

A SELF-CONSISTENT THEORY FOR MODELLING INTERFACIAL AND BULK PROPERTIES

BY

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A Dissertation Presented to the
COLLEGE OF GRADUATE AND INTERDISCIPLINARY STUDIES
KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

DOCTOR OF PHILOSOPHY

In

CHEMICAL ENGINEERING

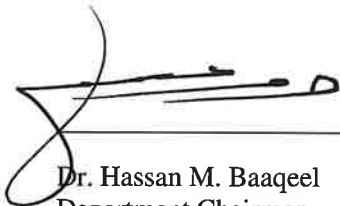
DECEMBER 2023

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

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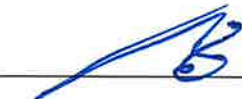

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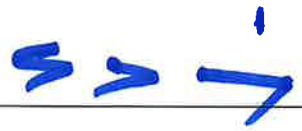
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Dedication

This work is dedicated to my late father Hassan Ali Al-Rashidy, my mother Sanaa Al-Dakak, my wife Nourhan Al-Shatby, my newborn Kenan Al-Rashidy and my brother Mahmoud Al-Rashidy for their constant support, love, and patience.

ACKNOWLEDGMENTS

All praise and gratitude are due to Almighty Allah for endowing me with strength, endurance, and patience, enabling me to successfully complete this work. I am profoundly grateful for His guidance throughout my career and the numerous blessings bestowed upon me. Subsequently, I express my sincere appreciation to King Fahd University of Petroleum and Minerals for providing me the opportunity to pursue my PhD studies. I extend my deepest gratitude to my thesis advisor, Dr. Nayef Mesnad Alsaifi, for his exceptional guidance, inspiration, and motivation. His academic support has been invaluable, and I am particularly thankful for his belief in me during moments of self-doubt. I am also immensely grateful to my thesis co-advisor, Dr. M. Mozahar Hossain, for his insightful feedback and encouragement, which fortified my resolve to overcome challenges throughout this research. My advisors' patience and faith in my abilities have been pivotal to my progress. Further, I extend my gratitude to my committee members: Dr. Mamdouh Al-Harthi, Dr. Sagheer Onaizi, and Dr. Abdullah Sultan, for their invaluable contributions to my academic journey. Lastly, I am profoundly thankful to my mother, who has endured significantly during this period and always believed in me. I express my heartfelt thanks to my wife for her unwavering support and to my late father, whose memory inspired me to continue my graduate studies. I also wish to thank my brother, friends, extended family, and the members of the KFUPM Egyptian society for their continuous support.

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LIST OF ABBREVIATIONS

DGT	:	Density Gradient theory
DFT	:	Density Functional Theory
OZ	:	Ornstein Zernike Integral Equation
IET	:	Integral Equation Theory
PY	:	Percus–Yevick Closure
MSA	:	Mean Spherical Approximation Closure
HNC	:	Hypernetted-Chain Equation Closure
MS	:	Martynov and Sarkisov Closure
RY	:	Rogers and Young Closure
SMSA	:	Soft Core-MSA Closure
HMSA	:	HNC-SMSA Closure
KH	:	Kovalenko and Hirata Closure
DUH	:	DUH and Haymet Closure
MV	:	Modified Verlet Closure
MHNC	:	Modified-HNC
VM	:	Vompe Martynov Closure
ZSEP	:	Lloyd L. Lee Approximation

$g(r)$	:	Radial Distribution Function
$h(r)$	:	Total Distribution Function
$c(r)$	:	Direct Distribution Function
$\gamma(r)$	:	Indirect Distribution Function
CPE	:	Coupling Parameter Expansion Method
TPT	:	Thermodynamic Perturbation Theory

ABSTRACT

Full Name : [Ahmed Hassan Ali El-Rashidy]
Thesis Title : [A Self-Consistent Theory for modelling Interfacial and Bulk properties]
Major Field : [Chemical Engineering]
Date of Degree : [December 2023]

The Ornstein-Zernike (*OZ*) equation and its related statistical mechanical closures are utilized for studying bulk and interfacial properties for Lennard-Jones fluid. The common obstacles associated with predicting the spinodal decomposition curve and gas-liquid phase transition are overcome by implementing the coupling-parameter expansion (*CPE*). The overcome of such obstacles made it possible to conduct extensive evaluation of thermodynamic and structural properties from *OZ* equation for 14 closures such as Verlet, Mean spherical approximation, hypernetted chain equation (*HNC*) and their modifications. The prediction of thermodynamic properties and structural properties are compared against molecular simulation data for the closures with and without *CPE*. The study reveals that the Modified Verlet (*MV*) is the most accurate closure in predicting structural and thermodynamic properties including spinodal decomposition curves, phase coexistence and the critical point.

The study is extended to the prediction of the interfacial properties using the Kirkwood-Buff-Fowler theory for Lennard-Jones fluid. Because the structural property of the pair correlation function is needed as input for the interfacial calculations, the modified Verlet is used for this purpose. It is found that the pair correlation function obtained from the *MV* closure significantly enhances the accuracy of the surface tension from the Kirkwood-Buff-Fowler theory. The results are more accurate than those usually obtained from fitted pair correlation function.

To extend the Kirkwood-Buff-Fowler theory beyond Gibbs dividing surface and to account of the interfacial thickness, six theories are considered including Lenker-Henderson, McLellan, Fitts and Berry et al. The density profiles are approximated by linear, cubic and exponential functions. The use of an exponential density profile within the interfacial thickness emerged as the most accurate approach for depicting the density distribution in the interfacial region. This conclusion leads to predicting more accurate surface tension and surface energy. The accuracy of these quantities is found to be sensitive to the cut-off distances.

ملخص الرسالة

الاسم الكامل: أحمد حسن علي الرشيد

عنوان الرسالة: نظرية متسقة ذاتيًا لنمذجة الخصائص الواجهية والجملة

التخصص: الهندسة الكيميائية

تاريخ الدرجة العلمية: ديسمبر 2023

معادلة أورنشتاين-زينرنيك (OZ) والإغلاقات الميكانيكية الإحصائية المتعلقة بها تُستخدم لدراسة خصائص الجملة والواجهة لسائل لينارد-جونز. تم التغلب على العقبات الشائعة المرتبطة بتنبؤ منحني التحلل اللاحق وانتقال الطور الغازي-السائل من خلال تنفيذ توسعة معامل الاقتران (CPE). التغلب على هذه العقبات جعل من الممكن إجراء تقييم واسع للخصائص الديناميكية الحرارية والبنوية من معادلة OZ لـ 14 إغلاقًا مثل Verlet، تقريب الكروي المتوسط، معادلة سلسلة hypernetted (HNC) وتعديلاتهم. يتم مقارنة توقعات الخصائص الديناميكية الحرارية والبنوية مقابل بيانات المحاكاة الجزيئية للإغلاقات مع وبدون CPE. الدراسة تكشف أن Verlet المعدل (MV) هو الإغلاق الأكثر دقة في توقع الخصائص البنوية والديناميكية الحرارية بما في ذلك منحنيات التحلل اللاحق، تواجد الأطوار والنقطة الحرجة.

تم تمديد الدراسة لتشمل توقع الخصائص الواجهية باستخدام نظرية كيركوود-باف-فاولر لسائل لينارد-جونز. نظرًا لأن الخاصية البنوية لدالة الارتباط الزوجية مطلوبة كمدخل للحسابات الواجهية، فقد تم استخدام Verlet المعدل لهذا الغرض. تبين أن دالة الارتباط الزوجية التي تم الحصول عليها من إغلاق MV تحسن بشكل كبير من دقة التوتر السطحي من نظرية كيركوود-باف-فاولر. النتائج أكثر دقة من تلك التي يتم الحصول عليها عادة من دالة الارتباط الزوجية الملائمة.

لتوسيع نظرية كيركوود-باف-فاولر إلى ما بعد سطح تقسيم Gibbs ولمراعاة سمك الواجهة، تم النظر في ست نظريات بما في ذلك Lenker-Henderson، McLellan، Fitts و Berry وآخرين. يتم تقريب ملفات الكثافة بواسطة دوال خطية، تكعيبية وأسية. استخدام ملف كثافة أسي ضمن سماكة الواجهة ظهر كأفضل نهج لتصوير توزيع الكثافة في المنطقة الواجهية. هذا الاستنتاج يؤدي إلى توقع توتر سطحي وطاقة سطحية أكثر دقة. تبين أن دقة هذه الكميات حساسة لمسافات القطع.

Chapter 1

INTRODUCTION

1.1 Motivation

The study of interfacial properties plays a significant role in various types of applications such as absorption, adsorption and multi-phase equilibria (Safran, 2018). For instance, the study of surface tension is important in detergent industry. Detergents improve in performance as the water surface tension is decreased (Birdi, 2013). Surface tension is also very important in paints to produce defect free coatings on surfaces (Lambourne and Strivens, 1999). The study of surface tension plays a major role in tablet coating, drug solubility and stability in the pharmaceutical industry (Karbowski *et al.*, 2006; Schweizer and Kistler, 2012; Cross and Plunkett, 2014). In oil and gas industry, the determination of interfacial properties provides a guide for selecting the proper surfactants to enhance oil recovery (Pasquarelli and Wasan, 1981; Speight, 2020; Saxena and Mandal, 2022).

Because of its significant role, several experimental studies have been conducted to measure interfacial properties of certain compounds. Jasper (1972) compiled surface tension data for 2200 pure fluid compounds at different temperatures. Korosi and Kovats (1981) measured the surface tension of 83 pure organic compounds. More recent studies have been focused on specialized compounds like ionic liquids (Kolbeck *et al.*, 2010; Almeida *et al.*, 2016; Shimizu *et al.*, 2018; Setiawan *et al.*, 2021). Bowers *et al* (2004) measured the surface tension of different ionic liquids to investigate their aggregation behaviour. Ghatee and Zolghadr (2008) conducted surface tension measurements of imidazolium-based ionic liquids at liquid–vapor equilibrium.

The study of interfacial properties has also found a great interest in nanofluids, which have a wide range of applications from enhanced oil recovery to thermal applications in heat exchangers and power systems (Lee, 2007; Huminic and Huminic, 2012; Kuang *et al.*, 2018; Wahab *et al.*, 2019; Sun *et al.*, 2020; Wu *et al.*, 2020; Kumar *et al.*, 2022). In a recent study, Wanic *et al.* (2020) measured the surface tension of ethylene glycol-based nanofluids containing various types of nitrides. There have also been some studies of interfacial tension directed toward paraffins with nanofluid emulsions because of their importance in the process of enhanced oil recovery. Sharma and Sangwai (2017) measured the surface tension reduction of paraffin oils in the presence of silica nanofluids with polyacrylamide as a dispersing agent. Cabaleiro *et al.* (2019) measured the surface tension of paraffin in water nano emulsions. Yan *et al.* (2020) studied the effect of multi-walled carbon nanotubes (MWCNTs) on the surface tension of paraffins.

Furthermore, surface tension is an essential property in the field of fuel additives and clean flues. Chaparro *et al.* (2020) measured the surface tension for a mixture cyclopentyl methyl ether, ethanol and hexane to investigate the mixtures capability of being an additive to gasoline. Zhao *et al.* (2020) measured the surface tension of binary mixtures of n-hexadecane with methyl decanoate and methyl butyrate to investigate them as fuel additives.

Irrespective of the devoted effort, experiments are generally limited to certain compounds. Indeed, the measurements barely cover a wide temperature and pressure ranges. Furthermore, the experimental measurements of interfacial properties can also be costly and not practical if many types of mixtures are needed. For certain mixtures and conditions, it is quite difficult to measure the interfacial properties. For these reasons, the development of

thermodynamic theories for predicting interfacial properties has remained a subject of interest over the years.

Gibbs (1879) was one of the first scholars who developed a thermodynamic theory of capillarity. Subsequently, Van der Waals (1893) developed his theory for inhomogeneous fluids which paved the way for the density gradient theory (*DGT*) (Rowlinson, 1979). Cahn and Hilliard (1958) applied the *DGT* to a planar interface of a Lennard-Jones fluid situated between two coexisting phases. The main idea of the *DGT* theory is to minimize the grand potential to determine the equilibrium density profile at the interface (Llovell *et al.*, 2010). The use of *DGT* needs the so-called influence parameter, which is usually taken as an adjustable parameter. This makes *DGT* lacking of predictive power (Rowlinson and Widom, 2013). This is why more attention has been paid to a more successful approach known as the density functional theory (*DFT*). The *DFT* methods are also based on the formulation of a free energy functional of the single particle density describing thermodynamics properties of an inhomogeneous system. This makes the *DFT* methods very accurate however they are complex and computationally very challenging (Gross, 2009).

An alternative but simpler theory was originally developed by Fowler (1937) and extended by Kirkwood and Buff (1949) to mixtures. This theory is mathematically much simpler than *DFT* and *DGT*. It has also the flexibility of computing the surface energy. The Fowler's approximation is based on the mechanical definition of surface tension instead of the thermodynamic definition. From the mechanical perspective, surface tension is the interfacial tension of the phase boundary resulting from a uniform pressure acting normal to the interface between two fluid phases. Based on Fowler's approximation, the surface tension is related to the pair correlation function $g(r)$ of the homogeneous fluid (Fowler, 1937; Lekner and Henderson,

1977). The Fowler's approximation was tested for hard sphere and Lennard-Jones fluids using different approaches for the pair correlation function (Shoemaker *et al.*, 1970; M. V Berry *et al.*, 1972; Freeman and McDonald, 1973; Salter and Davis, 1975). The comparison with experimental and molecular simulation data showed reasonable accuracy at some certain points.

The Fowler's approximation has been modified by several studies to improve its accuracy. One of the earliest modifications was made by Maclellan (1952) who incorporated the pair correlation functions for both liquid and the vapor phases. Because Fowler's approximation was originally developed by considering zero density for the vapor side, Lekner and Henderson (1977) modified Fowler's approximation by considering the vapor density contribution. They also derived a relation where the direct correlation function $c(r)$ is used instead of the pair correlation function. Gray and Gubbins (1975) extended Fowler's approximation to various types of interfaces. The Fowler's approximation has also been extended and evaluated for molten salts (Pastor and Goodisman, 1978). Although extensive analysis has been made, the Fowler's approximation was unsuccessful to predict accurate results for molten salts.

Fowler's approximation and their modifications are closely related to the pair correlation function. Therefore, their accuracy depends on the accuracy of the pair correlation function. It is well-known that one way to obtain the pair correlation function is through integral equations theories using the Ornstein-Zernike Equation (OZ) with a closure with a certain intermolecular potential (Ornstein and Zernike, 1914). There are common closures used with the OZ equations such as Percus-Yevick (1958), Hypernetted chain (van Leeuwen *et al.*, 1959) and Mean Spherical Approximation (J L Lebowitz and Percus, 1966). The use of these closures with the modified Fowler's approach does not give good agreement for the surface tension with the molecular simulation data or experimental data for the two phase coexistence region (Lekner

and Henderson, 1977). One potential reason is that these studies ignored the fact that these closures are not accurate for the two-phase coexistence region. Many closures have been studied in the literature for the Lennard-Jones potential. The majority of these closures failed to give an accurate phase diagram (Caccamo, 1996). Despite the use of different numerical techniques, it was not possible to obtain the pair correlation function needed for the full phase diagram especially close to the critical region. Therefore, there are computational obstacles limiting the use of integral Equation theories. These obstacles made it difficult to evaluate available closures for the Lennard-Jones potential; not only for pure liquids but also for the vapour-liquid equilibrium region needed for predicting interfacial properties. This is why most closures used in the literature are approximate and lacking thermodynamic consistency.

The prediction of surface tension using Fowlers' approximation was not completely satisfied in the literature. The use of an accurate closure with Fowler's approximation and its modification can increase its accuracy. We can also study the reasons behind the failure of Fowler's approximation with any compound including molten salts and other types of salts. If a combination of an accurate closure and Fowler's approximation succeeds, this gives us a great opportunity to study the role of interfacial properties in various types of physical phenomena observed in mixed systems such as phase separation. Furthermore, unlike other interfacial theories, the prediction of surface energy is straightforward by Fowler's approximation. Therefore, in this work, we are motivated by studying various types of closures and finding the most accurate in terms of two-phase properties and thermodynamic consistency.

Irrespective of the accuracy of any closure, it is imperative to realize that the problems of integral Equation theories are not only computational. In fact, some theories may not have feasible solutions at certain fluid regions such as the critical region. To overcome this problem,

we employ coupling parameter expansion (*CPE*) (Ramana, 2013; Ramana and Menon, 2013) to facilitate the determination of the complete phase envelope. Zhou (2006) introduced an enhanced version of *CPE* using thermodynamic perturbation theory (*TPT*) , especially for short-range potentials.

In this thesis, the enhanced version is utilized with integral Equation theories to obtain the full phase diagram for Lennard-Jones fluid. We apply *CPE* to fifteen closures. Six of these closures were originally developed for hard sphere potential; namely, Percus-Yevick (*PY*) (Percus and Yevick, 1958) the Hypernetted-Chain Equation (*HNC*) (Rushbrooke and Scoins, 1953; Morita and Hiroike, 1960), the Mean Spherical Approximation (*MSA*) (J. L. Lebowitz and Percus, 1966), the Martynov and Sarkisov closure (*MS*) (Martynov and Sarkisov, 1983), the Verlet closure (Verlet, 1980) and the Rogers and Young closure (*RY*) (Rogers and Young, 1984). The other nine closures were initially developed for systems with soft sphere potentials and were subsequently evaluated and tested for their applicability to the Lennard-Jones fluid. These closures involve the soft core *MSA* (*SMSA*) (Madden and Rice, 1980), the HNC-SMSA closure (*HMSA*) (Zerah and Hansen, 1986), the Kovalenko and Hirata closure (*KH*) (Kovalenko and Hirata, 1999), the DUH and Haymet closure (*DUH*) (Duh and Haymet, 1995), the modified DUH (Duh and Henderson, 1996), the modified Verlet (*MV*) (Choudhury and Ghosh, 2002), the modified-HNC (*MHNC*) (Rosenfeld and Ashcroft, 1979), the Vompe Martynov closure (*VM*) (Martynov *et al.*, 1999) and finally a modified version of the Lloyd L. Lee Approximation (*ZSEP*) (Lee, 1995; Lee *et al.*, 1996).

Therefore, in this thesis, the solutions of 15 closures with *OZ* Equation are obtained with and without *CPE* for Lennard-Jones potential. A detailed comparison with molecular simulation data is also made to select the most accurate closure for the Lennard-Jones fluid. The comparison

includes both structural properties such as the pair correlation function and key thermodynamic properties like internal energy and chemical potential. Moreover, the study is extended to test thermodynamic consistency of each theory and to predict the metastable region by predicting the spinodal lines. The most accurate closure is then utilized for the calculations of the interfacial properties.

1.2 Research Objectives

The ultimate objectives of the thesis are threefold: first, to overcome the prediction limitations of solving Ornstein-Zernike Equation for various types of closures for Lennard-Jones fluid by employing coupling parameter expansion. The second objective is to review and investigate the limitations of fifteen closures by studying structural and thermodynamic properties. The third objective is to predict the interfacial properties using the most accurate closures.

Based on the three objectives, the specific objectives can be summarized under different categories:

- **Development of Numerical Codes:**
 - To devise numerical algorithms (*CPE*) capable of predicting structural and thermodynamic properties for the Lennard-Jones fluid. In pursuing this goal, various closures (15 closures) are tested to identify the most accurate closure for modeling this system.
- **Prediction of Phase Diagrams and thermodynamic properties:**
 - To predict the phase diagram of the Lennard-Jones fluid by employing a range of Ornstein-Zernike (*OZ*) closures with and without *CPE*.

- To predict various types of thermodynamic properties including internal energy, isothermal compressibility, thermal pressure coefficient, thermal expansion coefficient, chemical potential, Joule-Thomson coefficient, Grüneisen coefficient, Speed of sound, isobaric heat capacity, and the isochoric heat capacity.
- **Validation Against Molecular Simulation Data:**
 - To validate the results obtained from *OZ* closures with available molecular simulation data.
- **Prediction of interfacial properties:**
 - To incorporate the most accurate and thermodynamically consistent *OZ* closure with Fowler's approximation for Lennard-Jones fluid systems and compare with available simulation data.

1.3 Thesis Organization

This Thesis will be organized as follows:

Chapter 2: Theoretical background

- This chapter will present a comprehensive overview of prior scholarly research related to various Ornstein-Zernike (*OZ*) closures. Additionally, it will delve into an in-depth exploration of the mathematical framework that forms the basis of *OZ* Equation closures.

Chapter 3: Thermodynamic properties from Integral equation theories

- In this chapter, a detailed description of the thermodynamic properties of for the Lennard-Jones fluid via the *OZ* integral equation theory.

Chapter 4: Coupling-Parameter Expansion and computational methods for

Ornstein–Zernike equation

- In this chapter, a detailed description of the numerical method employed to solve the Ornstein-Zernike (OZ) Equation with various closures for the Lennard-Jones potential is provided. Additionally, the chapter delves into thermodynamic calculations based on the pair correlation function and outlines the methodology used for phase diagram calculations.

Chapter 5: Results of Ornstein–Zernike equation with and without CPE for Lennard-Jones fluid

- This chapter will be dedicated to the presentation of outcomes, focusing on phase diagrams resulting from the application of various closures. It will also encompass an analysis of multiple thermodynamic properties and the evaluation of their consistency.

Chapter 6: Kirkwood-Buff-Fowler theory

- Chapter 6 will expound upon the theoretical and mathematical foundations that underlie the Kirkwood-Buff-Fowler approximations. These insights are pivotal for a comprehensive understanding of the subsequent results.

Chapter 7: Results of Interfacial properties

- This chapter will serve as the platform for presenting the outcomes derived from the Fowler approximations, in conjunction with a comparative analysis against results achieved through diverse closure methodologies.

Chapter 7: Conclusion and Prospective Directions

- In the final chapter, we will synthesize our findings and offer conclusions based on the results. Additionally, we will outline avenues for potential future research and applications in this field.

Chapter 2

THEORETICAL BACKGROUND

The pioneering work of Ornstein and Zernike had a tremendous impact on liquid solution theories. Their Equation has provided a powerful insight into thermodynamic and structural properties. In statistical mechanics, fluid structure represents the spatial arrangement of molecules in terms of probabilistic quantities such as the radial distribution function. The radial distribution function gives the time-averaged spatial arrangement of the molecules in a gas, liquid or solid. The theoretical approaches in this thesis depend on radial distribution functions. Hence, it would be essential to give a theoretical overview about molecular distribution functions and the related integral Equation theories, which are based on Ornstein and Zernike equation.

Perhaps, the most important molecular distribution function is the so-called pair correlation function $g(r)$. In terms of probability, the pair correlation function gives the probability of how two molecules are different apart in space. It can also be interpreted as how a certain particle is surrounded by other particles. For example, if a particle exists at a position $\mathbf{r}_1$ the density at $\mathbf{r}_2$ would be $g(|\mathbf{r}_1 - \mathbf{r}_2|) \equiv \rho g_{12}$. As the distance between $\mathbf{r}_1$ and $\mathbf{r}_2$ tends to infinity $g_{12} = 1$.

The pair correlation function can be obtained from three different methods; namely, x-ray and neutron scattering experiments, computer simulation, and integral Equation theories (Sandler, 2010; Lee, 2016). Integral Equation theories and computer simulations handle hypothetical fluids with specific presumed pairwise potential (e.g., hard-sphere, square well, and Lennard-Jones potentials). Whereas, scattering experiments deal with real fluids (Fowler, 1939; Sandler, 2010; Lucas, 2013; Lee, 2016). Our focus in this thesis is directed into pair correlation

function from integral Equation theories. The molecular simulation data will also be used for the sake of comparison with different integral Equation theories.

2.1 Pair correlation function

In the phase space of a canonical ensemble, the probability that the i^{th} cell contains a phase point, representing a specific spatial configuration and momentum distribution, is expressed as:

$$dp^{(N)}(p^N, r^N) = \frac{\exp[-\beta H_N(p^N, r^N)] dp^N dr^N}{N! h^{3N} Z_N} \quad 2.1-1$$

where h is the Planck constant, H_N is the Hamiltonian, Z_N is the partition function and $\mathbf{p}^N$ is the momenta variables and $\mathbf{r}^N$ is the spatial variables. This general expression allows for the derivation of various specialized probabilities by performing marginalization over the phase space coordinates (Hill, 1956; Gray *et al.*, 1984). The Hamiltonian, H_N , for spherically monatomic molecules with a symmetric potential is defined as

$$H_N(p^N, r^N) = \sum_{i=1}^N \frac{p_i^2}{2m} + V_N(r_1, \dots, r_N) \quad 2.1-2$$

The classical canonical partition function is then defined as

$$Z_N = \frac{Q_N}{N! \Lambda^{3N}} \quad 2.1-3$$

where the configurational integral, Q_N is defined as

$$Q_N = \int dr_1 \dots dr_N \exp[-\beta V_N(r_1, \dots, r_N)] \quad 2.1-4$$

where V_N is the total potential energy. This quantity possesses dimensions of volume raised to the power of N , denoted as V^N . In the case of an ideal gas, where there are no interactions

between particles the $Q_N = V^N$. The configurational marginal probability, which is the probability independent of particle momenta, is given by:

$$dp^{(N)}(\mathbf{r}^N) = \frac{1}{Q_N} \exp [-\beta V_N(\mathbf{r}_1, \dots, \mathbf{r}_N)] d\mathbf{r}_1 \dots d\mathbf{r}_N \quad 2.1-5$$

The integration has been carried out over the momentum coordinates $d\mathbf{p}_1$ through $d\mathbf{p}_N$. The term $dp^{(N)}(\mathbf{r}^N)$ represents the configurational probability of a specific molecular configuration, that is, the spatial arrangement of molecules, without consideration of their momenta. When a subset of n molecules is chosen from a larger system of N molecules, where n is less than N , the probability of these n molecules being located at positions $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n$, while disregarding the positions of the remaining $(N-n)$ molecules, can be calculated by performing an integration over the $N-n$ unspecified positions:

$$dp^{(n)}(\mathbf{r}^n) = \frac{1}{Q_N} d\mathbf{r}_1 \dots d\mathbf{r}_n \left[\int d\mathbf{r}_{n+1} d\mathbf{r}_{n+2} \dots d\mathbf{r}_N \exp (-\beta V_N(\mathbf{r}^N)) \right] \quad 2.1-6$$

The differential probability $dp^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n)$ quantifies the likelihood that molecule 1 is located within the differential volume $d\mathbf{r}_1$ centered at position $\mathbf{r}_1$, and simultaneously, molecule 2 is within $d\mathbf{r}_2$ at $\mathbf{r}_2$, and so on, up to molecule n . However, if our interest lies in the presence of a molecule, without regard to specific labels, at a particular position (with N molecules to choose from), along with another unlabeled molecule occupying $\mathbf{r}_2$ (with $N-1$ choices), and so on, up to molecule n , then this probability is greater than the one defined in Equation (2.1-6). In fact, it is $N(N-1)(N-2)\dots(N-n+1)$ times the value given by Equation (2.1-6)

$$dp_g^{(n)}(\mathbf{r}^n) = \frac{N!}{(N-n)!} dp^{(n)}(\mathbf{r}^n) \quad 2.1-7$$

This new probability, denoted as $p_g^{(n)}$, is termed the generic probability because it accounts for molecules without regard to their specific labels. This perspective is particularly realistic,

especially when dealing with identical molecules, as permutations of these molecules do not alter the overall molecular state.

The n-Body Generic Density Function $\rho^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n)$ is therefore defined as $p_g^{(n)}(\mathbf{r}^n)$

$$\rho^{(n)}(r_1, \dots, r_n) \equiv \frac{N!}{(N-n)! Q_N} \int dr_{n+1} \dots dr_N \exp(-\beta V_N(r^N)) \quad 2.1-8$$

The frequently employed density functions in the context of molecular systems are the one-body, two-body, and three-body density functions. The one-body density function, denoted as $\rho^{(1)}(\mathbf{r}_1)$ and often referred to as the singlet density and the two-body density function $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ is called the pair density.

From the pair density and the singlet density, the pair correlation function $g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ is defined as

$$g^{(2)}(r_1, r_2) = \frac{\rho^{(2)}(r_1, r_2)}{\rho^{(1)}(r_1)\rho^{(1)}(r_2)} \quad 2.1-9$$

The pair correlation function has certain properties especially at high temperature limit, the low-density limit, and the ideal gas limit. As the $T \rightarrow \infty, \beta \rightarrow 0, \beta V_N \rightarrow 0$

$$\lim_{T \rightarrow \infty} g^{(n)}(r_1, \dots, r_n) = \rho^{-n} \frac{N!}{(N-n)!} \frac{\int dr_{n+1}, \dots, dr_N \exp(-\beta V_N)}{\int dr_1, \dots, dr_N \exp(-\beta V_N)} = 1 - O\left(\frac{1}{N}\right) \quad 2.1-10$$

therefore,

$$\lim_{T \rightarrow \infty} g^{(2)}(r) = 1 - O\left(\frac{1}{N}\right) \quad 2.1-11$$

In the thermodynamic limit, as the number of particles N approaches infinity (at constant ρ), terms of order $O(1/N)$ become negligible and vanish (Lee, 2016).

As the density, approaches zero, it can be demonstrated from the cluster expansion of the pair correlation function $g^{(2)}(r)$ that

$$\lim_{\rho \rightarrow 0} g^{(2)}(r) = \exp(-\beta u(r)) \quad 2.1-12$$

And finally, the at the ideal gas limit

$$g^{(n)}(r_1, \dots, r_n) = 1 \quad 2.1-13$$

2.2 The Ornstein–Zernike (OZ) equation

The interest of integral equations has been appeared since the development of the Yvon-Born-Green hierarchy (YBG) and the Bogoliubov–Born–Green–Kirkwood–Yvon hierarchy (BBGKY) (Hansen and McDonald, 2013). In these integral equations, $g^{(n)}$ is not computed unless prior knowledge of $g^{(n+1)}$ is available. To obtain a solution, it becomes necessary to close the hierarchy by introducing an approximation that establishes a relationship between $g^{(n+1)}$ and $g^{(n)}$.

For the pair correlation function, the Born-Green (BG) Equation utilizes the Kirkwood superposition approximation to remove the triplet correlation function. This approximation entails a simple breakdown of the triplet correlation function into a product of three pair correlation functions. It is important to note that this approximation is only partially dependable under high-density conditions.

The shortcomings of the BG Equation initiated substantial efforts to enhance the Kirkwood superposition approximation for its use in the YBG equation. Yet, these endeavors resulted in progressively complex treatments. As a result, an alternative and more effective approach emerged, focusing on the use of approximate integral equations. This method leverages the exact Ornstein-Zernike (OZ) equation. In fact, the entire domain of integral Equation theories for the study of the liquid state fundamentally relies on the application of the OZ equation.

The OZ integral Equation is one of the most popular integral equations for predicting the pair correlation function for pure and mixture fluids (Ornstein and Zernike, 1914). The total correlation function $h(r_{12}) = g(r_{12}) - 1$, quantifies the localized influence of one molecule (molecule 1) on another molecule (molecule 2) at a distance r_{12} . Unlike the radial distribution function $g(r)$, which approaches unity as the separation r increases, $h(r_{12})$ diminishes to zero at larger separations.

Ornstein and Zernike (1914) introduced a division of the total correlation function, $h(r_{12})$, into two components: a direct part and an indirect part ($h(r) = \gamma(r) + c(r)$). The direct part is described by a function $c(r_{12})$ known as the direct correlation function. The indirect part ($\gamma(r)$) accounts for the influence that propagates directly from molecule 1 to molecule 3, which then impacts molecule 2, either directly or indirectly through interactions with other particles. This effect is weighted by density and averaged across all possible positions of molecule 3. With this decomposition of $h(r_{12})$, it can be expressed as follows:

$$h(r_{12}) = c(r_{12}) + \int dr_3 c(r_{13}) \rho(r_3) h(r_{23}) \quad 2.2-1$$

This Equation is known as the Ornstein-Zernike (OZ) Equation and serves as the fundamental Equation for the direct correlation function. This Equation basically describes the total correlation function as a result of the direct correlation between any two particles and the higher-order effects brought in due to the presence of other particles (Lucas, 2013; Lee, 2016). In the case of an isotropic liquid, where the directions become irrelevant, the distances can be reduced to the scalar separation distance, r , between the two molecules in question. As a result, the Ornstein-Zernike Equation simplifies to:

$$h(r) = c(r) + 4\pi\rho \int dr' r'^2 c(r - r') h(r') \quad 2.2-2$$

The concept of the direct correlation function was originally introduced in the context of critical phenomena, where the pair correlation function exhibits long-range behavior. However, it is important to note that this long-range nature is mediated through intervening solvent or liquid molecules, while the direct correlation function, which arises from the intermolecular interactions between the two specific molecules of interest, remains short-ranged function. Even in the vicinity of the critical point, the direct correlation function retains its short-range character. Consequently, the direct correlation function plays a crucial role in distinguishing and segregating the correlations associated with short-range and long-ranged interactions. The Ornstein-Zernike (OZ) Equation articulates that the long-range aspect can be described by summing over all the intervening molecules, as indicated by the integration process.

The Ornstein-Zernike (OZ) equation, on its own, is not particularly useful because it links two unknown functions, $h(r)$ and $c(r)$, with a single equation. To make it practical, we require an additional relationship that connects $h(r)$ and $c(r)$ to close the equation. Various approximate integral equations have been developed to fulfill this role.

The OZ Equation with an additional Equation of direct correlation function $c(r)$ in terms of the intermolecular potential, $u(r)$, produces a system of non-linear equations that are solved to get the total correlation function $h(r)$. This additional relation is called a closure:

$$h(r) = \exp [-\beta u(r) + h(r) - c(r) + B(r)] - 1 \quad 2.2-3$$

where $B(r)$ is called the Bridge function. The OZ Equation is solved numerically for most closures; however, analytical solutions are present for some closures. The accuracy of the calculated $g(r)$ greatly depends on the closure used.

2.3 The Bridge Function

The bridge function, $B(r)$, has been established as a summation of an infinite series of terms. Each of these terms involves integrals with kernels that consist of products of correlation functions, and the complexity of these products increases progressively as one moves through the series. This infinite series is often represented visually through diagrams known as "bridge" diagrams, from which the function $B(r)$ derives its name. The expression $h(r) - c(r) + B(r)$ is commonly known as the negative excess potential of mean force, denoted as $\omega(r)$ (Martynov, 1992). The diagrams contributing to the negative excess potential of mean force can be classified based on the number of h bonds associated with particle 1. This infinite series of $\omega(r)$ diagrams are represented by (Attard, 1993):

$$\omega(r_{12}) = \sum_{n=1}^{\infty} \omega^{(n)}(r_{12}) \quad 2.3-1$$

It's crucial to note that $\omega^{(1)}(r)$, which corresponds to the indirect correlation function $\gamma(r)$. Regrettably, even though we understand the types of diagrams involved, the resulting series cannot be converted into a manageable analytical formula or accurately evaluated through numerical methods. Therefore the calculated $g(r)$ is not exact and there are always thermodynamic inconsistencies involving different routes in calculating thermodynamic properties.

2.4 Ornstein-Zernike (OZ) Closures

2.4.1 Inconsistent OZ closures

2.4.1.1 Percus-Yevick, Hypernetted-Chain Equation and Mean Spherical Approximation

The two most famous closures are the Percus-Yevick (*PY*) (Percus and Yevick, 1958) and the hypernetted-Chain Equation (*HNC*) (Rushbrooke and Scoins, 1953; Morita and Hiroike, 1960). The *PY* and *HNC* equations are derived by the diagrammatic analysis of $g(r)$. The *HNC* is

also derived by minimizing a free energy functional. Whereas the *PY* Equation can be derived through expansions of the generating functionals which is the singlet density. This makes the *HNC* more thermodynamically consistent than the *PY* Equation but still not as consistent compared to perturbation theories (Sandler, 2010; Lucas, 2013; Bagchi, 2018). An integral Equation is consistent when the isothermal compressibility obtained from the virial pressure calculated from the $g(r)$ (virial equation) is equal to the isothermal compressibility obtained from the compressibility Equation (Bomont, 2008; Lee, 2016). The *PY* and *HNC* closure equations are provided below:

$$c(r) = g(r)[1 - \exp(-\beta u(r))] \quad 2.4-1$$

$$h(r) = \exp[-\beta u(r) + h(r) - c(r)] - 1 \quad 2.4-2$$

where $\beta = 1/k_b T$ and $u(r)$ is the pairwise potential. The *HNC* closure can also be derived from Equation (2.2-3) by setting $B(r)$ to zero.

The *PY* closure Equation (2.4-1) and the *OZ* integral Equation (2.2-2) make up a system of equations that are often solved using numerical iterative approaches. In the particular situation of a hard-sphere (*HS*) fluid, an analytical solution is obtained (Thiele, 1963; Wertheim, 1963, 1964; Nezbeda, 1974; Henderson *et al.*, 2019). This theory performs best for short-ranged potentials, where it can predict both the structural and thermodynamic features of the examined system with a good degree of precision (Barker and Henderson, 1976; Caccamo, 1996). The *PY* can also be solved analytically for hard sphere mixtures (Lebowitz, 1964; Hansen and McDonald, 2013). The *PY* closure is also used to find the radial distribution function for gases of hard sticks, hard squares, hard cubes as demonstrated by Verlet (1964). Although the *PY* closure shows good results in structure and thermodynamic properties for the hard sphere potential, still thermodynamic inconsistency is present between different calculation routes. The *PY* closure is

also solved analytically for adhesive hard sphere fluid by Baxter (1967a, 1968b). In the case of the Lennard-Jones potential the *PY* closure is not solved analytically and is only solved numerically.

The adequacy of the *PY* closure for the Lennard-Jones potential has been investigated by many in the literature. Broyles (1961a, 1961b) has shown that the $g(r)$ calculated from the *PY* closure are more accurate and in line with the molecular simulation than the Born-Green integral equation. Khan (1964) has studied the *PY*-Lennard-Jones combination to compute the radial distribution function of argon for different thermodynamic states under the critical point. Khan and Broyles (1965) did similar work for xenon. Mikolaj and Pings (1965) used the experimental radial distribution function of argon and obtained the associated potential using the *PY* closure. The obtained potential was found to be a function of density which implies considerable non-additive contribution. Mikolaj and Pings conclude that for the *PY* closure to be valid, the potential used should be state dependent especially in density. Throop and Bearman (1966) however, showed that the state points used by Mikolaj and Pings were all in the region of high temperature and high density where thermodynamic inconsistency exists for the *PY* closure. Throop and Bearman concluded that the *PY* closure for the Lennard-Jones fluid is adequate at high temperatures and moderate densities. For temperatures below the critical point, Throop and Bearman reported that the *PY* closure becomes thermodynamically inconsistent especially at higher densities. Morita and Hiroike (1960) derived the *HNC* from a variational principle and in theory doing so would ensure that the thermodynamic properties obtained are thermodynamically consistent. In a similar manner Baxter (1967b) derived the pressure for the *PY* approximation with the Lennard-Jones potential. The pressure calculated is equivalent to the inverse isothermal compressibility derived from the direct correlation function $c(r)$. This shows

that calculating the Equation of state from the $c(r)$ using the PY closure is more accurate than the virial route. Watts (1968) showed that pressure-density data calculated using the Equation derived by Baxter (1967b) is adequate near the critical point. However, Watts used a truncated potential at a cut off r_c which was in the region of 3.5σ . Above this value the PY approximation worsens drastically. This was done to ensure that the $c(r)$ vanishes at the same r_c as the potential. Watts (1969b) has shown that the pressure derived from the inverse compressibility Equation with the truncated Lennard-Jones potential is suitable to describe structure and thermodynamic properties of argon. In contrast to the work of Watts (1969b), Mandel et al. (1970) showed that the Equation of state calculated by the compressibility Equation was not comparable to molecular dynamic data at state points below the critical point. However, in Mandel et al. work the potential was not truncated and the $g(r)$ was forced to 1 after a r distance of 6σ . This shows that for the PY approximations, using a truncated Lennard-Jones potential and using a short-ranged correlation function would produce somewhat accurate thermodynamic and structure properties for a range of state points at the vicinity of the critical point.

