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Classical and Statistical Thermodynamics of Gas Solubility in Polar Fluids.

Christopher Paul Williams

Louisiana State University and Agricultural & Mechanical College

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Classical and statistical thermodynamics of gas solubility in polar fluids

Williams, Christopher Paul, Ph.D.
The Louisiana State University and Agricultural and Mechanical Col., 1987
CLASSICAL AND STATISTICAL THERMODYNAMICS
OF GAS SOLUBILITY IN POLAR FLUIDS

A Dissertation
Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in
The Department of Chemical Engineering

by
Christopher Paul Williams
B.Sc. Exeter University, England, 1981
M.S. Louisiana State University, 1984
May 1987
Dedicated to my parents Alec and Emily Joyce
Acknowledgement

I would like to express my most sincere thanks to my major professor Dr. Edward McLaughlin for the opportunity to attend L.S.U. and for his guidance both intellectual and personal. I feel compelled to recognize the immense help offered to me by my office-mate for the last two years, Dr. Sumnesh K. Gupta. Thanks to John Coon for his constant questioning, suggestions and friendship. One of my lasting memories of the department will be the companionship and comaraderie of the graduate students. I wish them all the best.

Last, but of course not least, I must thank my parents for the innumerable sacrifices they have made, their encouragement and love without which I simply couldn’t have done this.

Thanks to Carol Fowler for typing this dissertation. And good luck to Baton Rouge Rugby Football Club. Thanks for the memories.
Publications and Presentations

(1) "The Solubility of Aromatic Hydrocarbons in Mixtures of Benzene and Cyclohexane"
P.B. Choi, C.P. Williams, K. Buehring and E. McLaughlin

(2) "Perturbation Theory of Liquids"
C.P. Williams and S. Gupta

(3) "High Pressure Solubility of Gases and Gas Mixtures in Liquids"
C.P. Williams, P.B. Choi and E. McLaughlin
In preparation

(4) "Perturbation Theory and Computer Simulation of Polar Fluids"
C.P. Williams, S. Gupta and E. McLaughlin
Submitted to Journal of Chemical Physics

(5) "Improved Experimental Techniques for High Pressure Vapor-Liquid Equilibria"
C.P. Williams, P.B. Choi and E. McLaughlin,
Presented at A.I.Ch.E. Annual National Meeting, Chicago, IL.
November 1985.

(6) "Computer Simulation of Diatomic Fluids"
S.K. Gupta, J.E. Coon, C.P. Williams and E. McLaughlin
Presented at A.I.Ch.E. Spring National Meeting, New Orleans, LA.
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Symbol List - Classical Thermodynamics

\[ A \] - Helmholtz free energy

\[ A_{ij} \] - Scatchard-Hildebrand equation parameter

\[ f \] - fugacity

\[ G \] - Gibbs free energy

\[ g \] - molar Gibbs free energy

\[ \bar{g} \] - partial molar Gibbs free energy

\[ H \] - Henry's Law constant

\[ N \] - number of particles

\[ n \] - number of moles

\[ P \] - pressure

\[ R \] - molar gas constant

\[ T \] - temperature

\[ V \] - volume

\[ v \] - molar volume

\[ \bar{v} \] - partial molar volume

\[ X \] - liquid phase composition

\[ Y \] - vapor phase composition

Greek Symbols

\[ \beta \] - coefficient of isothermal compressibility

\[ \gamma \] - activity coefficient

\[ \phi \] - fugacity coefficient

\[ \Lambda \] - Wilson's equation parameter
Superscript

E - excess property
id - ideal fluid value
l - liquid phase
o - pure component
pg - perfect gas value
res - residual property
s - saturation value
v - vapor phase
\textasteriskcentered - unsymmetric convention
\infty - infinite dilution

Subscripts

i,j,k - component indices
ij - binary interaction index
r - reference
Symbol List - Statistical Thermodynamics

A - Helmholtz free energy

A0, A1, A2 - Terms in Zwanzig's expansion for the Helmholtz free energy

d - hard-body diameter

g - radial distribution function

h - Planck's constant

k - Boltzmann's constant

m - molecular mass

N - number of particles

n - unnormalized distribution function

P - pressure

P( ) - probability

Q - canonical partition function

r - interparticle separation

Δr - separation shell size

T - temperature

U - total intermolecular potential

u - binary intermolecular potential

X - composition

X( ) - configuration property

Y - spherical harmonic coefficient

y - background correlation function

Zc - configurational integral

Greek Symbols

α - Barker-Henderson perturbation expansion parameter
\( \beta \) - Boltzmann factor \((1/kT)\)
\( \gamma \) - Barker-Henderson perturbation expansion parameter
\( \varepsilon \) - Lennard-Jones potential energy parameter
\( \lambda \) - square-well potential parameter
\( \phi \) - azimuthal angle
\( \Phi() \) - averaged potential
\( \eta \) - Zwanzig's perturbation parameter
\( \Theta \) - Euler angle
\( \mu \) - dipole moment
\( \rho \) - particle density
\( \sigma \) - Lennard-Jones potential separation parameter
\( \omega \) - combined Euler angle representation

**Superscripts**

BH - Barker-Henderson
d - hard-body diameter
HB - hard-body fluid
HS - hard-sphere fluid
LJ - Lennard-Jones
o - reference
p - perturbation
WCA - Weeks-Chandler-Anderson
\( \star \) - dimensionless property or complex conjugate

**Subscripts**

\( i,j,k,\ell \) - component indexes
\( ij \) - binary interaction index
ABSTRACT

The solubilities of argon and of three binary gas mixtures of nitrogen and methane, 25%CH₄ - 75%N₂, 50%CH₄ - 50%N₂ and 75%CH₄ - 25%N₂, in water have been measured at a temperature of 323K for pressures up to 124.1 MPa.

The data have been correlated using the established forms of the Krichevsky-Kasarnovsky and Krichevsky-Ilinskaya equations and are in agreement with previous studies. The performance of the Krichevsky-Ilinskaya equation has been improved by using Wilson's equation in place of the two-suffix Margules equation to predict the non-ideality associated with the solute gas in the solution. A simple predictive method for ternary mixtures, based on an extension of the Krichevsky-Kasarnovsky equation, has been proposed.

The thermodynamic properties of pure polar fluids, a preliminary to the treatment of aqueous solutions, have been studied using statistical mechanics. A perturbation theory using a nonspherical reference potential has been derived and results have been compared to other perturbation theories and computer simulation studies. The extension of this theory to use a nonspherical reference fluid is described but remains as yet untested.

The thermodynamic properties of the reference fluids in the perturbation theories mentioned above have been determined by Monte Carlo computer simulation. A comparison of the results from the two sources suggests that the accuracy of the perturbation theories could be improved by a more accurate calculation of these reference properties.
Due to the inevitable depletion of existing reserves of energy the investigation of alternative, and hence usually obscure, sources is of great interest and practical importance. One such source currently being studied is the exploitation of the solubility of natural gas in brine solutions, a situation found in so-called geothermal natural gas aquifers. The aquifers may be found at considerable distances beneath the surface and hence will be subject to substantial overburden pressures. Estimates of the amount of recoverable natural gas range from a 6- to 50-year supply at current rates of consumption\(^1\). Obviously, any economic evaluation and estimation of the potential recovery from such aquifers requires an accurate and reliable prediction of the high pressure phase equilibria for such a natural gas-brine system and the effect of a second solute on the solubility.

Experimental studies of such systems, and simple systems chosen to resemble the actual solutions, at conditions corresponding to those expected, are to say the least scarce, particularly at pressures greater than 68.9 MPa. Therefore, as part of this study, the solubilities of pure argon (chosen for its sphericity) in water and of three gas mixtures of methane and nitrogen in water have been determined at 323K for pressures up to 124.1 MPa. The gas mixtures were studied to gain some insight into the effect of the presence of one solute gas on the solubility of another similar gas in the same solvent. The solubilities of both pure methane and pure nitrogen have been determined by a previous investigator\(^2\).
Experimental investigation is one of the three methods available for studying the behavior and thermodynamic properties of fluids. In addition, these properties may be studied using theoretical analyses or by the technique of computer simulation, and the interrelation of all three methods can be conveniently illustrated by figure 1.1(3). The question of whether computer simulation ought to be regarded as a theoretical or an experimental investigation is constantly argued(3) and is best answered when considering the use to which computer simulation results are put. When comparing theoretical and computer simulation studies, based on the same intermolecular potential model, the simulation can be regarded as providing "experimental" data with which to test the theoretical approximations. Alternatively, in comparing simulation with experimental results, the simulation acts as a "theory" and the comparison serves to test the model used for the intermolecular potential. It is the first of these applications, the use of computer simulation data as experimental results, that is employed in this study.

The prediction and correlation of high-pressure solubilities using macroscopic classical thermodynamics essentially involves determining the Poynting correction to a standard state Henry's law constant using expressions describing the effect of pressure on the fugacity. Such equations were first derived independently by Krichevsky and Kasarnovsky(4) and Dodge and Newton(5). Improvements to the original Krichevsky-Kasarnovsky equation have been made by including a term for the non-ideal behavior of the dissolved solute(6) and a term for the compressibility of the partial molar volume(2) of the solute gas in the solution using the equation of Namiot(7).

Rather than use the two-suffix Margules equation to predict the solute non-ideality, as done by Krichevsky and Ilinskaya(6), the
Figure 1.1. Three methods of studying the thermodynamics of a fluid.
Wilson equation for the excess Gibbs free energy has been used in a manner similar to that for solid solubilities\(^{(8)}\). Further, a modified form of the Krichevsky-Kasarnovsky equation\(^{(4)}\) has been extended and applied to the correlation of the solubility of binary gas mixtures in a pure solvent.

The equations described above, contain macroscopic thermodynamic properties and as such are independent of any intermolecular potential model chosen to describe interparticle interactions, and thereby do not fit the scheme described by figure 1.1. However one alternative to the treatment of gas solubility is to use a statistical mechanical perturbation theory which has been an area of tremendous progress primarily due to the recent development and availability of high-speed computers.

First suggested over thirty years ago by Longuet-Higgins\(^{(9)}\), perturbation theories have been successfully applied to non-polar spherical fluids by Barker and Henderson\(^{(10)}\) and Weeks, Chandler and Anderson\(^{(11)}\), with the biggest improvement of late being the numerical solution of the Ornstein-Zernicke equations, under various closures, for "soft-sphere" potentials\(^{(12,13)}\). Unfortunately, attempts to derive similar theories for polar fluids have not been as successful, with problems particularly in the convergence of the perturbation expansion series. A perturbation theory that uses a nonspherical reference potential, thereby ensuring a non-zero first-order term in the expansion, has been developed that predicts the Helmholtz free energy of the polar fluid. Results of the theory are compared with existing computer simulation data and values from other perturbation theories. Literature values for computer simulation of the fluids
studied here are again scarce, and where neither Monte Carlo nor molecular dynamics simulation data were found, values have been generated using programs developed during the research.

Experimental data for the reference and perturbation contributions to the total free energy, in addition to information about the structure of the reference fluids, has been obtained by substituting the same perturbed intermolecular potential into the Monte Carlo simulations as is used in the perturbation theory. This therefore provides a valuable comparison not just of the overall performance of the perturbation theory when compared to "experimental" values but also of the accuracy of the perturbation theory in describing the reference and perturbation fluid contributions.

In an effort to determine the structural dependence of the reference fluids caused by the orientation dependent electropolar contributions to the intermolecular potential, as well as the difference between the structures due to the full and that due to the reference potentials, the spherical harmonic coefficients have been calculated for both situations. The spherical harmonic expansion provides a description, in terms of one-dimensional coefficients, of the multidimensional distribution function. This investigation ought to provide some insight into the relative successes or failures of the perturbation theories described in this study.
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Chapter II

THEORY

Whenever one considers the equilibrium distribution or solubility of a solute $i$, in our case a pure gas or one of a mixture of gases, between a liquid and vapor phase, by definition the fugacity of this component must be the same in both phases\(^{(1)}\).

\[
\frac{f_i^V}{f_i^L} = f_i^0
\]  

Therefore, the task of predicting and correlating the solubility of gases in liquids is, in essence, simply a question of determining the liquid and vapor phase fugacities of the solute $i$. Two approaches have been taken in solving this problem, using classical thermodynamics and statistical mechanics, and are discussed in detail in the following sections.

2.1 Classical Theory of Gas Solubility

The fugacity of component $i$ in the liquid phase, $f_i^L$, can be related to the activity coefficient $\gamma_i$ and the fugacity of pure $i$, $f_i^0$, by equation (2.2)\(^{(1)}\)

\[
f_i^L = \gamma_i X_i f_i^0
\]  

and from the definition of the vapor phase fugacity coefficient, $\phi_i^V$, a similar expression may be written for the vapor phase fugacity,

\[
f_i^V = \phi_i^V y_i P
\]
where \( P \) is the total system pressure. For a supercritical solute, that is a solute whose critical temperature is lower than the system temperature, a typical plot of fugacity against composition is shown in figure 2.1, where the composition dependence of \( f_1 \) and \( f_2 \) is known for only part of the composition range. Since the value of the fugacity of the pure solvent as a liquid, \( f_1^0 \), is known, the ideal solution fugacity, \( f_{id} \), is best given by the Lewis-Randall rule

\[
f_{id} = f_1^0 x_1.
\]  

(2.4)

However for the solute, component 2, no experimental value for \( f_2^0 \), the fugacity of pure solute as a liquid, is known and suggests a supercritical liquid. Alternatively, the tangent at \( x_2 = 0 \) is easily constructed giving the line referred to as Henry's Law. Therefore, the Lewis-Randall rule for ideal-solution behavior is not suitable, and Henry's Law is used instead

\[
f_2^{id} = x_2 H_2(T,P)
\]  

(2.5)

where \( H_2(T,P) \) is the Henry's constant, and is best regarded as the fugacity of pure component 2 in a hypothetical liquid state.

One consequence of this is seen when applied to the definition of activity coefficients, as in equation (2.6)

\[
y_i = \frac{f_i}{f_{id}}
\]  

(2.6)

The ideal fugacity, \( f_{id} \), defined by the Lewis-Randall rule is given by equation (2.4) written for component \( i \) and therefore substituting into equation (2.6) gives
Figure 2.1  Fugacity as a function of limited solubility of solute (2) in a solvent (1).
with the accompanying condition that when \( X_i = 1 \), \( f_i = f_i^o \) and therefore \( \gamma_i = 1.0 \). However, when the ideal solution behavior for component \( i \) is defined according to Henry's Law, the following is obtained

\[
\gamma_i^* = \frac{f_i}{X_i f_i^o} = \frac{(f_i / X_i)}{H_i} \tag{2.8}
\]

Therefore, when \( X_i = 0 \), \( \gamma_i^* = 1 \) by L'Hopital's rule,

\[
\lim_{X_i \to 0} \left( \frac{df_i}{X_i} \right) = \frac{df_i}{dX_i} \bigg|_{X_i = 0} = H_i \tag{2.9}
\]

This method of defining the activity coefficients of different species differently, is the so-called "unsymmetric convention" and the fugacity of component \( i \) in the liquid phase is given by equation (2.10)

\[
f_i^o = \gamma_i^* X_i H_i \tag{2.10}
\]

At low pressures the dependence of the Henry's constant on pressure may be assumed negligible. However, at high pressures, the effect is no longer negligible and it is then necessary to consider the effects of pressure on \( H_i \), obtained from the pressure dependence of the fugacity \( f_i^o \), given by equation (2.11),

\[
\left\{ \frac{\partial \ln f_i^o}{\partial \bar{v}_i} \right\}_{T,X} = \frac{\bar{v}_i}{RT} \tag{2.11}
\]

where \( \bar{v}_i \) is the partial molar volume of solute \( i \) in the liquid phase. Integrating from a reference pressure \( P_r \) to the system pressure \( P \),
\[ \ln f_i^p = \ln f_i^{p^R} + \int_{p^R}^P \frac{\tilde{\nu}_i}{RT} dP \quad (2.12) \]

and combining equations (2.10) and (2.12) gives,

\[ \ln \frac{f_i}{X_i} = \ln H_i^{p^R} + \ln \gamma_i^{p^R} + \int_{p^R}^P \frac{\tilde{\nu}_i}{RT} dP \quad (2.13) \]

As the solute concentration approaches zero, this system pressure approaches the solvent saturation pressure \( P_i^S \), and it is therefore convenient to use this pressure as the reference, and as such, equation (2.13) can then be written as

\[ \ln \frac{f_i}{X_i} = \ln H_i^{p^L} + \ln \gamma_i^{p^L} + \int_{p^L}^P \frac{\tilde{\nu}_i}{RT} dP \quad (2.14) \]

From equation (2.1), we know that at equilibrium the fugacities of component \( i \) in the liquid and vapor phases are equal, and \( f_i \) at the system pressure may be obtained from equation (2.15),

\[ f_i^L = f_i^V = \phi_i Y_i^P \quad (2.15) \]

where \( \phi_i \) and \( Y_i \) are the fugacity coefficient and concentration of component \( i \) in the vapor phase respectively.

The activity coefficient, \( \ln \gamma_i^* \), is a partial molar property with respect to the excess Gibbs free energy \((g^E/RT)^*\), both defined according to the unsymmetric convention. However, the equations that correlate \( \ln \gamma_i^* \) are derived from expressions for \( g^E/RT \) defined according to the symmetric convention. For a multicomponent system, the activity coefficient is related to the excess Gibbs free energy by
and may be more conveniently expressed using mole fractions as the independent variable.

\[ \text{RT} \ln \gamma_i = \frac{g_i}{\gamma_i} = \sum_{k \neq i} x_k \frac{\partial g}{\partial x_k} \bigg|_{T,P,n_{j \neq i}} \]  

(2.16)

(2.17)

It has been shown\(^1\) that the symmetric and unsymmetric activity coefficients are related by equation (2.18),

\[ \ln \gamma_i^* = \ln \gamma_i - \lim_{X_i \to 0} \ln \gamma_i \]

(2.18)

and as such provides a connection between expressions for the excess Gibbs free energy and the unsymmetric activity coefficient \( \gamma_i^* \), via \( \gamma_i \).

### 2.1.1 Binary Systems

For the case of a binary system of a gaseous solute(2) in a solvent(1), equation (2.14) may be written as

\[ \ln \frac{f_2}{X_2} = \ln \gamma_2^* \frac{P^S}{P} + \int_{P_1}^{P} \frac{P - \nu_2}{RT} dP \]  

(2.19)

Assuming that the partial molar volume of the solute gas, \( \bar{\nu}_2 \), is equal to the partial molar volume at infinite dilution, i.e.

\[ \bar{\nu}_2 = \nu_2^\infty \]  

(2.20)

and further that
then equation (2.19) may now be written, after performing the integration, as

\[ \ln \frac{f_2}{X_2} = \ln H_2 + \ln \gamma_2 + \frac{-\infty p^S}{RT} (P - p^S) . \]  

(2.22)

By setting the activity coefficient, \( \gamma_2^{p^S} \), equal to unity in equation (2.22), Krichevsky and Kasarnovsky obtained

\[ \ln \frac{f_2}{X_2} = \ln H_2 + \frac{-\infty p^S}{RT} (P - p^S) . \]  

(2.23)

Equation (2.23) was also derived independently by Dodge and Newton.

From equation (2.17), the activity coefficient of the solute gas in the liquid may be written as

\[ RT \ln \gamma_2 = g - \int \frac{dg_1}{dX_1} \]  

(2.24)

and if the two-suffix Margules equation is used to represent the molar excess Gibbs free energy as

\[ g^* = A_{12} X_1 X_2 \]  

(2.25)

the symmetric activity coefficient, \( \gamma_2 \), is obtained by substituting equation (2.25) into equation (2.24).
\[ \text{RTln} \gamma_2 = A_{12} \chi_1^2 \]  

(2.26)

The corresponding unsymmetric activity coefficient is found by substituting equation (2.26) into equation (2.18)

\[ \ln \gamma_2^* = \frac{A_{12}}{RT} (\chi_1^2 - 1). \]  

(2.27)

Substituting equation (2.27) into equation (2.22) gives the Krichevsky-Ilinskaya\(^{(4)}\) equation

\[ \ln \frac{\mathbf{f}_2}{X_2} = \ln \frac{\mathbf{F}_2^s}{X_2} + \frac{A_{12}}{RT} (\chi_1^2 - 1) \]  

\[ + \frac{v_2^s}{v_1^s} (P - P_1^s). \]  

(2.28)

Alternatively, Wilson's equation\(^{(5)}\) can be used to predict the molar excess Gibbs free energy and hence, through equations (2.24) and (2.18), the unsymmetric activity coefficient which is given below as equation (2.29). The details of this derivation are given in appendix A.

\[ \ln \gamma_2^* = - \ln \left\{ \frac{(X_1 \Lambda_{21} + X_2)}{\Lambda_{21}} \right\} - \frac{\Lambda_{12}}{X_1 + X_2 \Lambda_{12}} - \]  

\[ \frac{\Lambda_{21}}{X_1 + X_2} - \frac{(\Lambda_{12} - 1)}{X_1}. \]  

(2.29)

Upon substitution into equation (2.22) an expression similar to equation (2.28) is obtained but is not given here. Krichevsky and Ilinskaya\(^{(4)}\) defined an apparent partial molar volume, \( v_2^* \), such that

\[ v_2^*(P - P_1^s) = v_2^p (P - P_1^s) + A_{12} (X_1^2 - 1) \]  

(2.30)
combining equations (2.28) and (2.30) gives

\[
\ln \frac{f_2}{X_2} = \ln H_2^1 + \frac{\nu^\infty}{RT(P - P^S_1)} \tag{2.31}
\]

the modified Krichevsky-Kasarnovsky equation \(^4\). Krichevsky and Ilinskaya also measured the true partial molar volume at infinite dilution of a solute gas in both water and methanol. It was observed that these measured values differed from those obtained from a plot of experimental solubility data according to equation (2.23). This discrepancy was thus attributed to the non-ideal behavior of the solute gas in the solvent, as predicted by equation (2.30).

Rather than assume the solute partial molar volume to be constant, Choi\(^6\) defined the pressure dependence of \(\nu^\infty_2\) to be that suggested by Namiot\(^7\) as in equation (2.32)

\[
-\nu^\infty_2 = -\nu^\infty_1 \left\{ 1 - \beta_2(P - P^S_1) \right\} \tag{2.32}
\]

where \(\beta_2\) is the coefficient of isothermal compressibility of the partial molar volume of the solute in solution. Substituting equation (2.32) into (2.19) and neglecting terms having products of \(\beta_2\) and \(P^S_1\), Choi\(^6\) obtained

\[
\ln \frac{f_2}{X_2} = \ln H_2^1 + \ln \gamma_2^\infty + \frac{\nu^\infty_1 P^S_1}{RT(P - P^S_1)} - \frac{\beta_2 \nu^\infty_1 P^S_1}{2RT} \tag{2.33}
\]

the extended Krichevsky-Ilinskaya equation. A similar expression has been independently derived by Coco and Johnson\(^8\). Equations (2.27) and
(2.29) may be substituted for $\ln \gamma_{21}^p$ in equation (2.33) above with the appropriate changes in the expression for the apparent partial molar volume $v_2^\ast$.

2.1.2. Ternary Systems

Equations (2.28) and (2.33) can easily be extended to ternary systems of a solvent (1) and two solute gases (2) and (3) by substituting the appropriate expression for $\ln \gamma_{21}^p$ and $\ln \gamma_{31}^p$, written from the appropriate recursive formulas for both the two-suffix Margules and Wilson's (5) equation in appendix A. However, the number of independent parameters to be determined can be as high as eight for the extended Krchevsky-Ilinskaya equation with the unsymmetric activity coefficient given by Wilson's equation. This would appear to prohibit the use of these equations to predict the solubilities of gas mixtures.

An interesting alternative is found upon recognizing that equation (2.31), the modified Krchevsky-Kasarnovsky equation, may be used for ternary as well as binary systems without any additional determination of parameters by assuming that the apparent partial molar volume, $v_1^\ast$, is independent of the solute composition and is therefore the same in both binary and ternary systems, i.e.

$$\ln \frac{f_2}{X_2} = \ln H_2^1 + \frac{v_2^\ast}{2RT}(P - P_1^S) \quad (2.34)a$$

and

$$\ln \frac{f_3}{X_3} = \ln H_3^1 + \frac{v_3^\ast}{3RT}(P - P_1^S) \quad (2.34)b$$
The gas phase fugacity of a binary system is taken to be that of the solvent free, pure gas solute $i$, and therefore for the solutes used, experimental P-V-T data can be used in its determination. In effect, we may write for binaries

$$f_i = f^0_i$$ (2.35)

where $f^0_i$ represents the fugacity of pure $i$.

Equation (2.31) can be rearranged to be explicit in the liquid phase solubility of solute $i$ as

$$X_i = \frac{f^0_i}{P_i \exp \left\{ \frac{v_i^\infty}{R_i T} (P - P_i^S) \right\}}$$ (2.36)

which may be written as

$$X_i^o(P) = f_i^o(P) \psi(H_i^1, v_i^\infty, P)$$ (2.37)

Therefore, for the solutes (2) and (3), each in a binary system with a solvent (1), equations (2.34)a and b become,

$$X_2^o(P) = f_2^o(P) \psi(H_2^1, v_2^\infty, P)$$ (2.38)a

$$X_3^o(P) = f_3^o(P) \psi(H_3^1, v_3^\infty, P)$$ (2.38)b

Similarly, for a ternary system, the respective solubilities of solutes (2) and (3) are

$$X_2(P) = f_2(P, Y_2) \psi(H_2^1, v_2^\infty, P)$$ (2.39)a
The Lewis-Randall fugacity rule (9) relates the fugacity of component $i$ in a mixture to the pure component fugacity and its composition in that mixture

$$f_i = Y_i f_i^0.$$  \hspace{1cm} (2.40)

Assuming equation (2.40) applies to the vapor phase of the systems being studied, again assumed solvent free, then upon substitution into equations (2.39)a and b, and further simplification using equation (2.38)a and b, one obtains

$$X_2(P) = Y_2 X_2^0(P) \hspace{1cm} (2.41)a$$

$$X_3(P) = Y_3 X_3^0(P) \hspace{1cm} (2.41)b$$

Therefore, if the solubility data of the binary systems of each solute gas with the solvent, is fitted to some function, the solubility in the solvent of each solute gas of the ternary system can be readily determined.

The accuracy of the Lewis-Randall rule, equation (2.40), can be determined to some extent by obtaining the fugacity, $f_i$, by some independent means such as an equation of state, and comparing the predicted values of $X_i$ by each method.
2.2 Perturbation Theory

The idea of using perturbation theory, that is the expansion of an unknown real system about some known reference system, was first suggested over thirty years ago by Longuett-Higgins (10) who related the free energy of a non-ideal solution to that of an ideal one by expanding the free energy in terms of a perturbation potential, and independently by Barker (11) who expanded the partition function of a polar fluid about that of isotropic molecules. Later Zwanzig (12) showed how the free energy of a dense atomic fluid, interacting with some isotropic pair potential \( U(r) \) could be related to that of a hard-sphere fluid with a potential \( U^0(r) \) by performing a Taylor's series expansion of the canonical partition function of the system \( Q_c \)

\[
Q_c = \frac{\lambda^{3N}}{N!} Z_c \tag{2.42a}
\]

where \( \lambda = \hbar/(2\pi mkT)^{1/2} \) and in particular on the configurational integral \( Z_c \)

\[
Z_c = \int \cdots \int \exp(-\beta U(r)) \, dr \tag{2.43}
\]

A review of Zwanzig's derivation is given in appendix B. Zwanzig obtained the following expression for the Helmholtz free energy of a fluid,

\[
A = A_0 + \frac{(N\rho/2)}{F} \int U^P(r) g^O(r) \, dr + \left\{ \begin{array}{c} \text{Higher Order} \\ \text{Terms} \end{array} \right\} \tag{2.44}
\]

where \( A_0 \) is the Helmholtz energy of the reference system, \( U^P(r) \) is the perturbation potential, \( g^O(r) \) is the radial distribution function of the reference system, \( N \) the number of particles, \( \rho \) is the number density and
is the intermolecular separation vector. The second term on the r.h.s. of equation (2.44) above, is the first-order expansion term $A_1$, and so on for higher terms, $A_2$, $A_3$, etc.

### 2.2.1 Perturbation Theory of Spherical Molecules

Initial attempts to apply Zwanzig's expansion to the perturbation theory of spherical molecules were unsuccessful, except for the case of hot dense gases\(^\text{(13)}\) and proved to be due to the poor selection of the reference and perturbation potentials. By recognizing the importance of the repulsive part of any interaction potential in determining the structure of a fluid and by carefully choosing the reference potential to reflect this Barker and Henderson\(^\text{(14)}\) were able to obtain good agreement with computer simulation data. For the case of the square-well potential shown in figure 2.2, Barker and Henderson\(^\text{(14)}\) modified Zwanzig's expansion and obtained the following expression for the free energy of a square well fluid,

$$
\frac{A}{NkT} = \frac{A_0}{NkT} + \frac{\rho \varepsilon}{2kT} \int_0^{\lambda \sigma} g^0(r) dr + \left\{ \begin{array}{c} \text{Higher} \\
\text{order terms} \end{array} \right\}
$$

(2.45)

where $\varepsilon$ is the depth of the potential well, and $\lambda$ determines the width of the well in relation to the hard-core diameter $\sigma$. The total potential was split into a reference or unperturbed potential, $U^0(r)$, and a perturbation potential, $U^P(r)$, according to the following

$$
U^0(r) = \begin{cases} 
\infty & \text{for } r < \sigma \\
0 & \text{for } r > \sigma
\end{cases}
$$

(2.46)
Figure 2.2. Potential for square-well interaction.
\[ U^P(r) = 0 \quad \text{for} \quad r < \sigma \quad (2.46)c \]
\[ = -\epsilon \quad r < \sigma < \lambda \sigma \quad (2.46)d \]
\[ = 0 \quad r > \lambda \sigma \quad (2.46)e \]

The success of this approach when compared to existing simulation data, even at low temperatures, showed that the failure of previous approaches (e.g. McQuarrie and Katz\textsuperscript{(13)}) was indeed due to the separation of the total interaction potential into its reference (repulsive) and perturbation (attractive) parts and prompted Barker and Henderson\textsuperscript{(15)} to apply their adaptation of Zwanzig’s expansion to fluids with 'soft-sphere' repulsive forces, given by the Lennard-Jones 12:6 potential, where the split of the potential is shown in figure 2.3 and described by equations (2.47)a-d.

\[ U^O(r) = U(r) \quad \text{if} \quad U(r) > 0 \quad (2.47)a \]
\[ U^P(r) = 0 \quad (2.47)b \]
\[ U^O(r) = 0 \quad \text{if} \quad U(r) < 0 \quad (2.47)c \]
\[ U^P(r) = U(r) \quad (2.47)d \]

The configurational integral was expanded in a double power Taylor series, in terms of an inverse steepness parameter \( \alpha \) and a depth parameter \( \gamma \),

\[ A = A_0 + \alpha \left\{ \frac{\partial A}{\partial \alpha} \right\}_0 + \gamma \left\{ \frac{\partial A}{\partial \gamma} \right\}_0 + \ldots \quad (2.48) \]

where the parameter \( \alpha \) varies the steepness of a modified potential and \( \gamma \) varies the depth of the potential in the attractive region. Barker and Henderson thereby obtained
Figure 2.3  Split of total interaction potential into the perturbation (dashed line) and reference (solid line) terms according to Barker-Henderson.
The hard-sphere or Barker-Henderson diameter, $d_{BH}$, is chosen so that the first-order expansion term in the inverse steepness parameter, $\omega$, is zero. This diameter is therefore given by

$$d_{BH} = \int_0^\sigma (1 - \exp[-\beta U^0(r)]) dr$$  \hspace{1cm} (2.50)$$

and is dependent only on the system temperature.

The higher order terms of equation (2.49) above, depend on three and four-body distribution functions and as a simplification Barker and Henderson suggested two approximations for the second-order terms, the macroscopic compressibility and the local compressibility approximations, and indicated the latter to be the more appropriate.

With this approximation of the second-order term, and using equation (2.50) to define the equivalent hard-sphere diameter, Barker and Henderson obtained

$$A \frac{NkT}{NkT} = \frac{A_0}{NkT} + 2\pi \rho \int_0^\infty g^0(r)U^P(r)r^2 dr$$  
$$\hspace{1cm} + \gamma 2\pi \rho \beta \int_0^\infty g^0(r)U^P(r)r^2 dr + \left\{ \text{Higher order terms} \right\}.$$  \hspace{1cm} (2.49)$$

The values predicted by the above equation compared favorably with the existing molecular dynamics (MD) and Monte Carlo (MC) results, as well
as experimental data for argon, for all fluid temperatures and densities.