Another approach to calculate the pressure for the Lennard-Jones Potential using the PY closure, is to calculate the internal energy from the following internal energy Equation (Energy equation):

$$U = \frac{3}{2}NKT + 2\pi N\rho \int_0^\infty u(r)g(r)r^2 dr \quad 2.4-3$$

and then integrating the internal energy with respect to inverse temperature β to get the free energy. The free energy is differentiated with respect to volume to get the pressure. The pressure through this route is more accurate than the virial route and the compressibility route because the PY closure gives fairly accurate $g(r)$ and therefore accurate internal energy (Barker *et al.*, 1970; Henderson and Chen, 1970). Henderson et al. (1970) used the pressure and the free energy

derived from the energy Equation to calculate phase equilibrium of the Lennard-Jones fluid. The phase diagram was nearly exact to argon experimental data (Guggenheim, 1945; Guggenheim and McGlashan, 1960). This can be attributed to the fact that the n th order perturbation expansion of the $g(r)$ in terms of pressure or compressibility produces n th order perturbation terms in thermodynamic properties. Whereas, $g(r)$ expansion in terms of energy gives rise to $(n+1)$ th order perturbation term in thermodynamic properties. The *PY* closure combined with energy Equation is an excellent theory for the liquid state. However, this is only for the Lennard-Jones potential and is not the case for other potential like the square-well potential (Chen *et al.*, 1969; Henderson and Chen, 1970).

In contrast to the *PY* closure the *HNC* closure for the Lennard-Jones potential is less accurate in calculating $g(r)$ and thermodynamic properties as shown by Broyles *et al.* (1962). Klein and Green (1963) derived the virial coefficient for the Equation of state of the *HNC* through the virial route (using the $g(r)$) and the compressibility route (using the $c(r)$). The second and the third coefficients were identical but the fourth was not. This is due to the approximation of the $B(r) = 0$. They also calculated the isothermal compressibility singularity points (points at infinite isothermal compressibility) and compared them with experimental data of argon. A considerable deviation is noticed. The behavior of the *HNC* inside the liquid-vapor coexistence curve is inferior to the accuracy of the *PY* closure even if the Lennard-Jones potential is truncated. Watts (1969a) has studied the *HNC* closure with different truncation of the Lennard-Jones potential has shown that the critical point produced by the *HNC* is higher than the *PY* closure and is different by an order of 15°-20°C to argon. Watts also found that the compressibility calculated using the compressibility Equation does not diverge at the critical point as observed with the *PY* closure. The *HNC* pressure-density curves calculated from the

virial Equation of state are extremely poor compared with the simulation and experimental data as the case with the *PY* closure. The $g(r)$ calculated using the *HNC* is in better agreement with the simulation data than the *PY* closure given that the potential is not truncated (Madden and Fitts, 1974).

Another important closure is the mean spherical approximation (*MSA*) (J. L. Lebowitz and Percus, 1966). Lebowitz and Percus (1966) introduced a generalization of the mean spherical model for Ising ferromagnets by Lewis and Wannier. The *MSA* was developed for intermolecular potential with hard core. The *MSA* when equipped with the hard sphere potential reduces to the *PY* closure. It is found to be more accurate than the *PY* and *HNC* closure when dealing with potentials with a hard core (J. L. Lebowitz and Percus, 1966; Andersen *et al.*, 1976). Analytical solution for the hard sphere potential with permanent electric dipole moments were formulated by Wertheim (1971). The *MSA* is found to be accurate for a number of model Hamiltonians one of which is the restricted primitive model (ions of opposite charges but equal in size) (Blum, 1975). Blum and Høye (1977) obtained the explicit form of the *MSA* for asymmetric electrolytes. Extensive studies has been done in the literature for electrolytes by the aid of the *MSA* and modified versions of the *MSA* (Blum, 1975, 1988; Blum and Høye, 1977; Copeman and Stein, 1986; Sanchez-Castro and Blum, 1989; Lu *et al.*, 1993; Sun *et al.*, 1994; Simonin *et al.*, 1996; Taghikhani and Vera, 2000; Yu *et al.*, 2003). In the original theory of the *MSA* the total correlation function $h(r)$ is forced to be (-1) in the hard sphere region. This is not suitable for soft core potentials like the Lennard-Jones.

Narten *et al* (1974) solved the *MSA* for the Lennard-Jones fluid but instead of forcing the total correlation function to -1 in the hard sphere region they used the direct correlation function of the *PY* closure. They called it the soft core *MSA*. In terms of structure properties, it showed

better accuracy than the *PY* and *HNC*. In a similar manner but slightly different way, Madden and Rice (1980) generalized the *MSA* for continuous potentials concentrating on the Lennard-Jones potential. The Lennard-Jones potential is split into a reference potential and a perturbing potential according to the Weeks *et al* (1971) high temperature high density approximation (Andersen *et al.*, 1971). Madden and Rice therefore generalized the *MSA* by using the splitting scheme and setting the radial distribution function of the fluid equal to the radial distribution function of the reference potential at high density and/ or high temperature as shown by Weeks *et al.*. Thus, the *SMSA* incorporates two key components:

- The partitioning of the potential energy into "reference" and "perturbation" parts.
- The approximation of the *SMSA* bridge function, achieved by applying the "unique functionality" assumption.

To begin, the partitioning of the Lennard-Jones potential energy is carried out according to the Weeks *et al* (1971) (*WCA*) partition scheme

$$u(r) = u_r(r) + u_a(r) \quad 2.4-4$$

$$u_r(r) = \begin{cases} u(r) - u(r_m), & r \leq r_m \\ 0, & r > r_m \end{cases} \quad 2.4-5$$

$$u_a(r) = \begin{cases} u(r_m), & r \leq r_m \\ u(r), & r > r_m \end{cases} \quad 2.4-6$$

where the r_m is the position of the potential minimum.

Furthermore, the *SMSA* bridge function is defined as follows

$$g(r) = [1 - \exp(\beta u_r(r))]^{-1} [c(r) + \beta u_a(r)] \quad 2.4-7$$

Using the $s(r) = \gamma(r) - \beta u_a(r)$ function

$$B^{SMSA}(r) \approx B^{SMSA}(s) = \ln(1 + s) - s \quad 2.4-8$$

This generalized *MSA* “named after as soft-*MSA* (*SMSA*)” was better suited to deal with the Lennard-Jones potential compared to the *PY* and *HNC* closures. However, the problem of thermodynamic consistency persists with the *MSA* and the *SMSA*. Another drawback of the *SMSA* is whenever the condition of the radial distribution function at high density and/or high temperature is not equal to the radial distribution function of the reference potential the *SMSA* becomes inaccurate. Therefore, the *SMSA* is not suitable in dealing with highly polar fluids or high concentration ionic mixtures.

2.4.1.2 Martynov–Sarkisov Approximation (*MS*).

Martynov and Sarkisov (1983) proposed a *OZ* closure where Equation 2.3-1 is truncated to the second order $n = 2$. The *MS* approximation, initially developed for the hard sphere (*HS*) system, is characterized by the absence of adjustable parameters. In the high-density region, it has been demonstrated that the *MS* approximation enhances the results obtained from the *PY* and *HNC* closures, notably reducing the thermodynamic inconsistencies observed in both methods.

2.4.1.3 Verlet closure

Verlet (1980) devised a semi-phenomenological closure with a two adjustable parameters. The parameters were adjusted in just a way where the fourth and fifth virial coefficients of the hard sphere fluid are calculated near their accurate values. The Verlet closure is more accurate when dealing with the hard sphere potential than the *PY* closure. However, the verlet closure in its original form where the parameters are adjusted to the hard-sphere potential is not suitable for the Lennard-Jones potential.

Table 2-1 Most common closures used for the Hard Sphere fluid.

Closure	B(r)	
<i>PY</i>	$B(r) = \ln[1 + \gamma(r)] - \gamma(r)$	2.4-9
<i>HNC</i>	$B(r) = 0$	2.4-10
<i>MSA</i>	$c(r) = \begin{cases} -\gamma - 1, & r < \sigma \\ -u(r), & r \geq \sigma \end{cases}$	2.4-11
<i>Verlet</i>	$B(r) = \frac{-\gamma^2(r)}{2(1 + \frac{4}{5}\gamma(r))}$	2.4-12
<i>MS</i>	$B(r) = [1 + 2\gamma(r)]^{0.5} - \gamma(r) - 1$	2.4-13

Note that *MSA* is easily presented using the direct correlation function $c(r)$ and σ is the Hard sphere diameter.

Table 2-1 shows the closures which are mainly developed for the hard sphere potential. They are not thermodynamically consistent for the Lennard-Jones fluids. These closures are presented in the form of Equation 2.2-3, with each closure having a distinct bridge function.

2.4.2 Mixed closures

2.4.2.1 Rogers and Young

Several closures were devolved in the literature to improve the consistency of those closures with respect to classical fluids. For the hard sphere potential, the *PY* and the *HNC* are the most accurate and most suited. The *PY* Equation is mostly suited for small interparticle distances and the *HNC* is most appropriate for large interparticle distances (Rosenfeld and Ashcroft, 1979). It is reasonable to say that mixing the two closures would produce a more accurate theory for purely repulsive potentials. This mixed closure is introduced by Rogers and Young (1984) (*RY*) by using a mixing parameter which ensures at large interparticle distances the *HNC* is predominant and at lower interparticle distances the *PY* is the predominant closure. This mixing parameter is determined by iteration at the freezing density until the isothermal

compressibility from the virial route and the compressibility route are equal. This forces the closure to be more thermodynamically consistent. The *RY* gives accurate results for the hard sphere potential and purely repulsive inverse power potentials. However, the *RY* closure is not thermodynamically consistent with the Lennard-Jones potential (Zerah and Hansen, 1986). The *RY* bridge function is expressed as follows

$$B(r) = \ln \left[1 + \left(\frac{(\exp(\gamma(r)f(r) - 1))}{f(r)} \right) \right] - \gamma(r) \quad 2.4-14$$

$f(r) = 1 - \exp(-\alpha r)$ is a simple switching function where α is an adjustable parameter to achieve thermodynamic consistency.

2.4.2.2 Hypernetted-Chain Equation-soft core Mean Spherical Approximation

For the Lennard-Jones potential Zerah and Hansen (1986) took a similar approach to Rogers and Young but instead of mixing the *PY* and *HNC* closures they mixed the *SMSA* and the *HNC* closures. The reason behind this is that the *SMSA* has shown more promise for dealing with the Lennard-Jones potential. The mixing parameter is treated the same way as the *RY* closure. The *HMSA* shows better results than the *SMSA* closure for the Lennard-Jones fluid. C Caccamo *et al.* (1993) calculated the phase diagram for the Lennard-Jones potential. The phase diagram faired satisfactory when compared with simulation experiments. The *HMSA* Bridge function is presented as follows

$$B(s) = -s(r) + \ln \left[1 + \frac{\exp(f(r)s(r)) - 1}{f(r)} \right] \quad 2.4-15$$

where $f(r)$ is the same as the switching function used in the *RY* closure.

2.4.2.3 Kovalenko and Hirata

In the context of combining elements from both the *HNC* and *PY* closures, Kovalenko and Hirata (1999) introduced a closure that achieved this mixing without the need for adjustable parameters. Their closure method relied on the value of the total distribution function. In regions characterized by low density, where $h(r)$ was less than zero, the closure predominantly exhibited *HNC* characteristics. Conversely, in regions of high density where $h(r)$ was greater than zero, the closure predominantly displayed *PY*-like behavior. The *KH* bridge function is expressed as

$$B(r) = \begin{cases} \ln(1 + d(r)) - d(r), & d(r) \leq 0 \\ 0, & d(r) > 0 \end{cases} \quad 2.4-16$$

Where $d(r) = -\beta u(r) + \gamma(r)$.

2.4.3 Modified *HNC* (*MHNC*) and Reference *HNC* (*RHNC*)

Concerning the consistency problem, one of the most consistent closures for Lennard-Jones potential is the Reference *HNC* (*RHNC*) (Lado, 1973) or Modified *HNC* (*MHNC*) (Rosenfeld and Ashcroft, 1979). Lado (1973) calculated the perturbed free energy and pair correlation function of a separated potential assuming that the properties of the reference part is known. In his calculations he used the *HNC* for the perturbed part and assumed that the reference part would be any purely repulsive potential. The hard sphere potential for the reference part is an excellent choice as accurate parametrizations of the hard sphere pair distribution function are available in the literature.

In a similar manner Rosenfeld and Ashcroft (1979) proposed the (*MHNC*), if the $B(r)$ is replaced by the correct sum of elementary graphs, the *MHNC* becomes exact and therefore becomes more thermodynamically consistent. However, the exact $B(r)$ is difficult to obtain. Therefore, Rosenfeld and Ashcroft used the unique functionality assumption especially for the

hard-sphere potential and constructed an excess free energy functional and proceeded to minimize it with respect to the $g(r)$. Which lead to the $B(r)$ used in the *MHNC* closure:

$$B(r) = g(r)_{HS} - 1 - \ln [-c(r)_{HS}] \quad 2.4-17$$

This is the bridge function of the *PY* closure. Lado (1976) results showed excellent accuracy when using the *PY* bridge function in an *HNC* setting dealing with charged hard spheres.

In the (*MHNC*) approach, the $B(r)$ term, which is equal to 0 in the *HNC* closure, is replaced with $B^{HS}(r, \eta^*)$ (the hard sphere bridge function). Here, η^* is defined as $\eta^* = \pi/6\rho(\sigma^*)^3$, with σ^* representing the hard sphere diameter. The value of σ^* is determined by enforcing thermodynamic consistency to ensure the accuracy of the approach. The hard sphere bridge function is easily obtained. Several parametrizations of the hard sphere bridge function are present in the literature. The easiest to implement is the Malijevský and Labík (1987) hard sphere bridge function parameterization.

Lado *et al* (1983) used the Reference Hypernetted Chain (*RHNC*) method, where they departed from determining the hard sphere (*HS*) diameter by enforcing thermodynamic consistency. Instead, they minimized the free energy, leading to the following equation

$$\int dr [g(r) - g^{HS}(r)] \frac{\partial B^{HS}(r, \sigma^*)}{\partial \sigma^*} \quad 2.4-18$$

Accurate results are obtained for the Lennard-Jones pair correlation function and thermodynamic properties. Furthermore, Caccamo (1995) calculated the phase diagram using the *MHNC* for the Lennard-Jones fluid. Caccamo used the Verlet and Weis (1972) parameterization of the hard sphere bridge function. Lomba (1989) calculated the phase diagram using *RHNC* and incorporating the Malijevský and Labík (1987) hard sphere bridge function parameterization. Lomba also traced a region in the liquid-vapor phase where no solutions were obtained using the

RHNC. This is a common feature for all *OZ* integral Equation closures. Moreover, Lomba *et al.* (1992) incorporated the Verlet closure for the reference part of the *RHNC* (*RHNC-VM*). There was no difference found in the results between using the Verlet closure for the reference part and using any hard sphere parametrization Equation in terms of structure. In fact, the *RHNC-VM* showed worse thermodynamic properties when dealing with soft core potentials (Lombardero *et al.*, 1992).

2.4.4 Renormalized closures

2.4.4.1 *DUH and Haymet*

Upon further investigations in the literature, it is recognized that the unique functionality assumption of the bridge function as hypothesized by Rosenfeld and Ashcroft is not actually true for all liquids (Foiles *et al.*, 1984; Ichiye and Haymet, 1988; Attard and Patey, 1990; DUH and Haymet, 1992). The work of DUH and Haymet (1992) in electrolytes concluded that the unique functionality assumption is true when the potential is split into a reference part and an appropriate attraction potential and the bridge function is renormalized using this attraction part of the potential. Renormalization of the bridge function is done when the bridge function in terms of $(\gamma = h - c)$ [the indirect correlation function] is replaced with the same bridge but in terms of $s(r) = \gamma(r) - u^a(r)$ where $u^a(r)$ is the attraction part of the potential. The bridge function they used for electrolytes was obtained by fitting simulation data. DUH and Haymet (1995) did the same for the Lennard-Jones potential and obtained a bridge function from simulation data (Llano-Restrepo and Chapman, 1992). Furthermore, Duh and Haymet proposed a density dependent $u^a(r)$ (Duh and Haymet, 1995; *DUH* and Henderson, 1996). Duh and Haymet calculated the phase diagram using their closure and was more accurate than the phase diagram

obtained using the Madden and Rice (1980) generalized *MSA* closure. Compared to simulation data, accurate structure and thermodynamic properties were easily obtained.

Duh and Haymet (1995) proposed the bridge function and the new partition scheme via numerical inversion of simulation data. The attractive part of the potential is as follows

$$u_a(r) = -4\varepsilon \left(\frac{\sigma}{r}\right)^6 \exp\left[\frac{-1}{\rho} \left(\frac{\sigma}{r}\right)^6\right] \quad 2.4-19$$

and the proposed bridge function

$$B(s) = \frac{-s^2}{2 \left[1 + \left(\frac{5s + 11}{7s + 9}\right)s\right]} \quad 2.4-20$$

The rationale behind selecting the function $u_a(r)$ is rooted in the following physical considerations:

- At higher densities, the system is primarily influenced by the repulsive component of the potential, which becomes the dominant force governing particle interactions.
- In contrast, at lower densities, the attractive component of the potential begins to play a more significant role in determining the behavior of the system.

This choice of $u_a(r)$ encapsulates the interplay between these two competing factors, allowing for an effective description of the system's behavior across a range of densities.

2.4.4.2 Modified DUH

The closure method introduced by DUH and Hayme (1995) can be viewed as a Padé 3-2 approximant. This closure is constructed based on an approximation of the expansion of the bridge function as a series $s(r)$.

It's worth noting that Padé approximants typically exhibit singularities in their expressions. In the case of the closure proposed by DUH and Hayme, there are two singularities at $s = -3/5$ and $s = -3$. These singularities are generally not problematic for pure Lennard-Jones (*LJ*) fluids. However, the singularity at $s = -3/5$ may lead to significant errors when applied to mixtures under specific conditions (Duh and Henderson, 1996).

Duh and Henderson (1996) introduced a modified closure that preserves the original *DUH* closure when dealing with positive values of $s(r)$. However, for negative values of $s(r)$, this modified closure utilizes only the first-order Taylor expansion for the function $B(s)$. Consequently, the closure takes the following form:

$$B(s) = \begin{cases} -\frac{-s^2}{2 \left[1 + \left(\frac{5s + 11}{7s + 9} \right) s \right]}, & s \geq 0 \\ -\frac{1}{2} s^2, & s < 0 \end{cases} \quad 2.4-21$$

Duh and Henderson (1996) also modified the $u_a(r)$ according to the following criterion

$$\left(\frac{\partial u_a}{\partial r} \right) \Big|_{r=\sigma} = 0 \quad 2.4-22$$

thus

$$\left(\frac{\partial u_r}{\partial r} \right) \Big|_{r=\sigma} = \left(\frac{\partial u}{\partial r} \right) \Big|_{r=\sigma} \quad 2.4-23$$

To clarify, the introduction of the "perturbation" potential does not alter the inter-particle force at the distance $r = \sigma$. Consequently, the expression for $u_a(r)$, which is now extended to mixtures, can be defined as follows:

$$u_a(r) = -4\varepsilon \left(\frac{\sigma}{r}\right)^6 \exp\left[\frac{-1}{\rho} \left(\frac{\sigma}{r}\right)^{6\rho}\right] \quad 2.4-24$$

The utilization of the function $s(r)$ was initially validated by Zerah and Hansen (1986). They demonstrated that the (SMSA) can be retrieved through the functional Taylor expansion framework originally proposed by Percus (1964). Additionally, Llano-Restrepo and Chapman (1994) extended this line of inquiry, suggesting that for the Lennard-Jones (*LJ*) bridge function, the approximation $B(r) = B(s)$ could provide a superior representation, especially when dealing with non-zero perturbation potentials $u^a(r)$. This assertion gains further credence from the favorable outcomes associated with the bridge function introduced by *DUH* and Haymet (1995).

2.4.4.3 Modified Verlet

Choudhury and Ghosh (2002) adopted the $u^a(r)$ function initially put forward by Duh and Haymet to renormalize the bridge function introduced by Verlet. This approach was designated as the Modified Verlet closure (*MV*). It's important to note that the *MV* closure reverts to the Verlet closure when $u_a(r)$ is set to zero. Remarkably, the *MV* closure exhibited exceptional performance in predicting both structural and thermodynamic properties, particularly when applied to the Lennard-Jones fluid. Furthermore, Choudhury and Ghosh calculated the phase diagram for the Lennard-Jones fluid, and the results were in excellent agreement with data obtained from simulation data.

The modified the Verlet closure, originally intended for the hard sphere potential, to apply it to the Lennard-Jones fluid. Choudhury and Ghosh (2002) introduced the following form for the $B(r)$ function:

$$B(r) = B(s) = \begin{cases} \frac{-s^2(r)}{2(1 + \alpha\gamma(r))}, & s \geq 0 \\ -\frac{1}{2}s^2, & s < 0 \end{cases} \quad 2.4-25$$

where $\alpha = 1.0175 - 0.275\rho$. In the original Verlet closure, the parameter α was an adjustable parameter used to ensure that the fourth and fifth virial coefficients were accurately computed. However, in the modified *MV* closure, it appears that α was determined through numerical inversion of simulation data involving the exact bridge function for the Lennard-Jones potential, similar to the approach used in the *DUH* closure. This method allowed for a more precise estimation of α for the specific case of the Lennard-Jones fluid. The $s(r)$ function is precisely the same as the modified *DUH* closure with the same $u_a(r)$ potential.

2.4.4.4 Martynov and Vompe

Martynov et al. (1999) introduced a bridge function by considering the expansion of the bridge function in relation to the negative excess potential of mean force, denoted as $\omega(r|2)$. They incorporated the asymptotic characteristics of the bridge function, which are most prominently evident at the critical point. Through this analysis, they derived the asymptotic behavior of $\omega(r|2)$. Subsequently, they demonstrated that utilizing the second term of Equation 2.3-1 but in terms of $\omega(r) - u_a(r)$ offered advantages in their approach. The bridge function is presented as follows

$$B(r) = [1 + 2s(r)]^{0.5} - s(r) - 1 \quad 2.4-26$$

The attraction part of the potential is according to the *WCA* scheme.

2.4.4.5 Zero-separation theorems for hard spheres

The consistency condition, where the pressure calculated through the virial route is equated to the pressure obtained via the compressibility route, has been employed in various closure models, including the *RY* and *HMSA* closures. However, it is worth noting that this consistency condition is not entirely effective, particularly in the core region of the system ($r < \sigma$) (Lee *et al.*, 1996). This lack of effectiveness can be attributed to the fact that the pressure (P) receives significant contributions primarily from the correlation function values at ($r > 0.8\sigma$). Furthermore, the calculated chemical potential is sensitive to $B(r)$, $\gamma(r)$ and $y(r)$ (cavity function) inside the core ($r < \sigma$). The cavity function is presented as:

$$\ln y(r) \equiv \ln g(r) + \beta u(r) = h(r) - c(r) + B(r) \quad 2.4-27$$

For general intermolecular potentials, the cavity function can be regarded as the "excess chemical potential." This term represents the energy needed to insert a dimeric molecule, with a bond length of L , into a medium consisting of individual monomers. The excess chemical potential quantifies the additional energy required for this dimer insertion compared to inserting the two constituent monomers separately (Boublík, 1986; Lee *et al.*, 1996):

$$-\ln y(L) = \beta \mu'_2(L) - 2\beta \mu'_1 \quad 2.4-28$$

As the bond length L approaches zero, the dimer essentially combines into a monomer with twice the strength or potential energy (2ε), while maintaining the same size (σ) as a regular monomer. This signifies the limit where the dimer behaves like a monomer with intensified potential energy. Therefore

$$-\ln y(0) = \beta \mu'_2(0) - 2\beta \mu'_1 \quad 2.4-29$$

In the case of hard spheres, the potential energy is either equal to ∞ or 0. When we double the potential energy, it remains either ∞ or 0, thus $\beta \mu'_2(0) = \beta \mu'_1$. Consequently, this result leads to

the recovery of the well-known zero-separation theorem for hard spheres $\ln y_{HS}(0) = 2\beta\mu'_1$ (Meeron and Siegert, 1968; Grundke and Henderson, 1972).

The function $\gamma(r)$ satisfies the OZ Equation at all values of r , including $r=0$. Thus

$$\gamma(0) = \frac{\partial \beta P}{\partial \rho} - 1 - 2 \frac{\beta U}{N} + \rho \int d\mathbf{r} g(r)[c(r) + \beta u(r)] \quad 2.4-30$$

The bridge function at $r=0$ can be therefore obtained from cavity function Equation 2.4-27. Thus

$$B(0) = \beta\mu'_2(0) - 2\beta\mu'_1 - \gamma(0) \quad 2.4-31$$

Lee (1995) and Lee *et al.* (1996) proposed a closure similar to the verlet closure for the Lennard-Jones fluid but with three adjustable parameters. They also used $B(s)$ instead of $B(r)$. The Bridge function proposed is

$$B(r) = -\frac{\xi s^2}{2} \left(1 - \frac{\alpha \varphi s(r)}{(1 + \alpha s(r))} \right) \quad 2.4-32$$

where ξ , α and φ are the adjustable parameters. The parameters are estimated by ensuring three conditions:

- Equation 2.4-31 is determined either through molecular simulation data or by utilizing a precise empirical Equation of state. It is set equal to the bridge function at $r=0$, as specified in Equation 2.4-32
- The pressure calculated through the virial route is equated to the pressure obtained via the compressibility route.
- The internal energy calculated is equal to the internal energy from simulation data.

They also used the WCA partition scheme for the $s(r)$ function.

This closure is difficult to implement for large number of state points especially if the phase diagram is to be calculated. Therefore, a new closure similar to the *ZSEP* is proposed where instead of using three adjustable parameters, two density functions are used and fitted to a limited amount of state points using simulation data for the bridge function. The new modified lee closure is as follows

$$B(r) = -\frac{\xi s^2}{2} \left(1 - \frac{\alpha s(r)}{(1 + \alpha s(r))} \right) \quad 2.4-33$$

where $\xi = x_1 + x_2 \rho$ and $\alpha = x_3 + x_4 \rho$, x_1 , x_2 , x_3 and x_4 are adjustable parameters determined using the same conditions above. Furthermore, *DUH* partition scheme is used here instead of the *WCA*.

Chapter 3

THERMODYNAMIC PROPERTIES FROM INTEGRAL EQUATION THEORIES

3.1 Lennard-Jones Potential

The Lennard-Jones potential is one of the most used intermolecular potentials in simulation experiments.

$$u_{LJ} = 4\varepsilon \left(\left[\frac{\sigma}{r} \right]^v - \left[\frac{\sigma}{r} \right]^u \right) \quad 3.1-1$$

where ε is the depth of the attractive well and σ is the interparticle distance. This form of the potential was initially proposed by Jones and Chapman (1924a, 1924b) to try and describe the interaction energy of noble gas crystals such as argon. Later in (1931) Lennard-Jones proposed the final form of the potential where $v = 12$ and $u = 6$ after London (1930) found that the attractive interaction between atoms decays at r^{-6} . It was discovered that the Lennard-Jones potential was not a good potential to describe the interaction between argon atoms (Maitland and Smith, 1971). However, the first Monte Carlo simulation on argon using the Lennard-Jones potential was performed by Wood and Parker (1957) and the first Molecular Dynamics simulation done by Rahman (1964) showed unexpected good agreement with liquid argon experimental data. In the last decade or more, the Lennard-Jones potential has been used extensively as the model potential for any simulation experiment describing simple symmetric atoms or molecules. The Lennard-Jones potential has also been used in describing interactions for some unsymmetric molecules and in some cases nano-colloids with less accuracy. The Lennard-Jones potential is not without disadvantages, particularly in computer simulation experiments. One drawback is

that the potential is of infinite range and hence many truncate the potential to a distance r_c where $r_c = 2.5\sigma$ or whatever they see fit. Thermodynamic and structural data produced from different simulations of the Lennard-Jones potential at different r_c differ up to 30%. Another disadvantage is that for some complicated systems the range of attraction is very high compared to the effective particle diameter (Barker *et al.*, 1971; Wang *et al.*, 2020). With integral Equation theories, the Lennard-Jones potential is truncated at a larger distance. However, the accuracy of the structural and thermodynamic data calculated greatly depends on the theory used (Fowler, 1939; Sandler, 2010; Lee, 2016).

There are a lot of simulation and experimental studies conducted for the Lennard-Jones potential. The first-ever Monte Carlo calculation for molecules interacting according to the Lennard-Jones potential was done by Wood and Parker (1957). Following that, (Rahman, 1964) conducted the first molecular dynamic simulation on Liquid Argon molecules interacting with Lennard-Jones potential. Rahman assumed that the Lennard-Jones Potential had an interacting range of 2.25σ . Rahman verified his results by comparing the obtained diffusion constant with the experimental diffusion constant of liquid Argon which was in good agreement. He also compared the dependency of the diffusion constant with temperature and got a good agreement with the experimental values. Lastly, Rahman compared the peaks of the $g(r)$ Fourier transform with the x-ray scattering experiment for Liquid Argon. In (1968) Verlet devised an extrapolation technique to calculate the direct correlation function $c(r)$ beyond the Lennard-Jones cut-off range. He used either the Percus-Yevik Equation or the Mayer f -function. Verlet in his paper showed that the peaks of the total correlation function Fourier transform are affected by the values of the obtained $g(r)$ after the cutoff range which also has an impact on the thermophysical properties obtained from the $g(r)$. However, Verlet showed that the structural properties are not

greatly impacted if the cut-off was increased from 2.5σ to 3.3σ . Several simulation experiments have different ranges to cut off the Lennard-Jones Potential. For example, Mountain and Haan (1979) truncated the Lennard-Jones potential at 2σ , Barker *et al.* (1971) truncated the potential at 2.5σ , Bamdad *et al.* (2006) used a cut off of 2.5σ and most recently, Gottschalk (2021) used a cut off range of 4.5σ and 5σ in his simulation. To counter the effect of cutting off the potential and to get a fairly accurate $g(r)$ beyond the cut-off range a large number of particles is used and a long-range potential correction is added to the simulation. Doing this will increase the computation load but will not have an adverse effect on the short repulsive range of the $g(r)$ as shown in the simulation done by Verlet (1968). Different simulations of the Lennard-Jones potential calculate different structural properties and different thermophysical properties. Therefore experimental data are used to differentiate between different simulations and different results calculated by integral Equation theories.

Argon has been used extensively to test the Lennard-Jones potential through simulation calculation and experiments. Verlet (1968) and Rahman (1964) have shown that the Lennard-Jones potential produces satisfactory structural results for argon. However, there are discrepancies when comparing thermophysical properties. This is especially true at high densities where the repulsive short-range forces have a higher impact on the calculated properties. The Lennard-Jones Potential is a pairwise additive potential meaning many-body interactions are neglected. The many-body interactions have a little effect on the $g(r)$ (Green, 1960). Whereas, the many-body interactions affect the internal energy, pressure, and enthalpy. Furthermore, as the polarizability of the molecules increased the deviation between the simulated and experimental results increased (Barker *et al.*, 1971; Barker, 1986a, 1986b; Ermakova *et al.*, 1995b, 1995a). One of the best experimental studies in the literature is the work done by Yarnell *et al.* (1973).

They reported the structure factor of argon around its triple point. The calculation of accurate structure factor data depends on how accurate the $g(r)$ is calculated in the short repulsive range and the long attractive tail of the potential. Hence, provides a strict test on the accuracy of the simulation method or the integral Equation used. In this regard, the Fourier transform of the total correlation provides a similar test.

3.2 Thermodynamic Properties

The interpretation of macroscopic thermodynamic properties in terms of molecular forces can be achieved through three primary routes based on molecular distribution functions:

- The energy equation, which relates the system's internal energy to molecular interactions.
- The pressure equation, which connects the system's pressure to the molecular behavior.
- The isothermal compressibility equation, which links the compressibility of the system to molecular forces and density fluctuations.

These equations express thermodynamic properties using molecular correlation functions. The core idea is that if we possess information about molecular spatial distributions and their interaction energies, we can determine the total energy by summing the energies between molecules over their intermolecular distances, as prescribed by the distribution function.

In the case of pressure, the quantity being summed relates to the virial, which accounts for molecular interactions. In contrast, for isothermal compressibility, the focus is on number fluctuations. While for the first two properties (energy and pressure), the canonical ensemble

(*CE*) is appropriate, for studying number fluctuations, the grand canonical ensemble (*GCE*) is the more suitable thermodynamic ensemble to use.

For the Lennard-Jones potential the thermodynamic properties represented below are all in reduced form. Table 3-1 presents the properties and their reduced form.

Table 3-1 Reduced for the basic thermodynamic properties.

Property	Reduced form
Temperature	$T^* = \frac{\kappa T}{\varepsilon}$ 3.2-1
Pressure	$P^* = \frac{P\sigma^3}{\varepsilon}$ 3.2-2
Density	$\rho^* = \left(\frac{N}{V}\right)\sigma^3$ 3.2-3
Helmholtz Free Energy	$A^* = \frac{A}{N\varepsilon}$ 3.2-4
Internal Energy	$U^* = \frac{U}{N\varepsilon}$ 3.2-5

where N is the particle number, V is the volume, and the Lennard-Jones size and energy parameters are σ and ε

All the thermodynamic properties in this thesis are in reduced form even if they are not superscript with the asterisk sign (*).

3.2.1 The Internal Energy

The differential relation of the internal energy in the *CE* is presented as (Lee, 2016):

$$U = \langle E \rangle = - \left(\frac{\partial \ln Z_N}{\partial \beta} \right) \Big|_{V,N} \quad 3.2-6$$

The partition function for the pairwise additive potentials

$$Z_N = \frac{1}{N! \Lambda^{3N}} \int d\mathbf{r}_1 \dots d\mathbf{r}_N \exp \left[-\beta \sum_{i < j} \sum_j^N u(\mathbf{r}_{ij}) \right] \quad 3.2-7$$

Performing the differentiation with respect to β

$$\frac{-1}{Z_N} \left\{ \frac{1}{N! \Lambda^{3N}} \int d\mathbf{r}^N \left[-\beta \sum_{i < j}^N u(\mathbf{r}_{ij}) \right] \exp(-\beta V_N) - \frac{3NZ_N}{\Lambda} \frac{\partial \Lambda}{\partial \beta} \right\} \quad 3.2-8$$

In the case of identical particles, the interaction potential $u(\mathbf{r}_{ij})$ is equal to $u(\mathbf{r}_{km})$ for all combinations of i, j, k , and m as long as $\mathbf{r}_{ij} = \mathbf{r}_{km}$. In the summation, there are $N(N-1)/2$ distinct pairs. Thus

$$U = \frac{1}{Q_N} \frac{N(N-1)}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N u(\mathbf{r}_{12}) e^{-\beta V_N} + \frac{3N}{\Lambda} \frac{\partial \Lambda}{\partial \beta} \quad 3.2-9$$

Using Equation 2.1-8 for the pair density $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ and noting $\frac{\partial \Lambda}{\partial \beta} = \frac{\Lambda}{2\beta}$ thus

$$U = \frac{1}{Q_N} N\kappa T + \frac{1}{2} \int d\mathbf{r}_1 \int_V d\mathbf{r}_2 u(r_{12}) \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \quad 3.2-10$$

For an isotropic and homogeneous fluid, the pair correlation function, denoted as $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$, can be expressed as $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \rho^2 g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \rho^2 g^{(2)}(r_{12})$. The integration with respect to $\int d\mathbf{r}_1 d\mathbf{r}_2$ can be transformed into $\int d\mathbf{r}_1 d\mathbf{r}_{12} = V \int d\mathbf{r}_{12}$. Thus

$$U = \frac{3}{2} N\kappa T + \frac{\rho^2 V}{2} \int d\mathbf{r}_{12} u(r_{12}) g^{(2)}(r_{12}) \quad 3.2-11$$

3.2.2 Virial Pressure

The pressure in the *CE* is presented as (Lee, 2016):

$$P = \kappa T \left(\frac{\partial \ln Z_N}{\partial V} \right) \Big|_{T, N} \quad 3.2-12$$

Assuming that the particle or molecules are in a container which is cubic with a volume $V = L^3$.

The length is scaled in units of

$$r_i^* = \frac{r_i}{L} \quad 3.2-13$$

The intermolecular potential $u(\mathbf{r}_{ij})$ depends on

$$r_{ij} = |\mathbf{r}_j - \mathbf{r}_i| = \left\{ L^2 \left[(r_{jx}^* - r_{ix}^*)^2 + (r_{jy}^* - r_{iy}^*)^2 + (r_{jz}^* - r_{iz}^*)^2 \right] \right\}^{1/2} = L |\mathbf{r}_j - \mathbf{r}_i| = L r_{ij}^* \quad 3.2-14$$

The partition function can be expressed as

$$Z_N = \frac{L^{3N}}{N! \Lambda^{3N}} \int_{V^*} d\mathbf{r}_1^* \dots d\mathbf{r}_N^* \exp(-\beta V_N) \quad 3.2-15$$

where V^* is the unit volume. Given that $L=V^{1/3}$

$$\frac{\partial \ln Z_N}{\partial V} = \frac{1}{Z_N} \frac{\partial Z_N}{\partial V} = \frac{N}{V} - \frac{\beta V^N}{Q_N} \int d\mathbf{r}^{*N} \exp(-\beta V_N) \left[\sum_{i < j} \sum \frac{\partial u}{\partial V} \right] \quad 3.2-16$$

The derivative

$$\frac{\partial u(r_{ij})}{\partial V} = \frac{V^{-2/3}}{3} \mathbf{r}_{ij}^* u' = \frac{\mathbf{r}_{ij}}{3V} u' \quad 3.2-17$$

where $u' = du(r)/dr$. Since the particles are identical, the summation involves $N(N-1)/2$ terms, and each of these terms contributes the same value after integration. Thus

$$\left(\frac{\partial \ln Z_N}{\partial V} \right) \Big|_{T,N} = \frac{N}{V} - \frac{\beta V^N N(N-1)}{2Q_N} \int d\mathbf{r}^{*N} \exp(-\beta V_N) \frac{\mathbf{r}_{12}}{3V} u'(\mathbf{r}_{12}) \quad 3.2-18$$

Upon restoring $r^*=r/V$

$$\frac{P}{\kappa T} = \frac{N}{V} - \frac{\beta}{6V} \int d\mathbf{r}_1 d\mathbf{r}_2 r_{12} \frac{du(r_{12})}{dr} \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \quad 3.2-19$$

Thus

$$\frac{\beta P}{\rho} = 1 - \frac{\beta \rho}{6} \int dr 4\pi r^3 \frac{du(r)}{dr} g(r) \quad 3.2-20$$

This Equation is known as the *virial pressure* equation. It expresses the pressure in terms of the pair correlation function $g(r)$ and the derivative of the pair potential. The quantity $\mathbf{r} \cdot \nabla \mathbf{u}$ is referred to as the virial. As $g(r)$ provides information about the radial distribution of molecules around a central molecule, Equation (3.2-20) represents the averaged virial ($\mathbf{r} \cdot \nabla \mathbf{u}$ weighted by $g(r)$).