By recognizing fully the significance of the repulsive forces in determining the equilibrium structure of simple fluids, Weeks, Chandler and Andersen\(^{(16)}\) proposed a first-order perturbation theory, neglecting the contributions of multiple body interactions. In splitting the potential into its respective repulsive and attractive contributions, they assumed that the region of action of the repulsive (reference) forces was bounded by the location of the minimum of the potential, \(r_{\text{min}}\). The splitting is shown in figure 2.4 and is described by equations (2.51)a-d,

\[
\begin{align*}
U^0(r) &= U(r) + \varepsilon \quad \text{for } r < r_{\text{min}} \\
&= 0 \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \text{for } r > r_{\text{min}} \\
U^P(r) &= -\varepsilon \quad \text{for } r < r_{\text{min}} \\
&= U(r) \quad \quad \quad \quad \quad \quad \text{for } r > r_{\text{min}}
\end{align*}
\]

where \(\varepsilon\) is the value of \(U(r)\) at the minimum and \(r_{\text{min}}\) is the location of this minimum.

Compared to the B-H split of the potential, the perturbation potential now varies slowly, particularly within the core of the unperturbed potential, with the result that the importance of fluctuations, and hence higher order terms, is diminished. Convergence is therefore much faster, and is assumed to occur after the first-order term. The free energy is then given by Zwanzig's expansion as

\[
\frac{A}{NkT} = \frac{A_0}{NkT} + 2\pi \rho \int_0^\infty g^0(r)U^P(r)r^2dr
\]

(2.52)
Figure 2.4  Split of the total interaction potential into its perturbation (dashed line) and reference (solid line) terms according to Weeks-Chandler-Andersen.
The biggest drawback of this method is that the properties of the reference system are not well known and \( A_0 \) and \( g^0(r) \) were taken to be the properties of hard spheres,

\[
A_0 = A^{\text{HS}}
\]

\[
g^0(r) = \exp\left\{-\beta U^0(r)\right\} y^{\text{HS}}(r)
\]

where \( y^{\text{HS}}(r) \) is the background correlation function of the hard spheres defined by equation (2.54).

The equivalent hard-sphere diameter, \( d^{\text{WCA}} \), is now dependent on both temperature and density and is determined from a 'blip-expansion' of the soft-sphere system about an equivalent hard-sphere system defined by

\[
\int d^{\text{WCA}} \left\{ y^d(r) \left[ \exp\left(-\beta U^0(r)\right) - \exp\left(-\beta U^{\text{HS}}(r)\right) \right] \right\} dr = 0
\]

and illustrated in figure 2.5.

This technique is based on the fact that the so-called Mayer f-functions, the product of the background correlation function and the exponential of the Boltzmann weighted potential, of the reference and hard-sphere systems are similar. Equation (2.55) can also be regarded as equating the compressibilities of the two systems. Again the results have been compared to simulation data, and shown to be as accurate as the second-order Barker-Henderson theory, equation (2.51).

Both the Barker-Henderson and the Weeks-Chandler-Andersen theories have been extended to mixtures by Leonard, Henderson and Barker\(^{(17)}\) and Lee and Levesque\(^{(18)}\) respectively. The first-order expressions for both theories are given below.
Figure 2.5 Illustration of blip-expansion to determine hard-sphere (HS) diameter equivalent to reference (REF) fluid.
Leonard-Barker-Henderson (LHB)

The first-order perturbation expansion for the free energy is of the form

$$\frac{A}{NkT} = \frac{A_0}{NkT} - 4n_0 \chi_1 \chi_2 d_{12}^2 g_0 \left( d_{12} - \delta_{12} \right)$$

$$+ 2n_0 \beta \Lambda \chi \int_0^\infty \sum_{\sigma_i} u_{ij}^p(r) g_{ij}^o(r) r^2 dr$$

(2.56)

where

$$\delta_{ij} = \int_0^{\sigma_{ij}} \left\{ 1 - \exp\left[ -\beta u_{ij}^0(r) \right] \right\} dr$$

(2.57)

By putting

$$d_{ii} = \delta_{ii}$$

(2.58)

the contribution of like attractions to the second term on the rhs of equation (2.56) cancel and the unlike hard-sphere diameter is then given by

$$d_{12} = (d_{11} + d_{22})/2$$

(2.59)

Lee and Levesque (LL)

Lee and Levesque \(^{18}\) approximated the radial distribution function of the reference soft-sphere system by

$$g_{ij}^o(r) = \exp\left\{ -\beta u_{ij}^0(r) \right\} y_{d_{ij}}^d(r)$$

(2.60)

The equivalent hard-sphere diameters, \(d_{ii}\), were again given by blip-expansions about hard-sphere systems, as in equation (2.55), and the free energy of the mixture is then given to first-order by
One significant improvement in the perturbation theory of spherical molecules has been achieved by Fischer (19,20) who obtained a numerical solution to the Percus-Yevick equations for soft-sphere reference potentials of pure fluids and mixtures. This solution has also been obtained independently by Monson (21). Therefore, this allows the reference system, and the corresponding properties, to be calculated for a reference potential chosen as either the BH or WCA part of the full potential and the distribution functions determined for this reference rather than an equivalent hard-sphere system. Therefore, by allowing the reference to resemble more closely the actual system, and in particular the repulsive part of the potential, the accuracy of the perturbation theories ought to be significantly improved.

2.3 Perturbation Theory of Nonspherical Molecules

2.3.1 Spherical Reference Potential

Perturbation expansions for molecular liquids were first suggested as early as 1951 by Barker (11) and later by Pople (22) who both expanded the free energy in powers of an anisotropic potential, \( U^P \), corresponding to

\[
U(r,\omega_1,\omega_2) = U^0(r) + \eta U^P(r,\omega_1,\omega_2)
\]

where \( r \) is the distance between molecular centres, \( \omega_1 \) is the orientation of molecule \( i \) and \( \eta \) is the perturbation parameter. \( U^0(r) \) is a spherically symmetric reference potential defined according to
\[ U^0(r) = \langle U(r, \omega_1, \omega_2) \rangle_{\omega_1, \omega_2} \]  \tag{2.63} 

where \( U(r, \omega_1, \omega_2) \) is the full pair potential and \( \langle \ldots \rangle_{\omega_1, \omega_2} \) indicates an unweighted average over the molecular orientations given by,

\[ \langle U(r, \omega_1, \omega_2) \rangle = \frac{\iint U(r, \omega_1, \omega_2) d\omega_1 d\omega_2}{\iint d\omega_1 d\omega_2} \]  \tag{2.64} 

and the normalizing factor by,

\[ \iint d\omega_1 d\omega_2 = 8\pi . \]  \tag{2.65} 

Equation (2.63) is often referred to as the \( u \)-expansion.

An important consequence of this expansion is that the angle-averaged perturbation potential is zero and as a result the first-order perturbation term in the series expansion for the Helmholtz free energy is itself zero

\[ \langle U^p(r, \omega_1, \omega_2) \rangle_{\omega_1, \omega_2} = 0 \]  \tag{2.66a} 

\[ A_1 = 0 \]  \tag{2.66b} 

The total Helmholtz free energy is then given by

\[ A = A_0 + A_2 + A_3 + \ldots \]  \tag{2.67} 

The complex second-order term \( A_2 \) involves integrals over two- and three-body reference correlation functions and requires further simplifying assumptions for its evaluation. A detailed description of this theory has been given by Gubbins and Twu (23) and Twu and Gubbins (24).
The third-order term, $A_3$, has been found to be of similar magnitude and of opposite sign to $A_2$, and therefore must be maintained in the perturbation expansion. Consequently the convergence of the series is slow, particularly for strongly polar molecules. Stell et al.\(^{(25)}\) have improved the convergence of the series by the use of a Padé approximant

$$A = A_0 + \frac{A_2}{(1 - A_3/A_2)}$$

(2.68)

and the results have been found to agree well with computer simulation data for fluids with strong electrostatic forces provided that the molecules possess spherical or near-spherical cores. The theories of molecular fluids have been comprehensively reviewed in detail by Gray and Gubbins\(^{(26)}\).

An alternative method of defining the reference potential $U^0(r)$ is to use an unweighted average of the Boltzmann factor over all orientations

$$\exp\left\{ -\beta U^0(r) \right\} = \langle \exp(-\beta U(r,\omega_1,\omega_2)) \rangle_{\omega_1,\omega_2}$$

(2.69)

Equation (2.69) above is called the $f$-expansion and is also referred to as the RAM (reference average Mayer function) theory and has the immediate advantage of giving the correct value of the second virial coefficient and includes an averaged contribution from the anisotropic part of the potential. However, the angle-averaged perturbation potential and hence the first-order term, $A_1$, are still both zero as in equations (2.66) a and b.
2.3.2 Nonspherical Reference Potential

Using spherical reference potentials for perturbation theories appears unsatisfactory, particularly for systems with highly anisotropic interactions, and convergence of the series will, at best, be poor. One alternative is to use a nonspherical reference potential such as that used by Mo and Gubbins\(^{(27)}\), chosen so that it resembles the structure of the real system as closely as possible, thereby decreasing the size and fluctuation of the perturbation terms.

Based on the success of the Weeks-Chandler-Andersen (WCA) theory for atomic fluids, Mo and Gubbins\(^{(27, 28)}\) proposed a generalization of this method to molecular fluids. For each orientation the potential is divided into repulsive reference and an attractive perturbation terms according to

\[
U(r, \omega_1, \omega_2) = U^0(r, \omega_1, \omega_2) + \eta U^P(r, \omega_1, \omega_2)
\]

(2.70)

where \(U^0\) is the reference potential given by

\[
U^0(r, \omega_1, \omega_2) = U(r, \omega_1, \omega_2) + \varepsilon(\omega_1, \omega_2) \quad r < r_{\text{min}}(\omega_1, \omega_2)
\]

(2.71)a

\[
U^0(r, \omega_1, \omega_2) = 0 \quad r > r_{\text{min}}(\omega_1, \omega_2)
\]

(2.71)b

where \(\varepsilon(\omega_1, \omega_2)\) and \(r_{\text{min}}(\omega_1, \omega_2)\) are the depth and location of the minimum of the full potential, as in the WCA theory for atomic fluids, but are now functions of the orientations \(\omega_1\) and \(\omega_2\). The Helmholtz free energy is then given by the first-order expansion, equation (2.44).

To calculate the reference free energy term, \(A_0\), of the nonspherical reference molecules Mo and Gubbins performed a blip expansion about a hard, nonspherical molecule followed by a Bellmans\(^{(29)}\).
expansion about a hard sphere. By analogy to the WCA approach, the pair correlation function for the reference fluid, $g^O(r, w_1, w_2)$ was assumed to be given by

$$g^O(r, w_1, w_2) = \exp\left\{ -\beta u^O(r, w_1, w_2) \right\} y^d(r, w_1, w_2)$$ \hspace{1cm} (2.72)

where $y^d(r, w_1, w_2)$ corresponds to a system with a hard, nonspherical potential. The reference free energy, $A^d$, and correlation function, $y^d(r, w_1, w_2)$, are then determined using Bellemans' perturbation expansion about a hard sphere. Mo and Gibbins performed calculations for Lennard-Jones potentials plus an anisotropic term, where the anisotropy was given by dipole-dipole, quadrupole-quadrupole, or anisotropic overlap interactions.

A similar approach has been developed by Kohler and Quirke who used a slightly different form of the orientation dependent reference potential. The method was applied to polar Lennard-Jones diatomic fluids and as a special case involving zero elongations, Lennard-Jones dipolar and quadrupolar fluids have been studied. To obtain $A^O$, a hard dumbell fluid was used to model the reference fluid, which of course reduces to a hard-sphere for the case of zero elongations.

Kohler and Quirke noted that the $u$-expansion, equation (2.63), gave values of the Helmholtz free energies that were too positive, and that the $f$-expansion, equation (2.69), gave values too negative. Following these observations, Kohler and Quirke split the dipole-dipole interaction into $U_{\mu\mu}$ for attractive configurations and $U_{\mu\mu} e^{-\beta U_{\mu\mu}}$ for repulsive configurations. However, for small separations the Boltzmann factor $e^{-\beta U_{\mu\mu}}$ cuts out too much of the repulsive potential,
making the resulting potential too negative. Kohler and Quirke therefore replaced the Boltzmann factor by a function that does not tend to zero for large values of $\beta U^{\mu\mu}$ and chose the Langevin function $L(\beta U^{\mu\mu})$ which is linear for small $\beta U^{\mu\mu}$ and approaches a constant for large values of $\beta U^{\mu\mu}$. The reference potential was then written as

$$U^o(r,\omega_1,\omega_2) = U^{LJ}(r) + U^{\mu\mu} e^{-3/2L(2\beta U^{\mu\mu})}H(\beta U^{\mu\mu})$$

(2.73)

where $H(\beta U^{\mu\mu})$ is a step function to indicate that the exponential only applies for positive values of $\beta U^{\mu\mu}$. Results of this theory are given later in section 5.2.

Due to the poor convergence of many perturbation expansions, particularly noticeable for highly anisotropic molecules, coupled with recent improvements associated with the calculation of fluid correlation functions (31), an attempt has been made to derive a simple and accurate first-order perturbation theory applicable to polar fluids.

The Barker-Henderson recipe for splitting the total interaction potential into repulsive and attractive parts, has been generalized for orientation dependent potentials, and is given by equations (2.74) a and b.

$$U^o(r,\omega_1,\omega_2) = U(r,\omega_1,\omega_2) \text{ for } U(r,\omega_1,\omega_2) > 0$$

(2.74)a

$$U^p(r,\omega_1,\omega_2) = 0$$

$$U^o(r,\omega_1,\omega_2) = 0 \text{ for } U(r,\omega_1,\omega_2) < 0$$

(2.74)b

$$U^p(r,\omega_1,\omega_2) = U(r,\omega_1,\omega_2)$$

One immediate advantage of this split is its simplicity for the situation where the minimum in the total potential, if it exists at all
for a specific orientation, necessary for performing a WCA-type split, is unknown. The potential of the polar fluid has been described by the Stockmayer potential, equation (2.75),

\[ U(r,\omega_1,\omega_2) = U_{LJ}(r) + U_{MULT}(r,\omega_1,\omega_2) + \ldots \]  

(2.75)

where \( U_{MULT}(r,\omega_1,\omega_2) \) is the electrostatic, orientation dependent, multipolar potential. The dipole-dipole, \( U^{\mu\mu} \), and the quadrupole-quadrupole, \( U^{QQ} \), potentials are given by

\[ U^{\mu\mu} = -\frac{\mu^2}{r^3} (S_1 S_2 C_{12} - 2C_1 C_2) \]  

(2.76)

\[ U^{QQ} = \frac{3}{4} \left( \frac{Q^2}{r^5} \right) (1 - 5C_1^2 - 5C_2^2 - 15C_1^2 C_2^2 + 2(S_1 S_2 C_{12} - 4C_1 C_2)^2) \]  

(2.77)

In equations (2.76) and (2.77) above, \( S_1 = \sin \theta_1, \ C_1 = \cos \theta_1, \ C_{12} = \cos \phi_{12} \), where \( \theta_1 \) and \( \theta_2 \) are the orientations of molecular centers with the center of mass vector between molecular centers and \( \phi_{12} \) is the azimuthal angle as illustrated in figure 2.6. The Lennard-Jones 12:6 potential is given as usual by

\[ U_{LJ} = 4\epsilon \left\{ \left( \frac{a}{r} \right)^{12} - \left( \frac{a}{r} \right)^6 \right\} \]  

(2.78)

The division of potentials according to equations (2.74) a and b for the case of dipolar \((\mu^*=\mu/(\epsilon \sigma^3)^{1/2}=1.0)\) and quadrupolar \((Q^*=Q/(\epsilon \sigma^5)^{1/2}=1.0)\) fluids is shown in figures 2.7 and 2.8 for various orientations.

Zwanzig's first-order expansion for the free energy can be written, using the orientation dependent potential and correlation functions, as
Figure 2.6 Illustration of Separation and Orientation of Polar Interactions
Figure 2.7  Separation of a dipolar Lennard-Jones potential into reference (solid lines) and perturbation (dashed lines) potentials for various orientations: line 1 is for $\theta_1 = 0$ and $\theta_2 = 180$; line 2 is for $\theta_1 = 0$ and $\theta_2 = 90$; and line 3 is for $\theta_1 = 0$ and $\theta_2 = 0$. 