The first term, "1", represents the kinetic contribution to the pressure, which corresponds to the ideal-gas behavior. The second term is attributed to the interaction energies among the molecules and is termed the configurational contribution. When the potential energy $u(r)$ is equal to zero ($du/dr = 0$), Equation (3.2-20) simplifies to $PV/NkT = 1$, which is the ideal-gas equation. Thus, the ideal gas is recognized as a system of noninteracting particles.

3.2.3 Isothermal compressibility

In the GCE the average number $\langle N \rangle$ (Lee, 2016):

$$\langle N \rangle = \kappa T \left(\frac{\partial \ln Z}{\partial \mu} \right) \Big|_{T,V} \quad 3.2-21$$

where μ is the chemical potential and Z is the grand canonical partition function.

The variance around the mean number is presented as follows:

$$\langle N^2 \rangle - \langle N \rangle^2 = (\kappa T)^2 \left(\frac{\partial^2 \ln Z}{\partial \mu^2} \right) \Big|_{T,V} = \kappa T \left(\frac{\partial \langle N \rangle}{\partial \mu} \right) \Big|_{T,V} \quad 3.2-22$$

at constant temperature $d\mu = v dP$ where v is the specific volume (V/N), thus

$$\left(\frac{\partial \mu}{\partial v} \right) \Big|_T = v \left(\frac{\partial P}{\partial v} \right) \Big|_T \quad 3.2-23$$

and

$$-\frac{N^2}{V} \left(\frac{\partial \mu}{\partial N} \right) \Big|_{T,V} = v \left(\frac{\partial P}{\partial v} \right) \Big|_{N,T} \quad 3.2-24$$

then

$$\left(\frac{\partial N}{\partial \mu} \right) \Big|_{T,V} = -\frac{N^2}{V^2} \left(\frac{\partial V}{\partial P} \right) \Big|_{N,T} \quad 3.2-25$$

The Isothermal compressibility K_T is defined as

$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right) \Big|_{N,T} \quad 3.2-26$$

then

$$\left(\frac{\partial N}{\partial \mu} \right) \Big|_{V,T} = \frac{N^2}{V} K_T \quad 3.2-27$$

From Equation 3.2-22

$$\langle N^2 \rangle - \langle N \rangle^2 = \langle N \rangle \rho \kappa T K_T \quad 3.2-28$$

The pair density $\rho^{(2)}$ in the *GCE* is defined as

$$\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = Z^{-1} \sum_{N \geq 2} \frac{z^N}{(N-2)!} \int d\mathbf{r}_3 \dots d\mathbf{r}_N \exp(-\beta V_N) \quad 3.2-29$$

where z called the activity $z \equiv \exp(\beta \mu) / \Lambda^3$. Integration of $\rho^{(2)}$ over $\mathbf{r}_1$ and $\mathbf{r}_2$ gives

$$\int d\mathbf{r}_1 d\mathbf{r}_2 \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = Z^{-1} \sum_{N \geq 2} N(N-1) \left[\frac{z^N Q_N}{N!} \right] \quad 3.2-30$$

The factor $Z^{-1} \left[\frac{z^N Q_N}{N!} \right]$ represents the probability of having N particles in the open system. Thus

$$\int d\mathbf{r}_1 d\mathbf{r}_2 \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \langle N^2 - N \rangle = \langle N^2 \rangle - \langle N \rangle \quad 3.2-31$$

thus

$$\langle N^2 \rangle = \int d\mathbf{r}_1 d\mathbf{r}_2 \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) + \langle N \rangle = \langle N \rangle \rho \kappa T K_T + \langle N \rangle^2 \quad 3.2-32$$

The Isothermal compressibility is therefore defined as follows:

$$\rho \kappa T K_T - 1 = \frac{\rho}{V} \int d\mathbf{r}_1 d\mathbf{r}_2 g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \langle N \rangle \quad 3.2-33$$

For an isotropic fluid

$$\rho \kappa T K_T - 1 = \rho \int_0^\infty dr 4\pi r^2 [g(r) - 1] \quad 3.2-34$$

This is the isothermal compressibility equation. Knowledge of the pair correlation function allows for the direct calculation of the isothermal compressibility. Additionally, one can integrate K_T to obtain the pressure.

Now, two methods are available for computing the pressure: the virial (pressure) Equation (3.2-20) and the isothermal compressibility Equation (3.2-34). When the pair correlation function is exact, the pressures obtained from either Equation (3.2-20 or 3.2-34) are identical, indicating internal consistency.

3.2.4 Inverse Isothermal Compressibility

The inverse isothermal compressibility, denoted as β_T , is defined as

$$\Pi_T = \beta \left(\frac{\partial P}{\partial \rho} \right) \Big|_T \quad 3.2-35$$

For isotropic functions, the three-dimensional Fourier transforms of $h(r)$ and $c(r)$ are expressed as

$$\check{h}(k) = \int d\mathbf{r} \exp(i\mathbf{k} \cdot \mathbf{r}) h(r) = \frac{4\pi}{k} \int_0^\infty dr r \sin(kr) h(r) \quad 3.2-36$$

where $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ and $r = |\mathbf{r}|$. Furthermore,

$$\check{c}(k) = \int d\mathbf{r} \exp(i\mathbf{k} \cdot \mathbf{r}) c(r) = \frac{4\pi}{k} \int_0^\infty dr r \sin(kr) c(r) \quad 3.2-37$$

The Fourier transform of the OZ Equation (2.2-2)

$$\check{h}(k) = \frac{\check{c}(k)}{1 - \rho \check{c}(k)} \quad 3.2-38$$

Rearranging gives

$$1 + \rho \check{h}(k) = \frac{1}{1 - \rho \check{c}(k)} \quad 3.2-39$$

Taking the limit of $\rho \check{h}(k)$ as the wave vector (k) approaches zero

$$\begin{aligned} \lim_{k \rightarrow 0} \rho \check{h}(k) &= \lim_{k \rightarrow 0} 4\pi\rho \int dr r^2 \frac{\sin(kr)}{kr} h(r) \\ &= 4\pi\rho \int_0^\infty dr r^2 h(r) = \rho \kappa T K_T - 1 \end{aligned} \quad 3.2-40$$

Therefore

$$\rho \kappa T K_T = 1 + \rho \check{h}(0) = \frac{1}{1 - \rho \check{c}(0)} \quad 3.2-41$$

$$1 - \rho\check{c}(0) = \frac{1}{\rho\kappa T K_T} = \Pi_T$$

The inverse isothermal compressibility is therefore defined as

$$\beta \left(\frac{\partial P}{\partial \rho} \right) \Big|_T = 1 - 4\pi\rho \int_0^\infty dr r^2 c(r) \quad 3.2-42$$

The isothermal compressibility can be easily calculated from this equation.

3.2.5 Chemical Potential

The calculation of the excess chemical potential $\beta\mu_{ex}$ is not a straightforward process and requires a specialized analysis. The majority of theories in the literature are grounded in the Kirkwood charging formula (Kirkwood, 1935). In the context of the Kirkwood charging formula, the excess chemical potential is formulated as

$$\beta\mu_{ex} = \rho \int_0^1 d\lambda \int \frac{\partial \beta u(r, \lambda)}{\partial \lambda} g(r, \lambda) d\mathbf{r} \quad 3.2-43$$

where $g(r, \lambda)$ represents the pair correlation function between a system of partially coupled particles and a system of fully coupled particles, within a system of fully coupled particles having a diameter d . To insert a test particle into the fluid, a cavity must be formed, gradually increasing its diameter from 0 to d . The quantity $\beta\mu_{ex}$ represents the work required to create such a cavity with a diameter of d . The parameter λ is commonly referred to as the charging or coupling parameter, which governs the degree of coupling between a test particle and the other particles within the system. When $\lambda = 0$, it signifies that the test particle is absent from the system. Conversely, when $\lambda = 1$, it indicates that the test particle is fully coupled to the system, becoming indistinguishable from the other particles. The parameter λ smoothly varies between these two cases, representing intermediate coupling strengths. As an initial estimation, the increasing cavity diameter, d_g , can be approximately equal to λd . It's worth noting that there are

alternative representations for d_g (Attard, 1993). The direct use of Equation (3.2-43), necessitates a numerical integration along a specific integration path. This integration process involves repeatedly computing the pair correlation function $g(r, \lambda)$ for various values of λ , which demands a substantial computational effort.

The selection of a specific integration path for the coupling parameter λ is an important concept of topological homotopy. This crucial idea, which encapsulates the idea of a continuous transformation of a curve connecting two fixed points, has been elucidated by Kjellander and Sarman (1989) and also discussed by Lee (1992). Indeed, these authors suggested employing a straightforward linear relationship with " λ " for the correlation functions, where $h(r, \lambda) = \lambda h(r)$ and $c(r, \lambda) = \lambda c(r)$. In other words, they implicitly assume that " d_g " is equal to " λd ". However, the calculated $\beta\mu_{ex}$ is considered an approximate and not exact.

The chemical potential can also be evaluated using Classical Thermodynamic Integration. For a given thermodynamic state point (ρ_0, T_0) the excess Helmholtz free energy A^{ex} can be obtained from the following

$$\beta A^{ex}(\rho_0, T_0) = \rho \int_0^{\rho_0} \left(\left(\frac{\beta P(\rho, T_0)}{\rho} \right) - 1 \right) \frac{d\rho}{\rho} \quad 3.2-44$$

the excess chemical potential is then determined from $\mu_{ex} = A^{ex} + P/\rho$, with the pressure in this context being either the virial pressure or the pressure derived from the compressibility equation. It's important to emphasize that Equation 3.2-44 is applied along the isotherm of T_0 . Therefore, if the density is close to the liquid phase, Equation 3.2-44 may not be applicable since numerical techniques used to solve the OZ Equation like the Picard method and Newton Raphson methods fail in the region of the spinodal and the coexisting phases. However, the *CPE* method is proficient in solving the OZ Equation within these regions. In the subsequent sections of this

thesis, the primary approach for computing the chemical potential will be Equation 3.2-44. In the low-density vapor region, Equation 3.2-44 is adequate for calculating the chemical potential using any method. However, in the liquid region, Equation 3.2-44 becomes inapplicable due to the nature of the integration path. Therefore, for the liquid region, the chemical potential is calculated with the assistance of the internal energy, employing the following equation

$$\beta A^{ex}(\rho, T) = \beta A^{ex}(\rho, T_{ref}) - \int_{T_{ref}}^T \beta U^{ex} \frac{dT'}{T'} \quad 3.2-45$$

where T_{ref} represents a selected reference state point, and the integration is performed on an isochore from T_{ref} to the desired state point T . Typically, the chosen reference state is a supercritical state point, as the $g(r)$ at such a point is readily calculable from the OZ Equation using various methods.

Additional thermodynamic properties will be based on the properties previously described. These properties, along with their corresponding equations, are detailed in Table 3-2.

Table 3-2 Various thermodynamic properties

Property	Equation	
Isochoric Heat Capacity (C_v)	$\left(\frac{\partial U}{\partial T}\right)_v$	3.2-46
Isobaric Heat Capacity (C_p)	$C_v + T \frac{\left(\frac{\partial P}{\partial T}\right)^2}{\rho^2 \frac{\partial P}{\partial \rho}}$	3.2-47
Speed of Sound (ω)	$\sqrt{\frac{C_p}{C_v} \frac{\partial P}{\partial \rho}}$	3.2-48
Joule-Thomson coefficient (μ_{JT})	$\frac{1}{\rho C_p} \left(T \frac{\frac{\partial P}{\partial T}}{\rho \frac{\partial P}{\partial \rho}} - 1 \right)$	3.2-49
Grüneisen coefficient (Γ)	$\frac{\left(\frac{\partial P}{\partial T}\right)_\rho}{\rho C_v}$	3.2-50
Thermal Pressure coefficient (γ)	$\left(\frac{\partial P}{\partial T}\right)_\rho$	3.2-51
Thermal Expansion coefficient (α)	$\frac{\frac{\partial P}{\partial T}}{\rho \frac{\partial P}{\partial \rho}}$	3.2-52

3.3 Phase Diagram Calculation

For pure components, the conditions for the coexistence of two phases, labeled as phase 1 and phase 2, in contact with each other are established by the following criteria:

$$T_1 = T_2; \quad P_1 = P_2; \quad \mu_1 = \mu_2 \quad 3.3-1$$

where, T_i , P_i , and μ_i represent the temperature, pressure, and chemical potential, respectively, of the i th phase (either phase 1 or phase 2). Equation 3.3-1 represents the thermal, mechanical, and chemical equilibrium between the two phases (Elliott *et al.*, 2012).

The condition of phase stability for a one-component system can be articulated through the behavior of the Helmholtz free energy, by asserting that:

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,N} = -\left(\frac{\partial P}{\partial V}\right)_{T,N} = \frac{1}{VK_T} > 0 \quad 3.3-2$$

In Equation 3.3-2, a positive value of the isothermal compressibility, K_T , indicates the mechanical stability of the system. In a standard depiction of a van der Waals isotherm, the points where K_T equals infinity correspond to the maximum and minimum points on the isotherm. These points collectively form the spinodal line. The binodal line, on the other hand, delineates the volumes of coexisting liquid and vapor at each temperature. These volumes can be determined either through the Maxwell construction or by equating the chemical potentials of the two phases (Elliott *et al.*, 2012).

3.4 Thermodynamic Consistency

The aim is to achieve exact outcomes at both structural and thermodynamic levels, as the thermodynamic variables are determined from integrals over $g(r)$ and $c(r)$. One must recognize that achieving self-consistency in a theory does not inherently guarantee its exactness in both structural and thermodynamic contexts at the same time. The primary strategy adopted is essentially to compel the theory to conform to certain equalities pertaining to the pressure as derived from the structure (Bomont, 2008).

Multiple methods exist for computing pressure. It can be determined using Equation 3.2-20, known as the virial equation, or through the integration of the isothermal compressibility with respect to density as indicated by the subsequent equation.

$$\rho \left(\frac{\partial P}{\partial \rho}\right) \Big|_T = \frac{1}{K_T} \quad 3.4-1$$

Pressure calculated via the virial Equation is indicated as $\left(\frac{\beta P}{\rho}\right)_v$, while pressure determined from Equation 3.4-1 is signified as $\left(\frac{\beta P}{\rho}\right)_c$. Additionally, the isothermal compressibility, K_T , is computed using

Equation 3.2-34. A third approach is centered around the employment of the excess internal energy, U^{ex} , which is connected to the excess Helmholtz free energy, A^{ex} . The relationship is defined as $U^{ex} = [\partial(\beta A^{ex})/\partial\beta]_v$. Subsequently, U^{ex} can be integrated with respect to the inverse temperature β along an isochoric path to obtain A^{ex} . The excess pressure, P^{ex} , is then derived from this relationship. Pressure calculated via this energy route is indicated as $\left(\frac{\beta P}{\rho}\right)_E$. An exact $g(r)$ ensures that all the aforementioned quantities attain an identical value.

Isothermal compressibility may serve as an alternative to pressure in order to maintain consistency between the virial and compressibility routes, as outlined by the following relationship

$$\beta \left(\frac{\partial P}{\partial \rho} \right) \Big|_T = \frac{1}{\rho \kappa T K_T} \quad 3.4-2$$

This approach is adopted to circumvent the need for integration. Moving forward, this Equation is utilized to ensure consistency within specific closures that require it. The computation of $\left(\frac{\beta P}{\rho}\right)_E$ is notably computationally intensive and thus, may not be practical for integration into a working theory, particularly when the objective is to calculate the phase diagram.

Chapter 4

COUPLING-PARAMETER EXPANSION AND COMPUTATIONAL METHODS FOR ORNSTEIN– ZERNIKE EQUATION

4.1 Introduction

The solution of integral equation theories has a long history of challenges and difficulties that affect their use as a major tool for liquid solution theories. While the early attempts were dedicated to simple interparticle pair potential, the analytical solution was not possible except for a few cases related to simple fluids such as hard sphere fluid. This is why the major interest has been paid to numerical techniques. At first, it may appear that the advances in computers can make integral equation theories accessible for studying liquid solution theories; nonetheless, it turns out that even the numerical methods have major obstacles that are tedious and difficult to overcome. It has been recognized at early stages that the solution in Fourier space is more convenient than that of real space. However, two major problems appeared, the first one is related to solution convergence and the second one is the existence of solutions. Because integral equations theories are approximate, the most efficient numerical techniques does not guarantee the existence of solution. In this chapter, we introduce the so-called coupling-parameter expansion (*CPE*) and how it can be employed to Lennard-Jones fluid. Then, we give an overview about the utilized numerical methods.

4.2 Numerical Methods in real and Fourier spaces

The *OZ* Equation necessitates numerical solutions, making the use of a numerical iteration method indispensable. Two primary types of iteration methods are usually employed; namely the Picard method and the Newton-Raphson method in real and Fourier spaces.

The Picard method is a well-regarded scheme extensively used for solving coupled integral equations, similar to the *OZ* equation. The objective of the Picard iteration method is to resolve the presented equations

$$c(r) = F[\gamma(r)] \quad 4.2-1$$

$$\tilde{\gamma}(k) = \frac{\rho \tilde{c}(k)^2}{k - \rho \tilde{c}(k)} \quad 4.2-2$$

where $F[]$ corresponds to the closure relation given by Equation 2.2-3. The Picard method is a straightforward direct iteration technique, where an initial projection of the $\gamma(r)$ function is used as the input for Equation 4.2-1. The resultant $c(r)$ is then transformed into $\tilde{c}(k)$ through Fourier transform and then incorporated into Equation 4.2-2, which is the Fourier-transformed version of the *OZ* equation. The resulting $\tilde{\gamma}(k)$ is then reconverted to $\gamma(r)$ using the inverse Fourier transform and reintroduced into Equation 4.2-1. This constitutes a single iteration. The procedure is repeated until successive iterations of $\gamma(r)$ meet a specified convergence criterion. When dealing with a radially symmetric function $f(r)$, the Fourier transforms, and inverse transforms are calculated using the Fourier-Bessel transformation

$$\tilde{f}(k) = 4\pi \int_0^\infty f(r) \frac{\sin(kr)}{kr} r^2 dr \quad 4.2-3$$

$$f(r) = \frac{1}{2\pi^2} \int_0^\infty \tilde{f}(k) \frac{\sin(kr)}{kr} k^2 dk \quad 4.2-4$$

The Picard method is recognized for its lower consumption of computing resources and disk space compared to other iteration methods. Nonetheless, its robustness can be a concern, as it may lead to divergent solutions even when dealing with non-stiff equations. This is due to its lack of dependency on minimizing any Equation parameters to diminish the residual vector, indicating that it does not exert control over the iterative process. To address stiff problems, a mixing function between $\gamma(r)$ iterations is proposed as follows

$$\gamma(r)^{i+1} = \alpha\gamma(r)^i + \gamma(r)^{i-1} \quad 4.2-5$$

In this case, α , ranging between 0 and 1, represents the mixing parameter. Adjusting this parameter allows for the regulation of how the new solution is combined with the previous one. Nonetheless, even with this control, robust convergence cannot be assured. Convergence is found to be satisfactory only near the ideal gas state. For conditions of higher densities and lower temperatures, selecting an extremely precise initial estimate becomes crucial, and it may be necessary to dampen or even extrapolate the successive approximations to ensure accuracy (Broyles, 1960).

An alternative approach for solving the OZ Equation involves applying Equation 2.2-2 in a discrete format and resolving a set of non-linear equations using the Newton-Raphson (NR) method. This method can achieve rapid convergence when a reliable initial estimate is provided. However, it typically requires solving a big number of equations, often ranging from 100 to 1000 (Smith *et al.*, 1974).

A modified approach is to utilize the Baxter's forms of the Ornstein-Zernike (OZ) Equation (Baxter, 1967a, 1968a). Watts (1968) used Baxter's Equation and developed a modified Newton-Raphson (NR) method. In comparison to earlier approaches, this method reduced the number of equations by approximately half, but calculating the involved matrix was laborious. In

a similar manner, Kohler *et al.* (1975) implemented a direct iterative process but with an alternative form of Baxter's OZ equation (1968a). Despite the extensive effort, challenges associated with convergence were again faced, particularly in the liquid region.

Unlike the others who focused on either Picard or Newton methods, Gillan (1979) introduced a technique that combines elements of both methods. The Gillan's method focused on $\gamma(r)$ function, which was decomposed into two components: a 'coarse' part, expressed as an expansion in roof functions P_j , and a 'fine' part, denoted as $\Delta\gamma(r)$

$$\gamma(r) = \sum_{j=1}^M a_j P_j(r) + \Delta\gamma(r) \quad 4.2-6$$

The coefficients a_j were then determined using the Newton-Raphson (NR) method, while the $\Delta\gamma(r)$ was calculated through direct iterations. Typically, M , varies from 6 to 10. The function $\Delta\gamma(r)$ tends to be close to zero, ensuring that the direct iterations converge quickly.

Labik *et al.* (1985) used a similar approach to the Gillan's method but instead of using the roof function as basis function they used the sine function as a basis function. The use of sine functions for expansion is considered more intuitive than using roof functions, a distinction that is evident in the computational process. Unlike Gillan's method, the calculation of the Jacobian matrix in this approach is significantly faster, and importantly, Fourier transformations are not required in the Newton-Raphson (NR) iterations. While these benefits are somewhat balanced by an approximately threefold increase in the number of equations (ranging from 15-30 instead of 6-10), it has been demonstrated that the total number of arithmetic operations in the NR iteration process is reduced by about a factor of ten. Labik *et al.* (1985) method is also centered around the $\gamma(r)$ function. The $\Gamma(r_i)$ function is represented as $r_i\gamma(r_i)$ and its inverse Fourier transform in the discrete form

$$\Gamma_i = \frac{\Delta k}{2\pi^2} \sum_{j=1}^{N-1} \tilde{f}_j \sin\left(\frac{\pi}{N} ij\right) \quad i = 1, 2, \dots, N-1 \quad 4.2-7$$

where $\Gamma_i = \Gamma(r_i)$ and $\tilde{\Gamma}_j = \tilde{\Gamma}(k_j)$. The function $C(r_i) = C_i = r_i c(r_i)$ and Equation 2.2-3 can be written as

$$\mathbf{c}(\mathbf{r}) = \exp[-\boldsymbol{\beta} \mathbf{u}(\mathbf{r}) + \mathbf{h}(\mathbf{r}) - \mathbf{c}(\mathbf{r}) + \mathbf{B}(\mathbf{r})] - \mathbf{1} \quad 4.2-8$$

Thus $C_i = f(\Gamma_i)$ and its Fourier transform in the discrete form

$$\tilde{C}_j = \tilde{C}(k_j) = 4\pi\Delta r \sum_{i=1}^{N-1} C_i \sin\left(\frac{\pi}{N} ij\right) \quad j = 1, 2, \dots, N-1 \quad 4.2-9$$

where $ri = i\Delta r, kj = j\Delta k$ and $\Delta r\Delta k = \pi/N$. The first-order expansion of the function C_i in Equation 4.2-8 around the point Γ_i^0 is expressed as follows:

$$C_i = C_i^0 + \phi_i^0 (\Gamma_i - \Gamma_i^0) \quad 4.2-10$$

where

$$\phi_i^0 = \left(\frac{df}{d\Gamma_i} \right)_{\Gamma_0=\Gamma_i^0} \quad \text{and} \quad C_i^0 = F(\Gamma_i^0) \quad 4.2-11$$

The Fourier transform of Equation 4.2-10 is given by:

$$\tilde{C}_j = \tilde{C}_j^0 + 4\pi\Delta r \sum_{i=1}^{N-1} \phi_i^0 (\Gamma_i - \Gamma_i^0) \sin\left(\frac{\pi}{N} ij\right) \quad 4.2-12$$

Equation 4.2-7 is used for Γ_i and Γ_i^0 in terms of

$$\tilde{C}_j = \tilde{C}_j^0 + \sum_{k=1}^{N-1} \tilde{C}_{j,k} (\tilde{\Gamma}_k - \tilde{\Gamma}_k^0) \quad 4.2-13$$

where

$$\tilde{C}_{j,k} = \frac{2}{N} + \sum_{i=1}^{N-1} \phi_i^0 \sin\left(\frac{\pi}{N} ik\right) \sin\left(\frac{\pi}{N} ij\right) \quad 4.2-14$$

By replacing the terms in Equation 4.2-2 with $\tilde{C}_j$ from equations 4.2-13 and 4.2-14, we obtain a series of $(N - 1)$ non-linear equations for the unknown $\tilde{T}_j$. This method is efficient and tends to converge readily, provided the initial estimate of $\tilde{T}_j$ is appropriately chosen. A significant limitation of this method, as well as all other methods employed to solve the OZ equation, is their inability to describe the phase coexistence and metastable regions. Hence, it has been obvious that the solution cannot be obtained with only efficient numerical techniques.

4.3 The Coupling-Parameter Expansion

4.3.1 Theory foundation

The Coupling Parameter Expansion method (*CPE*) successfully addresses the limitations of the Labik method, enabling the effective calculation of the numerical solutions within the phase coexistence region. In the initial formulations of Thermodynamic Perturbation Theory (*TPT*), it is assumed that the structural and thermodynamic properties of the reference system are known, and the thermodynamic properties of the actual system are calculated as minor deviations from the reference system. This approach presumes that the structure of both the reference and actual systems are identical. However, within this framework, it is not feasible to extend beyond the second-order term in the perturbation series, as this would necessitate higher-order correlation functions (Barker and Henderson, 1967a, 1967b).

Zhou (2006) developed a technique in which the Helmholtz free energy of a system is expressed as a series expansion over the coupling parameter ζ . This method involves the calculation of derivatives of the pair correlation function at $\zeta = 0$. Zhou (2008) utilized the finite-difference method to compute these derivatives, enabling the derivation of terms in the perturbation series up to the sixth order. As one progresses to higher orders in this approach, numerical differentiation introduces errors, and the data sets of the derivatives of the pair

correlation function need extra smoothing to eliminate fluctuations. Consequently, it becomes challenging to compute the derivatives of the $g(r)$ to an arbitrary order.

Furthermore, for inter-particle potentials with very short ranges, the convergence of the free energy series slows down significantly, demanding the evaluation of higher order terms for accurate results. Ramana and Menon (2013) and Ramana (2013) approached the issue more fundamentally by incorporating the concepts of Integral Equation Theory (*IET*) and Thermodynamic Perturbation Theory (*TPT*). This combined approach aimed to address the limitations and challenges inherent in each individual theory. In their approach, it is assumed that the $g(r)$ and the $c(r)$ of a system can be expressed as Taylor series in the coupling parameter ζ , evaluated at $\zeta = 0$. It was demonstrated that the terms in the Taylor series of both $g(r)$ and $c(r)$ (i.e., their derivatives) can be determined by solving a straightforward set of equations. These equations are derived by differentiating the *OZ* Equation and the generalized closure with respect to ζ . Within this framework, the formula for free energy proposed by Zhou can also be derived, in addition to obtaining the $g(r)$ and $c(r)$ of the actual system.

Ramana and Menon (2013) successfully computed $g(r)$ and $c(r)$ within the spinodal and near the critical region, achieving this without any convergence issues in their iteration scheme, despite its simplicity. This accomplishment has prompted a reevaluation of the existence of solutions to the *OZ* Equation within the spinodal region. While Sarkisov (2001) hypothesized that solutions to the *OZ* Equation do exist in the spinodal region, as far as our knowledge goes, the spinodal lines have not been predicted from integral equation theories.

The $g(r)$ and $c(r)$ values in the two-phase region are particularly relevant in the density functional theory of fluids, notably in calculations like surface tension. These calculations require the $c(r)$ within the two-phase region (Evans, 1979). However, due to the lack of solutions

of integral Equation theories in certain parts of the phase envelope, previous calculations of surface tension often relied on an interpolation formula provided by Ebner *et al.* (1976) to ascertain $c(r)$ in the two-phase region.

4.3.2 Application to Lennard-Jones system

To apply *CPE*, let us assume a hypothetical pure system consisting of particles interacting by the Lennard-Jones potential at a temperature T and density ρ . The pair potential is split to a reference and perturbation terms and is given by

$$u(\zeta, r) = u_{ref}(r) + \zeta u_{pert}(r) \quad 4.3-1$$

where ζ is a coupling parameter. At $\zeta = 0$, the hypothetical system transforms into a reference system with the interaction potential $u_{ref}(r)$. When ζ is non-zero, it introduces a perturbation to $u_{ref}(r)$, as indicated in the previously mentioned equation. At $\zeta = 1$, the system reverts to its original, full potential that is the subject of the study. Therefore, the $g(r)$ and $c(r)$ of the system with a potential $u(r)$ can be formulated as a Maclaurin series in ζ . This series can be represented as follows:

$$c(\zeta, r) = c(0, r) + \zeta \left(\frac{\partial c}{\partial \zeta} \right)_{\zeta=0} + \frac{\zeta^2}{2!} \left(\frac{\partial^2 c}{\partial \zeta^2} \right)_{\zeta=0} + \dots \quad 4.3-2$$

$$g(\zeta, r) = g(0, r) + \zeta \left(\frac{\partial g}{\partial \zeta} \right)_{\zeta=0} + \frac{\zeta^2}{2!} \left(\frac{\partial^2 g}{\partial \zeta^2} \right)_{\zeta=0} + \dots \quad 4.3-3$$

From this point onward in this thesis, the n^{th} partial derivative of any function $X(\zeta, r)$ with respect ζ is denoted as $X^{(n)}(\zeta, r)$. Since $g(\zeta, r)$ and $c(\zeta, r)$ are expanded in terms of ζ , this implies that both $\gamma(\zeta, r)$ and $h(\zeta, r)$ are similarly expressed in a series of ζ . Consequently, the n^{th} order coefficient in the expanded series of $\gamma(\zeta, r)$ is represented by $\gamma^{(n)}(\zeta, r) = h^{(n)}(\zeta, r) - c^{(n)}(\zeta, r)$. Since the bridge function is function of $\gamma(\zeta, r)$, therefore the bridge

function is also a function of ζ ($B(\gamma) = B(\zeta, r)$). For the nonamilezed closures, the bridge function is defined as:

$$B(\zeta, r) = B[\gamma(\zeta, r) - \zeta u_a(r)] \quad 4.3-4$$

$u_a(r)$ could be the $u_{pert}(r)$ or any other attractive part of the Lennard-Jones potential used in the renormalization of the bridge function. The *Week-Chandler-Andersen* (WCA) is used for decomposing the potential in Equation 4.3-1 for the Lennard-Jones potential. The general formula for the n^{th} order derivative of $g(\zeta, r)$ is expressed in the following manner:

$$g^{(n)}(\zeta, r) = \sum_{m=0}^{n-1} B_m^{(n-1)} \psi^{(n-m)} g^{(m)}(\zeta, r) \quad n \geq 1 \quad 4.3-5$$

where $[B_m^{(n-1)}]$ is the binomial coefficient and the $\psi^{(n)}(\zeta, r)$ is the potential mean force derivatives and are denoted as

$$\psi^{(n-m)}(\zeta, r) = -\beta u_{pert}(r) \delta_{n,1} + \gamma^{(n)}(\zeta, r) + B^{(n)}(\zeta, r) \quad n \geq 1 \quad 4.3-6$$

where $\delta_{n,1}$ is the Kronecker delta. The $g^{(n)}(\zeta, r)$ values are calculated recursively using Equation 3.4-19. This process utilizes $\psi^{(n)}(\zeta, r)$, which is derived either from an initial guess or from the result of the previous iteration.

Since $c(\zeta, r) = g(\zeta, r) - \gamma(\zeta, r) - 1$, its n^{th} order derivative is

$$c^{(n)}(\zeta, r) = g^{(n)}(\zeta, r) - \gamma^{(n)}(\zeta, r) \quad n \geq 1 \quad 4.3-7$$

To establish a second set of relationships between $c^{(n)}(\zeta, r)$ and $\gamma^{(n)}(\zeta, r)$, the OZ Equation in Fourier space is employed as follows:

$$\tilde{h}(\zeta, k) = \frac{\rho \tilde{c}(\zeta, k)}{1 - \rho \tilde{c}(\zeta, k)} \quad 4.3-8$$

In this context, $\tilde{h}(\zeta, k)$ and $\tilde{c}(\zeta, k)$ represent the Fourier transforms of $h(\zeta, r)$ and $c(\zeta, r)$, respectively. Furthermore, the structure factor $\tilde{S}(\zeta, k)$ is defined as

$$\tilde{S}(\zeta, k) = \frac{1}{1 - \rho \tilde{c}(\zeta, k)} \quad 4.3-9$$

$$\tilde{S}(\zeta, k) = 1 + \rho \tilde{h}(\zeta, k) \quad 4.3-10$$

By differentiating Equation 4.3-9 n times, the resulting expression is obtained as follows:

$$\tilde{S}^{(n)}(\zeta, k) = \tilde{S}^{(0)}(\zeta, k) \rho \sum_{m=0}^{n-1} B_m^{(n-1)} \tilde{c}^{(n-m)}(\zeta, k) \tilde{S}^{(m)}(\zeta, k) \quad n \geq 1 \quad 4.3-11$$

Utilizing Equation 4.3-10, the derivatives of $\tilde{\gamma}(\zeta, k) = \tilde{h}(\zeta, k) - \tilde{c}(\zeta, k)$ can be expressed in the following manner:

$$\tilde{\gamma}^{(n)}(\zeta, k) = \rho^{-1} \tilde{S}^{(n)}(\zeta, k) - \tilde{c}^{(n)}(\zeta, k) \quad n \geq 1 \quad 4.3-12$$

Therefore, to acquire terms up to the n^{th} order in the Taylor series expansion of both $c(1, r)$ and $g(1, r)$, it is necessary to simultaneously solve N coupled linear equations in real space and N coupled linear equations in Fourier space, with ζ set to 0. The structure factor of the reference system, denoted as $\tilde{S}^{(0)}(\zeta, k)$ is derived by resolving the OZ equation with a chosen closure, but specifically for the reference part of the potential. In the case of the Lennard-Jones potential, the reference component is determined using the WCA partition scheme, and the OZ Equation is solved by employing the Labik method.

The CPE for the Helmholtz free energy density, $f(T, \rho) = -\beta \rho A^{ex\rho}$, of a homogeneous fluid at a specified temperature T , is given by (Hansen and McDonald, 2013):

$$f(T, \rho) = f_{ref}(\rho) + \frac{\rho^2}{2} \int_0^1 d\zeta \int dr u_{pert}(r) g(\zeta, r) \quad 4.3-13$$

In this equation, $f_{ref}(\rho)$ represents the free energy density of the reference system. By substituting Equation 4.3-3 into Equation 4.3-13 and then integrating over ζ , the resulting expression becomes:

$$f(T, \rho) = f_{ref}(\rho) + \frac{\rho^2}{2} \int dr u_{pert}(r) \left(g(0, r) + \frac{1}{2!} \left(\frac{\partial g}{\partial \zeta} \right)_{\zeta=1} + \frac{1}{3!} \left(\frac{\partial^2 g}{\partial \zeta^2} \right)_{\zeta=1} + \dots \right) \quad 4.3-14$$

Such a procedure is not only applicable for the direct correlation function $c(r)$ and the pair correlation function $g(r)$ but also the free energy density.

As will be shown in the next chapter, the implementation of CPE with integral equation theories can extend the solution of OZ equation to some regions that have not been explored before. For instance, it is possible to explore the metastable region and predict for the first time the spinodal lines and isotherms from the OZ equation with different closures. We explore 15 closures and predict the binodal and spinodal lines.

Chapter 5

ORNSTEIN–ZERNIKE EQUATION RESULTS FOR LENNARD-JONES FLUID

5.1 Introduction

Considerable attention has been paid to the development of integral equation theories for liquid solution theories over the years. The study of these theories may raise two questions: what is the most accurate theory for predicting structure and thermodynamic properties and what are the limitations of each theory?. To answer the first question, we begin with a quote from Malijevsk and Kolafa, who tried to answer the first question: “*it is not easy to answer the first question unambiguously. Different closures were tested on computer simulation data of different precision in different ranges of state variables by different authors.*” Their quote was related to hard sphere system, which is far simpler than that of Lennard-Jones system.

There are several factors that make the comparison difficult. However, one of the major obstacles is that it is hard to solve the *OZ* equation with different closures. In fact, Lomba (1994) concluded that most closures fail to give solution at certain regions for Lennard-Jones and other systems. To investigate these problems, extensive comparisons are made for 14 closures with the *OZ* equation for Lennard-Jones potential. Because it is known that the numerical solution may break down at certain regions, we implement the *CPE* for these closures.

Therefore, in this chapter, we present the results with and without *CPE*. To make it easy to distinguish the results, the solutions of the integral equations will be simply denoted by *CPE* if *CPE* is implemented to the closure. Otherwise, the results of integral equations will be denoted

by *non-CPE*. We emphasize that the *non-CPE* is basically the classical approach that has been used in the literature. For that, Labik numerical technique is utilized for solving the integral equations.

5.2 Approach for comparison

Table 5-1 summarizes the closures studied in this thesis. Their mathematical formulations were given in Chapter 2. The results will be given for these closures with *CPE* and *non-CPE*.

Table 5-1 Closures used in the analysis of Lennard-Jones fluid.

Author	Year	Closure
Percus and Yevick	1958	PY
Morita and Hiroike	1960	HNC
Rosenfeld and Ashcroft	1979	MHNC
Madden and Rice	1980	sMSA
Verlet	1980	Verlet
Martynov and Sarkisov	1983	MS
Rogers and Young	1984	RY
Zerah and Hansen	1986	HMSA
Duh and Haymet	1995	DUH
Duh and Henderson	1996	MDUH
Lee	1996	ZSEP
Kovalenko and Hirata	1999	KH
Martynov <i>et al.</i>	1999	VM
Choudhury and Ghosh	2002	MV

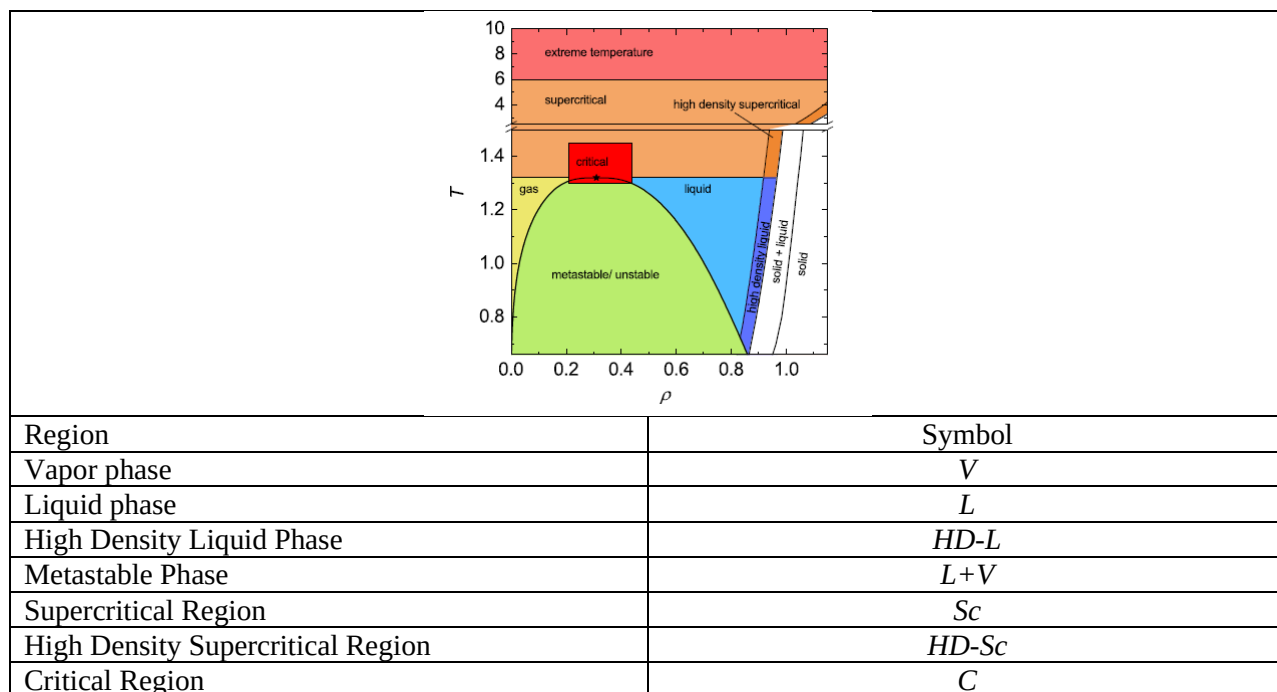
The results presented in this chapter include detailed comparisons between 14 closures, which are summarized in Table 5-1. The comparisons involve predictions of thermodynamic and structure properties. Table 5-2 summarizes the major quantities considered in this study for the comparisons. The comparisons are conducted by comparing the results of these quantities from the closures against molecular simulation data. Stephan *et al.* (2019) conducted a detailed assessment for the *LJ* simulation data in the literature. We use this detailed data for the comparison.