Pair Potential, $U/\epsilon$ 

$\mu^* = 1.0$ 

$r/\sigma$
Figure 2.8 Separation of a quadrupolar Lennard-Jones potential into reference (solid lines) and perturbation (dashed lines) potentials for various orientations: line 1 is for $\theta_1 = 90$, $\theta_2 = 63.4$, and $\phi = 90$; line 2 is for $\theta_1 = 0$ and $\theta_2 = 0$; line 3 is for $\theta_1 = 0$ and $\theta_2 = 90$. 
\[ A = A_0 + \frac{(Np/2)}{2} \int \langle U^P(r,\omega_1,\omega_2)g^0(r,\omega_1,\omega_2) \rangle_{\omega_1,\omega_2} dr \] (2.79)

where again the angle brackets, \( \langle \ldots \rangle \), indicate an unweighted average over all orientations \( \omega_1 \) and \( \omega_2 \). The second term on the right-hand side is referenced as \( A_1 \) hereafter.

The correlation function \( g^0(r,\omega_1,\omega_2) \) has been approximated according to the suggestion of Sung and Chandler (32), and successfully utilized by Fischer (19) for diatomic liquids, where the background correlation function, \( y^0(r,\omega_1,\omega_2) \), is assumed independent of orientation and therefore

\[ g^0(r,\omega_1,\omega_2) = y(r)\exp \left\{ -\beta U^0(r,\omega_1,\omega_2) \right\} \] (2.80)

Here \( y(r) \) is the background correlation function obtained from the numerical solution of the Percus-Yevick equation for a soft-repulsive potential obtained by Boltzmann averaging of the orientation dependent potential, as in equation (2.81).

\[ \exp \left\{ -\beta \Phi(r) \right\} = \langle \exp(-\beta U^0(r,\omega_1,\omega_2)) \rangle_{\omega_1,\omega_2} \] (2.81)

Angle-averaged values of the Boltzmann factor of the reference \( \langle \exp(-\beta U^0(r,\omega_1,\omega_2)) \rangle_{\omega_1,\omega_2} \) and the angle-averaged perturbation potential \( \langle U^P(r,\omega_1,\omega_2) \rangle_{\omega_1,\omega_2} \) for dipolar and quadrupolar fluids are shown in figure 2.9.

The reference free energy is obtained by expanding the reference about that of a hard-sphere fluid.
Figure 2.9  Angle-averaged Boltzmann factor, $e^{\beta \phi}$, and angle-averaged perturbation potential, $\langle U^P \rangle$, for a dipolar (solid lines) fluid with $\mu^* = 1.0$ and a quadrupolar (dashed lines) fluid with $Q^* = 1.0$. 
\[ A_0 = A^{HS} + 2\pi \rho \int y^{HS}(r) \left\{ \exp(-\beta U^0(r)) - \exp(-\beta U^{HS}(r)) \right\} r^2 dr \]  

(2.82)

and by choosing the hard-sphere diameter that satisfies the following equality through a trial-and-error procedure

\[ \int y^{HS}(r) \left\{ \exp(-\beta \phi(r)) - \exp(-\beta U^{HS}(r)) \right\} r^2 dr = 0 \]  

(2.83)

where \( y^{HS}(r) \) is again obtained from numerical solution of the Percus-Yevick equation but for the case of hard spheres. The free energy of the reference fluid is then given to first-order by,

\[ A_0 = A^{HS} \]  

(2.84)

where \( A^{HS} \), the Helmholtz free energy of the hard-spheres, is predicted using the Carnahan-Starling equation of state. By substituting equations (2.74)a and b, (2.80) and (2.84) into Zwanzig’s expansion, equation (2.44), one obtains

\[ A = A^{HS} + \left( N \rho / 2 \right) \int y(r) \langle U^P(r, \omega_1, \omega_2) \rangle_{\omega_1, \omega_2} dr \]  

(2.85)

Equation (2.85) is hereafter referred to as method I.

This approach is similar to the method of Kohler and Quirke with the biggest difference being in the choice of the reference potential and the calculation of the perturbation term and differs from the method of Sung and Chandler in the calculation of the first-order term \( A_1 \).

A slightly different approach to calculating the free energy of polar fluids can be obtained by observing that for dipolar fluids, the angle-averaged pair distribution function is similar to that for an
isotropic reference. To the zeroth-order, we may write the rather drastic assumption

\[ g^0(r,\omega_1,\omega_2) = g^{HS}(r) \]  

(2.86)

Substitution of this expression in the first-order expansion, equation (2.79), gives

\[ A = A^{HS} + \left( N\rho / 2 \right) \int g^{HS}(r) \langle u^P(r,\omega_1,\omega_2) \rangle_{\omega_1,\omega_2} \, dr \]  

(2.87)

where \( A^{HS} \) is given as before. Equation (2.87) is hereafter referred to as method II. Except for a slightly different definition of the hard-sphere diameter, method II reduces to the Barker-Henderson method for isotropic only interactions.
2.4 Monte Carlo Simulation in the Canonical Ensemble

In an effort to provide not only additional computer simulation data for comparing the performance of the perturbation theories, but also information on the structure and contribution of the reference fluid, a Monte Carlo technique has been developed to simulate the reference fluid and to determine the contribution of the perturbation potential to the total Helmholtz free energy. Along with values of the reference and perturbation Helmholtz free energies, the simulation also determines the spherical harmonic coefficients of the appropriate reference fluid, therefore allowing at least a qualitative description of its structure.

The canonical ensemble is defined as a system where the temperature $T$, the volume $V$ and the number of particles $N$ are held constant at some specified value. The canonical ensemble average of a mechanical property, $\langle f \rangle$, is then defined as

$$\langle f \rangle = \frac{\int \ldots \int f(\vec{x})P(\vec{x})d\vec{x}}{\int \ldots \int P(\vec{x})d\vec{x}} \quad (2.88)$$

where $\vec{x}$ is a multidimensional vector specifying the molecular configurations and $P(\vec{x})$ is an unnormalized probability density which, in this ensemble, is given by

$$P(\vec{x}) = \exp\left\{-\beta U(\vec{x})\right\} \quad (2.89)$$

Evaluation of $\langle f \rangle$ according to equation (2.88) would involve an integration over a $2N$-dimensional configuration space, therefore for $N$ of the order of 200 it is obviously impractical to carry out a several-hundred dimensional integration by the usual numerical
methods and so a method of integrating over a random sampling of points in the configuration space, the Monte Carlo method, has been developed\(^{(37)}\).

Randomly choosing a point in this 2-dimensional configuration space by putting each of the \(N\) particles at a random position and orientation in the phase space, and giving this configuration a weight \(\exp(-\beta U(x))\) is impractical for close packed, liquid-like configurations since it is highly probable that a configuration where \(\exp(-\beta U(x))\) is very small would be chosen. Therefore, Metropolis et al.\(^{(37)}\) proposed a modified Monte Carlo scheme where configurations are chosen with a probability \(\exp(-\beta U(x))\) and weighted evenly. Details of this procedure and the fortran program (MCVECQQ) code are given in appendix C.

To determine the configurational internal energy of the ensemble, the mechanical property \(f\) in equation (2.88) is the sum of all pairwise interactions,

\[
f = \sum_{i<j}^{N} u_{ij}
\]

and the pressure can be calculated by determining the average virial of the forces.

\[
f = \frac{1}{3} \sum_{i<j} \frac{\partial u_{ij}}{\partial r_{ij}} \left( \frac{\partial u_{ij}}{\partial r_{ij}} \right)
\]

Due to the absence of a satisfactory direct Monte Carlo technique for estimating the canonical configurational integral, the procedure for obtaining the Helmholtz free energy at a density \(\rho\) and temperature \(T\) has been that of thermodynamic integration\(^{(38)}\) where
\[
\frac{A(\rho, T)}{NkT} = \int_0^\rho \left[ \frac{P(\rho)}{\rho kT} - \frac{1}{\rho} \frac{\partial P}{\partial \rho} \right] \, d\rho
\]

which may be written in terms of the dimensionless quantities \( \rho^*, T^* \) and \( P^* \) as

\[
\frac{A^*}{T^*} = \int_0^\rho \left[ \frac{P^*(\rho^*)}{T^* \rho^*} - \frac{1}{\rho^*} \frac{\partial \rho^*}{\rho^*} \right] \, d\rho^*
\]

where

\[
\rho^* = \rho \sigma^3 \tag{2.94a}
\]

\[
T^* = kT/\epsilon \tag{2.94b}
\]

\[
P^* = \rho \sigma^3/\epsilon \tag{2.94c}
\]

and

\[
A^* = A/N\epsilon \tag{2.94d}
\]

This Metropolis Monte Carlo method\(^{(37)}\) has been used to provide an alternate independent value for the reference free energy term of the perturbation theories discussed in sections 2.3.2 and 2.3.3. To accomplish this the reference pair potential \( U_{ij}^0(r) \), defined according to the Barker-Henderson prescription shown in figure 2.3 and given by equations (2.47)a-d, has been substituted for the total interaction potential \( U(r) \) in the virial term, equation (2.91). The Monte Carlo simulation pressure is therefore the pressure of the reference fluid, \( P^0 \), and the reference Helmholtz free energy is given by equation (2.93), written as

\[
\frac{A^0}{T^*} = \int_0^\rho \left[ \frac{P^0(\rho^*)}{T^* \rho^*} - \frac{1}{\rho^*} \frac{\partial \rho^*}{\rho^*} \right] \, d\rho^*
\]
This value of $A_0$ then allows the accuracy of both spherical and nonspherical reference fluids, as approximations in the respective perturbation theories, to be determined.

The perturbation terms in Zwanzig's expansion, $A_1, A_2, \text{etc.}$, can be calculated directly from computer simulations using expressions given by McQuarrie. The first-order term, $A_1$, is given simply by the canonical ensemble average of the configurational perturbation potential, $U^p$, and the second-order term, $A_2$, is related to the fluctuation of the first-order term (see appendix B).

$$A_1 = \langle U^p \rangle \quad \text{(2.96)a}$$

$$A_2 = -\frac{1}{kT} \left\{ \langle U^p \rangle^2 - \langle U^p \rangle^2 \right\} \quad \text{(2.96)b}$$

In equations (2.96)a,b, $\langle \ldots \rangle$ again indicates an average over the canonical ensemble.

Calculation of the first order term is considerably simplified when the configurational perturbation potential, $U^p$, is taken to be the sum of the pair potentials, as given by equation (2.97)

$$U^p = \sum_{i<j} u^p_{ij}(r) \quad \text{(2.97)}$$

The higher-order terms, however, are considerably more awkward since they introduce third- and fourth-order distribution functions that arise due to terms of the form $u_{ij}(r)u_{jk}(r)$ and $u_{ij}(r)u_{kl}(r)$ respectively, that occur when $U^p$ is itself squared as in equation (2.96)b.
2.4.1 Reference Fluid Structure from Computer Simulation

The use of a nonspherical reference fluid in the perturbation theory to represent the anisotropies introduced by the orientational dependent electropolar interactions, is hindered by the lack of information concerning the structural effects of such interactions. This lack of understanding then continues into calculations of the reference fluid properties in the perturbation theory such as the shape and density of the equivalent hard-body fluid and the corresponding Helmholtz free energy, $A^{HB}$. To a certain extent these uncertainties and discrepancies can be removed by calculation of the reference fluid free energy by Monte Carlo computer simulation, following the procedure described in section 2.4. However, there still remains the difficulty of calculating this reference free energy term using one of the equations applicable to hard-body systems such as those given by Boublik$^{(35)}$.

A common method of extracting the structural properties of a fluid from computer simulation data is to describe the dependence of the total pair distribution function $g(r,\omega_1,\omega_2)$ upon the locations and orientations of the particles by using a spherical harmonic expansion. First suggested by Pople$^{(39,40)}$, this is a method by which functions with a large number of dependent variables are written as an infinite series of an appropriate orthonormal set. The coefficients of the expansion are functions only of the interparticle separation, $r$. Hence, for a fixed separation, the orientational dependence of any configurational property can be described by a series whose terms are analytic functions of the angles defining the relative orientations. Further, through an examination of the size and significance of the coefficients
of the expansion, it is possible to obtain an understanding of the structure and nonsphericity of the fluid under consideration.

Mo and Gubbins\(^{(28)}\) have applied a similar procedure to determine the effect of non-central forces, such as dipolar and quadrupolar interactions, on the contributions to the Helmholtz free energy expressed itself as an infinite series. A study of the orientational structure of dense, hard diatomic fluids has been performed by Streett and Tildesley\(^{(41)}\) who have calculated up to sixteen terms in the spherical harmonic expansion of \(g(r,\omega_1,\omega_2)\). Wojcik and Gubbins\(^{(42)}\) have performed a similar study for the case of pure quadrupolar dumbbell fluids.

The pair distribution function \(g(r,\omega_1,\omega_2)\) of a polar fluid is a function of the three angles \(\theta_1\), \(\theta_2\), \(\phi_{12}\) and the separation of the centers of mass, \(r_{12}\). As for any configurational property, the pair distribution function may be expanded as an infinite series of the spherical harmonics \(Y_{\ell m}(\theta_1,\phi_1)\)\(^{(43)}\).

\[
g(r_{12},\theta_1,\theta_2,\phi_{12}) = 4\pi \sum_{\ell\ell'} \sum_{m} g_{\ell\ell' m}(r_{12}) Y_{\ell m}(\theta_1,\phi_1) Y_{\ell' -m}^{*}(\theta_2,\phi_2)
\]

\((2.98)\)

where \(g_{\ell\ell' m}\) are the spherical harmonic coefficients of the expansion and are functions of the separation, \(r_{12}\), only. The sums over \(\ell\) and \(\ell'\) are from 0 to \(\infty\), while \(m\) is equal to or less than the lesser of \(\ell\) and \(\ell'\).

An explicit expression for the expansion coefficients \(g_{\ell\ell' m}\) may be obtained by multiplying both sides of equation \((2.98)\) by the complex conjugates of the spherical harmonics \(Y_{\ell m}^*(\theta_1,\phi_1)\) and \(Y_{\ell' -m}^*(\theta_2,\phi_2)\) and integrating over all angular space \(\theta_1\) and \(\phi_1\), using the orthonormal properties of the spherical harmonics.
One method of obtaining the coefficients $g_{\ell m}$ would be to sort each particle into the appropriate configurational space during the course of a computer simulation and then to calculate the coefficients by numerical integration. However such a procedure would require a prohibitively large amount of computer storage.

Calculation of the coefficients as ensemble averages presents a more feasible approach. The average of any configurational property, $X$, in a shell between $r_{12}$ and $r_{12} + dr_{12}$ is defined as

$$
<X> = \frac{\iint X(r_{12}, \omega_1, \omega_2) n^{(2)}(r_{12}, \omega_1, \omega_2) d\omega_1 d\omega_2}{\iint n^{(2)}(r_{12}, \omega_1, \omega_2) d\omega_1 d\omega_2}
$$

(2.100)

where $\omega_i$ has again been used to represent the Euler angles $\Theta_i$ and $\Phi_i$. In equation (2.100), $n^{(2)}(r_{12}, \omega_1, \omega_2)$ is the probability of finding a particle 2 in the shell space $dr_{12}$, a distance $r_{12}$ from particle 1.

Introducing a normalized distribution function $g^{(2)}(r_{12}, \omega_1, \omega_2)$ defined by

$$
g^{(2)}(r_{12}, \omega_1, \omega_2) = \frac{16\pi}{\rho^2} n^{(2)}(r_{12}, \omega_1, \omega_2)
$$

(2.101)

where $\rho$ is again the number density and defining the first expansion coefficient for the distribution function so that the pair distribution function for particle centers is given by

$$
g_{000}(r_{12}) = \frac{1}{(4\pi)^2} \iint g(r_{12}, \omega_1, \omega_2) d\omega_1 d\omega_2
$$

(2.102)
it follows that

$$\int \int X(r_{12}, w_1, w_2) g(r_{12}, w_1, w_2) dw_1 dw_2 = (4\pi)^2 g_{oo0}(r_{12}) \langle X \rangle_{\text{SHELL}}$$  \hspace{1cm} (2.103)

If the property $X$ is allowed to be the product of two normalized spherical harmonics, then from equation (2.99)

$$g_{\ell \ell' m}(r_{12}) = 4\pi g_{oo0}(r_{12}) \left\langle Y_{\ell m}^*(w_1) Y_{\ell' m}^*(w_2) \right\rangle_{\text{SHELL}}$$ \hspace{1cm} (2.104)

where the quantity in brackets is the average for all particles in the shell $r_{12}$ to $r_{12} + dr_{12}$ and is calculated in the form of a histogram every 5000 configurations during the course of the simulation. Values of the coefficients, $g_{\ell \ell' m}(r_{12})$, for values of $\ell$ and $\ell'$ up to 4 have been determined using expressions for the ensemble averages given by Streett and Tildesley (41).
2.5. Calculation of Henry's Law Constant from Statistical Mechanics

When attempting to predict the solubility of a solute in a solvent using the theory of statistical mechanics it is convenient to relate the Henry's law constant, $H_i$, to the chemical potential, $\mu_i$. The problem then becomes therefore one of determining the chemical potential of the system.

2.5.1 Relationship between Henry's Constant and Chemical Potential

For a perfect gas, it can be shown that the Gibbs free energy is given by

$$G^{PG}(T,P,n_i)/NkT = \ln\left(\frac{P_i}{kT}\right) + \Sigma X_i \ln X_i \quad (2.105)$$

and according to Gibbs, the chemical potential of the $i^{th}$ component of a mixture is, $\mu_i$, defined as

$$\mu_i = \left\{\frac{\partial G}{\partial n_i}\right\}_{T,P,n_{j\neq i}} \quad (2.106)$$

or one may say that the chemical potential of the $i^{th}$ component is equal to the partial molar Gibbs free energy of $i$. Substituting equation (2.105) into equation (2.106) gives the chemical potential of a perfect gas.

$$\frac{\mu_i^{PG}(T,P)}{kT} = \ln\left(\frac{P_i}{kT}\right) + \ln X_i \quad (2.107)$$

The chemical potential of a real gas is related to the fugacity, $f_i$, by equation (2.108)

$$d\mu_i = kTd(lnf_i) \quad (2.108)$$
which upon integration gives

\[ \mu_i(T,P_1) - \mu_i(T,P_2) = kT \ln \left\{ \frac{f_i(T,P_1)}{f_i(T,P_2)} \right\} \]  

(2.109)

and if \( P_2 \) is chosen such that equation (2.105) is applicable, then equation (2.109) may be written as

\[ \mu_i(T,P) - \mu_i^{pg} = kT \ln \left\{ \frac{f_i(T,P)}{X_i P} \right\} \]  

(2.110)

The residual function of a thermodynamic property, \( Y \), is defined according to equation (2.111)

\[ Y_{res} = Y_{real \ fluid} - Y_{pg} \]  

(2.111)

and combining the above with equation (2.110) gives

\[ \frac{\mu_i^{res}(T,P)}{kT} = \ln \left\{ \frac{f_i(T,P)}{X_i P} \right\} \]  

(2.112)

where the argument of the right hand side is the dimensionless fugacity coefficient. The Henry's law constant relates thermodynamic functions to the limiting case of solubility and is formally defined as

\[ H_i(T,P) = \lim_{X_i \to 0} \left( \frac{f_i}{X_i} \right) \]  

(2.113)

Therefore applying equation (2.113) to equation (2.112) gives an equation relating \( H_i(T,P) \) to the residual chemical potential of component \( i \) at infinite dilution.
The chemical potential, \( \mu_i \), is itself simply related to the Helmholtz free energy of the mixture, \( A \), by

\[
\ln \left\{ \frac{H_i}{\beta kT} \right\} = \frac{\mu_i^{\text{res}}}{kT} \tag{2.114}
\]

Therefore there exists a direct path relating the Helmholtz free energy to the Henry's law constant.

Neff and McQuarrie\(^{(45)}\) have calculated Henry's law constants of solute gases for mixtures described by the L.H.B. theory\(^{(17)}\). Uno et al.\(^{(46)}\) and Goldman\(^{(47)}\) have performed similar calculations using the Lee and Levesque\(^{(18)}\) extension to mixtures of the WCA Theory\(^{(16)}\).
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Chapter III

EXPERIMENTAL

3.1 Previous Work

The solubility of gases in liquids has been extensively studied at moderate pressures and temperatures. However for similar measurements at high pressures, experimental data are not very abundant.

3.1.1 Pure Gases

The solubility of methane in water was measured previously by Culberson et al. at pressures up to 68.9 MPa and at temperatures of 298K to 444K; by O'Sullivan and Smith up to 60.8 MPa at 323K to 398K; by Sultanov et al. up to 100.2 MPa at 423K to 633 K; and by Price up to 152 MPa at 427K to 627K. In addition the saturation composition of CH₄ in the vapor phase in equilibrium with liquid water, was determined by Olds et al. at pressures up to 68.9 MPa at temperatures of 310.7K to 510.8K; and by Rigby and Prausnitz up to 9.3 MPa at 298K to 373K. For the system of nitrogen in water, liquid phase solubilities were reported by Wiebe et al. for pressures up to 101.3 MPa at temperatures of 298K, 323K and 348K; O'Sullivan and Smith up to 60.8 MPa at 323K and 398K; Tsikilis and Maslennikova up to 354.6 MPa at 603K and 638K; and by Saddleton and Krase up to 30.4 MPa at 323K to 513K. Both Rigby and Prausnitz and Saddleton and Krase report values for the saturated vapor phase composition of the system as does Bartlett for pressures up to 101.3 MPa and at 323K. The solubility of argon in water has been determined by Namiot and Bondareva at temperatures of 283K, 298K and 323K for pressures up to 68.7 MPa. No
reports of vapor phase compositions have been found in the literature for the argon-water system.

3.1.2 Mixtures of Gases

Namiot and Bondareva\(^\text{(15)}\) have determined the solute concentrations in water of mixtures of argon and methane for pressures of 29.5 MPa and 49.1 MPa at 298K. The same authors\(^\text{(16)}\) have measured the equilibrium compositions of helium-methane mixtures in water at 298K for pressures up to 59.0 MPa. However no data reporting equilibrium measurements for mixtures of nitrogen and methane has been found in the literature.

3.2 Experimental Work

The gases and gas mixtures used in the solubility experiments were all 'Ultra High Purity' (U.H.P.) grade and were supplied by Matheson Co. except for the argon which was supplied by Liquid Carbonic. The gases and their respective purities, as specified by the suppliers, were argon (99.999\%) nitrogen (99.999\%) and methane (99.97\%). Distilled, deionized water was always used as the solvent.

3.2.1 Preparation

The high-pressure experimental equipment, shown schematically in figure 3.1, consists of a two-stage, diaphragm compressor C-1 which feeds compressed gas through valve V-4 into a ballast tank T-1. This tank provides an immediate source of pressurized gas, required during the sampling procedures. The pressure in the ballast tank is read using a Bourdon-type gage, PI-1.
Figure 3.1 High-Pressure Equipment
The equilibrium cell, T-2, is a Hastalloy-C lined vessel surrounded by an electrical heating jacket which is used to control the temperature of the cell. The pressure in the cell is read on a digital meter with a transducer PI-3 which was calibrated against a dead weight gage by the manufacturer. The equilibrium cell can also be put into a rocking motion to promote equilibration. Water can be fed into the equilibrium cell from the holding tank T-3. For the purpose of safety, all of the equipment shown in figure 3.1, except the gas cylinder and the liquid tank T-3, is enclosed in an explosion chamber. This chamber, made of one-quarter inch boilerplate shielded by one-half inch dense fiberglass board, is designed to contain fragments from an explosion or decompression which may result from a sudden rupture of the cell, T-2. Two bursting disc assemblies D-1 and D-2 are located within the chamber and are to prevent accidental overpressuring of the high pressure system. The chamber is also equipped with a methane gas detector which triggers an exhaust fan, drawing 10,000 cfm when the methane concentration reaches 20% of the lower explosive limit within the chamber, and an alarm when the concentration reaches 40%.

For each set of experiments using a particular solute gas, or after the changing of a gas cylinder feeding the compressor C-1, the high pressure system is completely evacuated back to V-1 via valve V-18, and then purged with solute gas and re-evacuated. This process is repeated several times to ensure complete removal of the previous solute gas and any atmospheric air. The system is then isolated from the vacuum by closing V-18 and filled with solute gas from the gas cylinder to about 100-200 psig to prevent any inward leaks. The equilibrium cell is again evacuated having isolated the ballast tank and compressor by closing
valves V-7 and V-8. The required amount of distilled water is then allowed to enter T-2, from the holding tank T-3, by way of V-21, filling about half of the cell (approximately 350cc of water). The amount of liquid introduced into the cell is measured by the corresponding liquid level decrease in tank T-3. Vacuum is maintained in the system after filling, and the distilled water degassed by continuing to evacuate the equilibrium cell and allowing the solvent to evaporate for a period of approximately 0.25 hours. After degassing is complete, valve V-18 is closed and the cell is immediately blanketed with solute gas from the ballast tank T-1 via V-7 and a metering valve V-10, to prevent air from leaking into the system.

When the gas pressure in T-2, read on the digital pressure indicator PI-2, reaches 500 psig, valve V-7 is closed. Water is then allowed to fill the liquid line from the equilibrium cell through valves V-15, V-16, V-17, V-11 to V-20 by opening V-20 to the atmosphere until a steady stream of solvent is observed. The flow of liquid is regulated by needle valve V-12. Valve V-20 is then reclosed and pressurizing continued. The solute gas is compressed by the compressor C-1, and the pressure in the equilibrium cell is increased to the desired value, at which time V-7 is closed. Allowance is made for the slight temperature increase in the cell above the set-point, due to compression of the gas, and the corresponding change in pressure. The pressure in the ballast tank T-1 is allowed to increase by approximately 1500 psi before the compressor is stopped in order to provide an immediate source of high pressure gas, required during the liquid phase sampling procedure.
3.2.2 Liquid Phase Sample

For a liquid phase sample, equilibrium is obtained by putting the cell into a rocking motion. Culberson et al.\(^{(17)}\) indicated that a period of about three hours was required to achieve equilibrium for a similar system. After this period the cell is allowed to remain stationary in the near vertical position for one hour, to ensure complete separation of the phases. After this time the pressure inside the equilibrium cell is increased by opening V-7 and adjusting the needle valve V-10. This creates non-saturation conditions in the cell immediately before sample removal, to ensure that the gradual displacement of the liquid sample, from the equilibrium cell along the liquid sampling line, and the corresponding decrease in pressure will not result in the flashing of dissolved solute gas from the liquid phase. The rate of displacement of the liquid sample can be controlled by adjusting the metering valve V-12 and the exit valve V-20. The initial pressure increase in the equilibrium cell must be maintained, and is done so by continuous adjustment of valves V-7 and V-10. When approximately 50cc of liquid have been collected (an amount equivalent to the volume of the line from the equilibrium cell to the outlet at V-20), valves V-15 and V-17 are closed to trap a liquid sample of approximately 5-6 cc.

During the sampling procedure the liquid buret system is thoroughly evacuated. The liquid sample is then expanded into the buret system where the water and water vapor are frozen in the receiving flask F-1 (see figure 3.2) using crushed dry ice. The gas and water vapor remaining in the sampling line and flask is transferred to a previously evacuated buret system of known volume by means of a Toepler pump. Once the transfer is complete, the buret system is closed off and the temperature and pressure recorded. The composition of this vapor is
Figure 3.2  Liquid Phase Sample Analysis
determined by gas chromatography. The number of moles of solute dissolved in the liquid sample can therefore be calculated from this data. The water frozen in the receiving flask is vaporized by heating under vacuum and frozen again in the pre-weighed cold-traps VT-1 and VT-2. When VT-1 and VT-2 have returned to ambient temperature, the weight of solvent in the sample is determined by reweighing. During the collection of the liquid sample all lines between the equilibrium cell and the cold-traps are heated by electrical heat-tracing to ensure complete vaporization and capture.

3.3 Experimental Results

The accuracy of the experimental system and techniques has been confirmed previously by Choi(18), for the liquid phase results. Further confirmation has been achieved by comparison of the liquid phase experimental results for the argon-water system at 323K, with values reported by Namiot and Bondareva(15) for pressures up to 68.7 MPa. This comparison is shown in table 3.1, and a plot of the average of the solubilities at each pressure is shown in figure 3.3.

The results for the liquid phase solubility of the three mixtures of CH₄ and N₂ solute gases are given in tables 3.2, 3.3 and 3.4. The average solubility at each pressure was calculated, and are plotted as figures 3.4, 3.5 and 3.6. These results may be used to further verify the accuracy of our experimental apparatus and techniques. The error bars of the data plotted as figures 3.3-3.6 are of the size of the symbols used in the plots and as such have not been shown.
Table 3.1 Comparison of Experimental Data with Literature Values for the Liquid Phase Composition.

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(a) ref. (15)
Figure 3.3  Liquid Phase Composition Argon(2) / Water(1) from Experiment (Points) and Literature (Dashed Line)
Table 3.2 Experimental Liquid Phase Compositions

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Figure 3.4  Liquid Phase Composition 25% Methane(2) 75% Nitrogen(3) / Water(1)
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Figure 3.5  Liquid Phase Composition 50% Methane(2) - 50% Nitrogen(3) / Water(1)
Table 3.4 Experimental Liquid Phase Compositions

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Figure 3.6  Liquid Phase Composition 75% Methane(2) - 25% Nitrogen(3) / Water(1)
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4.1 Correlation of Solubility Data

4.1.1 Binary Systems

The solubility data for the argon-water system has been correlated using equations (2.28), (2.31), (2.33) and an expression similar to equation (2.28) except that the unsymmetric activity coefficient, \( \gamma^*_2 \), has been predicted by Wilson's equation rather than the two-suffix Margules equation.

The fugacity of argon, as a function of pressure, required for the evaluation of the correlations, has been obtained from the experimental data of Namiot and Bondareva\(^{(1)}\), and is plotted in figure 4.1.

Using the fugacity of the solute gas, \( f_2 \), from figure 4.1, equation (2.28) can be used first to correlate the solubility data given in table 3.1. For convenience in extending the plot of equation (2.28) to zero pressure, Choi\(^{(2)}\) introduced a modified Henry's law constant according to King\(^{(3)}\), given by

\[
\ln H^*_2 = \ln H^*_2 - \frac{P^*_2}{RT} \left( \frac{v^*_2 p^*_1}{v^*_2 p^*_1} \right)
\]

and combining equations (4.1) and (2.28) gives

\[
\ln \left( \frac{f_2}{X_2} \right) = \ln H^*_2 + \frac{-v^*_2 p}{RT}
\]

The gas phase has been assumed free of any solvent (i.e. \( Y_1 = 0 \)) which has been found to introduce uncertainties significantly smaller than expected experimental errors, and by doing so allows the fugacity, \( f_2 \),
Figure 4.1  Fugacity Coefficient of Argon.
to be given simply by

\[ f_2 = f_2^{ov} = \phi_2^{op} \]  

(4.3)

substituting equation (4.3) into equation (4.2) gives

\[ \ln\left(\frac{\phi_2^{op}}{X_2}\right) = \ln h^*_2 + \frac{-v_2^*}{RT} \]  

(4.4)

and it is this equation that is used to plot the experimental data for the argon-water system and is shown in figure 4.2. The slope of the straight line gives the apparent partial molar volume, \( v_2^* \), and the Henry's law constant, \( h_2^1 \), may be read from the figure at the saturation pressure of water at the system temperature. These values are given in table 4.1, along with similar values for binary systems of methane and nitrogen with water taken from the work of Choi\(^{(2)}\) and included here for comparison.

The Krichevsky-Ilinskaya equation, in the form of equation (2.28), does not correlate the solubility data of Choi\(^{(2)}\) well. One alternative, as discussed in Chapter 2, is to use Wilson's equation in place of the two-suffix Margules equation to predict the unsymmetric activity coefficient, \( v_2^* \), and as such is given by equation (2.29). Substitution of this expression along with equation (2.31), into equation (2.22) gives

\[
\frac{(v_2^* - \infty^*_{P_1})}{RT} (P - P_1^S) = -\ln \left\{ \frac{(X_1 \Lambda_{21} + X_2)}{\Lambda_{21}} \right\}
\]

(4.5)
Figure 4.2  Solubility of Argon(2) in Water(1)
(Line is Linear Fit of Points)
\( T = 323 \text{K} \)

<table>
<thead>
<tr>
<th>Solute</th>
<th>Henry's Law Constant, ( H_2 ) ( \times 10^{-2} / \text{MPa/mol. frac.} )</th>
<th>Partial molar volume, ( \hat{v}_2^* ) ( \times 10^{-6} / \text{m}^3 \text{mol}^{-1} )</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Expt</td>
<td>S.P.T*</td>
<td>Expt</td>
</tr>
<tr>
<td>Argon</td>
<td>57.5</td>
<td>45.5</td>
<td>28.4</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>115.7 (a)</td>
<td>127.3</td>
<td>32.2</td>
</tr>
<tr>
<td>Methane</td>
<td>57.1 (a)</td>
<td>69.3</td>
<td>35.1</td>
</tr>
</tbody>
</table>

* Scaled Particle Theory of Reiss et al. (4,5)

(a) From reference (2)
(b) Predicted using method of Brelvi and O'Connell (4)
(c) From dilatometric experiments of Krichevsky and Ilinskaya (5)
(d) Predicted using method of Choi (2)

Table 4.1 Comparison of the Henry's law constant, \( H_2 \), and the apparent partial molar volume, \( \hat{v}_2^* \), from various sources.
Using the values of \( v_2^{\infty} \) found previously and given in column 4 of table 4.1, together with the values for \( v_2^{\infty} \) given in column 6, the solubility data for all three systems has been correlated by equation (4.5). The two independent parameters in this equation, \( \Lambda_{12} \) and \( \Lambda_{21} \), have been determined using an unconstrained optimization search technique, minimizing the total error between experimental and predicted solubilities. The resulting values of the parameters are given in table 4.2.