Table 5-2 The properties and correlation functions calculated for the analysis of Lennard-Jones fluid

Thermodynamic properties	
Quantity	symbol
Isothermal compressibility	K_T
Thermal Pressure coefficient	γ
Joule-Thomson coefficient	μ_T
Grüneisen coefficient	Γ
Speed of Sound	ω
Isobaric Heat Capacity	C_p
Isochoric Heat Capacity	C_v
Residual Internal Energy	U^{res}
Equation of State	P
Structure properties	
Function	symbol
Pair correlation function	$g(r)$
Bridge function	$B(r)$
Other criteria for comparisons	
▪ Thermodynamic consistently test ▪ Phase Diagram ▪ Critical point evaluation	

To proceed in a systemic manner, we follow the classification proposed by Stephan *et al.* (2019) who divided the fluid region into seven regions as shown in Table 5-3. To show these regions clearly, we inserted the figure into the table for easy access

Table 5-3 Region classification for the Lennard-Jones fluid



5.3 Results and Discussion

As previously discussed, the thermodynamic consistency constraint is established by equating the isothermal compressibility. This is achieved by differentiating the pressure, as calculated from Equation 3.2-20, with respect to density, and then comparing it with the isothermal compressibility calculated from Equation 3.2-34. This process is concisely encapsulated in Equation 3.4-2. Hence, Equation 3.4-2 serves as the objective function in scenarios involving closures that enforce thermodynamic consistency, such as the *HMSA*, *RY*, and *MHNC* closures. This function must be minimized for each state point, a task that becomes computationally demanding when dealing with a large number of state points.

For the *ZSEP* (Zero Separation Enforced closure for Perturbed chains) closure, we suggested a similar approach, but rather than ensuring the consistency conditions for every individual state point, we employed two functions to simultaneously fit a limited number of state

points. The proposed consistency conditions include Equation 3.4-2 and simulation data for the bridge function. Specifically, we utilized the simulation data from Llano-Restrepo and Chapman (1992). The objective function used in this fitting process is outlined as follows:

$$f_{obj} = \sum_j \frac{1}{n} \sum_i^n 0.6 |B_j^{sim}(r_i) - B_j^{ZSEP}(r_i)| + 0.4 |K_T^{virial}(r_i) - K_T^{comp}(r_i)| \quad 5.3-1$$

where j is the number of state points used in the minimization process.

In the case of the *MHNC* closure, two different parameterizations of the hard sphere bridge function were employed. The first one is the Verlet and Weis (1972) parameterization, denoted as *MHNC-V*, and the second one is the Maličevský and Labík (1987) parametrization, referred to as *MHNC-L*.

Classical approaches, such as the Labik method for solving the *OZ* integral equation, have traditionally been the standard. The *CPE* method, being a relatively new approach, necessitates a comparison with the Labik method. This comparison is conducted in the region where the Labik method is known to be effective and does not fail. In this regard the thermodynamic properties calculated from each approach are summarized in Table 5-4 and Table 5-5. On the other hand, the structure properties that are evaluated by each method for select closures are presented in **Error! Reference source not found.**, Figure 5-2, Figure 5-3, and Figure 5-4.

Table 5-4 Pressure, Internal Energy, and Isothermal compressibility at T=1.2 and $\rho = 0.07$

Closure	Pressure			Internal Energy			Isothermal compressibility		
	<i>Non-CPE</i>	<i>CPE</i>	<i>SIM</i>	<i>Non-CPE</i>	<i>CPE</i>	<i>SIM</i>	<i>Non-CPE</i>	<i>CPE</i>	<i>SIM</i>
<i>PY</i>	0.063	0.063	0.063	-0.590	-0.583	-0.587	23.667	23.307	23.475
<i>HNC</i>	0.063	0.063	0.063	-0.590	-0.583	-0.587	23.933	23.300	23.475
<i>SMSA</i>	0.059	0.059	0.063	-0.523	-0.523	-0.587	17.826	17.827	23.475
<i>DUH</i>	0.063	0.063	0.063	-0.588	-0.583	-0.587	23.296	23.042	23.475
<i>MDUH</i>	0.063	0.063	0.063	-0.590	-0.583	-0.587	23.671	23.065	23.475
<i>MS</i>	0.063	0.063	0.063	-0.590	-0.583	-0.587	23.670	23.309	23.475
<i>Verlet</i>	0.063	0.063	0.063	-0.590	-0.583	-0.587	23.668	23.308	23.475
<i>VM</i>	0.062	0.063	0.063	-0.589	-0.583	-0.587	23.583	23.284	23.475
<i>MV</i>	0.063	0.063	0.063	-0.590	-0.583	-0.587	23.670	23.309	23.475
<i>KH</i>	0.064	0.065	0.063	-0.525	-0.528	-0.587	18.336	18.663	23.475
<i>MHNC-V</i>	0.062	0.063	0.063	-0.590	-0.583	-0.587	23.838	23.300	23.475
<i>MHNC-L</i>	0.062	0.063	0.063	-0.589	-0.583	-0.587	23.816	23.300	23.475

Table 5-5 Pressure, Internal Energy, and Isothermal compressibility at T=0.9 and $\rho = 0.87$

Closure	Pressure			Internal Energy			Isothermal compressibility		
	<i>Non-CPE</i>	<i>CPE</i>	<i>SIM</i>	<i>Non-CPE</i>	<i>CPE</i>	<i>SIM</i>	<i>Non-CPE</i>	<i>CPE</i>	<i>SIM</i>
<i>PY</i>	2.924	2.924	1.806	-5.899	-5.899	-6.028	0.100	0.100	0.048
<i>HNC</i>	3.853	3.853	1.806	-5.671	-5.671	-6.028	0.122	0.122	0.048
<i>SMSA</i>	1.284	1.285	1.806	-6.119	-6.119	-6.028	0.041	0.041	0.048
<i>DUH</i>	1.933	1.932	1.806	-5.997	-5.997	-6.028	0.050	0.050	0.048
<i>MDUH</i>	1.881	1.865	1.806	-6.010	-6.014	-6.028	0.050	0.054	0.048
<i>MS</i>	2.964	2.951	1.806	-5.871	-5.925	-6.028	0.105	0.107	0.048
<i>Verlet</i>	3.014	3.006	1.806	-5.883	-5.884	-6.028	0.102	0.102	0.048
<i>VM</i>	2.014	2.014	1.806	-6.002	-6.002	-6.028	0.059	0.059	0.048
<i>MV</i>	1.754	1.754	1.806	-6.026	-6.026	-6.028	0.046	0.046	0.048
<i>KH</i>	4.789	4.875	1.806	-5.415	-5.405	-6.028	0.082	0.081	0.048
<i>MHNC-V</i>	1.692	1.693	1.806	-6.051	-6.051	-6.028	0.054	0.051	0.048
<i>MHNC-L</i>	1.824	1.824	1.806	-6.028	-6.028	-6.028	0.051	0.051	0.048

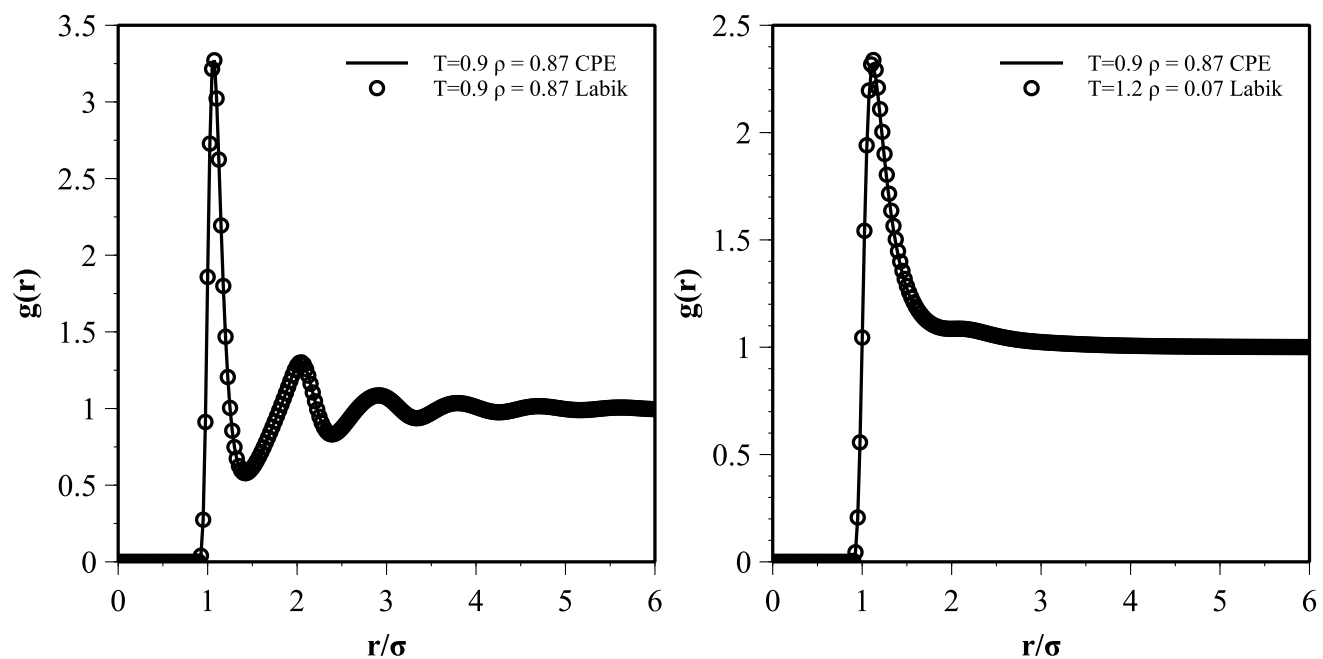


Figure 5-1 $g(r)$ calculated using PY closure.

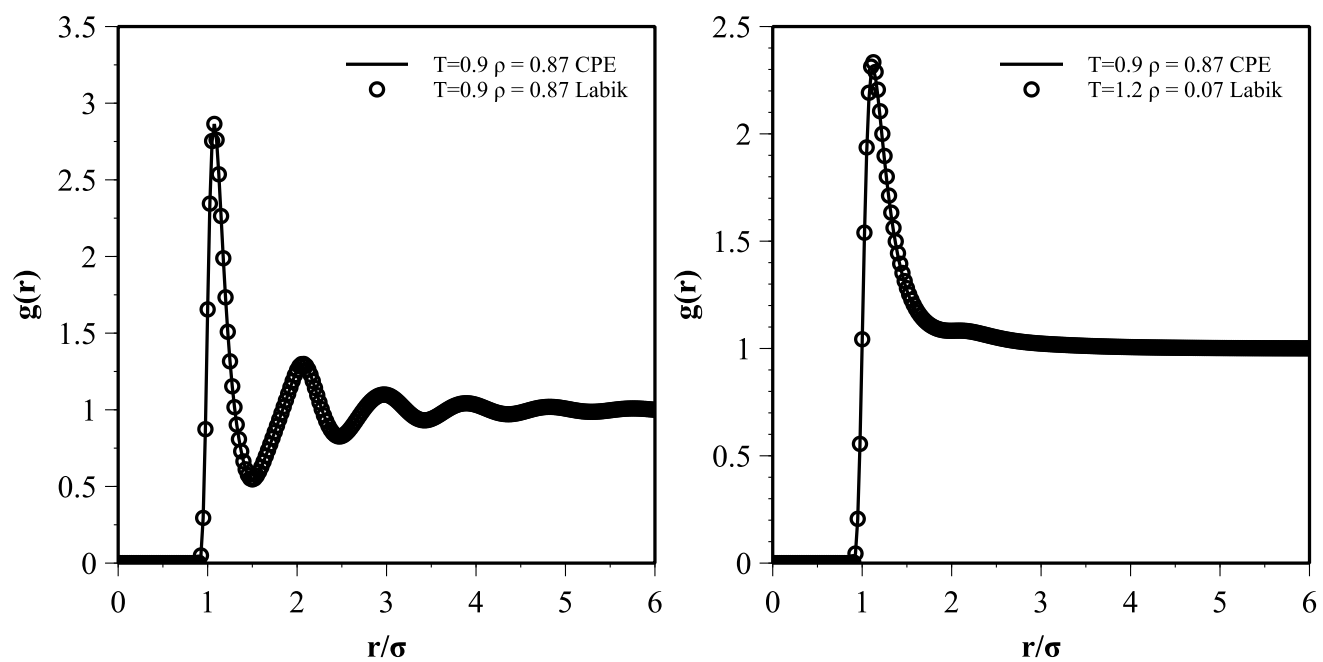


Figure 5-2 $g(r)$ calculated using DUH closure.

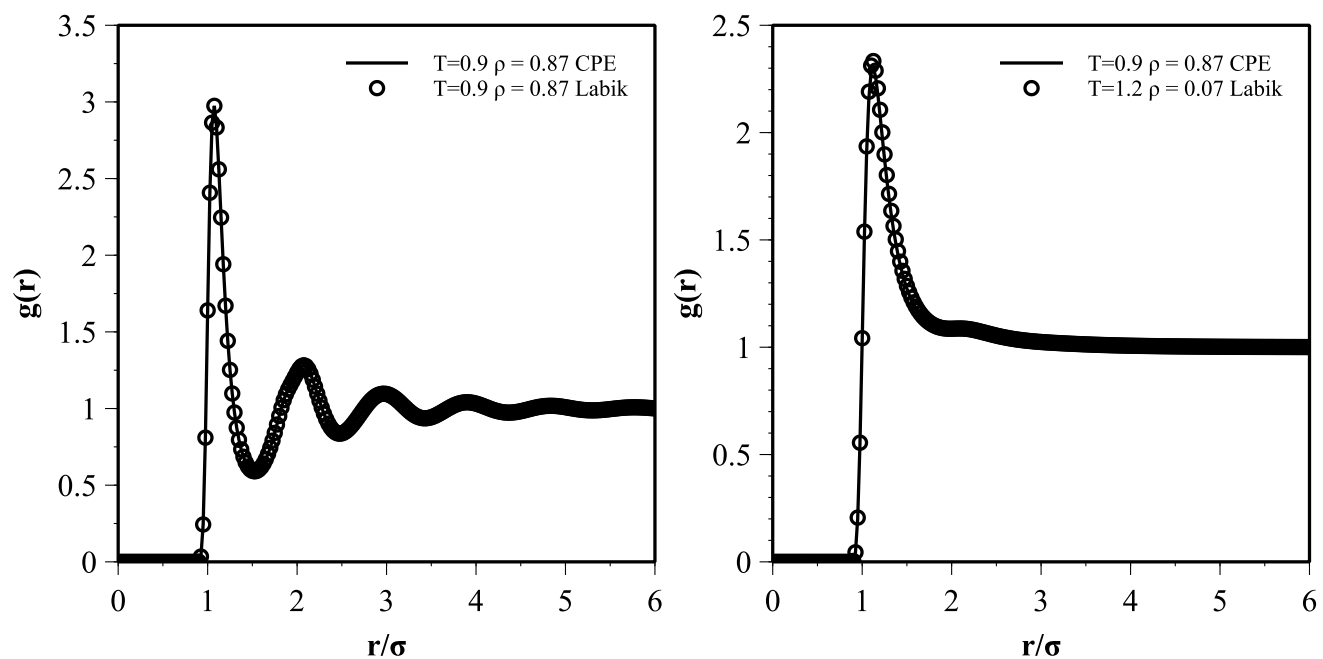


Figure 5-3 $g(r)$ calculated using MHNC-L closure.

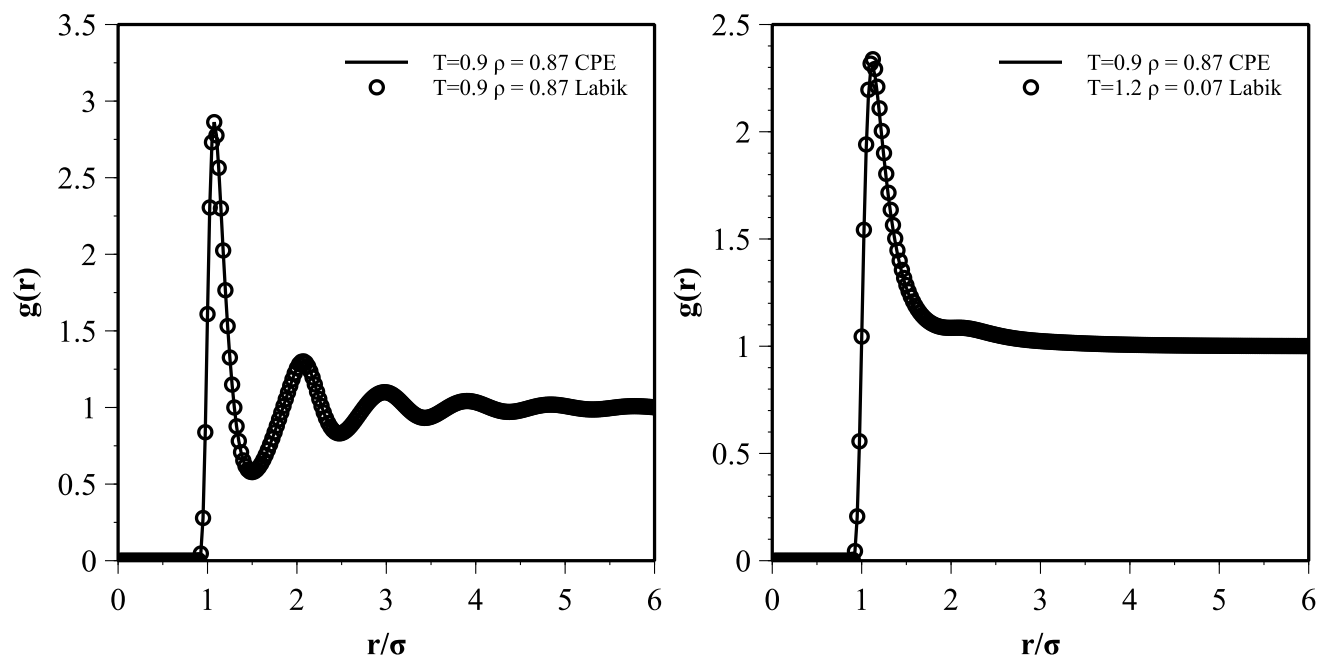


Figure 5-4 $g(r)$ calculated using MV closure.

It is easily shown that the Labik method and the *CPE* method are equivalent in terms of both structural and thermodynamic properties. The percentage difference between these two methods concerning thermodynamic properties does not surpass 5%. This equivalence is further underscored when comparing the results of the *MHNC-L* (Malijevský and Labík parametrization) and *MHNC-V* (Verlet and Weis parametrization) closures. Both the *MHNC-L* and *MHNC-V* closures involve an adjustable parameter, the hard sphere diameter, and it is noteworthy that both methods converge to the same hard sphere diameter when addressing the same objective function. In terms of structure the $g(r)$ evaluated using both the Labik method and the *CPE* are indistinguishable.

Table 5-4 and Table 5-5 in the study present data for two distinct state points. Table 5-4 focuses on a vapor phase, while Table 5-5 is concerned with a high-density liquid phase. This reveals that most closures applied to a Lennard-Jones fluid demonstrate accurate results for the vapor phase. However, there is a noticeable variance between the simulation data and the calculated thermodynamic properties for the high-density liquid phase. Among the closures presented in Table 5-5, the most accurate ones are identified as *MV*, *DUH*, *MDUH*, and *MHNC-L*. This indicates that while certain closures perform well in modeling vapor phase conditions, their accuracy can vary significantly when applied to high-density liquid phases, highlighting the importance of choosing the appropriate closure for different phases in the study of Lennard-Jones fluids.

In Table 5-4, it is noted that most closures perform accurately except for the *SMSA* closure. In a Similar manner to *MSA*, *SMSA* struggles at low densities. The failure of *MSA* in low-density conditions is attributed to its approximation of $g(r)$ as $1 - \beta u(r)$, which diverges from the more accurate expression $g(r) = \exp[-\beta u(r)]$. For *SMSA*, the issue at low densities stems from

the selection of the perturbation potential. As density decreases and $\gamma(r)$ approaches zero, $s(r)$ trends towards $-\beta u_a(r)$. Consequently, at the limit of low density ($\rho \rightarrow 0$), the bridge function $B^{SMSA}(r)$ is described as:

$$\lim_{\rho \rightarrow 0} B^{SMSA}(r) = \ln[1 - \beta u_a(r)] + \beta u_a(r) \quad 5.3-2$$

However, this expression is not valid, indicating a flaw in the *SMSA* approach, particularly at low densities. This discrepancy highlights the importance of accurately choosing and formulating the perturbation potential in closure methods, especially when dealing with various density regimes.

The *HMSA*, *RY*, *MSA*, and the modified *ZSEP* closures are not included in Table 5-4 and Table 5-5 for specific reasons:

1. *HMSA* and *RY* Closures: These involve a minimization process that significantly increases the computational effort when using the *CPE* (Coupling Parameter Expansion) method.
2. Modified *ZSEP* Closure *MZSEP*: This closure already encompasses a complex minimization procedure that includes states in the coexisting phase region, particularly in scenarios where the Labik method fails to converge.
3. *MSA* in the *CPE* Framework: When the Mean Spherical Approximation is treated within the *CPE* framework, it automatically converts into the *SMSA* (Soft Mean Spherical Approximation). This is because both the *SMSA* and the *CPE* are based on splitting the Lennard-Jones potential into reference and perturbing parts.

Consequently, the *MZSEP* is exclusively solved using the *CPE* method, while the *RY*, and *HMSA* are addressed using the Labik method only.

In order to distinguish between different closures based on their accuracy in representing structural properties, with the goal of identifying the most precise closure. By comparing the closures in terms of how accurately they capture structural details, such as $g(r)$, the most effective closure in terms of structural accuracy can be determined. Hence, the figures from Figure 5-5 to Figure 5-13 illustrate the $g(r)$ calculated by different closures at a temperature $T = 0.936$ and density $\rho = 0.88$, representing a high-density liquid phase. Figure 5-5, Figure 5-6 and Figure 5-7 represent closures, which can be classified as mixed closures. The figures up to Figure 5-11 show closures with normalized bridge functions, and the last two figures present the *MHNC-L* and *MHNC-V* closures.

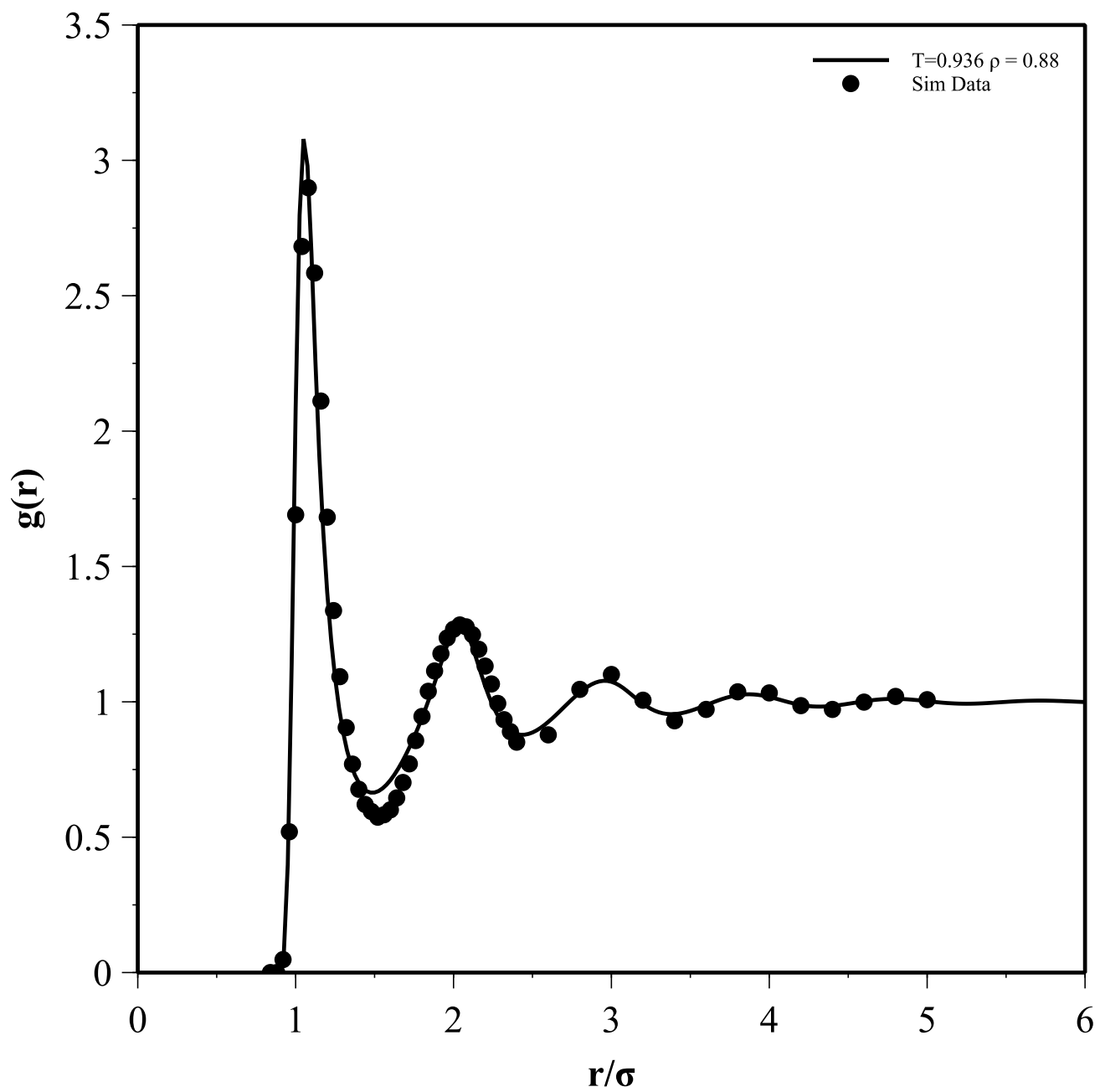


Figure 5-5 $g(r)$ calculated using *HMSA* closure.

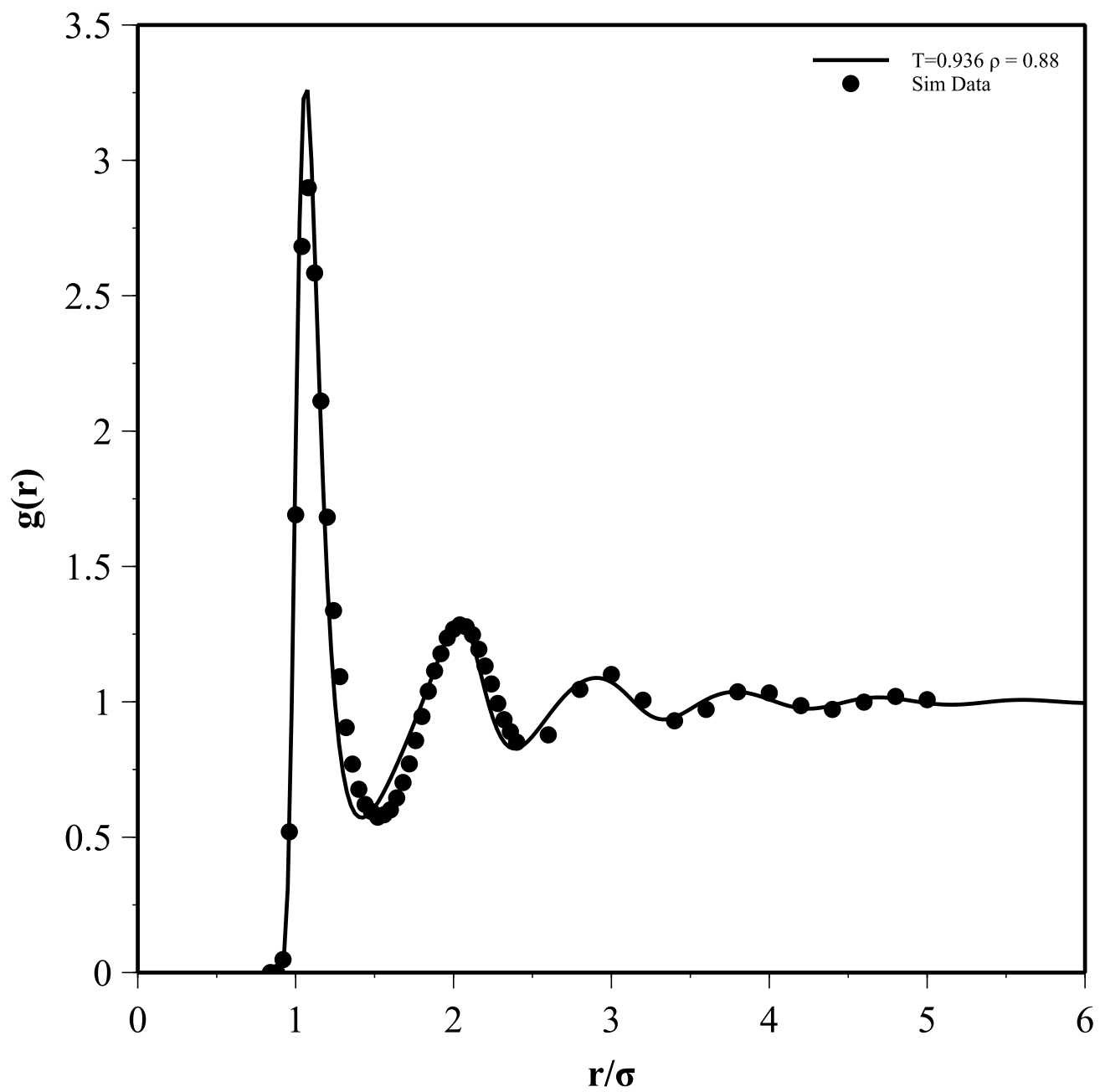


Figure 5-6 $g(r)$ calculated using *RY* closure.

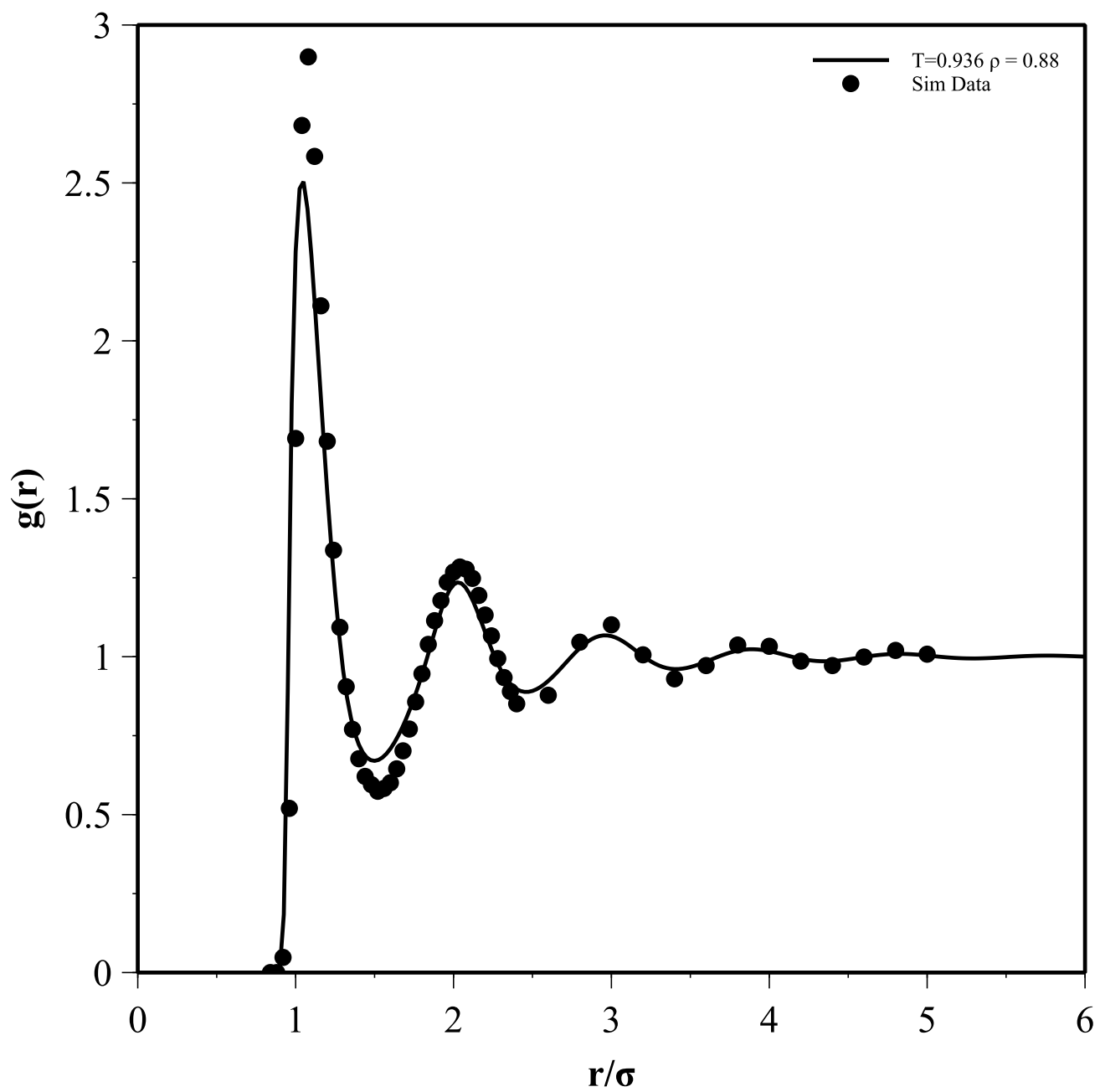


Figure 5-7 $g(r)$ calculated using KH closure.

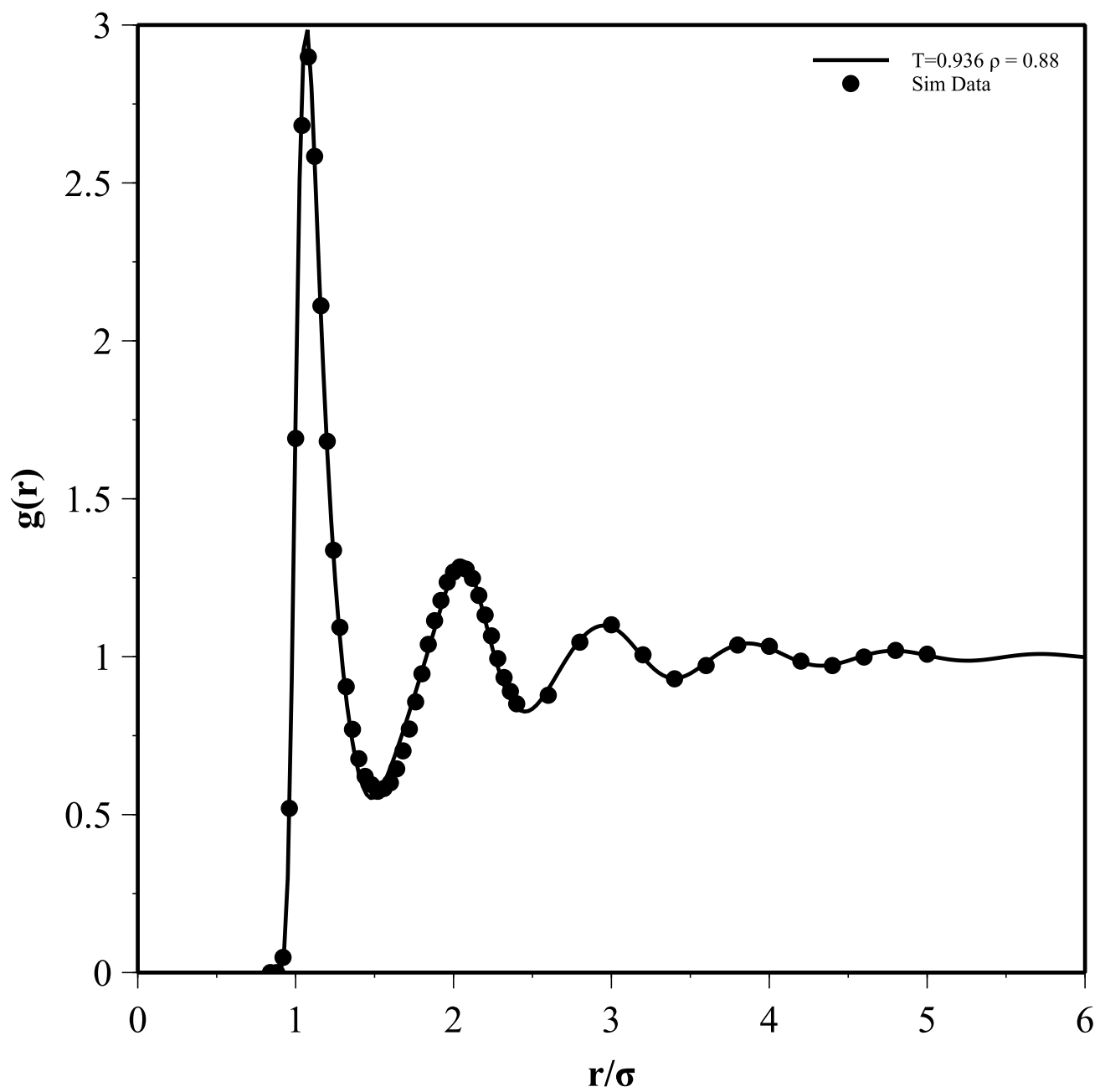


Figure 5-8 $g(r)$ calculated using VM closure.

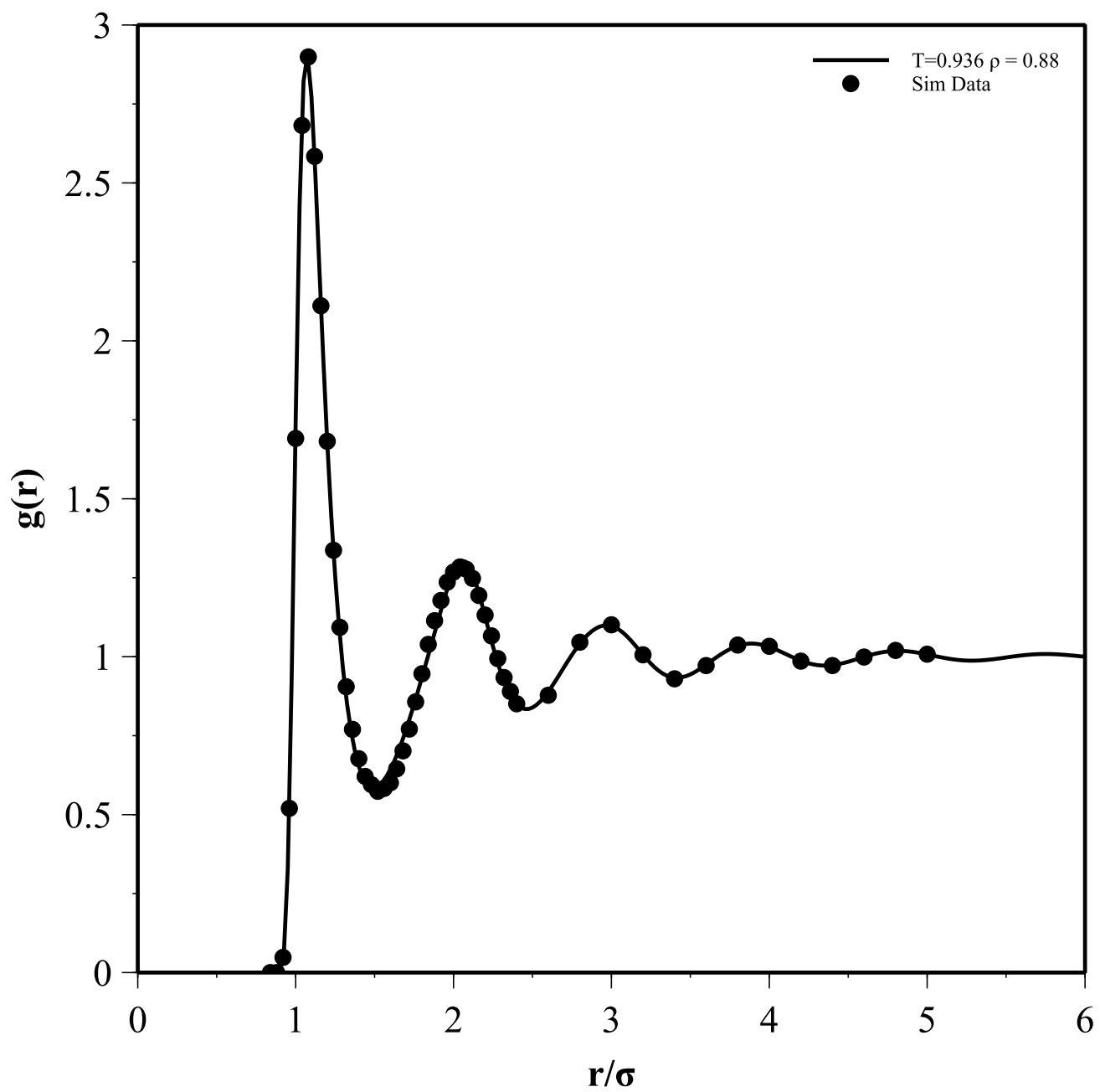


Figure 5-9 $g(r)$ calculated using *MDUH* closure.

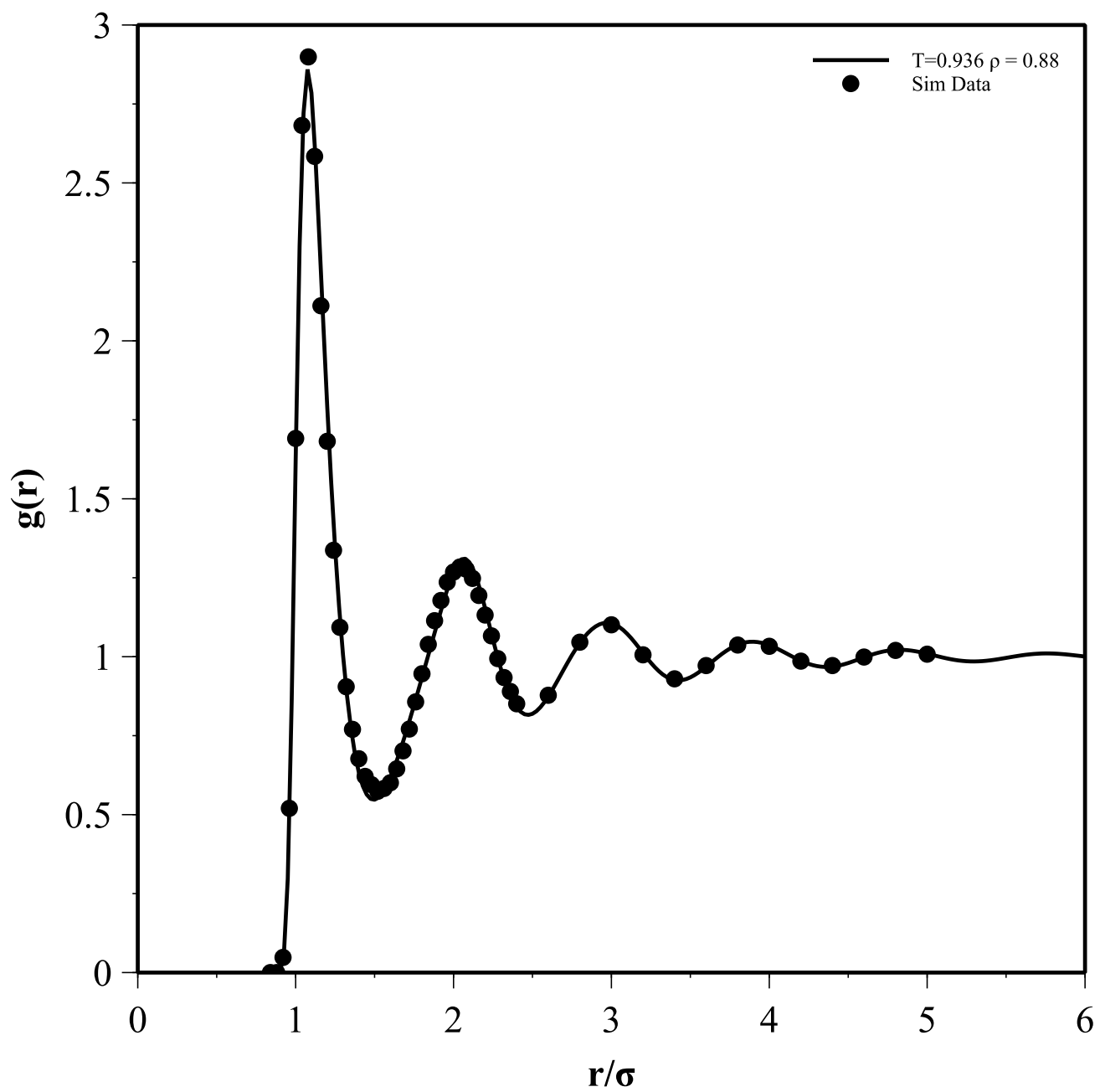


Figure 5-10 $g(r)$ calculated using *MZSEP* closure.

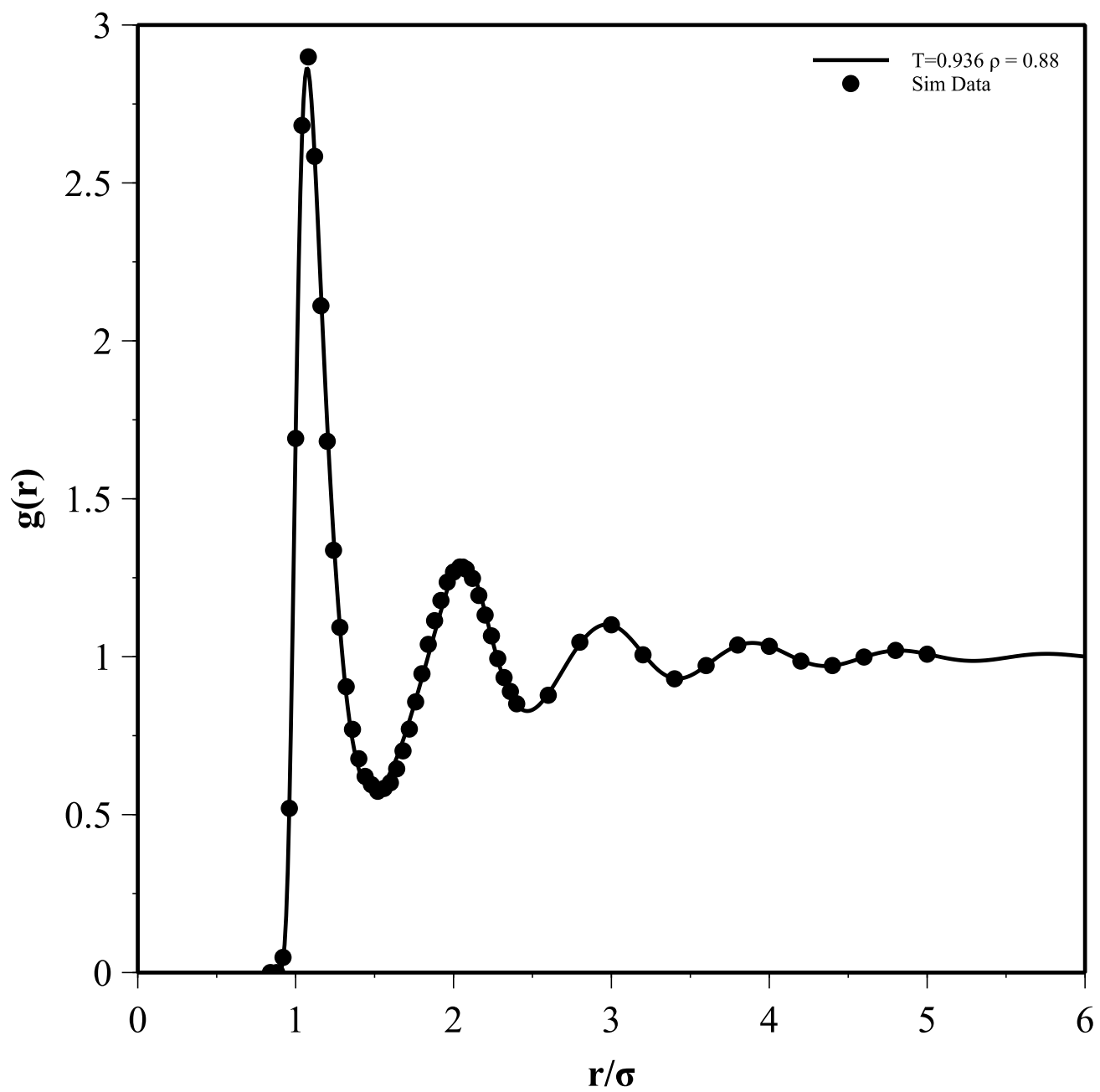


Figure 5-11 $g(r)$ calculated using MV closure.

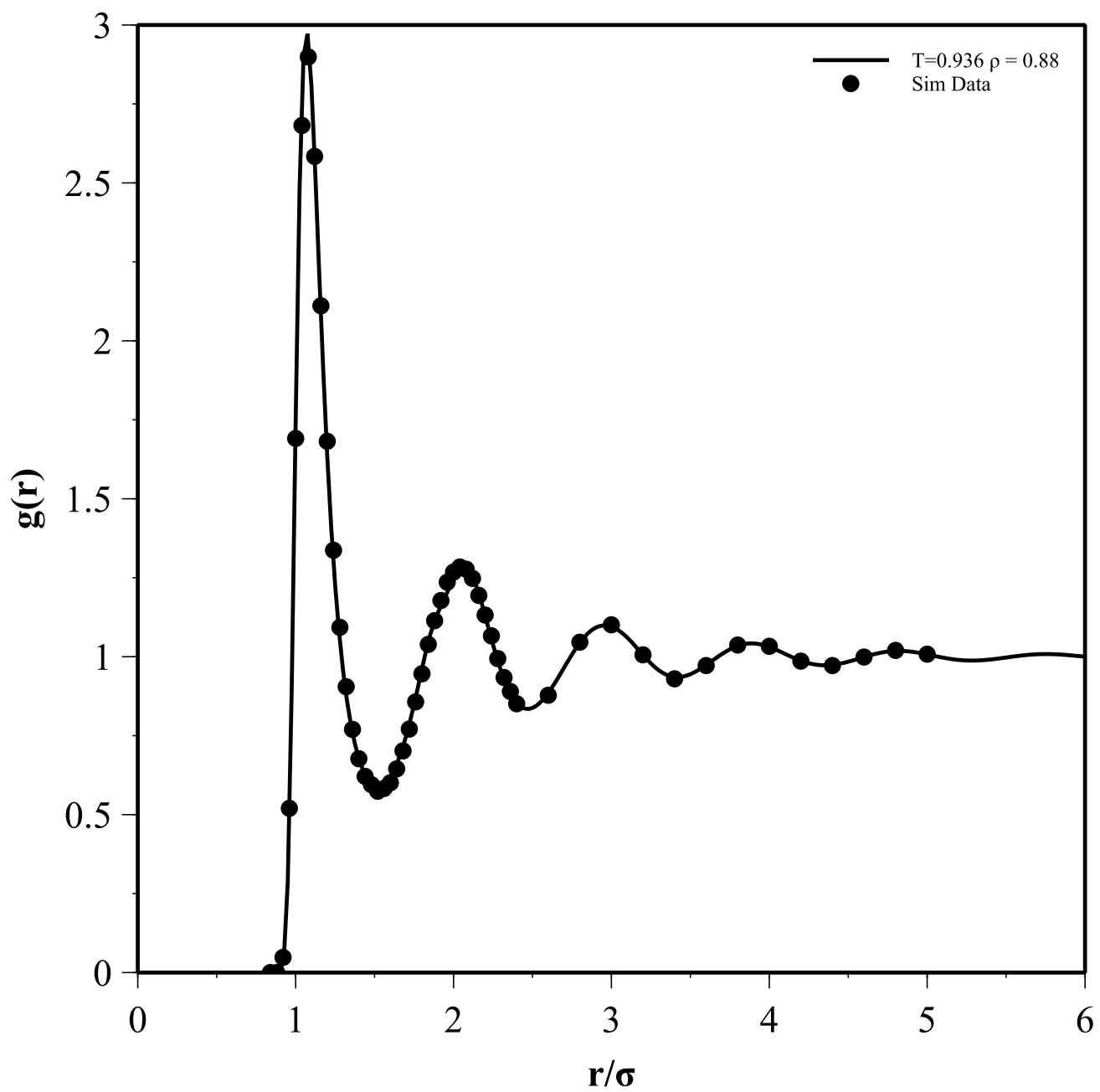


Figure 5-12 $g(r)$ calculated using $MHNC-L$ closure.

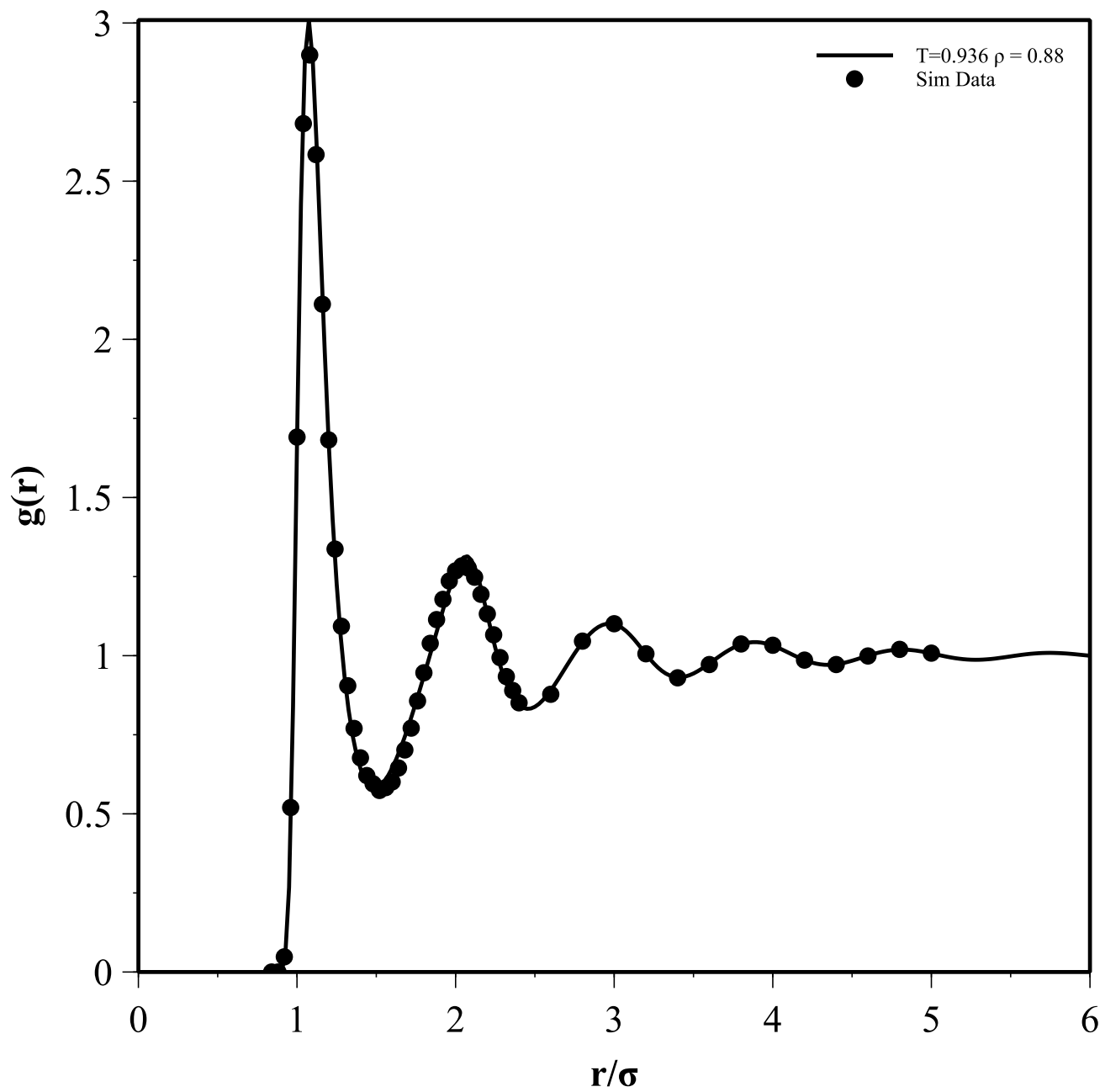


Figure 5-13 $g(r)$ calculated using *MHNC-V* closure.

From these figures, it is observed that the mixed closures are less precise compared to closures that include an $s(r)$ in their formulation. Notably, all closures that renormalize the bridge function, except for the *VM* closure, utilize the $u_a(r)$ proposed by DUH and Henderson (1996). The *VM* closure, on the other hand, normalizes the bridge function using the *WCA* $u_a(r)$.

The choice of $u_a(r)$ significantly impacts phase calculations, especially near the critical point, as will be evident in the phase diagram data presented later. In terms of structural accuracy, the *MHNC* closures outperform the mixed integral Equation closures and are relatively close to the accuracy of the renormalized bridge function closures, with some deviation at the first peak of the calculated $g(r)$.

Comparing the $g(r)$ calculated from *MHNC-L* and *MHNC-V*, it is found that they are quite similar, although the *MHNC-L* demonstrates more accurate thermodynamic properties, as shown in Table 5-5. This comparison shows small differences in accuracy between various closures, especially in the context of high-density liquid phases.

Table 5-6 and Table 5-7 in the thesis provide a clear comparison of various closures in computing thermodynamic properties. This is achieved by comparing the calculated thermodynamic properties to simulation data, utilizing the Mean Absolute Error (*MAE*) metric for each region on the phase diagram. This method allows for a quantitative assessment of the closures' accuracy in predicting thermodynamic behaviors.

The *MAE* is a standard statistical measure used to quantify the accuracy of predictions or calculations against actual values. The formula for the Mean Absolute Error is as follows:

$$MAE = \frac{1}{n} \sum_{i=1}^n |y_i - x_i| \quad 5.3-3$$

where n represents the number of data points, y_i is the i^{th} value of the property as obtained from the simulation data, and x_i is the i^{th} value of the same property as calculated by the thermodynamic model or method being assessed. The *MAE* provides an average magnitude of the errors in a set of predictions, without considering their direction. Lower *MAE* values indicate higher accuracy of the model in replicating the observed data, making it a useful metric for evaluating the performance of different models or methods across various regions of the phase diagram.

Table 5-6 *MAE* to various thermodynamic properties.

Region	PY	HNC	Verlet	MS	KH	SMSA	VM	DUH	MDUH	MZSEP	MV
K_T											
V	0.372	0.371	0.372	0.372	3.296	4.156	0.372	0.420	0.372	0.372	0.372
L	0.075	0.116	0.076	0.075	0.035	0.033	0.013	0.013	0.007	0.007	0.010
HD-L	0.028	0.056	0.037	0.020	0.028	0.054	0.022	0.020	0.019	0.015	0.014
Sc	0.162	0.146	0.162	0.163	0.447	0.560	0.171	0.184	0.163	0.152	0.162
HD-Sc	0.002	0.010	0.001	0.004	0.006	0.024	0.011	0.009	0.008	0.036	0.024
L+V	0.207	0.245	0.208	0.195	2.744	3.622	0.158	0.172	0.145	0.142	0.145
Overall	0.207	0.212	0.208	0.205	1.498	1.910	0.198	0.218	0.192	0.187	0.192
γ											
V	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000
L	4.676	0.421	4.441	3.915	2.479	0.396	1.600	4.009	3.872	0.760	0.832
HD-L	10.386	1.912	10.228	6.222	4.460	0.639	4.060	7.456	8.055	0.134	0.691
Sc	0.841	0.110	0.790	0.803	0.487	0.165	0.385	0.845	0.793	0.253	0.258
HD-Sc	6.841	1.398	6.101	5.309	2.866	1.075	1.683	6.315	6.290	0.091	0.433
L+V	0.624	0.075	0.337	0.521	0.324	0.063	0.137	0.502	0.450	0.074	0.060
Overall	1.810	0.270	1.707	1.352	0.878	0.182	0.675	1.492	1.499	0.195	0.253
μ_T											
V	0.107	0.085	0.106	0.106	1.526	1.239	0.105	0.121	0.106	0.107	0.106
L	0.160	0.141	0.110	0.215	0.082	0.029	0.028	0.125	0.107	0.023	0.024
HD-L	0.057	0.151	0.035	0.239	0.024	0.276	0.056	0.041	0.021	0.073	0.065
Sc	0.113	0.078	0.110	0.110	0.252	0.236	0.086	0.147	0.117	0.079	0.082
HD-Sc	0.083	0.110	0.096	0.102	0.026	0.244	0.081	0.084	0.083	1.444	0.315
L+V	0.151	0.065	0.133	0.129	2.382	1.788	0.102	0.148	0.133	0.100	0.100
Overall	0.114	0.092	0.104	0.131	0.775	0.652	0.085	0.127	0.105	0.111	0.088
Γ											
V	0.005	0.003	0.005	0.005	0.004	0.031	0.005	0.005	0.005	0.005	0.005
L	2.480	0.121	2.427	2.287	1.785	1.111	1.650	2.313	2.268	1.345	1.358
HD-L	3.481	1.028	3.394	2.811	2.210	1.089	2.046	2.899	2.981	1.153	1.333
Sc	0.662	0.048	0.635	0.637	0.433	0.263	0.432	0.680	0.642	0.375	0.371
HD-Sc	2.576	0.283	2.343	2.059	1.252	0.731	0.968	2.419	2.411	0.252	0.480
L+V	0.795	0.097	0.790	0.798	0.611	0.356	0.573	0.807	0.770	0.532	0.516
Overall	0.921	0.129	0.893	0.830	0.616	0.363	0.580	0.865	0.847	0.438	0.455
ω											
V	0.004	0.005	0.005	0.005	0.015	0.045	0.005	0.005	0.005	0.005	0.005
L	2.369	0.399	2.379	2.392	1.874	0.352	1.455	1.502	1.564	0.868	0.880
HD-L	2.076	1.315	2.326	2.292	2.754	2.508	1.769	2.490	2.476	1.115	1.402
Sc	0.765	0.181	0.761	0.767	0.555	0.160	0.445	0.618	0.593	0.331	0.319

HD-Sc	0.832	1.077	2.187	2.710	2.547	13.631	11.058	5.053	3.189	11.056	13.202
L+V	0.506	0.034	0.508	0.508	0.371	0.094	0.321	0.333	0.350	0.241	0.223
Overall	0.783	0.248	0.831	0.842	0.729	0.606	0.728	0.740	0.699	0.561	0.624
C_p											
V	0.058	0.033	0.057	0.057	0.303	0.228	0.056	0.061	0.056	0.054	0.056
L	1.040	3.842	0.824	1.004	0.598	0.558	0.768	0.674	0.910	0.900	0.814
HD-L	3.084	6.475	3.837	1.623	0.351	3.876	2.702	2.150	3.057	2.519	2.191
Sc	0.698	0.836	0.707	0.709	0.874	0.646	0.541	0.850	0.668	0.525	0.524
HD-Sc	0.476	2.141	0.683	0.837	0.288	1.411	0.536	0.501	0.502	3.061	1.696
L+V	0.496	1.152	0.136	0.022	0.492	0.176	0.147	0.250	0.225	0.178	0.159
Overall	0.711	1.409	0.728	0.560	0.585	0.750	0.560	0.641	0.661	0.606	0.541
C_v											
V	0.017	0.007	0.017	0.017	0.060	0.069	0.017	0.017	0.017	0.016	0.017
L	2.544	0.104	3.116	1.920	1.516	1.602	2.333	2.676	2.932	1.995	1.967
HD-L	3.107	0.220	3.445	0.664	1.768	1.714	2.357	3.648	4.615	1.987	2.073
Sc	0.484	0.034	0.443	0.440	0.237	0.252	0.360	0.518	0.515	0.345	0.339
HD-Sc	0.730	0.228	0.510	0.297	0.346	0.472	0.555	0.703	0.702	0.329	0.405
L+V	0.488	0.029	0.854	0.989	0.451	0.471	0.692	0.727	0.723	0.589	0.574
Overall	0.771	0.052	0.865	0.522	0.458	0.475	0.650	0.861	0.964	0.566	0.569
U^{res}											
V	0.001	0.001	0.001	0.001	0.022	0.026	0.001	0.001	0.001	0.001	0.001
L	0.078	0.204	0.085	0.078	0.384	0.041	0.019	0.041	0.010	0.011	0.001
HD-L	0.077	0.437	0.118	0.083	0.727	0.133	0.021	0.028	0.015	0.091	0.015
Sc	0.012	0.087	0.018	0.019	0.174	0.042	0.004	0.022	0.005	0.009	0.005
HD-Sc	0.240	0.873	0.001	0.051	1.355	0.473	0.125	0.006	0.016	0.472	0.179
L+V	0.016	0.028	0.016	0.015	0.077	0.019	0.004	0.011	0.002	0.002	0.001
Overall	0.026	0.112	0.027	0.025	0.210	0.051	0.008	0.017	0.005	0.022	0.007
P											
V	0.013	0.001	0.013	0.016	0.025	0.060	0.036	0.041	0.045	0.046	0.049
L	0.751	0.204	0.790	0.799	1.733	0.304	0.167	0.151	0.051	0.076	0.036
HD-L	0.795	0.437	1.009	0.945	3.541	0.807	0.130	0.108	0.059	0.648	0.177
Sc	0.122	0.087	0.162	0.169	0.643	0.179	0.023	0.066	0.019	0.047	0.028
HD-Sc	1.026	0.873	0.210	0.004	6.737	2.526	0.660	0.064	0.043	3.058	1.350
L+V	0.308	0.028	0.309	0.322	0.427	0.081	0.065	0.041	0.013	0.002	0.010
Overall	0.243	0.112	0.264	0.261	0.899	0.243	0.066	0.068	0.033	0.153	0.072

Table 5-7 Basic Thermodynamic properties for *MHNC* and *RY* closures

<i>MHNC-L</i>								
Region	ρ	T	K_T		U^{res}		P	
			Calculated	Sim	Calculated	Sim	Calculated	Sim
V	0.01	1.00	211.165	211.218	-0.046	-0.046	0.005	0.005
L	0.71	1.05	0.177	0.202	-4.919	-4.923	0.224	0.252
HD-L	0.86	0.85	0.080	0.056	-6.035	-6.031	1.263	1.263
Sc	0.6	2.00	0.169	0.170	-3.731	-3.747	1.777	1.760
HD-Sc	1.00	2.00	0.008	0.013	-4.881	-5.037	15.986	15.216
L+V	0.767	0.72	0.164	0.130	-5.591	-4.893	-0.734	-0.433
<i>MHNC-V</i>								
Region	ρ	T	K_T		U^{res}		P	
			Calculated	Sim	Calculated	Sim	Calculated	Sim
V	0.01	1.00	211.165	211.218	-0.046	-0.046	0.005	0.005
L	0.71	1.05	0.182	0.202	-4.936	-4.923	0.161	0.252
HD-L	0.86	0.85	0.083	0.056	-6.054	-6.031	1.146	1.263
Sc	0.6	2.00	0.176	0.170	-3.753	-3.747	1.721	1.760
HD-Sc	1.00	2.00	0.007	0.013	-5.087	-5.037	14.991	15.216
L+V	0.767	0.72	0.159	0.130	-5.595	-4.893	-0.783	-0.433
<i>HMSA</i>								
Region	ρ	T	K_T		U^{res}		P	

			Calculated	Sim	Calculated	Sim	Calculated	Sim
V	0.01	1.00	195.642	211.218	-0.027	-0.046	0.005	0.005
L	0.71	1.05	0.083	0.202	-4.742	-4.923	0.908	0.252
HD-L	0.86	0.85	0.049	0.056	-5.762	-6.031	2.667	1.263
Sc	0.6	2.00	0.092	0.170	-3.628	-3.747	2.018	1.760
HD-Sc	1.00	2.00	0.010	0.013	-4.831	-5.037	16.371	15.216
L+V	0.767	0.72	0.078	0.130	-5.359	-4.893	0.312	-0.433
<i>RY</i>								
Region	ρ	T	K_T		U^{res}		P	
			Calculated	Sim	Calculated	Sim	Calculated	Sim
V	0.01	1.00	211.188	211.218	-0.046	-0.046	0.005	0.005
L	0.71	1.05	0.341	0.202	-4.860	-4.923	0.906	0.252
HD-L	0.86	0.85	0.121	0.056	-5.889	-6.031	2.478	1.263
Sc	0.6	2.00	0.211	0.170	-3.732	-3.747	1.952	1.760
HD-Sc	1.00	2.00	0.011	0.013	-5.254	-5.037	14.311	15.216
L+V	0.767	0.72	0.609	0.130	-5.457	-4.893	0.550	-0.433

Key observations from these tables are as follows:

- Vapor Region (from Table 5-6): All closures exhibit low *MAE* in the vapor region across all calculated thermodynamic properties. This indicates that these closures are accurate for vapor phase regions.
- Liquid Phases (*L*, *HD-L*, and *L+V* regions): In the liquid phase (*L*), high-density liquid phase (*HD-L*), and the liquid+vapor coexistence region (*L+V*), closures that incorporate renormalized bridge functions demonstrate better *MAE* compared to those without renormalized bridge functions. This suggests that the renormalization of the bridge function enhances the accuracy of closures in these regions.
- Performance of Renormalized Closures: Among the renormalized closures, the *MV* closure generally shows a better *MAE* in most thermodynamic properties across various regions, with the exception of the high-density supercritical (*HD-Sc*) region. This trend holds true for all renormalized closures.
- Isothermal Compressibility, internal energy, and pressure (from Table 5-7): This table focuses on closures requiring multiple iterations to minimize an objective function, as

these are more time-consuming compared to other closures. The data illustrates how these closures perform in terms of isothermal compressibility, internal energy, and pressure.

- From both Table 5-6 and Table 5-7, it is evident that renormalized closures are more accurate for the Lennard-Jones fluid in most regions of the phase diagram compared to non-renormalized closures, including mixed-type closures and *MHNC* closures.
- Accuracy in Coexistence Region ($L+V$): Renormalized closures show heightened accuracy in the coexistence region compared to all other regions.

These observations highlight the importance of choosing the appropriate closure method based on the specific region of the phase diagram being studied. Renormalized closures, particularly the *MV* closure, appear to offer a more accurate modeling of the Lennard-Jones fluid across various phases, especially in liquid and coexistence regions.

The utilization of $s(r)$ correlation function in diagram expansions has a straightforward and practical rationale. The $h(r)$ diagrams associated with the bridge function involve an exponential factor $\exp[\omega(r) - u(r)]$ in the integrand expressions. Consequently, these diagrams can be expanded in terms of powers of the mean force, specifically in the form of $[\omega(r) - u(r)]$. To circumvent issues stemming from the uncontrolled growth of the pair potential within the core region, it proves advantageous to perform the expansion in powers of $[\omega(r) - u_a(r)]$.

The results in Table 5-6 indicate a notable difference in accuracy between closures that use the *WCA* partition scheme (such as *SMSA* and *VM*) and those that employ the *DUH* partition scheme, including *DUH*, *MDUH*, *MV*, and *MZSEP*.

The *DUH* partition scheme, which was developed based on fitting simulation data of the Lennard-Jones bridge function, appears to offer greater accuracy for the Lennard-Jones fluid. This suggests that the way the intermolecular potential is partitioned into reference and perturbation parts significantly influences the performance of the closure methods. The *DUH* scheme's ability to more accurately fit the characteristics of the Lennard-Jones potential seems to translate into better performance in calculating thermodynamic properties, as evidenced by the lower Mean Absolute Errors in the closures using this scheme. This comparison underscores the importance of the partitioning scheme in the effectiveness of the normalization of the bridge function.

Figure 5-14 to Figure 5-19 display the calculated bridge functions for the *PY*, *MV*, and *MZSEP* closures. These figures effectively illustrate the ability of the renormalization process to yield bridge functions that approximate the simulation data adopted from Llano-Restrepo and Chapman (1992) with reasonable accuracy.

While the bridge function predictions at subcritical temperatures by the *MV* and *MZSEP* closures may not be highly precise, they still offer better accuracy compared to the *PY* closure and other non-renormalized closures. This comparison highlights the advantage of renormalized closures in achieving a closer alignment with empirical data, particularly in the challenging area of accurately predicting bridge functions at various temperature conditions.

The advantage of renormalized closures becomes particularly evident in the core region of the system (where $r < \sigma$). In this region, the accuracy of the bridge function is crucial, and renormalized closures tend to provide more precise results than their non-renormalized counterparts. This enhanced accuracy in the core region has practical implications, especially in the calculation of the chemical potential.

The chemical potential is a key thermodynamic property that is highly sensitive to the values of both the $B(r)$ and the $g(r)$ in the core region. The improved accuracy of the bridge function in renormalized closures ensures that the calculations of the chemical potential are more reliable and closer to actual physical behaviors. This makes renormalized closures particularly valuable for studying systems where precise knowledge of the chemical potential is critical, such as in phase equilibrium calculations.

The accuracy of the bridge function plays a crucial role in determining the precision of the calculated $g(r)$, which in turn contributes to the overall consistency of a closure. As illustrated, particularly in Table 5-8, renormalized closures demonstrate a higher degree of thermodynamic consistency compared to non-renormalized closures.

While renormalized closures may not achieve absolute accuracy—meaning the calculated $g(r)$ is not perfectly exact—they still represent an improvement in terms of consistency. This is significant for studies where accurate modeling of intermolecular interactions and thermodynamic properties is essential.

Among the renormalized closures, the MV closure stands out as the most accurate and consistent. This distinction highlights the effectiveness of the MV closure in capturing the complex interplay of forces in a system and its utility in providing reliable predictions for thermodynamic properties.

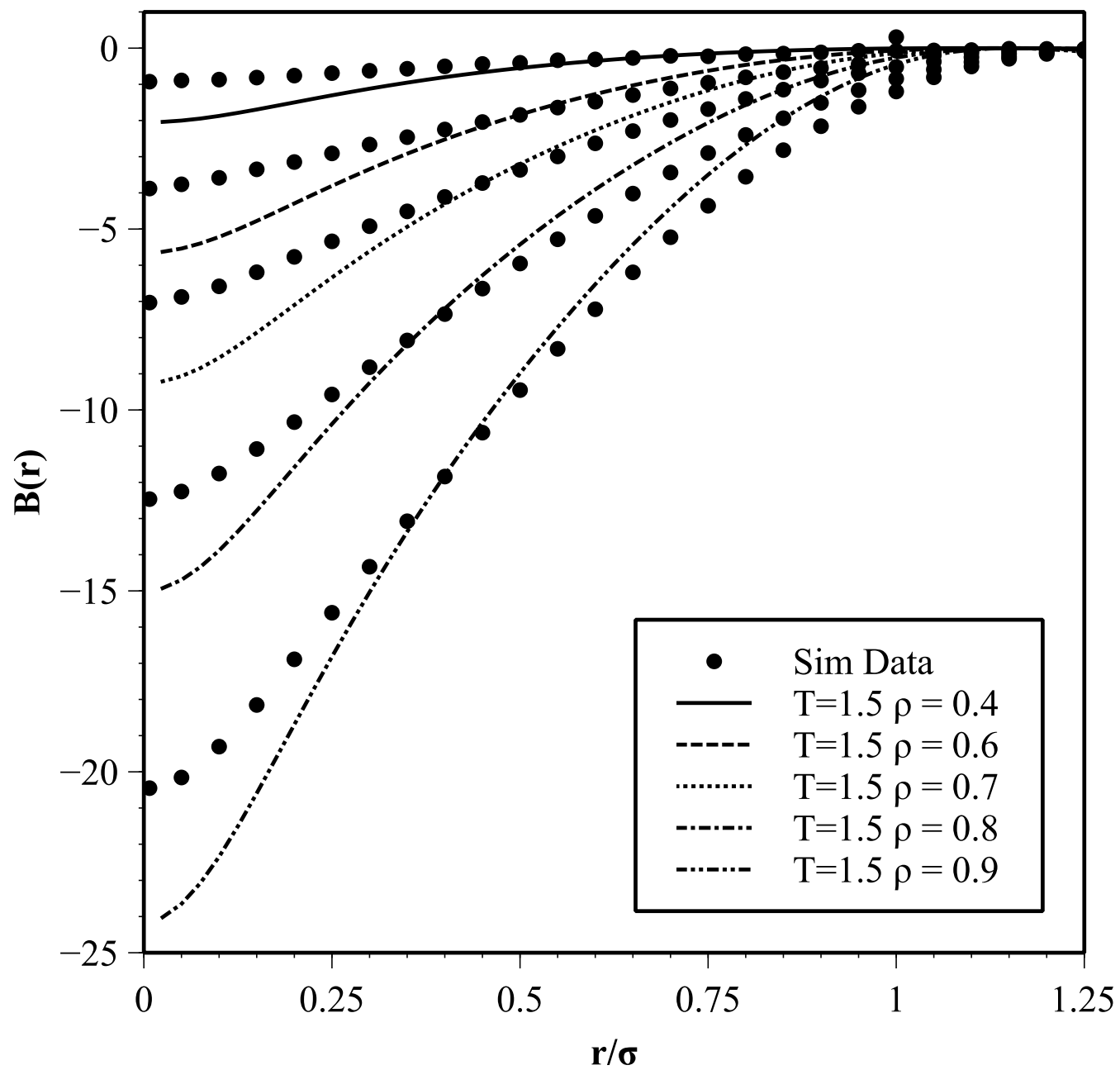


Figure 5-14 The bridge function of the *PY* closure at $T = 1.5$

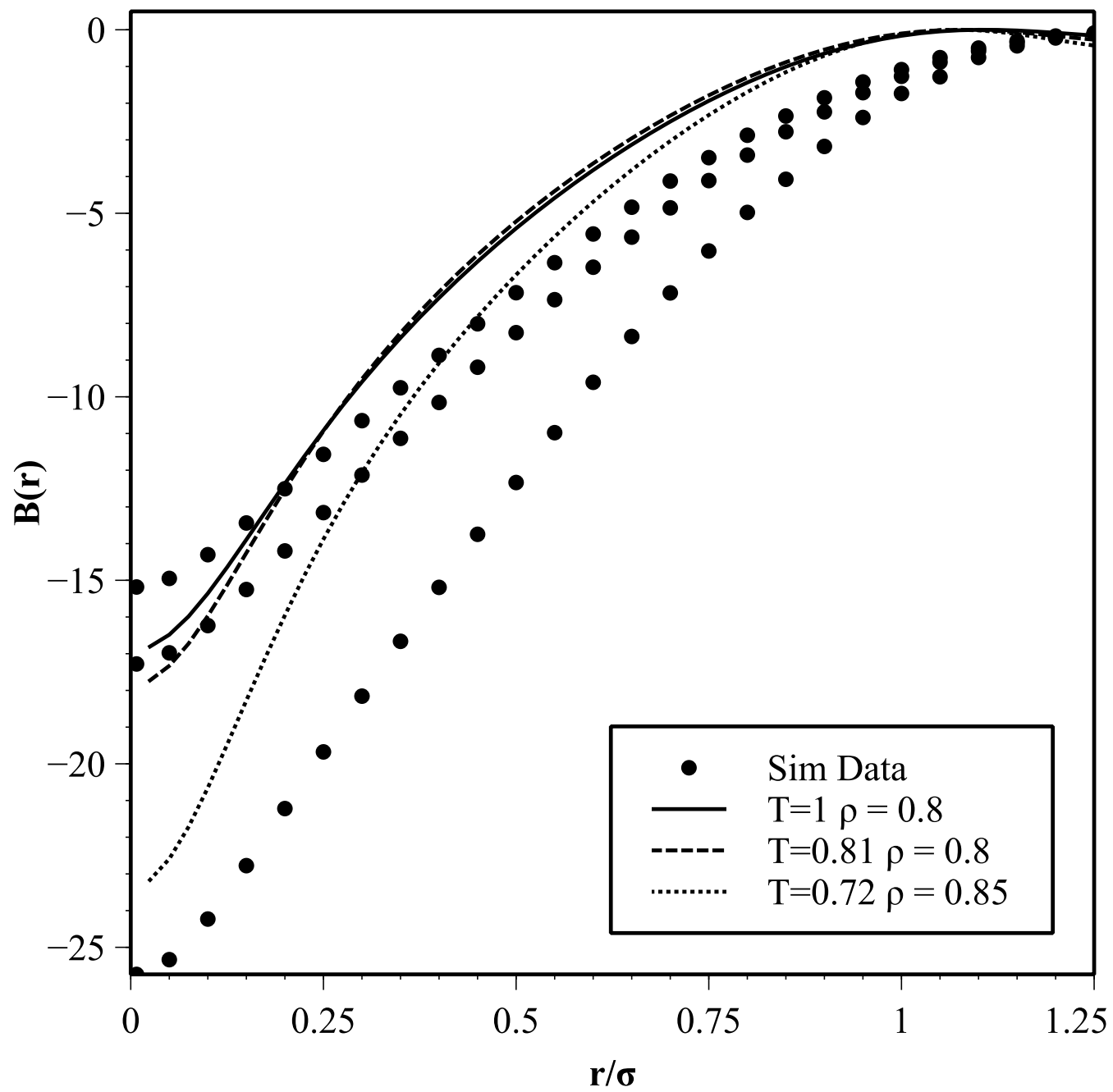


Figure 5-15 The bridge function of the *PY* closure at subcritical temperatures.