Choi attributed the failure of the Krichevsky-Illinskaya correlation, in conjunction with the two-suffix Margules equation, to the assumption of equation (2.21), i.e., a pressure-independent partial molar volume, and using the suggestion of Namiot derived equation (2.33). Combining equations (2.31) and (2.33) gives

\[
\frac{(v_2^{\infty} - v_2^{\infty})}{RT} (P - P_1^{\infty}) = \frac{\Lambda_{12}}{RT} (X_1^2 - 1) - \frac{\beta_2 v_2^{\infty} P_1^{\infty}}{2RT} \tag{4.6}
\]

Values of the Scatchard-Hildebrand binary parameter, and \( \beta_2 \), the coefficient of isothermal compressibility, found by a fit of the solubility data for each binary system to equation (4.6), are given in table 4.3.

4.1.2 Ternary Systems

Experimental P-V-T data for the ternary systems used in this study is not available from the literature, and hence the fugacities of the solute gases must be determined by some alternative method. The vapor phase fugacity coefficient of a solute \( i \) may be evaluated from equation (4.7)
\[ T = 323 \, \text{K} \]

### Wilson's Parameters

<table>
<thead>
<tr>
<th>Solute</th>
<th>( ^\wedge_{12} )</th>
<th>( ^\wedge_{21} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon</td>
<td>0.000</td>
<td>0.094</td>
</tr>
<tr>
<td>Nitrogen†</td>
<td>0.000</td>
<td>0.034</td>
</tr>
<tr>
<td>Methane†</td>
<td>0.000</td>
<td>0.107</td>
</tr>
</tbody>
</table>

† Using data of Choi (2)

Table 4.2 Wilson's parameters for Krichevsky-Illinskaya equation obtained from equation (4.5)
Table 4.3  Parameters from best fit of solubility data by equation (4.6), the extended Krichevsky-Ilinskaya equation of Choi

<table>
<thead>
<tr>
<th>Solute</th>
<th>$A_{12} \times 10^2$ (MPa m$^3$/mol)</th>
<th>$\beta_2 \times 10^3$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon</td>
<td>1.7</td>
<td>0.92</td>
</tr>
<tr>
<td>Nitrogen$^\dagger$</td>
<td>4.5</td>
<td>0.91</td>
</tr>
<tr>
<td>Methane$^\dagger$</td>
<td>1.4</td>
<td>0.75</td>
</tr>
</tbody>
</table>

$^\dagger$ From Choi$^{(2)}$
by using an equation of state to predict the P-V-T behavior of the vapor phase. Assuming, once again, that the vapor phase is solvent-free, the Redlich-Kwong equation of state has been used in equation (4.7) and the predicted fugacity coefficients used in the appropriate correlations. The Redlich-Kwong equation of state is written as

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

(4.8)

where the constants "a and b" are given by

$$ a = \frac{\Omega_a R^2 T_c^{2.5}}{P_c} $$

(4.9a)

$$ b = \frac{\Omega_b R T_c}{P_c} $$

(4.9b)

where $T_c$ and $P_c$ are the critical temperature and pressure respectively. The constants $\Omega_a$ and $\Omega_b$ used in equations (4.9)a,b are determined from a fit of the pure-component volumetric data of the saturated vapor rather than the inflexion point condition of the critical point which is far removed from the conditions being studied.

Using the fugacity coefficients of each solute $i$, $\phi_i^V$, predicted using equation (4.8), the experimental data given in tables 3.2-3.4 has been correlated by fitting the solubilities of each component to the modified Krjechevsky-Kasarnovsky equation written as

$$ \ln \left\{ \frac{y_i \phi_i^P}{X_i} \right\} = \ln \phi_i^V + \frac{v_i^*}{RT} (P - P_s) $$

(4.10)

and are plotted in figures 4.3-4.5.
Figure 4.3  Liquid Phase Solubility of 25%CH₄ - 75%N₂/H₂O System Correlated by the Modified Krichevsky-Kasarnovsky Equation for Ternary Systems. (Lines are Linear Fit of Points)
Liquid Phase Solubility of 50%CH₄ - 50%N₂/H₂O System Correlated by the Modified Krichevsky-Kaşarhovsky Equation for Ternary Systems. (Lines are Linear Fit of Points)
Figure 4.5 Liquid Phase Solubility of 75%CH₄ - 25%N₂/H₂O System Correlated by the Modified Krichevsky-Kasarnovsky Equation for Ternary Systems. (Lines are Linear Fit of Points)
The values of $v^*_1$ and $H^*_1$ obtained for each gas in the mixtures are given in table 4.4.

4.2 Prediction of Liquid Phase Solubility

4.2.1 Binary Systems

Prediction of the liquid phase solubility of the solute, $X_2$, by the modified Krichevsky-Kasarnovsky equation, requires values for the fugacity, $f_2$, the Henry's law constant, $H^*_2$, and $v^*_2$ the apparent partial molar volume. Choi [2] has discussed and evaluated various methods for determining these parameters independently and the corresponding values for $H^*_2$ and $v^*_2$ are given in columns (3) and (5) of table 4.1. The predicted values of $X_2$ are given in table 4.5 along with the percentage differences given by

$$\% \text{-Diff} = \left| \frac{X_{\text{Expt}} - X_{\text{Pred}}}{X_{\text{Expt}}} \right| \times 100 \quad (4.11)$$

As pointed out by Choi [2], prediction of $X_2$ by the extended Krichevsky-Ilinskaya equation requires two additional parameters, $A_{12}$ and $\beta_2$, and as yet no method is available for the prediction of $A_{12}$ for a binary system containing a polar component. Therefore equation (2.33) is not useful for solubility predictions but can still be applied to data correlation and interpolation.

4.2.2 Ternary Systems

The solubility of three binary mixtures of nitrogen and methane in water has been predicted using equations (2.41) a and b, where the pure
\( T = 323 \text{ K} \)

<table>
<thead>
<tr>
<th>System</th>
<th>( p^s_{H_1} \times 10^{-2} / \text{MPa/mol. frac (2)} )</th>
<th>( v^*_{1} \times 10^{-6} / \text{m}^3 \text{ mol}^{-1} (2) )</th>
<th>( \frac{v^*<em>{1}}{v</em>{H_1}} \times 10^{-6} / \text{m}^3 \text{ mol}^{-1} (3) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>25%CH(_4) (2) - 75%N(_2) (3)/H(_2)O</td>
<td>67.4</td>
<td>102.6</td>
<td>30.2  33.3</td>
</tr>
<tr>
<td>50%CH(_4) (2) - 50%N(_2) (3)/H(_2)O</td>
<td>62.3</td>
<td>119.7</td>
<td>34.5  29.3</td>
</tr>
<tr>
<td>75%CH(_4) (2) - 25%N(_2) (3)/H(_2)O</td>
<td>69.7</td>
<td>126.0</td>
<td>31.0  27.9</td>
</tr>
</tbody>
</table>

Table 4.4 Henry's law constants and partial molar volumes from modified Krichevsky-Kasarnovsky equation for ternary systems.
$T = 323 \, K$

<table>
<thead>
<tr>
<th>Press/MPa</th>
<th>$X_{\text{Expt}}$</th>
<th>$X_{\text{Pred}}^{(a)}$</th>
<th>$\Delta^{(a)}$</th>
<th>$X_{\text{Pred}}^{(b)}$</th>
<th>$\Delta^{(b)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.45</td>
<td>0.00283</td>
<td>0.00291</td>
<td>0.7</td>
<td>0.00357</td>
<td>26.2</td>
</tr>
<tr>
<td>42.42</td>
<td>0.00458</td>
<td>0.00455</td>
<td>0.6</td>
<td>0.00582</td>
<td>27.1</td>
</tr>
<tr>
<td>62.59</td>
<td>0.00576</td>
<td>0.00584</td>
<td>1.4</td>
<td>0.00752</td>
<td>30.5</td>
</tr>
<tr>
<td>83.22</td>
<td>0.00684</td>
<td>0.00695</td>
<td>1.5</td>
<td>0.00900</td>
<td>31.6</td>
</tr>
<tr>
<td>103.49</td>
<td>0.00777</td>
<td>0.00783</td>
<td>0.8</td>
<td>0.01021</td>
<td>31.4</td>
</tr>
<tr>
<td>123.82</td>
<td>0.00864</td>
<td>0.00851</td>
<td>1.5</td>
<td>0.01116</td>
<td>29.2</td>
</tr>
</tbody>
</table>

(a) $p_s^{(4.4)}$ and $v_s^{(4.4)}$ from fitting of equation (4.4)

(b) $p_s^{(4.5)}$ and $v_s^{(4.5)}$ from Scaled Particle Theory (4.5)

Table 4.5 Comparison of experimental and predicted solubilities in the argon-water system.
solute solubility data of each gas has been fitted to a second-order polynomial and the equations are given below

\[ X_2^\circ(P) = 8.0864 \times 10^{-4} + 7.3588 \times 10^{-5}P - 3.0295 \times 10^{-7}P^2 \]  
\[ X_3^\circ(P) = 4.3226 \times 10^{-4} + 5.1696 \times 10^{-5}P - 6.8821 \times 10^{-8}P^2 \]

(4.12)

(4.13)

The predicted solubilities have been compared to the experimental values according to equation (4.11) and are given in table 4.6.

4.3 Discussion

The success of the Krichevsky-Kasarnovsky equation in correlating the solubility of pure solute gases in water at high pressures has been shown previously by Choi \(^2\). This observation is further reinforced by the correlation of the solubility data given in table 3.1 for the argon-water system. As pointed out by Choi \(^2\), data correlated by the Krichevsky-Kasarnovsky equation, written as equation (4.4), should yield a straight line plot for \(\ln(\phi_2^\circ P / X_2)\) as a function of the pressure, \(P\), and as can be seen from figure 4.2, this is indeed the case. Values of the apparent partial molar volume, \(\bar{v}_2^\circ\), and the Henry's law constant, \(p_s^s\), obtained from figure 4.2 are given in table 4.1 along with the corresponding values for the nitrogen-water and methane-water systems \(^2\).

It is interesting to note that the value of \(p_s^{s_1}\) for argon is similar to that for methane, both spherical in shape whereas the value for nitrogen, which is dumbbell-shaped, is larger by a factor of approximately two. This comparison is also reflected in the values for \(p_s^{s_1}\) predicted
\[ T = 323 \text{ K} \]

<table>
<thead>
<tr>
<th>Press /MPa</th>
<th>( X_2 ) Expt</th>
<th>( X_2 ) Pred</th>
<th>( X_3 ) Expt</th>
<th>( X_3 ) Pred</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.56</td>
<td>.00047</td>
<td>.00056</td>
<td>.00127</td>
<td>.00114</td>
</tr>
<tr>
<td>42.15</td>
<td>.00085</td>
<td>.00084</td>
<td>.00195</td>
<td>.00187</td>
</tr>
<tr>
<td>62.55</td>
<td>.00113</td>
<td>.00106</td>
<td>.00257</td>
<td>.00255</td>
</tr>
<tr>
<td>82.48</td>
<td>.00125</td>
<td>.00120</td>
<td>.00301</td>
<td>.00317</td>
</tr>
<tr>
<td>103.08</td>
<td>.00141</td>
<td>.00129</td>
<td>.00355</td>
<td>.00377</td>
</tr>
<tr>
<td>123.85</td>
<td>.00153</td>
<td>.00132</td>
<td>.00401</td>
<td>.00433</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Press /MPa</th>
<th>( X_2 ) Expt</th>
<th>( X_2 ) Pred</th>
<th>( X_3 ) Expt</th>
<th>( X_3 ) Pred</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.89</td>
<td>.00109</td>
<td>.00114</td>
<td>.00073</td>
<td>.00077</td>
</tr>
<tr>
<td>42.22</td>
<td>.00158</td>
<td>.00169</td>
<td>.00118</td>
<td>.00125</td>
</tr>
<tr>
<td>63.91</td>
<td>.00205</td>
<td>.00214</td>
<td>.00187</td>
<td>.00173</td>
</tr>
<tr>
<td>84.32</td>
<td>.00218</td>
<td>.00243</td>
<td>.00201</td>
<td>.00215</td>
</tr>
<tr>
<td>104.35</td>
<td>.00261</td>
<td>.00259</td>
<td>.00245</td>
<td>.00254</td>
</tr>
<tr>
<td>125.12</td>
<td>.00280</td>
<td>.00264</td>
<td>.00270</td>
<td>.00291</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Press /MPa</th>
<th>( X_2 ) Expt</th>
<th>( X_2 ) Pred</th>
<th>( X_3 ) Expt</th>
<th>( X_3 ) Pred</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.79</td>
<td>.00145</td>
<td>.00170</td>
<td>.00036</td>
<td>.00038</td>
</tr>
<tr>
<td>42.10</td>
<td>.00220</td>
<td>.00253</td>
<td>.00060</td>
<td>.00062</td>
</tr>
<tr>
<td>62.52</td>
<td>.00290</td>
<td>.00317</td>
<td>.00086</td>
<td>.00085</td>
</tr>
<tr>
<td>83.29</td>
<td>.00340</td>
<td>.00363</td>
<td>.00105</td>
<td>.00107</td>
</tr>
<tr>
<td>103.31</td>
<td>.00389</td>
<td>.00388</td>
<td>.00123</td>
<td>.00126</td>
</tr>
<tr>
<td>123.52</td>
<td>.00421</td>
<td>.00396</td>
<td>.00142</td>
<td>.00144</td>
</tr>
</tbody>
</table>

Table 4.6 Comparison of experimental and predicted solubilities for ternary mixtures.
Figure 4.6 Comparison of Predicted (Lines) and Experimental (Points) Solubilities for 25%CH₄ - 75%N₂/H₂O System
Figure 4.7 Comparison of Predicted (Lines) and Experimental (Points) Solubilities for 50%CH\textsubscript{4} - 50%N\textsubscript{2}/H\textsubscript{2}O System
Figure 4.8  Comparison of Predicted (Lines) and Experimental (Points) Solubilities for 75%CH₄ - 25%N₂/H₂O System
predicted by the Scaled Particle Theory\(^{(6,5)}\) of which an important part is the "cavity-formation" term, where a cavity is created in the solvent fluid large enough to allow the insertion of a solute particle.

Choi\(^{(2)}\) has previously shown that the Krichevsky-Illinskaya correlation, using an activity coefficient predicted by the two-suffix Margules equation, is inappropriate for the correlation of the high-pressure solubility data presented here. In this work the correlation has been modified by using the Wilson's equation to predict the activity coefficient. Unfortunately, a visual test of the validity, or otherwise, of the correlation is impossible. However, the two Wilson parameters obtained from the unconstrained optimization of the solubility data, for all three binary systems, are given in table 4.2. As can be seen in the table, one of the two Wilson parameters, \(\Lambda_{12}\), is considerably smaller than the other, \(\Lambda_{21}\). Although written as such, it is not suggested that \(\Lambda_{12}\) is exactly zero, and indeed an examination of equations (4.14)a and b given below indicates such an occurrence would require an infinitely large interaction energy difference \((\lambda_{12} - \lambda_{11})\), in equation (4.14)a defining one of the two Wilson parameters,

\[
\Lambda_{12} = \left(\frac{v_2}{v_1}\right) \exp \left\{ -\frac{(\lambda_{12} - \lambda_{11})}{RT} \right\} \tag{4.14a}
\]

\[
\Lambda_{21} = \left(\frac{v_1}{v_2}\right) \exp \left\{ -\frac{(\lambda_{12} - \lambda_{22})}{RT} \right\} \tag{4.14b}
\]

where \(v_i\) is the molar volume of \(i\) and \(\lambda_{ij}\) represents the interaction energy between \(i\) and \(j\). Qualitatively one would expect the solvent-solvent interaction energy, \(\lambda_{11}\), to be substantially larger than that for solute-solute interactions, \(\lambda_{22}\), and the corresponding term for
the solvent-solute interactions, $\lambda_{12}$, to be of the same order of magnitude as $\lambda_{22}$. This would then result in a value of $\Lambda_{12}$ from equation (4.14a) that approached zero for all three solute gases, as is shown in table 4.2. Again the values of $\Lambda_{21}$ for argon and methane are similar, suggesting comparable values of the respective interaction energy differences. The lower value of $\Lambda_{21}$ for nitrogen can be explained by a lower solvent-solute interaction energy, presumably reflected in its lower solubility in water than both methane and argon.

The solubility in water of each solute gas in the gas mixture can be correlated by the Krichevsky-Kasarnovsky written as equation (4.10) and again the validity of this correlation for the data obtained in this study is indicated by the straight line plots, for each solute, in figures 4.3-4.5. The values of the apparent partial molar volume and the Henry's law constant, for each solute, obtained from the slope and intercept of each line respectively, are given in table 4.4 are comparable to the values previously given for the pure solute solubility data of Choi. This indicates that the assumption used in the prediction of the solubilities of the gas mixtures, given in table 4.6 and shown as figures 4.6-4.8, is valid.
References


(6) Brelvi, S.W. and J.P. O'Connell, "Corresponding States Correlations for Liquid Compressibility and Partial Molar Volumes of Gases at Infinite Dilution in Liquids" A.I.Ch.E.J., 18, 1239 (1972)


Chapter V

PERTURBATION THEORY AND COMPUTER SIMULATION RESULTS

The thermodynamic properties of Lennard-Jones fluids and electro-polar fluids have been calculated, at different state points and electropole moments, using the methods of perturbation theory as well as Monte Carlo and molecular dynamics computer simulation. Comparisons of the predicted values from the different methods, and with existing literature data, have been made.

Computer simulation of fluids is an accurate way to determine the properties of fluids for which the intermolecular potential is known. Monte Carlo computer simulations, using the same Barker-Henderson potential as that used in the perturbation theory calculations, can therefore be regarded as giving the 'exact' perturbation calculations within the precision of the simulations. Hence, a comparison of the results from both sources will not only provide a test of the perturbation methods themselves, but also of the assumptions inherent in the derivation of the methods.

To gain some insight into the effect of the splitting of the interaction potential into its 'repulsive' and 'attractive' parts, and therefore an understanding of the success or failure of the perturbation theory, the coefficients of the spherical harmonic expansion of the normalized distribution function have been calculated. A comparison of the coefficients for the full potential and Barker-Henderson potential should provide at least a qualitative description of the consequences of this split.
5.1 Perturbation Theory Results

The two versions of the perturbation theory used to determine the thermodynamic properties of the different fluids being studied here were derived in section 2.3.2. As was mentioned previously equation (2.85) is referred to as method I and equation (2.87) as method II.

Mo and Gubbins\(^{(1)}\) compared the anisotropic contribution to the internal energy, i.e. that part due to the additional electropolar potential, predicted by a nonspherical reference potential perturbation theory with the simulation data of Wang et al.\(^{(2)}\), at a state point near the triple point, for Lennard-Jones fluids with both dipolar and quadrupolar anisotropies. A similar comparison of the predicted anisotropic Helmholtz free energy with the Monte Carlo simulation results of Verlet and Weis\(^{(3)}\) has also been performed. Recently, Kohler and Quirke\(^{(4)}\) have compared the results of a perturbation theory for polar, nonspherical molecules with the results of Verlet and Weis\(^{(3)}\) for the special case of an elongation, $\xi = \ell/\sigma$, of zero, where $\ell$ is the separation of the molecule centers in dumbbells.

The reference and perturbation contributions to the total residual Helmholtz free energy of a pure Lennard-Jones fluid predicted by methods I and II, are given in table 5.1 for a reduced temperature of $T^* = 1.15$ and reduced densities of $\rho^* = 0.6, 0.7, 0.8$ and 0.85. Values of the equivalent hard-sphere diameter, calculated by equation 2.83, are also given in table 5.1. The residual Helmholtz free energy is defined by equation 5.1, when $(A/NkT)^{PG}$ is the free energy of a perfect gas, given by equation 5.2, at the same conditions.

\[
(\frac{A}{NkT})^{res} = \frac{A}{NkT} - (\frac{A}{NkT})^{PG} \tag{5.1}
\]
Table 5.1 Comparison of Residual Helmholtz Free Energy of Lennard-Jones 12:6 Fluid from Methods I and II with First-Order BH Theory and WCA Theory at $T = 1.15$

<table>
<thead>
<tr>
<th>$\rho$</th>
<th>$d^{HS}/\sigma$</th>
<th>$A_0/NkT$</th>
<th>$A_1/NkT$</th>
<th>$A_{res}/NkT$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>METHOD I</td>
<td>METHOD II</td>
</tr>
<tr>
<td>0.6</td>
<td>0.976</td>
<td>1.82</td>
<td>-3.43</td>
<td>-3.43</td>
</tr>
<tr>
<td>0.7</td>
<td>0.972</td>
<td>2.29</td>
<td>-4.03</td>
<td>-3.99</td>
</tr>
<tr>
<td>0.8</td>
<td>0.968</td>
<td>2.82</td>
<td>-4.59</td>
<td>-4.51</td>
</tr>
<tr>
<td>0.85</td>
<td>0.968</td>
<td>3.17</td>
<td>-4.85</td>
<td>-4.76</td>
</tr>
</tbody>
</table>

† From reference (5)
The residual Helmholtz free energy predicted by both the first-order Barker-Henderson theory and the Weeks-Chandler Anderson theory are also given for comparison (5).

Perturbation theory methods I and II have also been used to predict the contributions to the residual Helmholtz free energy of dipolar ($\mu^* = 1.00$ and $2.00$) fluids and quadrupolar ($Q^* = 0.6985$ and $1.3970$) fluids, at the same state points as table 5.1, and the results are given in tables 5.2 and 5.3 respectively.

5.2 Computer Simulation Results

Monte Carlo computer simulation of dipolar fluids in the canonical ensemble have been performed previously by McDonald (6) for a system of 108 particles. McDonald (6) reported values of the configurational internal energy, $U^*$, for dipolar fluids over a range of reduced densities up to $\rho^* = 0.9$ and at reduced temperatures of $T^* = 1.15$, $1.35$ and $2.75$ for $\mu^*$, the reduced dipole moment, equal to $1.0$ and at $T^* = 0.75$ for $\mu^* = 0.5$. Wang et al. (2) studied both dipolar and quadrupolar fluids at $T^* = 0.719$ and $\rho^* = 0.800$ for a system of 64 particles and recently Yao et al. (7) have reported a comparison with the results of McDonald (6) in addition to similar calculations performed in the grand canonical ensemble.

Although the thermodynamic properties usually reported for simulations performed in the canonical ensemble are the configurational internal energy and pressure, Verlet and Weis (3) reported values of
<table>
<thead>
<tr>
<th>$\rho^*$</th>
<th>$\mu^*$</th>
<th>$d^{HS}/\sigma$</th>
<th>$A_0/NkT$</th>
<th>Method I</th>
<th>Method II</th>
<th>$A^{res}/NkT$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>1.00</td>
<td>1.027</td>
<td>2.33</td>
<td>-4.11</td>
<td>-4.35</td>
<td>-1.78</td>
</tr>
<tr>
<td>0.7</td>
<td>1.00</td>
<td>1.018</td>
<td>2.92</td>
<td>-4.84</td>
<td>-5.13</td>
<td>-1.92</td>
</tr>
<tr>
<td>0.8</td>
<td>1.00</td>
<td>1.009</td>
<td>3.59</td>
<td>-5.54</td>
<td>-5.79</td>
<td>-1.95</td>
</tr>
<tr>
<td>0.85</td>
<td>1.00</td>
<td>1.001</td>
<td>3.88</td>
<td>-5.87</td>
<td>-6.07</td>
<td>-1.99</td>
</tr>
<tr>
<td>0.7</td>
<td>2.00</td>
<td>1.116</td>
<td>5.24</td>
<td>-11.94</td>
<td>-10.61</td>
<td>-6.69</td>
</tr>
<tr>
<td>0.8</td>
<td>2.00</td>
<td>1.089</td>
<td>6.10</td>
<td>-13.81</td>
<td>-12.36</td>
<td>-7.71</td>
</tr>
<tr>
<td>0.85</td>
<td>2.00</td>
<td>1.078</td>
<td>6.63</td>
<td>-14.74</td>
<td>-13.35</td>
<td>-8.10</td>
</tr>
</tbody>
</table>

Table 5.2 Contributions to the Residual Helmholtz Free Energy of Dipolar Fluids from Perturbation Theory at $T = 1.15$
<table>
<thead>
<tr>
<th>$\rho^*$</th>
<th>$Q^*$</th>
<th>$\frac{d}{\sigma}$</th>
<th>$A_0/NkT$</th>
<th>$A_{1/NkT}$</th>
<th>$A_{res/NkT}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>0.6985</td>
<td>0.976</td>
<td>1.82</td>
<td>-3.55</td>
<td>-3.53</td>
</tr>
<tr>
<td>0.7</td>
<td>0.6985</td>
<td>0.977</td>
<td>2.35</td>
<td>-4.18</td>
<td>-4.17</td>
</tr>
<tr>
<td>0.8</td>
<td>0.6985</td>
<td>0.978</td>
<td>2.99</td>
<td>-4.79</td>
<td>-4.77</td>
</tr>
<tr>
<td>0.85</td>
<td>0.6985</td>
<td>0.968</td>
<td>3.17</td>
<td>-5.08</td>
<td>-4.95</td>
</tr>
<tr>
<td>0.8</td>
<td>1.3970</td>
<td>1.017</td>
<td>3.77</td>
<td>-8.03</td>
<td>-7.30</td>
</tr>
<tr>
<td>0.85</td>
<td>1.3970</td>
<td>1.010</td>
<td>4.10</td>
<td>-8.62</td>
<td>-7.64</td>
</tr>
</tbody>
</table>

Table 5.3 Contributions to the Residual $\Delta$Helmholtz Free Energy of Quadrupolar Fluids from Perturbation Theory at $T = 1.15$
the anisotropic contribution to the Helmholtz free energy for $T^* = 1.15$ and $\rho^* = 0.85$ with reduced dipole moments of $\mu^* = 1.00$ and $2.00$.

The Monte Carlo simulations performed in this study were all started with the molecules in a face-centered cubic (FCC) lattice and an $\alpha$-orientation. To start, the total intermolecular potential, $U_{\text{tot}}$, was evaluated and then in order, beginning with particle 1, random displacements of particles were proposed and the resulting change in the total intermolecular potential, $\Delta U_{\text{tot}}$, determined. For the case of $\Delta U_{\text{tot}} < 0$, the move was accepted with unit probability. For the case of $0 < \Delta U_{\text{tot}} < H_{\text{max}}$, where $H_{\text{max}} = 20.0$, a random number, $\xi$, between 0 and 1.0 was generated and if $\exp(-\beta \Delta U_{\text{tot}})$ was greater than $\xi$, the move was accepted with probability $\exp(-\beta \Delta U_{\text{tot}})$. Otherwise, the proposed move was rejected and the old configuration accepted with unit probability. After a change in the position of each particle had been proposed a similar sequence was performed for the orientations of each particle. Even though this procedure required more computing time than the simultaneous changes in the positions and orientations of the molecules, and does not afford significantly improved convergence, this approach was followed to allow independent optimization of the acceptance rates of the proposed displacements and rotation.

The orientations of the molecules were described by the method of quaternions, rather than the usual Eulerian angles, to avoid preferential treatment of sampling in any one specific orientation. In all, 8000 displacements of the location and orientation of each particle were proposed in addition to 1000 such displacements for equilibration. To avoid excessive growth in computational errors, the total intermolecular potential was recalculated after every 20 proposed changes in the entire
ensemble. A truncated potential with a cut-off of 4.18 $\sigma$ was used and depending upon the density, systems of 256 or 500 particles were employed.

To confirm the accuracy of the Monte Carlo method developed here values of the configurational internal energy and the pressure for the full electropolar interaction potential have been compared with the results of Yao et al.\(^{(7)}\) and with results from a molecular dynamics computer simulation method previously developed and tested\(^{(9)}\). This comparison is shown in table 5.4.

For the case of a fluid described by the reference potential, $U^0$, defined by equations (2.74)a,b, the terms in the perturbation theory expansion can be calculated exactly, and Monte Carlo simulation is suitable since the reference potential is often discontinuous with respect to the separation, $r$. The first-order term in the expansion for the Helmholtz free energy, $A_1$, can be obtained straightforwardly by equation (2.88) written as

$$A_1^\ast = \left\langle U^P \right\rangle_{NVT} \tag{5.3}$$

where $\left\langle \ldots \right\rangle_{NVT}$ denotes a Monte Carlo average in the canonical ensemble and $U^P$ is the configurational perturbation potential again given by equations (2.74)a,b. Calculation of the reference Helmholtz, $A_0$, is rather more complicated and techniques such as the 'umbrella' sampling or test particle methods\(^{(12)}\) have been used to determine the free energy of dense fluids. However, such methods can provide unreliable results, and the method of thermodynamic integration has been used with $A_0^{\text{res}}$ given by equation (2.97) written as
<table>
<thead>
<tr>
<th>$\mu^*$</th>
<th>Internal Energy, $U^*$</th>
<th>Pressure, $P^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Monte Carlo</td>
<td>M.D.</td>
</tr>
<tr>
<td></td>
<td>Ref. (4)</td>
<td>THIS WORK</td>
</tr>
<tr>
<td>0.0</td>
<td>-5.40†</td>
<td>-5.43</td>
</tr>
<tr>
<td>0.5</td>
<td>-5.71</td>
<td>-5.71</td>
</tr>
<tr>
<td>0.8</td>
<td>-6.02</td>
<td>-6.05</td>
</tr>
<tr>
<td>1.0</td>
<td>-6.28</td>
<td>-6.31</td>
</tr>
</tbody>
</table>

† Obtained in this work

‡ Obtained using equation of Nicolas et al. (11)
\[ \left( \frac{A_0}{NkT} \right)^{\text{res}} = \frac{A_0^*}{T^*} = \int_0^{\rho^*} \left\{ \frac{P_0^*}{T^* \rho^*} - 1 \right\} \frac{d\rho^*}{\rho^*} \] (5.4)

where \( P_0^* \) is the reduced pressure of the reference fluid. The reliability of the results obtained from equation (5.4) depends simply upon the quality of the simulations performed.

The results of the simulations are shown in table 5.5 for the 256 particle simulation of the fluid obtained by a Barker-Henderson split of the Lennard-Jones 12:6 potential. Results for the reference fluid of dipolar fluids and quadrupolar fluids are given in tables 5.6 and 5.7 respectively. A temperature of \( T^* = 1.15 \) has been used throughout to allow a comparison with the results of Verlet and Weis (3). Results for the first-order term, \( A_1^* \), include tail-corrections for the Lennard-Jones interactions beyond the cut-off.