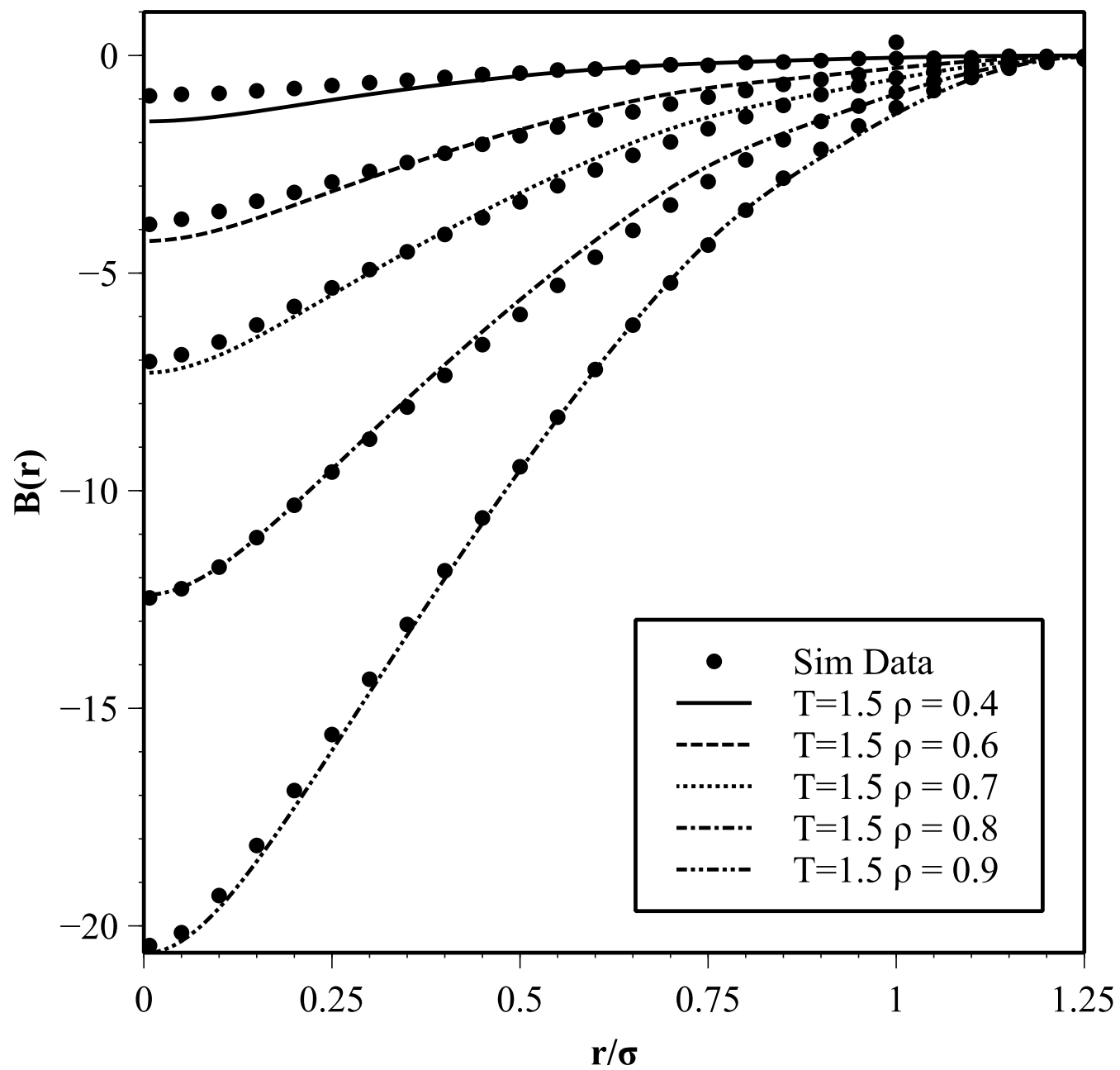


Figure 5-16 The bridge function of the *MV* closure at $T = 1.5$

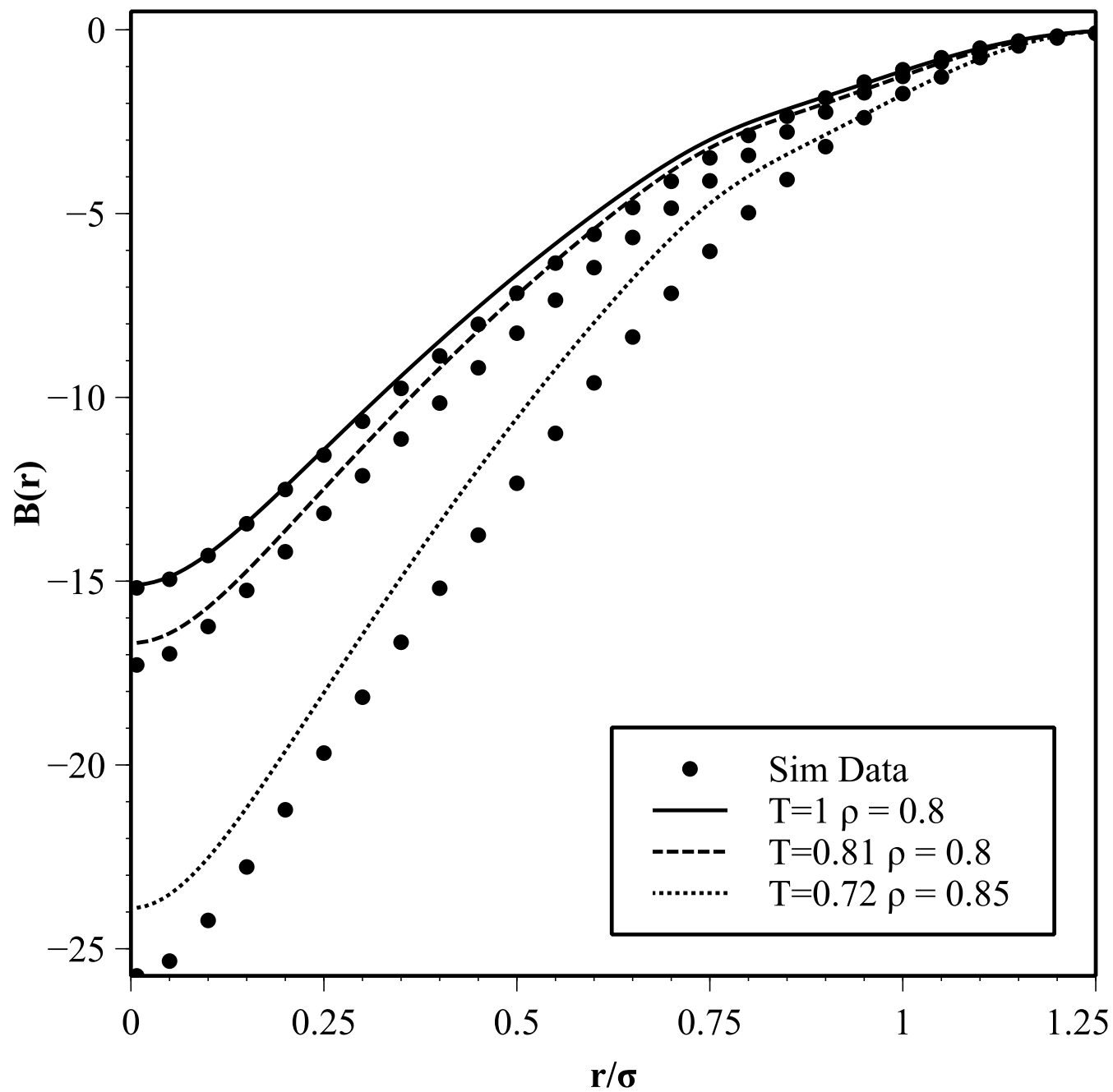


Figure 5-17 The bridge function of the MV closure at subcritical temperatures.

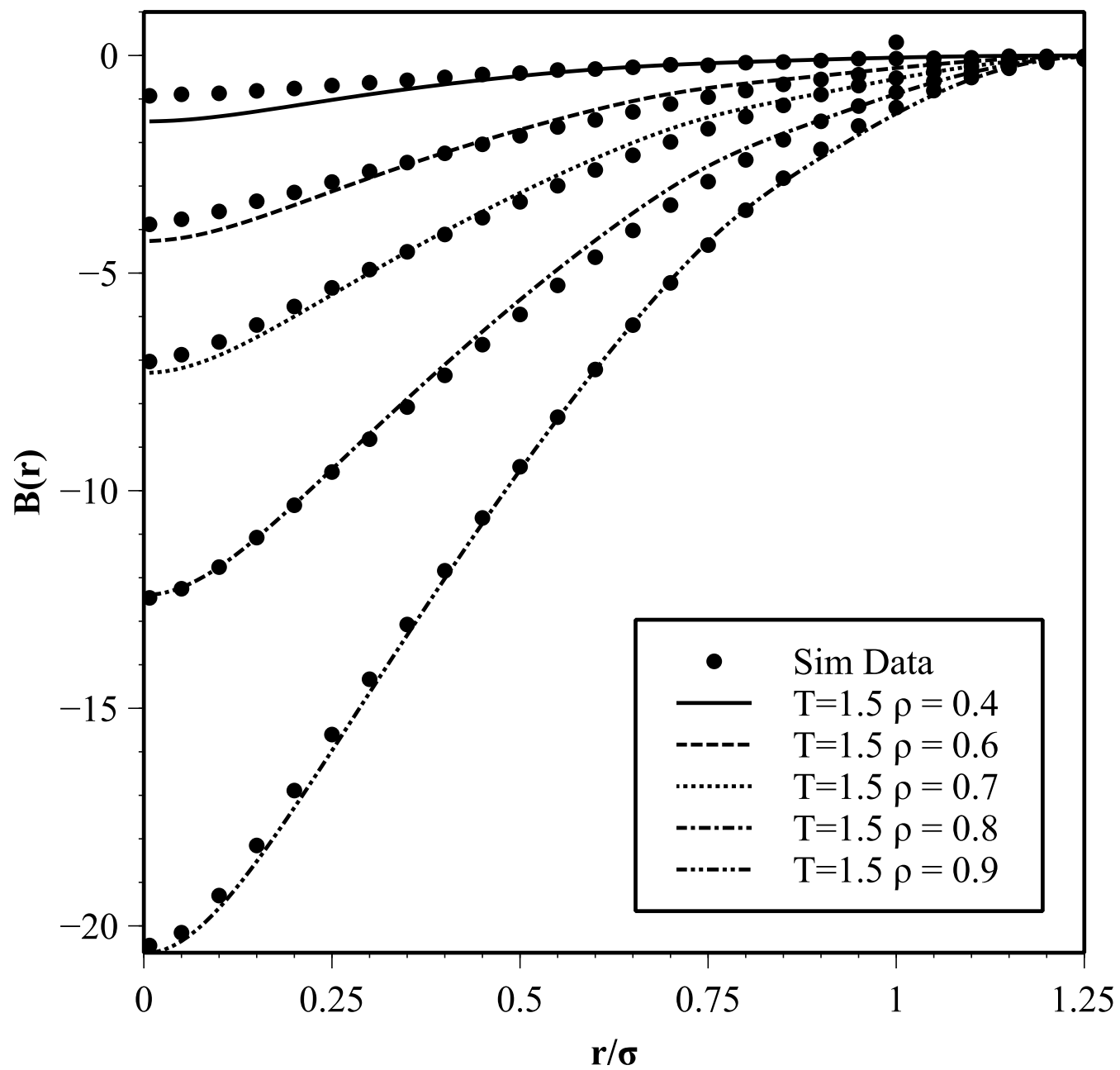


Figure 5-18 The bridge function of the *MZSEP* closure at $T = 1.5$

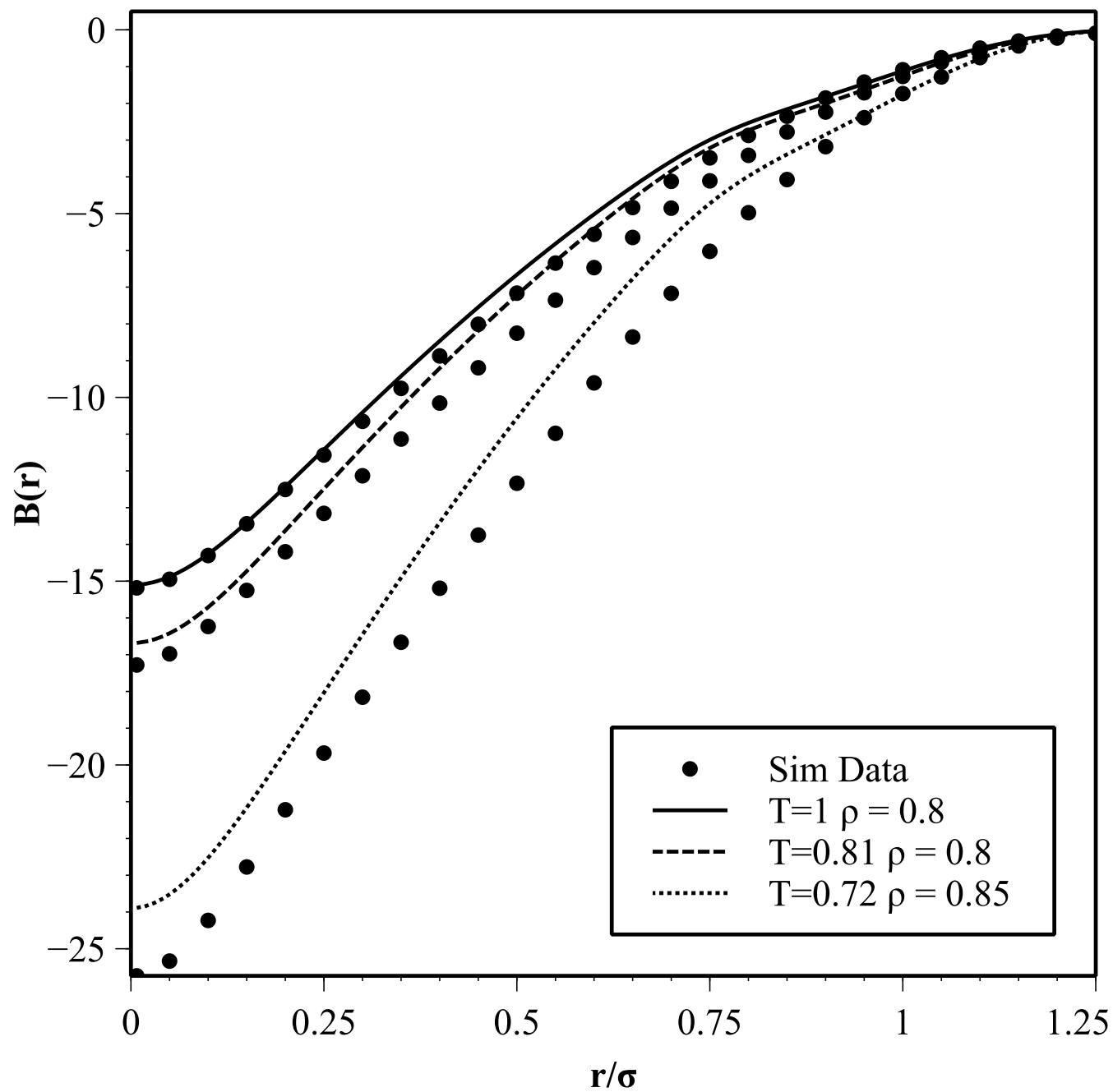


Figure 5-19 The bridge function of the *MZSEP* closure at subcritical temperatures.

Table 5-8 Isothermal compressibility via virial and compressibility routes.

Region	ρ	T	PY		Verlet		KH		HNC		MS	
			K_{TV}	K_{TC}	K_{TV}	K_{TC}	K_{TV}	K_{TC}	K_{TV}	K_{TC}	K_{TV}	K_{TV}
V	0.01	1.00	0.947	0.947	0.947	0.947	0.956	0.960	0.947	0.947	0.947	0.940
L	0.71	1.05	19.823	4.669	17.352	4.661	16.173	5.953	12.738	3.897	18.188	6.876
HD-L	0.86	0.85	52.694	10.093	39.202	8.675	34.725	12.034	27.302	7.842	33.964	16.842
Sc	0.6	2.00	13.590	8.039	13.266	8.003	15.340	8.744	12.949	7.031	13.396	8.873
HD-Sc	1.00	2.00	85.818	93.895	79.632	69.175	103.318	51.981	95.590	42.811	78.984	59.662
L+V	0.767	0.72	21.809	3.095	23.887	3.204	17.980	4.814	13.952	2.670	18.601	6.585
Region	ρ	T	SMSA		VM		MDUH		MV		MZSEP	
			K_{TV}	K_{TC}	K_{TV}	K_{TC}	K_{TV}	K_{TC}	K_{TV}	K_{TC}	K_{TV}	K_{TC}
V	0.01	1.00	0.940	0.966	0.947	0.947	0.947	0.947	0.947	0.947	0.947	0.947
L	0.71	1.05	6.876	9.799	8.796	6.578	6.050	7.534	5.785	7.695	5.628	7.400
HD-L	0.86	0.85	16.842	14.874	17.895	12.072	16.316	12.795	12.441	15.098	8.002	14.439
Sc	0.6	2.00	8.873	11.132	10.449	9.065	7.709	10.879	9.286	9.370	9.667	9.008
HD-Sc	1.00	2.00	59.662	-109.457	63.242	244.264	59.400	314.880	59.415	724.156	35.919	-87.549
L+V	0.767	0.72	6.585	10.715	7.853	5.725	7.697	4.317	7.628	8.047	2.779	7.972

K_{TV} indicates the isothermal compressibility via the virial route and K_{TC} is the isothermal compressibility via the compressibility route.

To highlight the disparities in how various closures predict the phase diagram of the Lennard-Jones fluid, and to showcase the advantages of the *CPE* over non-*CPE* methods like the Labik method, Figure 5-20 to Figure 5-34 are included in the thesis. These figures serve to visually demonstrate the comparative effectiveness of the *CPE* method against traditional approaches in accurately modeling the phase behavior of the Lennard-Jones fluid, especially the spinodal region.

The phase diagrams are computed using Equation 3.3-1. In this process, the pressure is determined by employing the virial Equation (equation 3.2-20), and the chemical potential is calculated using Equation 3.2-44 for the *CPE* method. However, for the Labik method the chemical potential for the vapor region is calculated using Equation 3.2-44 and for the liquid region Equation 3.2-45. The identification of the spinodal points is conducted as per the following method:

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,N} = -\left(\frac{\partial P}{\partial V}\right)_{T,N} = \frac{1}{VK_T} = 0 \quad 5.3-4$$

The prediction of the critical point is achieved by tracking the locus of spinodal points within both the liquid side and the vapor side. This involves identifying the points along the spinodal curve in each of these regions where the system's stability changes. The spinodal curve represents the limit of absolute stability of the homogeneous phase; beyond this curve, the fluid becomes unstable and phase separation occurs. By plotting these spinodal points for both the liquid and vapor regions and following their trajectories, the point where these two curves intersect is identified as the critical point. Table 5-9 show the calculated critical points for various closures. The critical point is presumed to be located at $T_c = 1.321 \pm 0.007$, $\rho_c = 0.316 \pm 0.005$, and $p_c = 0.129 \pm 0.005$ according to Stephan *et al.* (2019).

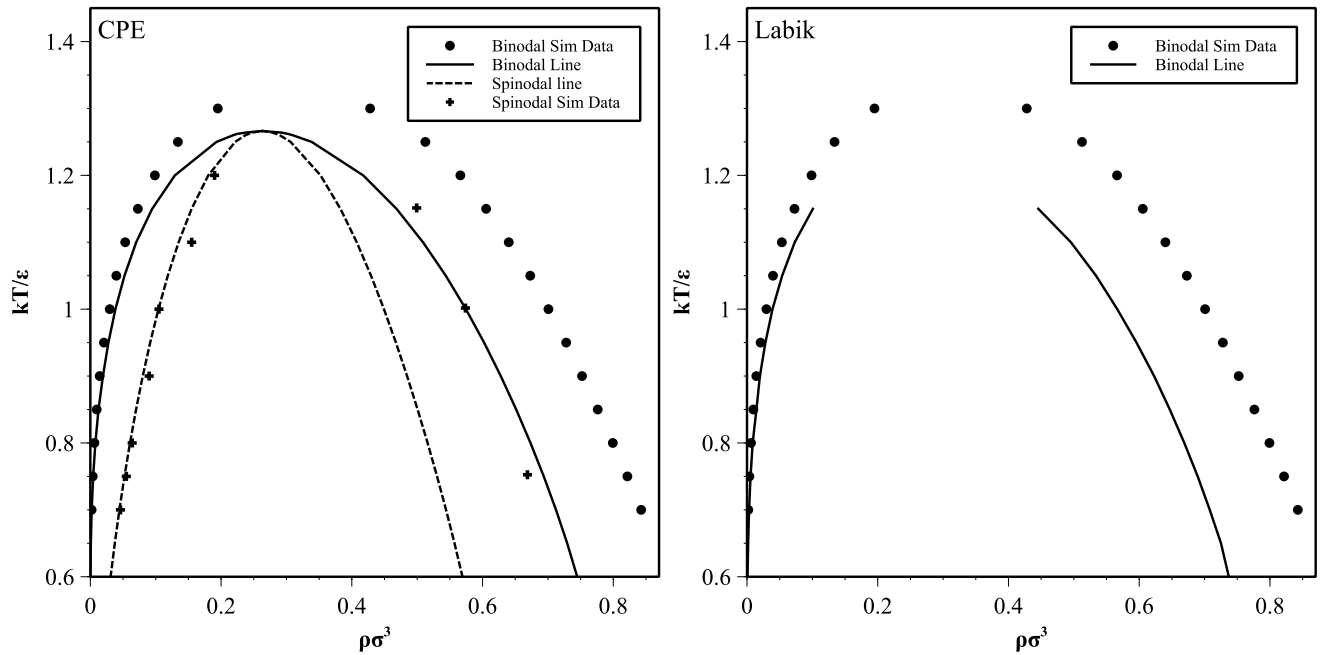


Figure 5-20 Lennard-Jones Phase Diagram using the *PY* closure.

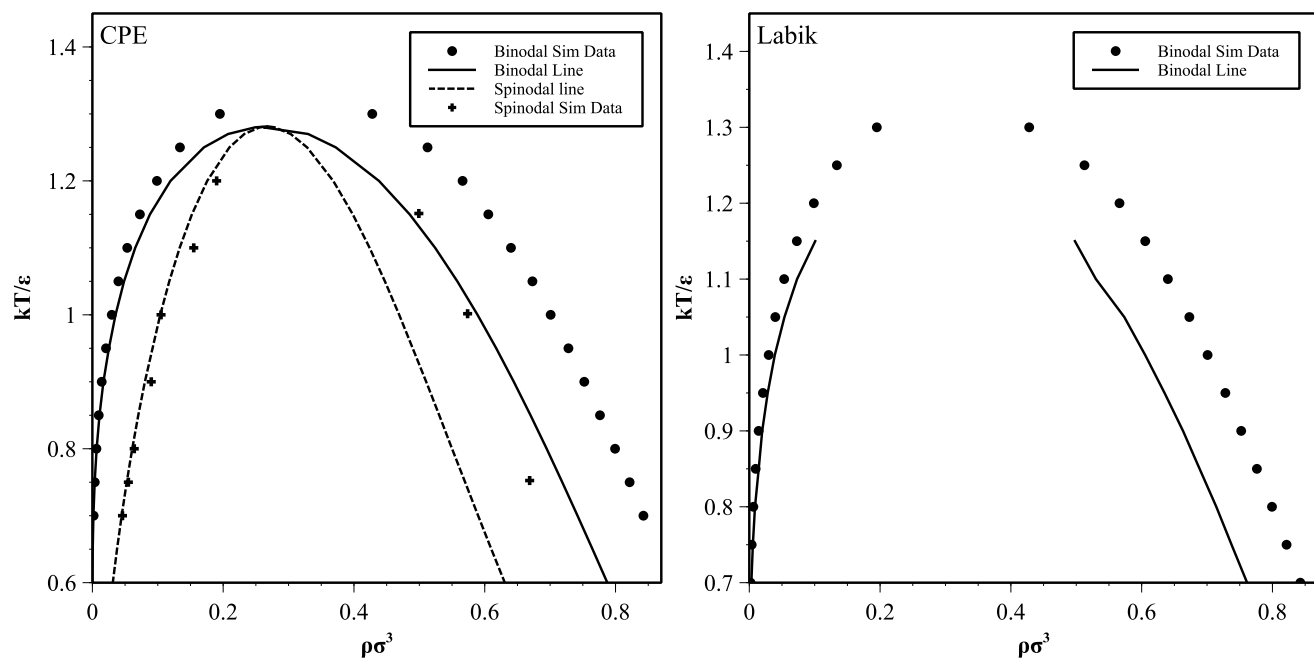


Figure 5-21 Lennard-Jones Phase Diagram using the *HNC* closure.

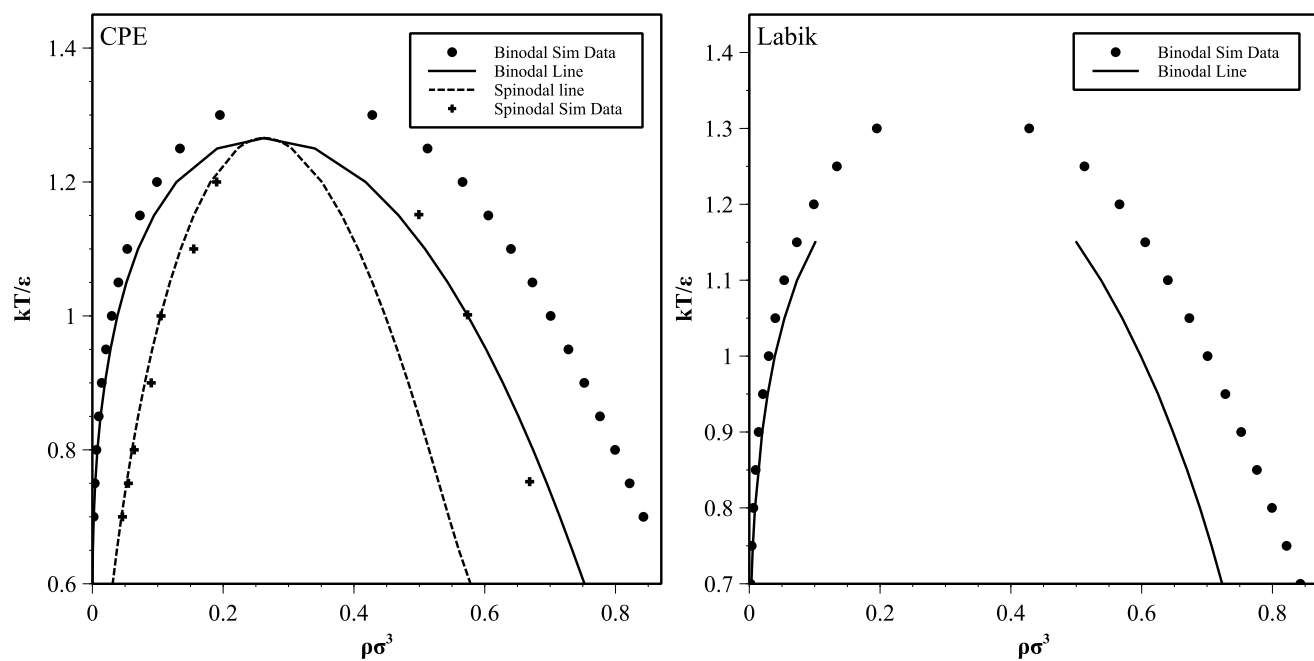


Figure 5-22 Lennard-Jones Phase Diagram using the *Verlet* closure.

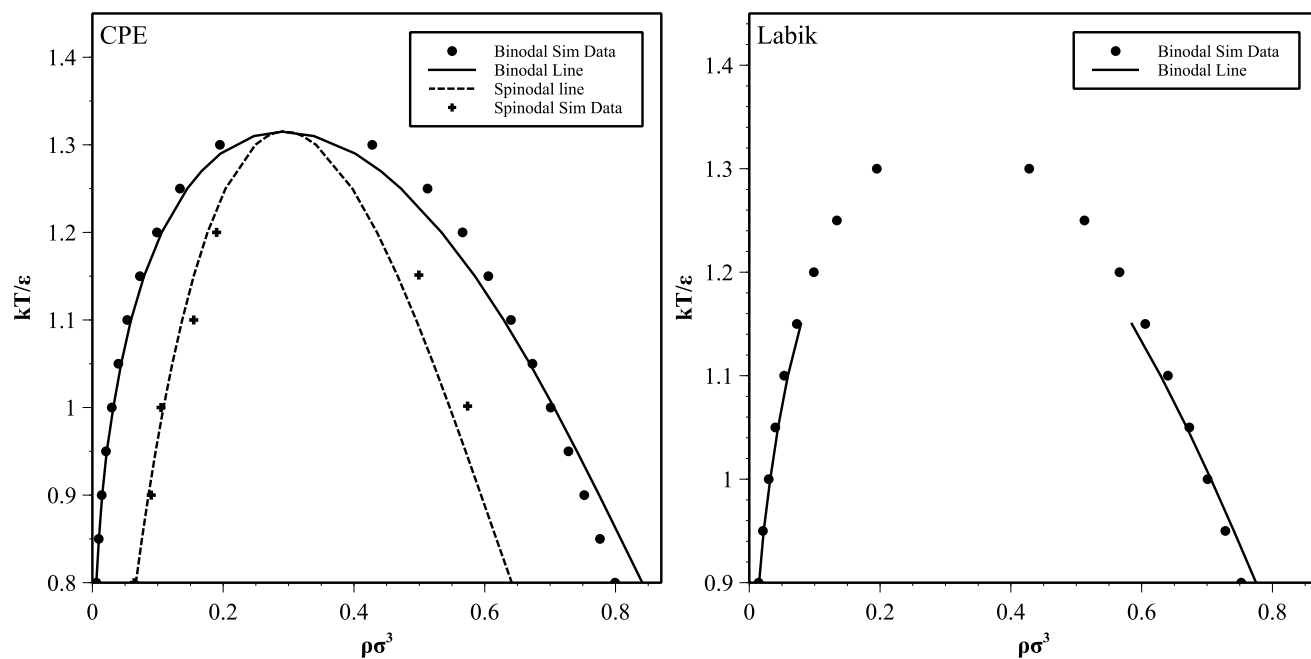


Figure 5-23 Lennard-Jones Phase Diagram using the *MS* closure.

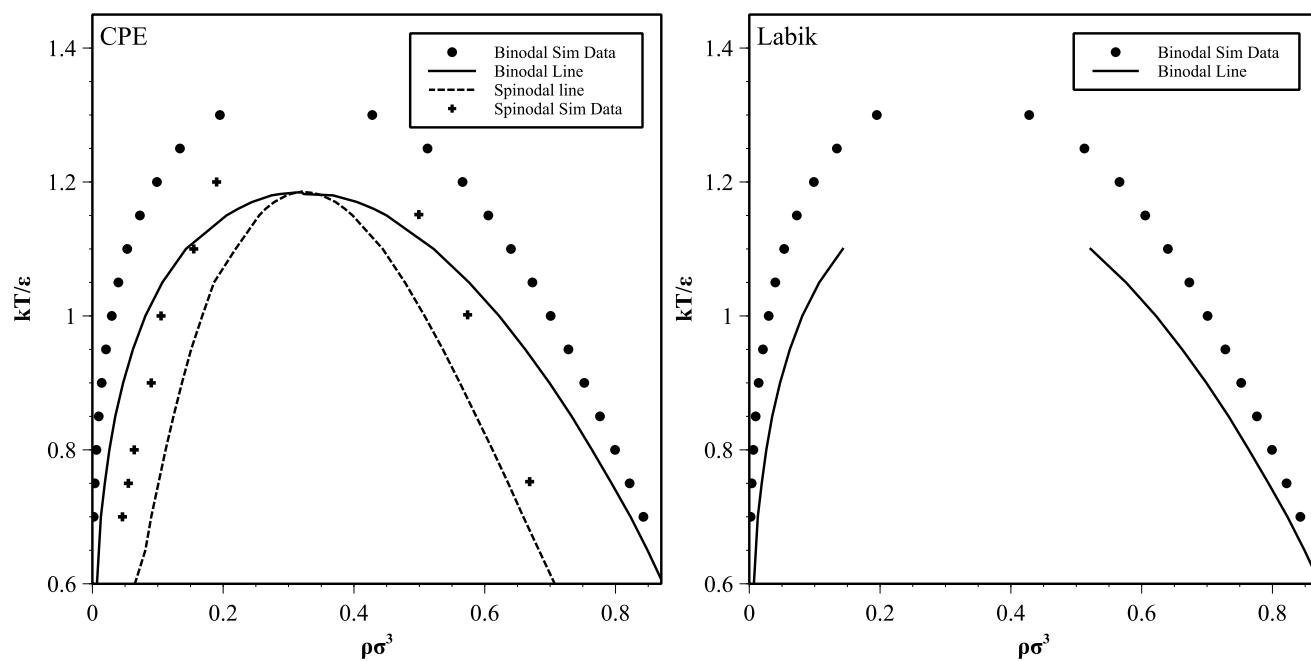


Figure 5-24 Lennard-Jones Phase Diagram using the *KH* closure.

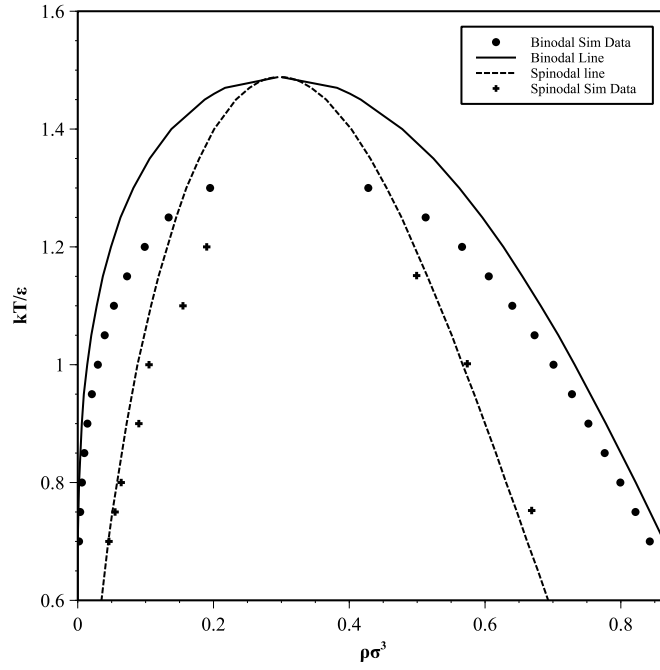


Figure 5-25 Lennard-Jones Phase Diagram using the SMSA closure.

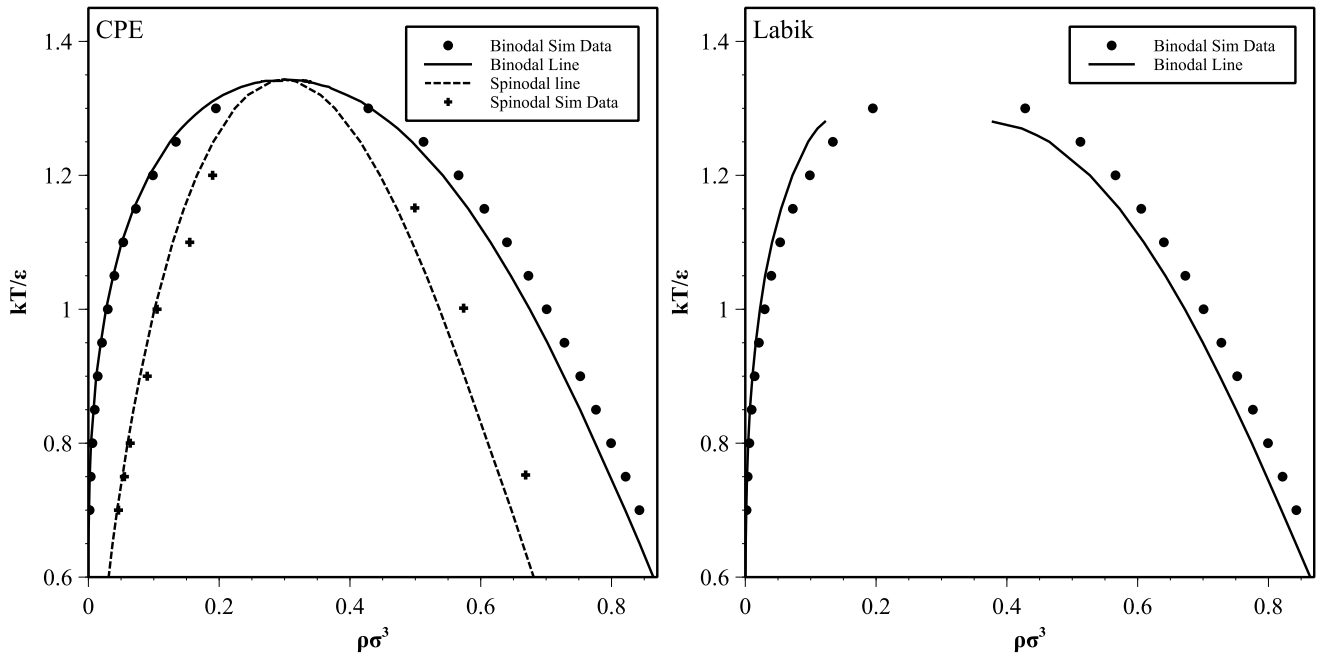


Figure 5-26 Lennard-Jones Phase Diagram using the VM closure.

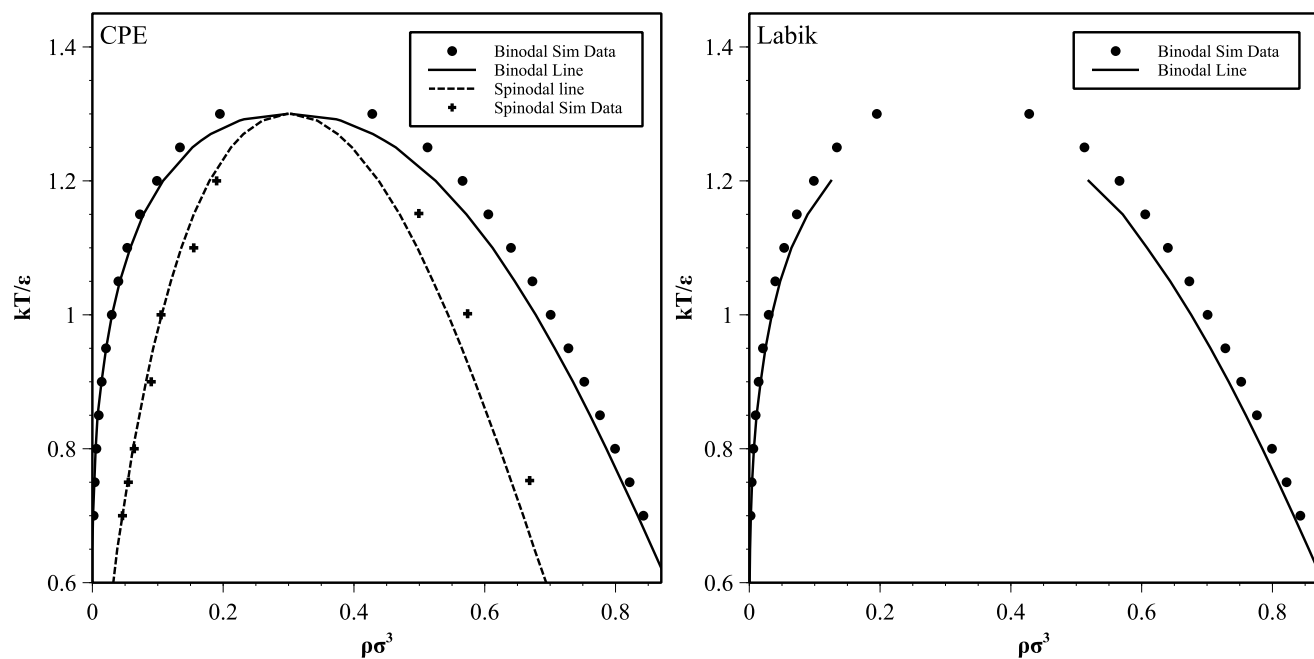


Figure 5-27 Lennard-Jones Phase Diagram using the *DUH* closure.

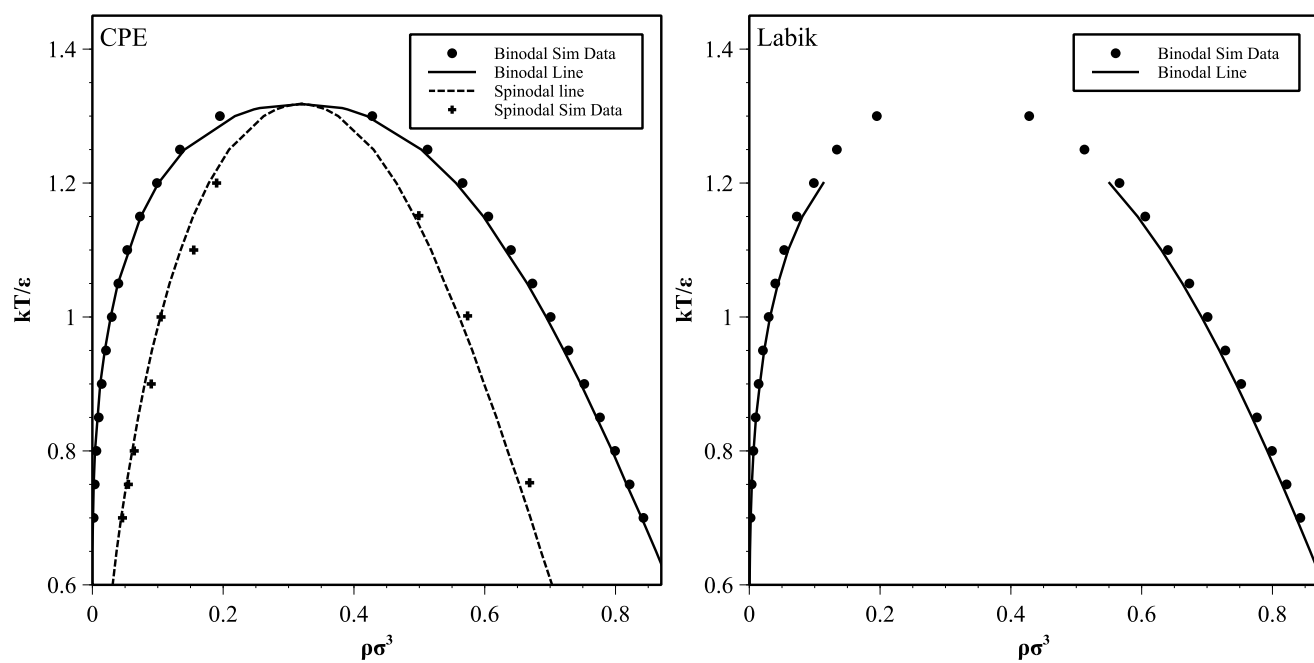


Figure 5-28 Lennard-Jones Phase Diagram using the *MDUH* closure.

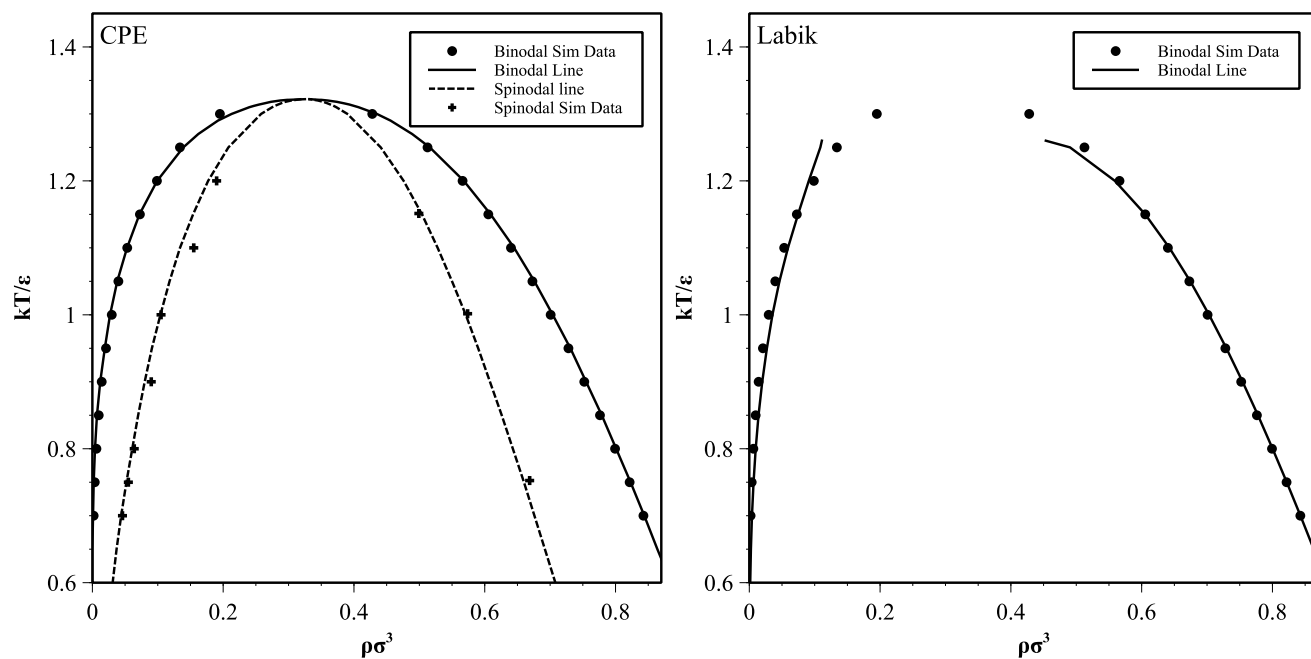


Figure 5-29 Lennard-Jones Phase Diagram using the *MV* closure.

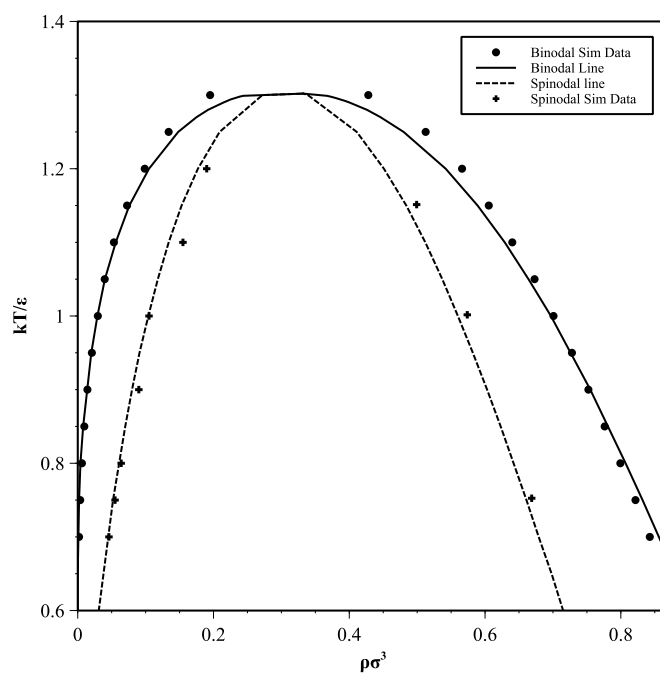


Figure 5-30 Lennard-Jones Phase Diagram using the *MZSEP* closure.

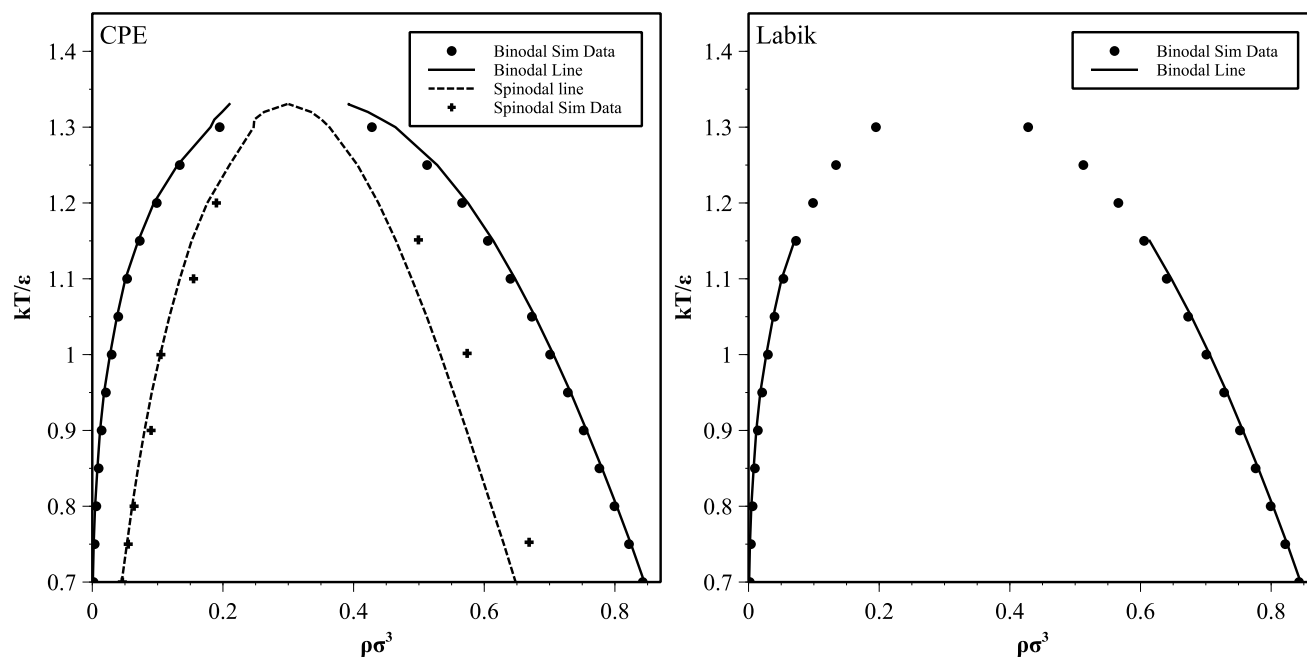


Figure 5-31 Lennard-Jones Phase Diagram using the *MHNC-L* closure.

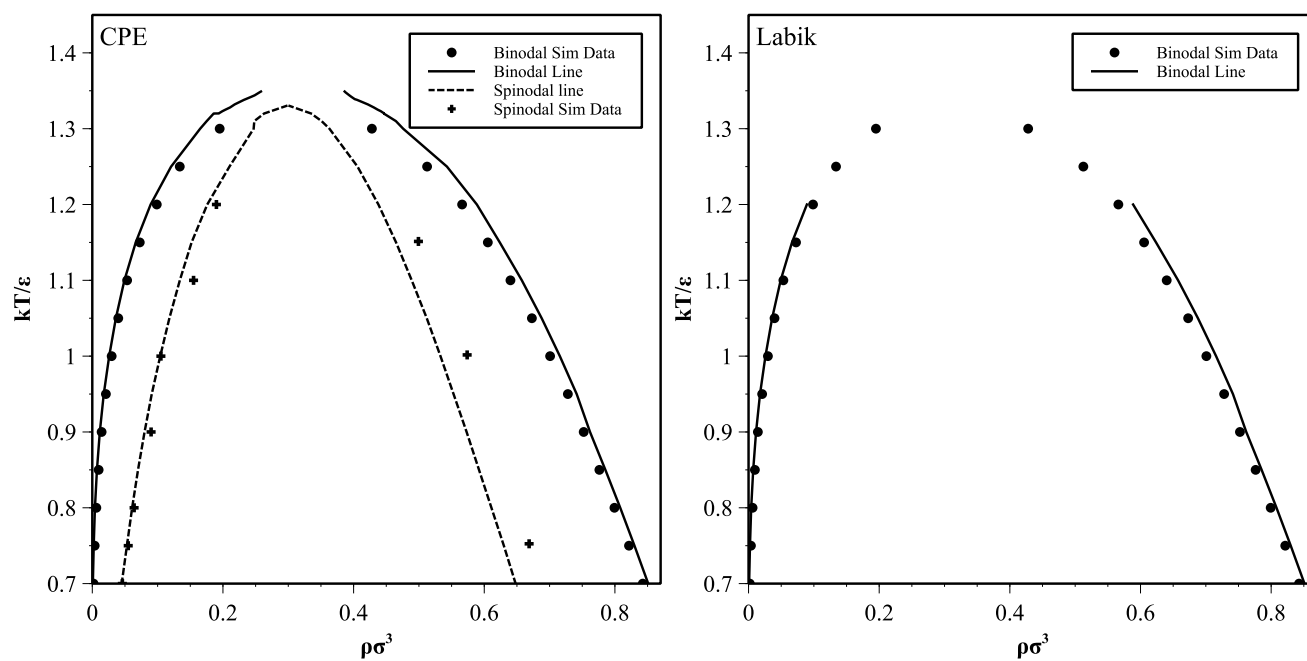


Figure 5-32 Lennard-Jones Phase Diagram using the *MHNC-V* closure.

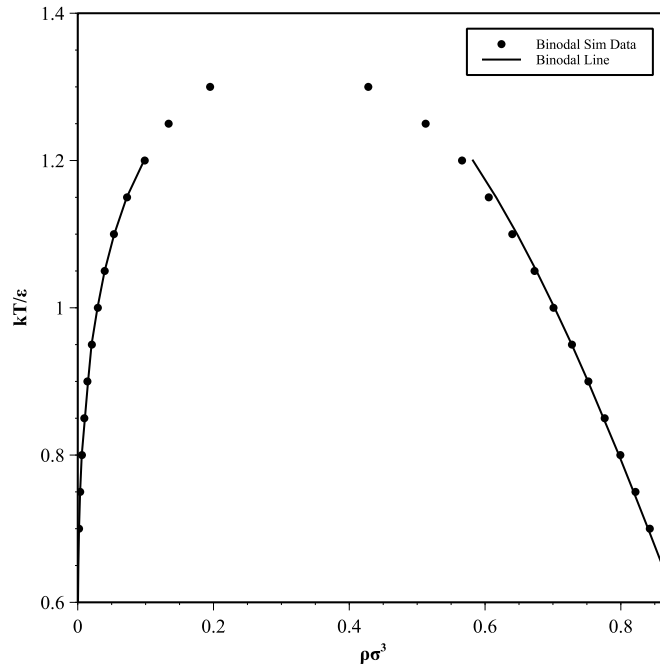


Figure 5-33 Lennard-Jones Phase Diagram using the *HMSA* closure.

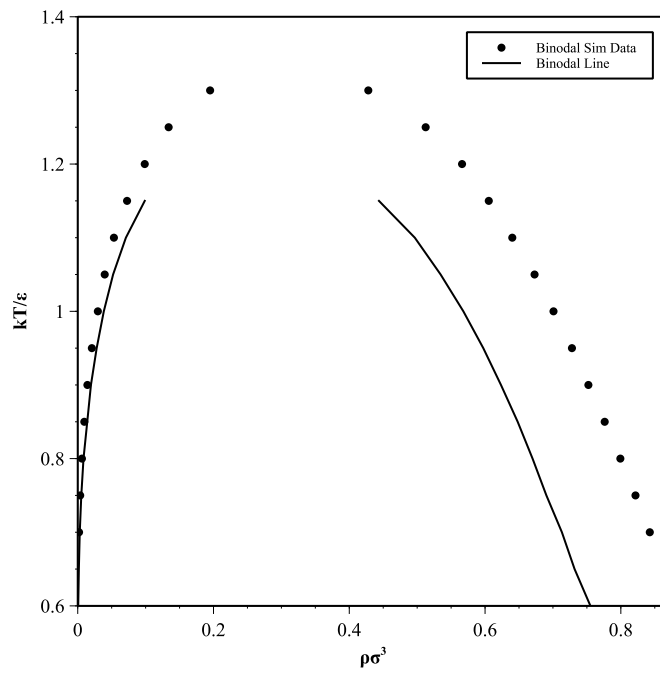


Figure 5-34 Lennard-Jones Phase Diagram using the *RY* closure.

Table 5-9 Critical point calculated by various closures.

Closure	Temperature	Density	Pressure
<i>PY</i>	1.266	0.263	0.114
<i>HNC</i>	1.281	0.267	0.118
Verlet	1.265	0.263	0.114
MS	1.263	0.269	0.113
KH	1.185	0.320	0.133
SMSA	1.488	0.301	0.159
VM	1.343	0.300	0.138
DUH	1.300	0.304	0.128
MDUH	1.318	0.320	0.135
MZSEP	1.302	0.332	0.127
MV	1.322	0.332	0.137
Simulation	1.321	0.316	0.129

Based on the analysis and the previous figures, it is straightforward to conclude that the MV closure exhibits superior accuracy in predicting the phase behavior, primarily attributed to the precise computation of the bridge function within the core region ($r < \sigma$). This precision in the bridge function leads to a more accurate estimation of the chemical potential, consequently resulting in reliable binodal and spinodal property calculations. Table 5-9 further corroborates the efficacy of the *MV* closure in accurately determining the critical point for the Lennard-Jones system. The selection of $u_d(r)$ plays a pivotal role in this process, especially since the direct correlation function $c(r)$ tends to asymptotically approach the negative long-range potential, particularly in the critical region (Berne, 2012). This aspect is critical in understanding the behavior of fluids near critical points. The *DUH* partition scheme of the Lennard-Jones potential, employed in closures such as *MV*, *DUH*, *MDUH*, and *MZSEP*, is instrumental in predicting the correct asymptotic behavior of the $c(r)$ function. This choice of partition scheme underpins the closures' ability to model the nuanced characteristics of the Lennard-Jones fluid accurately.

Additionally, the phase diagrams computed via the Labik method encounter convergence challenges in the coexistence phase region. The failure of the Labik method to converge at

certain points precludes these points from being valid representations of the true spinodal, as isothermal compressibility does not exhibit divergence at these locations. In contrast, the *CPE* method's determination of the spinodal is considered to be more accurate, reflecting the true spinodal as calculated by the closure. The discrepancies in spinodal accuracy among various closures are attributed to the specific closure characteristics rather than to the *CPE* method itself.

Furthermore, the Labik method primarily addresses long-range functions such as $g(r)$ and $\gamma(r)$, which cease oscillation beyond a certain distance. The *CPE* method, conversely, focuses on the derivatives of these functions relative to the coupling parameter exponent ζ , which are inherently short-ranged. This focus on short-range functions presents an advantage in resolving the *OZ* equation, as it prevents the singularity of the matrix required for solving simultaneous equations in Fourier space, a limitation often encountered with the Labik method. Figure 5-35 showcases $g(r)$ and its derivatives with respect to ζ . From this figure, it is evident that the derivatives are short-ranged when compared to $g(r)$, underscoring the effectiveness of the *CPE* method over the Labik method.

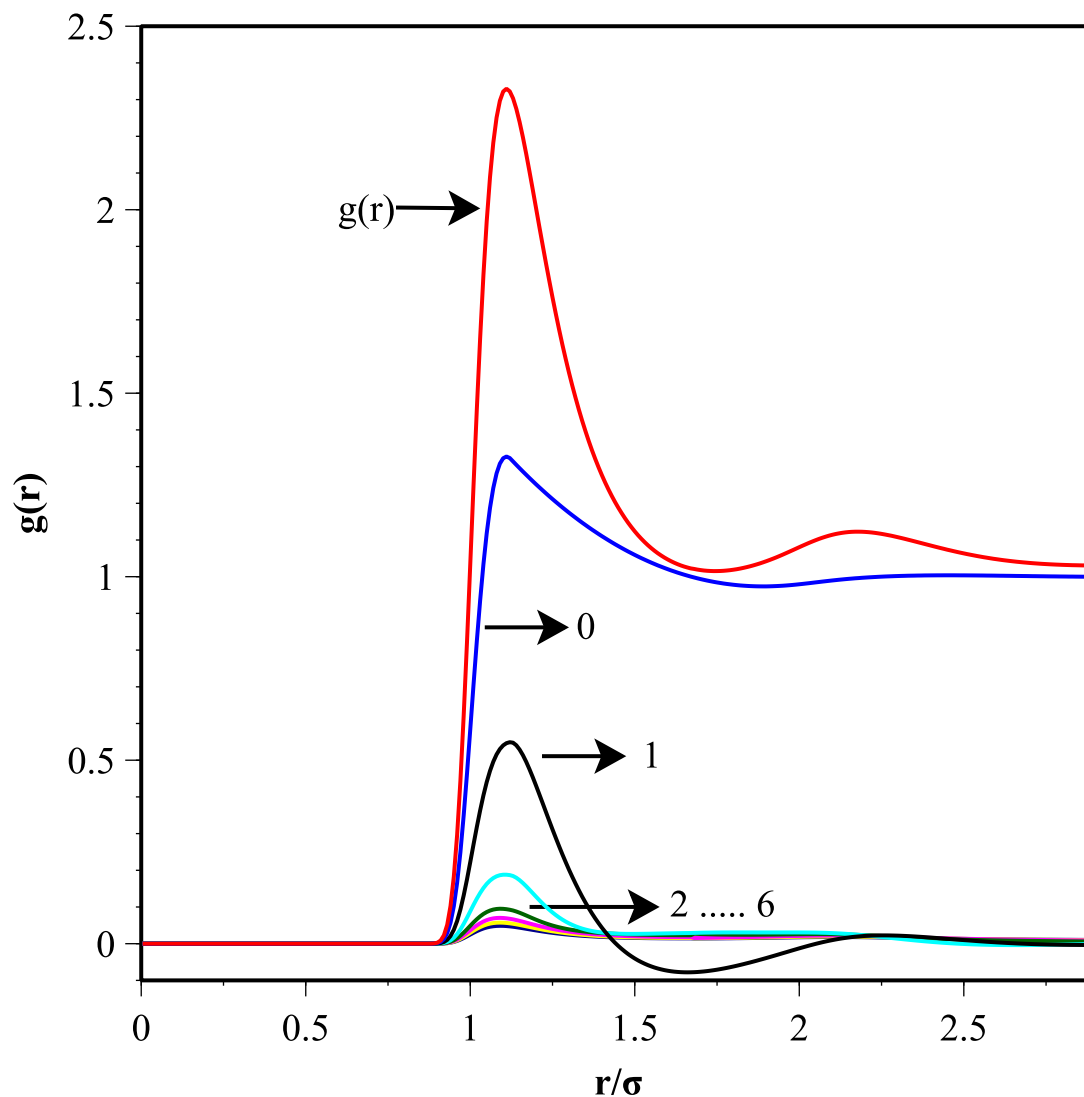


Figure 5-35 $g(r)$ and the 6 derivatives of $g(r)$ wrt ζ in terms of $g_n(r)/n!$ at $T = 1.1$ and $\rho = 0.25$

The occurrence of multiple solutions and singularities in the OZ equation within the liquid-vapor transition region has been thoroughly examined for the Lennard-Jones potential. This investigation has been conducted using the HNC closure, as referenced in Peplow *et al.* (2006). Peplow *et al.* has shown that the pseudo-arc-length continuation algorithm is essential for the direct application of Newton's method to the full potential, specifically for tracking the

singularities in the context of these studies. This algorithm allows for effective navigation through singular points. Indeed, the *OZ* equation exhibits more characteristic features in the liquid-vapor region, such as the 'fold-bifurcation' of solutions. However, the Coupling Parameter Expansion (CPE) method does not detect these singularities due to its foundational approach, which involves a series expansion about the repulsive component of the potential. This situation is somewhat akin to that of the van der Waals equation. While the van der Waals equation is free of singularities, it predicts a region of negative compressibility, demonstrating a similar limitation in capturing certain complexities of the system it models (Menon, 2021). Figure 5-36 shows case the pressure vs density phase diagram with three isotherms. The figure clearly shows how the *CPE* is able to capture the full isotherm and reach a solution inside the coexisting phase region.

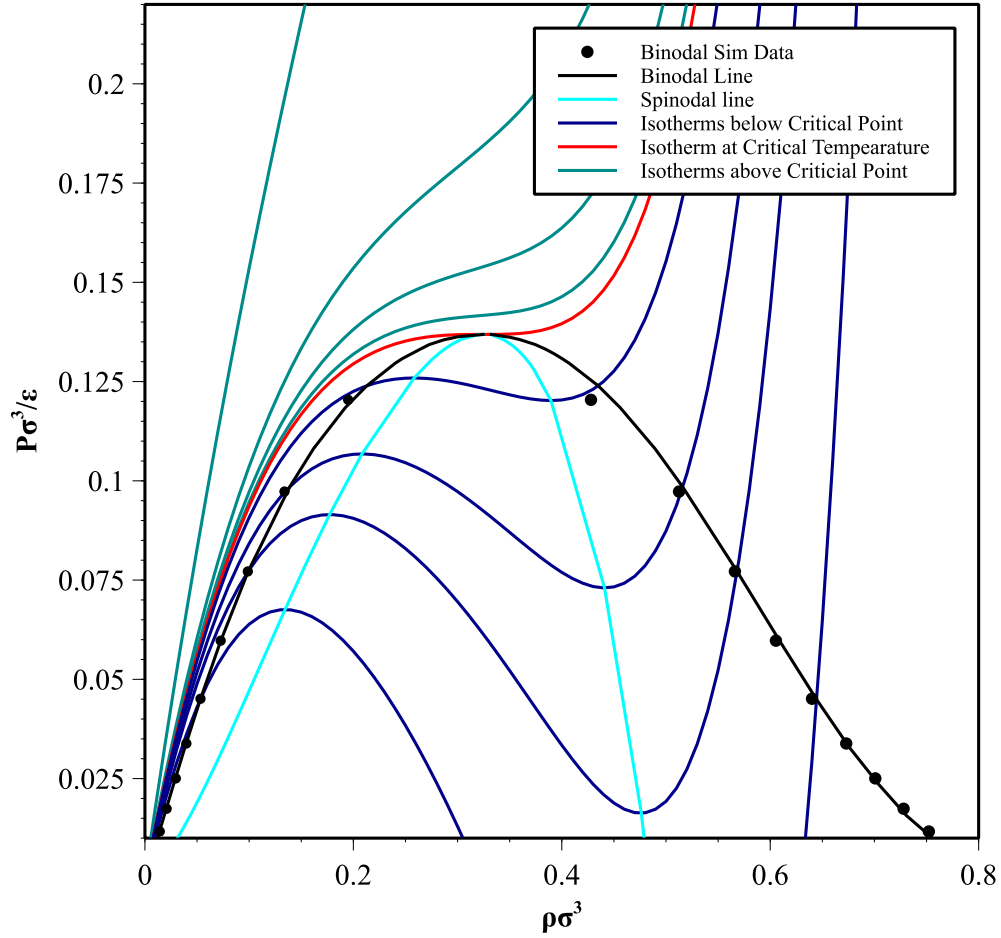


Figure 5-36 Pressure vs Density using the *CPE* for the *MV* closure.

The necessity of verifying whether the Coupling *CPE* yields any meaningful correlation functions, especially in the two-phase region, is therefore necessary. Figure 5-37 illustrates this assessment for the Lennard-Jones system, employing the *MV* closure. The figure shows the $c(r)$, the reference function $c^{(0)}(r)$ and six successive derivative terms $c^{(n)}(r)/n!$ at $T=1.1$ and $\rho=0.25$ corresponding to a state point inside the spinodal region. The expansion, as displayed, converges towards a well-defined function $c(r)$. Notably, the reference function $c^{(0)}(r)$ predominantly exhibits negative values. However, the positive aspect of $c(r)$ at $r > 1$, stemming from attractive interactions, contributes to the emergence of negative compressibility in the system. The

correlation functions derived in this context are considered nonphysical due to their generation of negative compressibility and the presence of a van der Waals loop in the pressure (Menon, 2021).

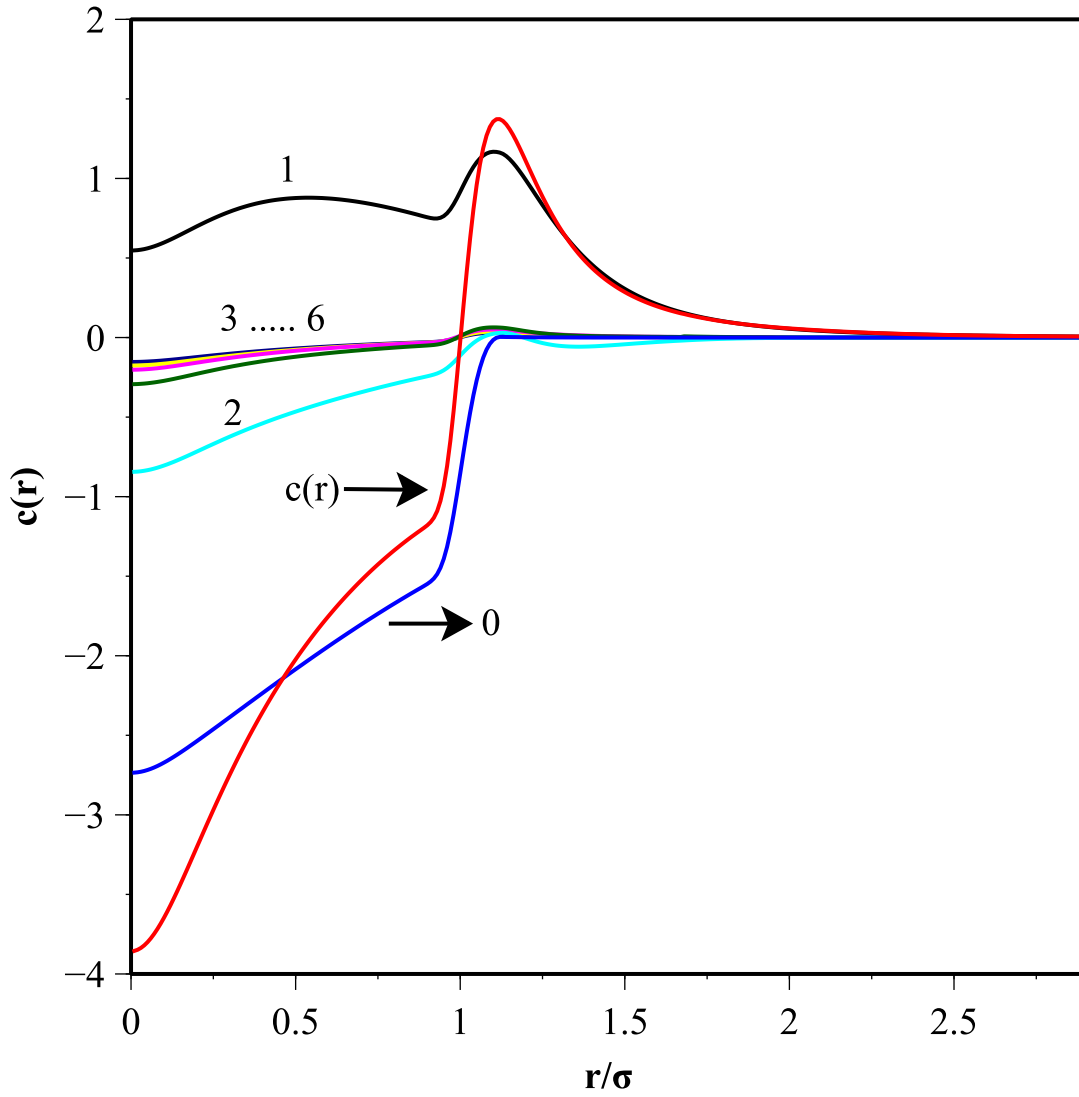


Figure 5-37 $c(r)$ and the 6 derivatives of $c(r)$ wrt ζ in terms of $g_n(r)/n!$ at $T = 1.1$ and $\rho = 0.25$

Chapter 6

KIRKWOOD-BUFF-FOWLER THEORY

6.1 Introduction

Surface tension at the liquid-vapor interface is a fundamental thermophysical property of fluids, deeply connected to a wide array of natural phenomena and a multitude of industrial applications. There have been numerous efforts to generalize and predict the behavior of experimental surface tension for pure substances. These efforts span a range of methodologies, from empirical to semi-empirical approaches. Such studies are crucial for understanding and utilizing the surface properties of fluids in both natural settings and various technological contexts. These generalized models and approaches play a significant role in advancing our knowledge and practical capabilities regarding the manipulation and application of fluids under different conditions (Reid *et al.*, 1987).

Surface tension, a key thermophysical property at the liquid-vapor interface, can be determined through methods grounded in statistical mechanics. These methods enable the calculation of surface tension by utilizing the intermolecular potential and analyzing key functions such as the radial distribution function $g(r)$ or the direct correlation function $c(r)$ within the liquid-vapor interface (Lekner and Henderson, 1977; Croxton, 1980; Rowlinson and Widom, 2013).

A primary challenge in calculating surface tension using statistical mechanics is determining the radial distribution function $g(r)$ or the direct correlation function $c(r)$. Typically, this problem has been addressed by focusing on the $g(r)$ or $c(r)$ of the liquid phase, especially for fluids characterized by a Lennard-Jones potential. The complexity lies in accurately modeling

these functions, as they are crucial in capturing the essence of molecular interactions and spatial distributions in the liquid phase. This approach to surface tension calculation, though challenging, is fundamental for understanding the microscopic underpinnings of surface phenomena in Lennard-Jones fluids, which are representative models for a wide range of real-world substances.

The simplest approximation for calculating surface tension and surface energy, especially near the triple point temperature, was proposed by Fowler (1937). This approximation considers a sharp, step transition from the liquid to vapor phases, without any interfacial zone or thickness. The essence of this approach is to simplify the model by ignoring the gradations and complexities of the interfacial region, which can be a suitable approximation under conditions close to the triple point. At such temperatures, the distinction between the liquid and vapor phases is more pronounced, making this abrupt transition model a reasonable approximation for studying surface phenomena. However, it's important to note that this model might not capture the nuances of the interfacial behavior at temperatures far from the triple point, where the interfacial zone plays a more significant role.

Qualitatively, it's evident that Fowler's approximation might introduce significant deviations, even at the triple-point temperature. This is primarily because it overlooks the interfacial thickness. To address this limitation, McLellan proposed a refinement. He introduced an expression for surface tension that incorporated the radial distribution functions (RDFs) of both vapor and liquid phases. In his approach, these RDFs were weighted using square-root functions, providing a more nuanced view than Fowler's stark liquid-to-vapor transition. McLellan's correction aimed to bring a more realistic representation of the interfacial behavior, recognizing the gradual change in density and structure across the liquid-vapor interface, thereby

enhancing the accuracy of surface tension calculations. This approach marked a significant step towards reconciling the simplicity of Fowler's model with the complex realities of phase interfaces.

The study by Freeman and McDonald (1973) provided values for surface tension and surface energy of Lennard-Jones fluids, computed using Fowler's approximation. Interestingly, their findings for surface tension showed a good alignment with experimental data for simple fluids near the triple point. This was somewhat unexpected, given the simplifications inherent in Fowler's model, particularly its neglect of interfacial thickness.

However, the study also revealed that their calculated values for surface energy deviated significantly from experimental results. This discrepancy highlights the limitations of the approximation, especially in contexts beyond the calculation of surface tension.

It is important to note that the computer simulations in Freeman and McDonald's study were converted into real units using Lennard-Jones parameters that differed from those used by other researchers. These specific Lennard-Jones parameters play a crucial role in determining the outcomes of such simulations and their subsequent comparison with experimental data. The choice of these parameters can significantly impact the validity and applicability of the simulation results, making it crucial to consider these factors when evaluating the accuracy and relevance of computational studies in the context of real-world fluids.

Fowler's approximation has seen diverse applications by various researchers, reflecting its utility in different contexts. Specifically, the $g(r)$ of the liquid phase has been determined through a variety of approaches. Studies like those by Shoemaker *et al.* (1970) and Berry *et al.* (1972) have utilized experimental data to obtain the $g(r)$ of the liquid phase. Salter and Davis

(1975) explored perturbative techniques to derive the $g(r)$. Perturbative methods, which involve small modifications to a known system to study changes in its behavior, offer a theoretical angle for understanding the liquid phase's properties within the framework of Fowler's approximation. The advancement in computer simulations has also been harnessed, as seen in the works of Gray and Gubbins (1975), Haile *et al.* (1976), and Rao and Berne (1979). These studies used computational models to simulate the conditions and properties of the liquid phase. The theoretical calculations employing Fowler's approximation have, in some instances, demonstrated alignment with experimental data to a certain degree. However, there are key considerations that must be taken into account when interpreting these findings. The Choice of Lennard-Jones parameters and the accuracy of the $g(r)$. These considerations imply that while theoretical calculations using Fowler's approximation can align with experimental data to some extent, the accuracy and reliability of these results are contingent upon the choices made in the parameters and the precision of the $g(r)$. Therefore, interpreting these results requires careful consideration of the methodologies and assumptions employed in each study.

6.2 Fowler's theory

In an attempt to study Macleod (1923) empirical Equation for surface tension from a statistical mechanical approach, Fowler (1937) developed an approximate theory for predicting the surface tension between vapor and liquid phases. The density of the vapor was neglected in his theory. Fowler (1937) started his theory by deriving an expression for the average total interaction energy between molecules located in a semi-infinite column (the interface) and molecules located in a semi-infinite volume at a fixed distance. He then proceeded to calculate the average force of repulsion between them. The surface tension was then calculated as a half of the work done in order to form a surface. The surface tension (γ^{sur}) was given by:

$$\gamma^{sur} = \frac{\pi\rho^2}{8} \int_0^\infty r^4 \frac{du}{dr} g(r) dr \quad 6.2-1$$

where, ρ is number density of the liquid phase, $u(r)$ is the intermolecular potential and $g(r)$ is the pair correlation function.

To derive a more general expression of the surface tension, Kirkwood and Buff (1949) used a rigorous approach using statistical mechanics. A Gibbs dividing surface with thickness l was defined in a rectangular coordinate system (x,y,z) as the (x,y) plane and z is normal to this plane. From the mechanical perspective, the interfacial tension is the sum of the actual stress (Σ_x) acting across a strip in the (y,z) plane parallel to the x direction and the contribution of the pressure normal to the interface. Therefore, the surface tension was expressed as follows:

$$\gamma = \Sigma_x + \int_{-l/2}^{l/2} p dz \quad 6.2-2$$

where, Σ_x was given by:

$$\Sigma_x = -kt \int_{-\frac{l}{2}}^{\frac{l}{2}} \rho^{(1)}(z) dz + \Sigma'_x \quad 6.2-3$$

The first term of Equation 6.2-3 is the contribution due to momentum transport, the second term Σ'_x is the intermolecular force transmitted across the strip and $\rho^{(1)}(z)$ is the singlet density which is a function of z normal to the interface.

Kirkwood and Buff (1949) estimated the pressures of the two homogeneous phases (α and β) from the common statistical mechanical definition of pressure:

$$p = kT\rho_\alpha^{(1)} - \frac{1}{6} \int r_{12} \left(\frac{du}{dr_{12}} \right) \rho_\alpha^{(2)}(r_{12}) dv_{12} \quad 6.2-4$$

$$p = kT\rho_\beta^{(1)} - \frac{1}{6} \int r_{12} \left(\frac{du}{dr_{12}} \right) \rho_\beta^{(2)}(r_{12}) dv_{12}$$

where, α, β two different phases and $\rho^{(2)}(r_1, r_{12})$ is the doublet density which is a function of the position of molecule 1 and the distance between molecule 1 and 2. Instead of expressing pressure for different phases by different equation, one Equation could express the pressure by defining a new singlet density ($\rho_{\alpha\beta}^{(1)}$) and doublet density ($\rho_{\alpha\beta}^{(2)}$) with respect to a Gibbs dividing surface:

$$\begin{aligned}\rho_{\alpha\beta}^{(1)} &= [1 - A(z)] \rho_{\alpha}^{(1)} + A(z) \rho_{\beta}^{(1)}, \\ \rho_{\alpha\beta}^{(2)} &= [1 - A(z)] \rho_{\alpha}^{(2)} + A(z) \rho_{\beta}^{(2)}, \\ A(z) &= 0, \quad z < 0, \\ A(z) &= 1, \quad z \geq 0,\end{aligned}\tag{6.2-5}$$

where, $A(z)$ is a unit step function. The pressure was then expressed as:

$$p = kT \rho_{\alpha\beta}^{(1)} - \frac{1}{6} \int r_{12} \left(\frac{du}{dr_{12}} \right) \rho_{\alpha\beta}^{(2)}(r_{12}) dv_{12}\tag{6.2-6}$$

To evaluate Σ'_x , the average force exerted by molecules in an element of volume (dv_{12}) above the strip in (y,z) plane on molecules in an element of volume (dv_1) below the strip was given by:

$$\rho^{(2)}(z_1, r_{12}) \nabla u(r_{12}) dv_1 dv_{12}\tag{6.2-7}$$

The component $d\Sigma'_x$ is then evaluated as:

$$d\Sigma'_x = \mathbf{e}_x \cdot \nabla u(r_{12}) \rho^{(2)}(z_1, r_{12}) dv_{12} dv_1\tag{6.2-8}$$

where, $\mathbf{e}_x$ is the unit vector parallel to the x direction. Integration of Equation 6.2-8 over all configuration r_1 below the (y,z) strip and over all configuration r_{12} above the strip led to the following expression:

$$\Sigma'_x = \frac{1}{2} \int_{-l/2}^{l/2} \int \frac{x_{12}^2}{r_{12}} \frac{du}{dr_{12}} \rho^{(2)}(z_1, r_{12}) dv_{12} dz\tag{6.2-9}$$

Equation 6.2-3 becomes:

$$\Sigma_x = - \int_{-\frac{l}{2}}^{\frac{l}{2}} p'(z) dz \quad 6.2-10$$

$$p'(z) = kT\rho^{(1)}(z) - 1/2 \int \frac{x_{12}^2}{r_{12}} \frac{du}{dr_{12}} \rho^{(2)}(z, r_{12}) dv_{12}$$

As l approaches infinity the surface tension is given by:

$$\gamma = \int_{-\infty}^{\infty} (p - p'(z)) dz \quad 6.2-11$$

Combining Equation 6.2-10 and Equation 6.2-6 leads to the following equation:

$$p - p'(z) = -kT\rho_s^{(1)}(z) + 1/2 \int \frac{x_{12}^2}{r_{12}} \frac{du}{dr_{12}} \rho_s^{(2)}(z, r_{12}) dv_{12} \quad 6.2-12$$

where, $\rho_s^{(1)}$ and $\rho_s^{(2)}$ were defined as the excess singlet and doublet densities with respect to the Gibbs dividing surface. The surface tension is then expressed by:

$$\begin{aligned} \gamma &= -kT \Gamma_s^{(1)} + 1/2 \int \frac{x_{12}^2}{r_{12}} \frac{du}{dr_{12}} \Gamma_s^{(2)}(r_{12}) dv_{12} \\ \Gamma_s^{(1)} &= \int_{-\infty}^{\infty} \rho_s^{(1)}(z) dz \\ \Gamma_s^{(2)} &= \int_{-\infty}^{\infty} \rho_s^{(2)}(z, r_{12}) dz \end{aligned} \quad 6.2-13$$

$\Gamma_s^{(1)}$ and $\Gamma_s^{(2)}$ are the superficial density and the pair superficial density. Equation (13) is a general theory for surface tension. The evaluation of γ greatly depends on the accuracy of $\Gamma_s^{(1)}$ and $\Gamma_s^{(2)}$.

$\Gamma_s^{(1)}$ and $\Gamma_s^{(2)}$ are difficult to evaluate accurately therefore approximation had to be made. For an equilibrium system of liquid and vapor, choosing a dividing surface of minimal thickness causes $\Gamma_s^{(1)}$ to vanish to zero. Furthermore, $\rho^{(1)}$ and $\rho^{(2)}$ are approximated by:

$$\begin{aligned}
\rho^{(1)}(z) &= \rho^{(1)}, & z &\leq 0 \\
\rho^{(1)}(z) &= 0, & z &> 0 \\
\rho^{(2)} &= \rho^{(1)}(z_1) \rho^{(1)}(z_1 + z_{12}) g^{(2)}(z_1, r_{12}) \\
g^{(2)}(z_1, r_{12}) &= g^{(2)}(r_{12})
\end{aligned}
\tag{6.2-14}$$

For pure fluids, the surface tension is then reduced to the same form derived by Fowler (1937) (equation 6.2-1).

6.3 Fowler's theory modifications

The surface energy U^{sur} and the surface tension γ^{sur} according to Fowler's approximation is given as follows:

$$U^{sur} = -\frac{\pi\rho_l^2}{2} \int_0^\infty r^3 u(r) g(r) dr \tag{6.3-1}$$

$$\gamma^{sur} = \frac{\pi\rho_l^2}{8} \int_0^\infty r^4 \frac{du}{dr} g(r) dr \tag{6.3-2}$$

Under Fowler's approximation, the expressions for calculating the surface energy U^{sur} and surface tension γ^{sur} of Lennard-Jones fluids can be further refined by including the contribution of the vapor density are given by Lekner and Henderson (1977) (LH):

$$U^{sur} = -\frac{\pi(\rho_l - \rho_v)^2}{2} \int_0^\infty r^3 u(r) g(r) dr \tag{6.3-3}$$

$$\gamma^{sur} = \frac{\pi(\rho_l - \rho_v)^2}{8} \int_0^\infty r^4 \frac{du}{dr} g(r) dr \tag{6.3-4}$$

where ρ_l and ρ_v are the coexisting densities of the liquid and the vapor phases.

McLellan (1952) proposed an alternative approach for calculating surface tension that involves a more subtle treatment of the radial distribution functions (RDFs) of both the vapor

and liquid phases. In his expression, McLellan introduced a method to weight these RDFs using square-root functions. McLellan (ML) expression is as follows:

$$\gamma^{sur} = \frac{\pi}{8} \int_0^\infty r^4 \frac{du}{dr} \left[\rho_l \sqrt{g_l(r)} - \rho_v \sqrt{g_v(r)} \right]^2 dr \quad 6.3-5$$

Given McLellan's expression for surface tension, the surface energy can be deduced from this Equation as follows:

$$U^{sur} = -\frac{\pi}{2} \int_0^\infty r^3 u(r) \left[\rho_l \sqrt{g_l(r)} - \rho_v \sqrt{g_v(r)} \right]^2 dr \quad 6.3-6$$

The modifications to the Fowler approach, as developed by Fitts (1969) and M. V. Berry *et al.* (1972), continue to consider the vapor-phase density as effectively zero, similar to the original framework. These revisions, however, introduce a new aspect in modeling the density within the surface transition zone. This is done through a continuous function $\rho(z)$, where z represents a coordinate perpendicular to the surface. In this model, the location of z relative to the interface is key: larger values of z ($z > 0$) are in the vapor phase, values of z less than zero ($z < 0$) are in the liquid phase, and z equal to zero is at the interface itself.

When computing the effect of surface thickness on surface tension, various density profiles can be utilized. Expressions for γ^{sur} have been derived using different forms of these profiles. A linear density profile, for example, implies a straightforward, proportional change in density across the surface transition zone. In contrast, a cubic profile provides a more complex model, where the rate of change in density varies in a cubic relationship across the interface, allowing for a more gradual transition. Additionally, an exponential density profile represents a scenario where the density changes more rapidly or gradually, depending on the distance from the interface. Fitts (1969) introduced the linear (FTL) and cubic density (FTC) profiles into the

Fowler theory, whereas the exponential density profile was introduced by M. V. Berry *et al.* (1972) (MVB) . The linear profile is given by:

$$\frac{\rho(z)}{\rho_l} = \begin{cases} \frac{1}{2} \left(1 - \frac{z}{b}\right) & -b \leq z \leq b \\ \rho_l & z < -b \\ 0 & z > b \end{cases} \quad 6.3-7$$

Therefore, the corresponding surface tension is given as:

$$\gamma^{sur} = \frac{\pi}{3} \rho_l^2 \int_0^{2b} r^4 \left(\frac{r}{5b} - \frac{r^2}{32b^2} \right) \frac{du(r)}{dr} g(r) dr + \frac{\pi}{8} \rho_l^2 \int_{2b}^{\infty} r^4 \frac{du(r)}{dr} g(r) dr \quad 6.3-8$$

The cubic profile is given by:

$$\frac{\rho(z)}{\rho_l} = \begin{cases} \left(\frac{z^3}{4b^3} - \frac{3z}{4b} \right) + \frac{1}{2} & -b \leq z \leq b \\ \rho_l & z < -b \\ 0 & z > b \end{cases} \quad 6.3-9$$

The corresponding surface tension for the cubic density profile is therefore given by:

$$\begin{aligned} \gamma^{sur} = & \pi \rho_l^2 \int_0^{2b} r^4 \left(\frac{2r}{25b} - \frac{r^3}{70b^3} + \frac{r^4}{256b^4} - \frac{r^6}{12800b^6} \right) \frac{du(r)}{dr} g(r) dr \\ & + \frac{\pi}{8} \rho_l^2 \int_{2b}^{\infty} r^4 \frac{du(r)}{dr} g(r) dr \end{aligned} \quad 6.3-10$$

The exponential profile is given by:

$$\frac{\rho(z)}{\rho_l} = \begin{cases} 1 - \frac{1}{2} \exp\left(\frac{z}{L}\right) & z \leq 0 \\ \frac{1}{2} \exp\left(-\frac{z}{L}\right) & z > 0 \end{cases} \quad 6.3-11$$

Therefore, the corresponding surface tension is as follows:

$$\gamma^{sur} = \pi \rho_l^2 \int_0^\infty \left(\frac{r^4}{L^4} - \frac{8r^2}{L^2} + 72 - \exp\left(\frac{-r}{L}\right) \left(\frac{4r^3}{L^3} + \frac{28r^2}{L^2} + \frac{72r}{L} + 72 \right) \right) \frac{du(r)}{dr} g(r) dr \quad 6.3-12$$

Lekner and Henderson (1977), in their study, made significant modifications to Fowler's theory to more accurately represent the properties of the liquid-vapor interface. Recognizing the limitations of Fowler's original assumption that vapor density is zero, they incorporated the vapor density into their model. Moreover, they accounted for the effect of surface thickness and the density profile within the interfacial zone, which are crucial for a realistic depiction of the interface.

To achieve this, Lekner and Henderson employed the thermodynamic definition of surface tension. In thermodynamics, surface tension is defined as the isothermal change in the Helmholtz free energy associated with the formation of a unit area of surface at constant volume. This perspective on surface tension allows for a more comprehensive understanding of the interfacial phenomena.

Lekner and Henderson's derivation of surface tension γ^{sur} was based on the deformation method originally proposed by Harasima (1953) and Toda (1955). They managed to simplify the general expression for γ^{sur} into a triple integral. This simplification was not just theoretical elegance; it also yielded a practical formula for calculating surface tension. In addition to γ^{sur} , they also derived a similar triple integral expression for the surface energy U^{sur} . Crucially, both γ^{sur} and U^{sur} in their model depend explicitly on several factors: the intermolecular potential, the radial distribution function $g(r)$, and the density profile $\rho(z)$ within the interface zone.

According to Lekner and Henderson derivation, the general expression for the surface tension and the surface energy for the Lennard-Jones fluid is given as follows:

$$U^{sur} = -\pi(\rho_l - \rho_v)^2 \int_0^\infty r^3 u(r) g(r) \left[-\frac{r^2}{2} + q_1(r) + q_2(r) \right] dr \quad 6.3-13$$

$$\gamma^{sur} = \frac{\pi(\rho_l - \rho_v)^2}{2} \int_0^\infty r^4 \frac{du}{dr} g(r) \left[\frac{r^4}{4} + p_1(r) + p_2(r) \right] dr \quad 6.3-14$$

Where the functions $q_1(r)$, $q_2(r)$, $p_1(r)$ and $p_2(r)$ are as follows:

$$q_1(r) = -2 \int_{-r}^r z \phi(z) dz - 2r \left[\int_r^\infty \phi(z) dz - \int_{-\infty}^r \phi(z) dz \right] \quad 6.3-15$$

$$q_2(r) = \int_{-\infty}^\infty \phi(z_1) dz_1 \int_{z_1-r}^{z_1+r} \phi(z_2) dz_2 \quad 6.3-16$$

$$p_1(r) = -2 \int_{-r}^r z \phi(z) (r^2 - z^2) dz \quad 6.3-17$$

$$p_2(r) = \int_{-\infty}^\infty \phi(z_1) dz_1 \int_{z_1-r}^{z_1+r} \phi(z_2) (r^2 - 3z_2^2) dz_2 \quad 6.3-18$$

with z is the distance along an axis perpendicular to the interface surface and $\phi(z)$ represents a correction to the step function $\phi_{step}(z)$ from liquid to vapor densities in order to produce the density profile in the interfacial zone. The density profile is then as follows:

$$\rho(z) = \phi_{step}(z) + \phi(z) \quad 6.3-19$$

Two models for the density profile are presented, the exponential model (*LHE*) and the Fermi's hyperbolic tangent model (Croxtan, 1980) (*LHF*). The exponential model is given by:

$$\rho(z) = \begin{cases} \rho_l - \frac{\rho_l - \rho_v}{2} \exp\left(\frac{z}{\lambda}\right) & z \leq 0 \\ \rho_v + \frac{\rho_l - \rho_v}{2} \exp\left(-\frac{z}{\lambda}\right) & z > 0 \end{cases} \quad 6.3-20$$

where $\lambda = (2 \ln 5)^{-1} t$, t is the 10-90 thickness. Lekner and Henderson (1978) shows that the parameter t is relatively insensitive to different choices of density profiles. Equation 6.3-20 is similar to Equation 6.3-11 except for the involvement of the vapor density in Equation 6.3-20.

Therefore $L = \lambda$ in Equation 6.3-11 and $2b = t$ in equations 6.3-8 and 6.3-10. The Fermi's hyperbolic tangent model is as follows:

$$\rho(z) = \frac{\rho_l + \rho_v}{2} - \frac{\rho_l - \rho_v}{2} \text{Tanh}\left(\frac{z}{2\delta}\right) \quad 6.3-21$$

where $\delta = (2\ln 9)^{-1}t$. The corresponding surface energy and the surface tension for the exponential density profile (equation 6.3-20) is presented by:

$$U^{sur} = -\frac{\pi(\rho_l - \rho_v)^2}{2} \int_0^\infty ru(r)g(r) \left\{ r^2 + \lambda^2 \left[4 - e^{-r/\lambda} \left(4 + \frac{r}{\lambda} \right) \right] \right\} dr \quad 6.3-22$$

$$\begin{aligned} \gamma^{sur} = & \frac{\pi(\rho_l - \rho_v)^2}{2} \int_0^\infty \frac{du}{dr} g(r) \left\{ \frac{r^4}{4} \right. \\ & \left. + \lambda^4 \left[18 - \frac{2r^2}{\lambda^2} - e^{-r/\lambda} \left(18 + \frac{18r}{\lambda} + \frac{7r^2}{\lambda^2} + \frac{r^3}{\lambda^3} \right) \right] \right\} dr \end{aligned} \quad 6.3-23$$

Furthermore, the corresponding surface energy and the surface tension for the Fermi's hyperbolic tangent model (equation 6.3-21) is as follows:

$$U^{sur} = -\frac{\pi(\rho_l - \rho_v)^2}{2} \int_0^\infty ru(r)g(r) \left[r^2 + 4\delta^2 \int_0^{r/\delta} x(e^x - 1)dx \right] dr \quad 6.3-24$$

$$\gamma^{sur} = \frac{\pi(\rho_l - \rho_v)^2}{2} \int_0^\infty \frac{du}{dr} g(r) \left[\frac{r^4}{4} + 2\delta^4 \int_0^{r/\delta} x \left(3x^2 - \frac{r^2}{\delta^2} \right) (e^x - 1)^{-1} dx \right] dr \quad 6.3-25$$

Chapter 7

RESULTS OF INTERFACIAL PROPERTIES

In this chapter of the thesis, the focus is on presenting the results of numerical calculations based on Fowler's theory and its subsequent modifications, particularly highlighting the application of the most accurate $g(r)$ obtained through the *MV* closure. These calculated results are then systematically compared with available simulation data, providing a benchmark for assessing the accuracy and applicability of the theoretical models.

Additionally, the chapter includes a comparative analysis with the *PY* closure. The *PY* closure is known to be inherently less accurate than the *MV* closure, especially in terms of modeling $g(r)$. By comparing the outcomes of the *PY* and *MV* closures, the chapter aims to demonstrate the significant impact that using a more accurate $g(r)$ model can have on the calculated values of surface tension and surface energy within the framework of Fowler's theory and its modifications.

This comparison not only underscores the importance of choosing an appropriate model for $g(r)$ in theoretical calculations but also illustrates how improvements in one aspect of the model, such as the radial distribution function, can enhance the overall predictive power and reliability of the theory when applied to complex fluid systems. The chapter, thus, contributes to a deeper understanding of the interplay between different theoretical components in the study of surface phenomena in fluids.

7.1 Methodology

The *MV* closure is implemented for the computation of $g(r)$ and the coexistent liquid and vapor densities in the Flower approximation and its variants. The 't' parameter in the equations,

where surface thickness is a factor, is taken from Baidakov *et al.* (2000)'s simulation data. This data selection is based on the extensive nature of the simulation, characterized by a high particle count, numerous time steps, considerable cut-off distance in interaction potential truncation, and a diverse temperature range. For surface tension comparison with simulation data, studies by Baidakov *et al.* (2000), Werth *et al.* (2017) and by Freeman and McDonald (1973) are referenced. Baidakov *et al.*'s approach involved molecular dynamic simulation with an explicit consideration of interfacial thickness, whereas Werth *et al.*'s study featured a simulation where gas and liquid phases were in direct contact. Similarly, Freeman and McDonald numerically solved Fowler's approximations using Monte Carlo integration. They used experimental $g(r)$ in their solution. The calculated surface energy will be juxtaposed with experimental data sourced from Stansfield (1958) and from the results obtained by Freeman and McDonald.

The calculated results are also compared with the results of the study conducted by Galán *et al.* (2005). The study of Galán *et al.* utilized the Fowler modifications Equation 6.3-22, Equation 6.3-23, Equation 6.3-24 and Equation 6.3-25. The $g(r)$ used in their study was the low density approximation (LDA) proposed by Lekner and Henderson (1977). They also used an approximation for the $g(r)$ proposed by Xu and Hu (1986) (XH) and an expression for the $g(r)$ proposed by Cuadros *et al.* (1998) (COS). Furthermore, for the coexisting vapor and liquid densities of Lennard-Jones fluid they used the expressions proposed by Okrasinski *et al.* (Okraśiński *et al.*, 2001b, 2001a).

7.2 Results

To demonstrate the critical role of the accuracy of $g(r)$ in the Kirkwood-Buff-Fowler theory, Figure 7-1 is presented. This figure shows the surface tension calculated using the Fowler approximation (equation 6.3-2), with both *MV* and *PY* closures for $g(r)$. The data from Figure 7-1

clearly indicates that the precision of $g(r)$ substantially affects the accuracy of the results. Specifically, the *MV* closure provides a more accurate $g(r)$, and consequently, γ^{sur} calculated using the *MV* closure's $g(r)$ is more precise than that obtained with the *PY* closure. Similarly, Figure 7-2, which depicts the surface energy computed using Equation 6.3-1, supports the same conclusion, highlighting the significant influence of the closure method on the accuracy of these calculations.

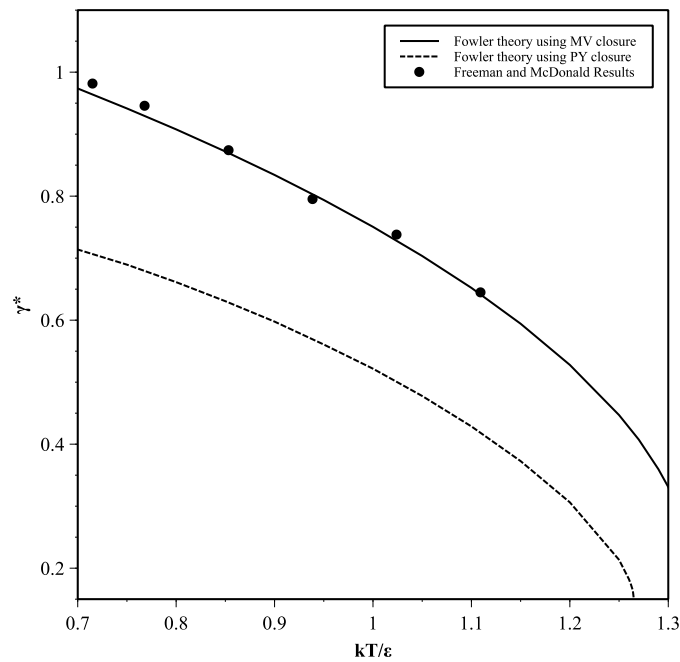


Figure 7-1 Surface tension for the Lennard-Jones fluid calculated using the *MV* closure for the $g(r)$.

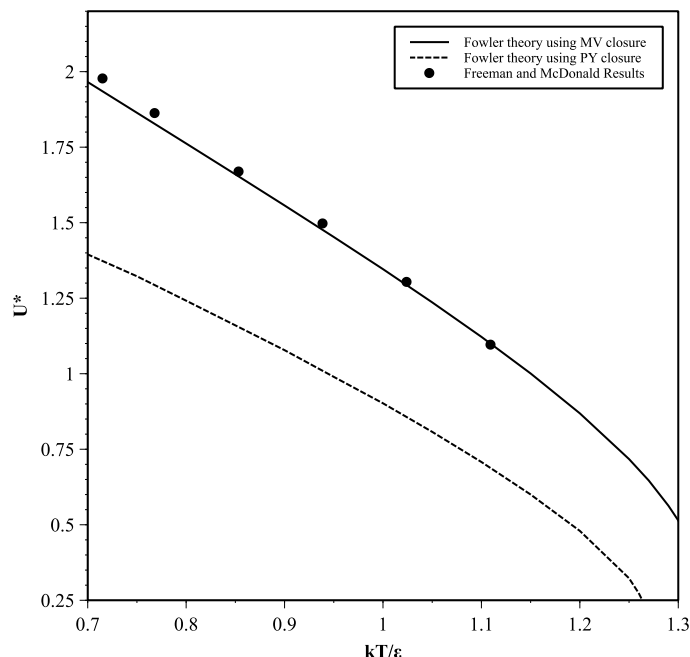


Figure 7-2 Surface Energy for the Lennard-Jones fluid calculated using the *MV* closure for the $g(r)$.

To explore the impact of interfacial thickness on surface tension, Figure 7-3 illustrates results from various Fowler modifications (Equation 6.3-4, Equation 6.3-5, Equation 6.3-8, Equation 6.3-10, Equation 6.3-12, Equation 6.3-23, and Equation 6.3-25), each using the *MV* closure for $g(r)$. Modifications that don't consider interfacial thickness (equation 6.3-4 and Equation 6.3-5) show less accuracy than others, except at the triple point. Accuracy of these modifications decreases with higher temperature. The linear density profile (Equation 6.3-8) proves slightly more accurate than the cubic density profile (Equation 6.3-10). Modifications with exponential density profiles (Equation 6.3-12 and Equation 6.3-23) are most accurate. In contrast, the modification using Fermi's hyperbolic tangent model (Equation 6.3-25) is least accurate.

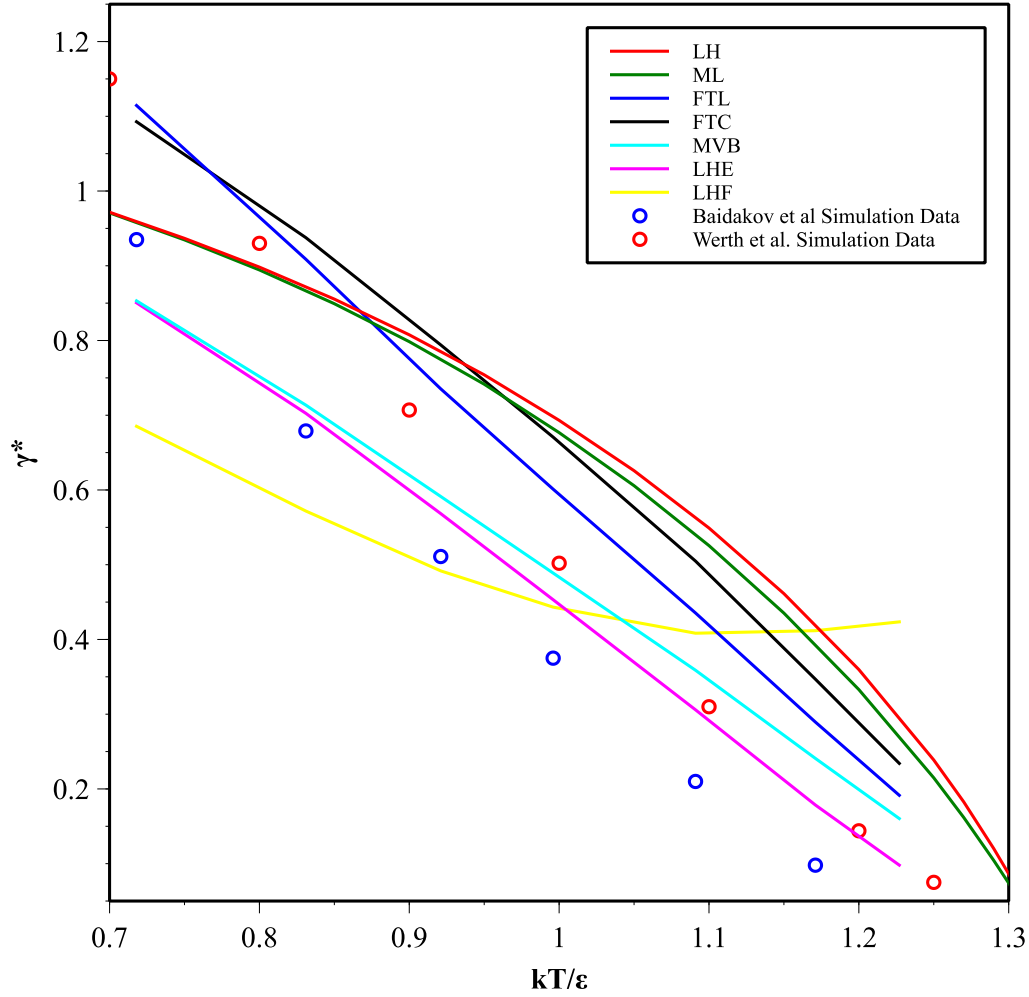


Figure 7-3 Surface tension calculated by various Fowler modification with the utilization of the *MV* closure for the $g(r)$

Figure 7-4 presents the calculation of surface energy using different Fowler modifications (equation 6.3-3, Equation 6.3-6, Equation 6.3-22, and Equation 6.3-24). In this analysis, it is observed that the modifications which do not incorporate surface thickness (equation 6.3-3 and Equation 6.3-6) are less precise compared to those that do. Notably, the model employing an exponential density profile (equation 6.3-22) emerges as the most accurate. In the context of surface energy, the modification utilizing Fermi's hyperbolic tangent model (equation 6.3-24)

delivers results that are comparable, yet still less accurate than those of the exponential density profile model.

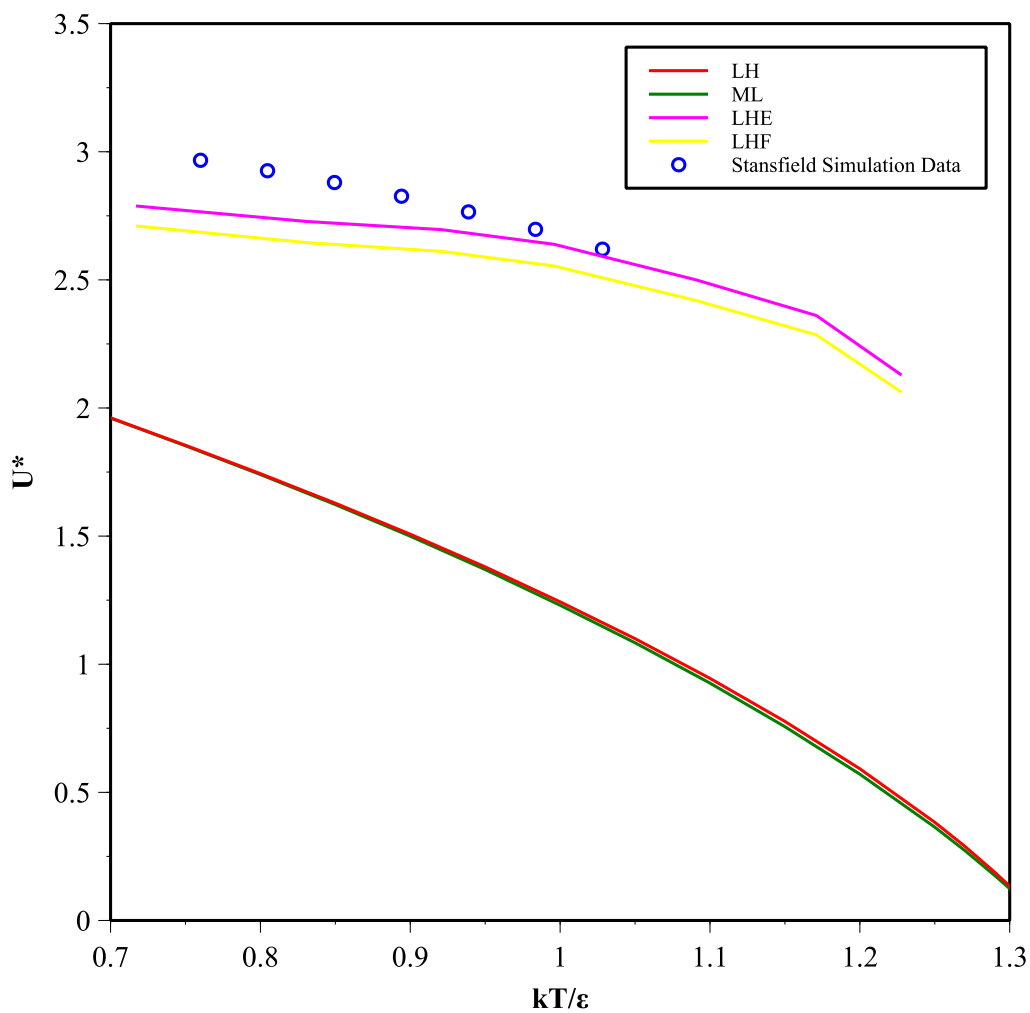


Figure 7-4 Surface energy calculated by various Fowler modification with the utilization of the MV closure for the $g(r)$

Table 7-1 the surface tension calculated using Equation 6.3-23, applying different approximations for the Lennard-Jones fluid $g(r)$ and the MV closure $g(r)$. The results demonstrate that the MV $g(r)$ leads to a notable enhancement in accuracy over other models, particularly at higher temperatures. The accuracy improvement of the MV $g(r)$ significantly enhances the calculated surface tension.

Furthermore, the COS $g(r)$ expression, as utilized by Galán *et al.*, shows improvement over other expressions, attributed to its being a fitted model to computer simulations specifically for the Lennard-Jones $g(r)$. However, Galán *et al.* required the use of two separate expressions to evaluate the coexisting liquid and vapor densities, highlighting a limitation in their approach.

The predictive power of the Ornstein-Zernike (OZ) integral Equation becomes evident in this context, as the vapor and liquid coexisting densities were evaluated using the MV closure itself. This aspect underscores the MV closure's capability to produce an accurate $g(r)$ that, in turn, yields more precise surface tension calculations, surpassing even those models that were directly fitted to simulation data.

Table 7-1 Surface tension calculated using Equation 6.3-23 with different $g(r)$ taken from Galán *et al.* and the $g(r)$ calculated from the MV closure. The simulation data are taken from Baidakov *et al.*

T	γ_{sim}^{sur}	γ^{sur}			
		MV	COS	LDA	XH
0.718	0.935	0.850	0.946	1.441	1.012
0.831	0.679	0.703	0.759	1.085	0.791
0.921	0.511	0.568	0.606	0.826	0.617
0.996	0.375	0.453	0.480	0.632	0.479
1.091	0.21	0.306	0.325	0.409	0.315
1.171	0.098	0.178	0.193	0.233	0.183
1.227	0.04	0.098	0.108	0.128	0.101

Chapter 8

CONCLUSION & RECOMMENDATIONS

8.1 Conclusion

In this work 15 *OZ* closures were studied by *CPE* and non-*CPE* methods to determine which closure was the most accurate in predicting the Lennard-Jones fluid thermodynamic and structure properties.

The *CPE* method is highly effective in calculating the radial distribution function ($g(r)$). *CPE* exhibits superiority over traditional methods such as the Picard and Newton-Raphson methods. The *CPE* enables straightforward calculation of $g(r)$ in regions of the phase diagram where the Picard and Newton-Raphson methods are ineffective. By employing the *CPE* method, both the spinodal and the critical points of the closures discussed in this thesis were successfully evaluated, tasks at which the conventional methods are inadequate.

The study emphasizes the superior performance of renormalized closures, especially in liquid and coexistence regions of the phase diagram. The *MV* closure is highlighted for its accuracy across various thermodynamic properties. In the context of renormalized closures, the selection of the partition scheme has significant impact on the accuracy of the closure. It was found that the closures that incorporate the *DUH* partition scheme have an enhanced accuracy over the closures that incorporated the *WCA* scheme. The *DUH* scheme is developed based on fitting simulation data of the Lennard-Jones bridge function.

For thermodynamic property prediction, all closures exhibit low Mean Absolute Error (*MAE*) in the vapor region. In contrast, renormalized closures with renormalized bridge functions demonstrate enhanced *MAE* in the liquid phase, high-density liquid phase, and the liquid+vapor

coexistence region. Furthermore, the accuracy of the bridge function in renormalized closures, especially in the core region, leads to more reliable calculations of the chemical potential, crucial for phase equilibrium calculations. The consequence of accurate bridge function in renormalized closures, especially in the core region, leads to more reliable calculations of the chemical potential, crucial for phase equilibrium calculations.

Finally, this work extends the analysis to surface tension and energy calculations using Fowler's theory and its modifications. It demonstrates that the precision of the radial distribution function ($g(r)$) substantially influences the accuracy of these calculations, with the *MV* closure providing enhanced precision.

Overall, the research contributes significantly to the field by providing a comprehensive evaluation of various closure methods, highlighting the importance of choosing the appropriate closure method based on the specific region of the phase diagram being studied. The detailed analysis of renormalized closures, particularly the *MV* closure, and the exploration of surface tension and energy calculations further enrich the understanding of the behavior of the Lennard-Jones fluid and similar systems.

8.2 Recommendations and Future Work

The findings and implications of this dissertation on the *OZ* closures for the Lennard-Jones fluid suggest several promising directions for future research. One area of exploration is the applicability of renormalized closure methods, particularly the *MV* closure, to more complex fluids such as polar or ionic liquids. Investigating these methods in diverse chemical environments could provide valuable insights into their versatility and limitations. Another significant aspect highlighted by this work is the importance of accurate bridge functions. Therefore, future research could focus on developing new and more accurate bridge function,

potentially enhancing the predictive power of the *OZ* for Lennard-Jones fluid. Additionally, the study suggests potential modifications to the Kirkwood-Buff-Fowler theory, which primarily employs the homogeneous liquid $g(r)$. By adapting this theory to specifically use the radial distribution function within the interfacial zone, it could become more relevant and accurate for a wider range of applications, offering a more detailed understanding of interfacial phenomena. These research directions aim not only to expand the theoretical framework but also to improve the practical applicability of these theories to more complex and realistic compounds.

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Publications Submitted

Integral Equation Theories for the Lennard-Jones Fluid, Nayef M. Alsaifi, Ahmad H. Alrashidy.

Publications under Review/Preparation

A Modified Closure for Lennard-Jones Fluid (Under Review).

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