Since Verlet and Weis (3) reported results for the Helmholtz free energy only at \( T^* = 1.15 \) and \( \rho^* = 0.85 \) and only for dipolar fluids, additional data has been generated using molecular dynamics computer simulation at different densities and for quadrupolar fluids, all at \( T^* = 1.15 \). These simulations were performed using 256 particles and a dipolar or quadrupolar potential truncated at \( 3.0 \sigma \). Production runs were made for 9000 time-steps after an equilibration of 1000 time-steps with a reduced time-step of \( \Delta t^* = 0.002 \). The rotational equation of motion was solved using the method of quaternions given by Evans and Murad (13). The programs used for these molecular dynamics simulations have been developed elsewhere (9).
<table>
<thead>
<tr>
<th>$\rho^*$</th>
<th>$P^0*$</th>
<th>$\langle U^0* \rangle$</th>
<th>$A^*_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.140</td>
<td>0.016</td>
<td>-0.579</td>
</tr>
<tr>
<td>0.2</td>
<td>0.343</td>
<td>0.036</td>
<td>-1.20</td>
</tr>
<tr>
<td>0.3</td>
<td>0.636</td>
<td>0.062</td>
<td>-1.85</td>
</tr>
<tr>
<td>0.4</td>
<td>1.06</td>
<td>0.096</td>
<td>-2.53</td>
</tr>
<tr>
<td>0.5</td>
<td>1.69</td>
<td>0.143</td>
<td>-3.23</td>
</tr>
<tr>
<td>0.6</td>
<td>2.54</td>
<td>0.201</td>
<td>-3.92</td>
</tr>
<tr>
<td>0.7</td>
<td>3.83</td>
<td>0.285</td>
<td>-4.59</td>
</tr>
<tr>
<td>0.8</td>
<td>5.67</td>
<td>0.398</td>
<td>-5.21</td>
</tr>
<tr>
<td>0.85</td>
<td>6.92</td>
<td>0.473</td>
<td>-5.50</td>
</tr>
</tbody>
</table>

Table 5.5 Monte Carlo simulation results at $T^* = 1.15$ for the nonspherical reference liquid obtained from a Barker-Henderson type split of the Lennard-Jones 12:6 potential.
<table>
<thead>
<tr>
<th>$\rho^*$</th>
<th>$p^o*$</th>
<th>$&lt;u^o*&gt;$</th>
<th>$a_l^*$</th>
<th>$p^o*$</th>
<th>$&lt;u^o*&gt;$</th>
<th>$a_l^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.146</td>
<td>0.148</td>
<td>-0.728</td>
<td>0.197</td>
<td>0.741</td>
<td>-1.75</td>
</tr>
<tr>
<td>0.2</td>
<td>0.372</td>
<td>0.302</td>
<td>-1.50</td>
<td>0.585</td>
<td>1.54</td>
<td>-3.66</td>
</tr>
<tr>
<td>0.3</td>
<td>0.702</td>
<td>0.461</td>
<td>-2.31</td>
<td>1.20</td>
<td>2.37</td>
<td>-5.66</td>
</tr>
<tr>
<td>0.4</td>
<td>1.17</td>
<td>0.628</td>
<td>-3.16</td>
<td>2.07</td>
<td>3.21</td>
<td>-7.68</td>
</tr>
<tr>
<td>0.5</td>
<td>1.86</td>
<td>0.812</td>
<td>-3.26</td>
<td>3.26</td>
<td>4.08</td>
<td>-9.71</td>
</tr>
<tr>
<td>0.6</td>
<td>2.82</td>
<td>1.01</td>
<td>-4.90</td>
<td>4.85</td>
<td>4.96</td>
<td>-11.8</td>
</tr>
<tr>
<td>0.7</td>
<td>4.20</td>
<td>1.23</td>
<td>-5.75</td>
<td>6.93</td>
<td>5.88</td>
<td>-13.7</td>
</tr>
<tr>
<td>0.8</td>
<td>6.21</td>
<td>1.48</td>
<td>-6.56</td>
<td>9.66</td>
<td>6.78</td>
<td>-15.7</td>
</tr>
<tr>
<td>0.85</td>
<td>7.49</td>
<td>1.63</td>
<td>-6.93</td>
<td>11.3</td>
<td>7.29</td>
<td>-16.6</td>
</tr>
</tbody>
</table>

Table 5.6 Monte Carlo simulation results at $T^*=1.15$ for the nonspherical reference fluid obtained from a Barker-Henderson type split of the dipolar Lennard-Jones 12:6 potential.
<table>
<thead>
<tr>
<th>$\rho^*$</th>
<th>$P_0^*$</th>
<th>$&lt;U_0^*&gt;$</th>
<th>$A_1^*$</th>
<th>$P_0^*$</th>
<th>$&lt;U_0^*&gt;$</th>
<th>$A_1^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.140</td>
<td>0.018</td>
<td>-0.593</td>
<td>0.152</td>
<td>0.115</td>
<td>-0.957</td>
</tr>
<tr>
<td>0.2</td>
<td>0.345</td>
<td>0.041</td>
<td>-1.23</td>
<td>0.395</td>
<td>0.252</td>
<td>-1.83</td>
</tr>
<tr>
<td>0.3</td>
<td>0.641</td>
<td>0.071</td>
<td>-1.90</td>
<td>0.758</td>
<td>0.378</td>
<td>-2.91</td>
</tr>
<tr>
<td>0.4</td>
<td>1.07</td>
<td>0.109</td>
<td>-2.61</td>
<td>1.27</td>
<td>0.525</td>
<td>-4.05</td>
</tr>
<tr>
<td>0.5</td>
<td>1.69</td>
<td>0.158</td>
<td>-3.31</td>
<td>1.99</td>
<td>0.679</td>
<td>-5.28</td>
</tr>
<tr>
<td>0.6</td>
<td>2.57</td>
<td>0.222</td>
<td>-4.06</td>
<td>2.98</td>
<td>0.843</td>
<td>-6.56</td>
</tr>
<tr>
<td>0.7</td>
<td>3.87</td>
<td>0.311</td>
<td>-4.77</td>
<td>4.33</td>
<td>1.02</td>
<td>-7.85</td>
</tr>
<tr>
<td>0.8</td>
<td>5.70</td>
<td>0.425</td>
<td>-5.45</td>
<td>6.13</td>
<td>1.21</td>
<td>-9.14</td>
</tr>
<tr>
<td>0.85</td>
<td>6.95</td>
<td>0.503</td>
<td>-5.76</td>
<td>7.23</td>
<td>1.30</td>
<td>-9.78</td>
</tr>
</tbody>
</table>

Table 5.7 Monte Carlo simulation results for the nonspherical reference fluid obtained from a Barker-Henderson type split of the quadrupolar Lennard-Jones 12:6 potential at $T = 1.15$. 
These simulations were used specifically to obtain the anisotropic contribution to the Helmholtz free energy again using the method of thermodynamic integration\(^\text{(12)}\),

\[
\Delta A = \int_\lambda^\Lambda \left\{ \frac{\partial U}{\partial \lambda} \right\} d\lambda
\]

(5.5)

where \(\lambda\) is the interaction coupling parameter, either \(\mu^{2}\) or \(Q^{2}\). Results for these simulations may then be combined with literature values\(^\text{(5)}\) of \(A_{LJ}^{*}\) to obtain the residual Helmholtz free energy.

The thermodynamic integration required in equation (5.4) to determine the reference Helmholtz free energy, was performed by fitting the simulation values of \(P^{\text{eq}}\) for each fluid, in the form of the integrand, to a fourth-order polynomial and then integrating analytically.

A comparison of the residual Helmholtz free energy from both perturbation theories, methods I and II, the exact perturbation calculations from Monte Carlo simulations and the molecular dynamics computer simulation values is given for pure, dipolar and quadrupolar fluids in tables 5.8, 5.9 and 5.10, respectively. A similar comparison of values for the anisotropic contribution to the Helmholtz free energy, defined as the difference between the properties of a bulk polar fluid and the corresponding nonpolar fluid at the same density and temperature, for dipolar and quadrupolar fluids is given in tables 5.11 and 5.12, respectively.
Table 5.8 Comparison of the residual Helmholtz free energy, $A_{\text{res}}/NkT$, from perturbation theory methods I and II, exact perturbation calculations from Monte Carlo (MC) and from molecular dynamics (MD) for a pure Lennard-Jones 12:6 fluid of $T^* = 1.15$

<table>
<thead>
<tr>
<th>$\rho^*$</th>
<th>METHOD I</th>
<th>METHOD II</th>
<th>MC</th>
<th>MD†</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>-1.61</td>
<td>-1.61</td>
<td>-1.63</td>
<td>-1.79</td>
</tr>
<tr>
<td>0.7</td>
<td>-1.74</td>
<td>-1.71</td>
<td>-1.72</td>
<td>-1.89</td>
</tr>
<tr>
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<td>-1.77</td>
<td>-1.69</td>
<td>-1.67</td>
<td>-1.84</td>
</tr>
<tr>
<td>0.85</td>
<td>-1.68</td>
<td>-1.59</td>
<td>-1.58</td>
<td>-1.79</td>
</tr>
</tbody>
</table>

† From Barker and Henderson (5)
### RESIDUAL HELMHOLTZ FREE ENERGY, $A^{\text{res}}_{NkT}$

<table>
<thead>
<tr>
<th>$\rho$</th>
<th>$\mu$</th>
<th>METHOD I</th>
<th>METHOD II</th>
<th>MC</th>
<th>MD</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>1.00</td>
<td>-1.78</td>
<td>-2.01</td>
<td>-2.13</td>
<td>-2.10</td>
</tr>
<tr>
<td>0.7</td>
<td>1.00</td>
<td>-1.92</td>
<td>-2.21</td>
<td>-2.32</td>
<td>-2.25</td>
</tr>
<tr>
<td>0.8</td>
<td>1.00</td>
<td>-1.95</td>
<td>-2.20</td>
<td>-2.36</td>
<td>-2.24</td>
</tr>
<tr>
<td>0.85</td>
<td>1.00</td>
<td>-1.99</td>
<td>-2.19</td>
<td>-2.31</td>
<td>-2.32$^+$</td>
</tr>
<tr>
<td>0.7</td>
<td>2.00</td>
<td>-6.69</td>
<td>-5.36</td>
<td>-5.94</td>
<td>-5.59</td>
</tr>
<tr>
<td>0.8</td>
<td>2.00</td>
<td>-7.71</td>
<td>-6.26</td>
<td>-6.49</td>
<td>-5.88</td>
</tr>
<tr>
<td>0.85</td>
<td>2.00</td>
<td>-8.10</td>
<td>-6.72</td>
<td>-6.67</td>
<td>-6.18$^+$</td>
</tr>
</tbody>
</table>

$^+$ MC data of Verlet and Weis$^{(3)}$

<p>| Table 5.9 | Comparison of the residual Helmholtz free energy, $A^{\text{res}}_{NkT}$, from perturbation theory methods I and II, exact perturbation calculations from Monte Carlo (MC) and from molecular dynamics (MD) for a dipolar Lennard-Jones 12:6 fluid of $T = 1.15$ |</p>
<table>
<thead>
<tr>
<th>$\rho^*$</th>
<th>$Q^*$</th>
<th>METHOD I</th>
<th>METHOD II</th>
<th>MC</th>
<th>MD</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>0.6985</td>
<td>-1.73</td>
<td>-1.71</td>
<td>-1.73</td>
<td>-2.03</td>
</tr>
<tr>
<td>0.7</td>
<td>0.6985</td>
<td>-1.84</td>
<td>-1.82</td>
<td>-1.86</td>
<td>-2.18</td>
</tr>
<tr>
<td>0.8</td>
<td>0.6985</td>
<td>-1.80</td>
<td>-1.78</td>
<td>-1.85</td>
<td>-2.19</td>
</tr>
<tr>
<td>0.85</td>
<td>0.6985</td>
<td>-1.91</td>
<td>-1.78</td>
<td>-1.78</td>
<td>-2.21*</td>
</tr>
<tr>
<td>0.7</td>
<td>1.3970</td>
<td>-4.26</td>
<td>-3.53</td>
<td>-4.25</td>
<td>-6.47</td>
</tr>
<tr>
<td>0.85</td>
<td>1.3970</td>
<td>-4.52</td>
<td>-3.54</td>
<td>-4.44</td>
<td>-6.80*</td>
</tr>
</tbody>
</table>

* MC data of Verlet and Weis (3)

Table 5.10 Comparison of the residual Helmholtz free energy, $A_{\text{res}}^{\text{res}}/NkT$, from perturbation theory methods I and II, exact perturbation calculations from Monte Carlo (MC) and from molecular dynamics (MD) for a quadrupolar Lennard-Jones 12:6 fluid of $T = 1.15$. 
<table>
<thead>
<tr>
<th>$\rho$</th>
<th>$\mu$</th>
<th>METHOD I</th>
<th>METHOD II</th>
<th>MC</th>
<th>MD</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>1.00</td>
<td>-0.173</td>
<td>-0.406</td>
<td>-0.506</td>
<td>-0.314</td>
</tr>
<tr>
<td>0.7</td>
<td>1.00</td>
<td>-0.182</td>
<td>-0.506</td>
<td>-0.604</td>
<td>-0.355</td>
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<tr>
<td>0.8</td>
<td>1.00</td>
<td>-0.180</td>
<td>-0.511</td>
<td>-0.689</td>
<td>-0.404</td>
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<tr>
<td>0.85</td>
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<td>-0.598</td>
<td>-0.733</td>
<td>-0.535</td>
</tr>
<tr>
<td>0.7</td>
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<td>-3.66</td>
<td>-4.23</td>
<td>-3.70</td>
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<tr>
<td>0.8</td>
<td>2.00</td>
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<td>-4.57</td>
<td>-4.82</td>
<td>-4.04</td>
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<tr>
<td>0.85</td>
<td>2.00</td>
<td>-6.43</td>
<td>-5.12</td>
<td>-5.10</td>
<td>-4.40</td>
</tr>
</tbody>
</table>

† MC data of Verlet and Weis$^{(3)}$

Table 5.11 Comparison of the anistropic contribution to the Helmholtz free energy, $\Delta A/NkT$, from perturbation theory methods I and II, exact perturbation calculations from Monte Carlo (MC) and from molecular dynamics (MD) for a dipolar Lennard-Jones 12:6 fluid of $T = 1.15$
ANISOTROPIC HELMHOLTZ FREE ENERGY, $\Delta A/NkT$

<table>
<thead>
<tr>
<th>$\rho^*$</th>
<th>$Q^*$</th>
<th>METHOD I</th>
<th>METHOD II</th>
<th>MC</th>
<th>MD</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>0.6985</td>
<td>-0.119</td>
<td>-0.099</td>
<td>-0.106</td>
<td>-0.239</td>
</tr>
<tr>
<td>0.7</td>
<td>0.6985</td>
<td>-0.100</td>
<td>-0.114</td>
<td>-0.142</td>
<td>-0.287</td>
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<tr>
<td>0.8</td>
<td>0.6985</td>
<td>-0.032</td>
<td>-0.097</td>
<td>-0.184</td>
<td>-0.354</td>
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<tr>
<td>0.85</td>
<td>0.6985</td>
<td>-0.229</td>
<td>-0.192</td>
<td>-0.208</td>
<td>-0.433</td>
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<tr>
<td>0.7</td>
<td>1.397</td>
<td>-2.49</td>
<td>-1.85</td>
<td>-2.59</td>
<td>-4.63</td>
</tr>
<tr>
<td>0.85</td>
<td>1.397</td>
<td>-2.84</td>
<td>-1.95</td>
<td>-2.87</td>
<td>-5.02</td>
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</tbody>
</table>

Table 5.12  Comparison of the anisotropic contribution to the Helmholtz free energy, $\Delta A/NkT$, from perturbation theory methods I and II, exact perturbation calculations from Monte Carlo (MC) and from molecular dynamics (MD) for quadrupolar Lennard-Jones 12:6 fluid of $T = 1.15$
5.3 Discussion

Method II and the exact perturbation calculations using Monte Carlo simulation show a reasonably close agreement with the simulation results for full potentials for the pure and dipolar Lennard-Jones 12:6 fluid results shown in tables 5.8 and 5.9. For \( \rho^* = 0.85 \) and \( \mu^* = 2.0 \) the deviation is about 8%. The agreement between method II and Monte Carlo values in table 5.9 suggests that method II works well for dipolar fluids. A similar comparison of the results from method I shows an underprediction for \( \mu^* = 1.00 \), just as in the case for Lennard-Jones 12:6 fluids, and a substantial overprediction for \( \mu^* = 2.0 \). A comparison of methods I and II with Monte Carlo perturbation calculations shows that deviations for method I increase as density increases at \( \mu^* = 2.0 \) and for the smaller dipole moment, \( \mu^* = 1.0 \), only a small change in deviations is seen as the density changes.

For quadrupolar Lennard-Jones 12:6 fluids, for which the results are given in table 5.10, all the methods consistently underpredict the residual Helmholtz free energy, however method I is closer to the Monte Carlo perturbation calculations than method II and in this case the density does not seem to affect the deviations in any systematic manner. A comparison of simulations using the full quadrupolar potential and Monte Carlo perturbation calculations shows an underprediction of as much 35% and this suggests that while a first-order expansion will perhaps work for the dipolar fluid, it will seriously underpredict the Helmholtz free energy for quadrupolar fluids.

A more severe test of these perturbation theories can perhaps be obtained by a comparison of the anisotropic contribution to the
Helmholtz free energy of the polar fluids. Although this is a less realistic test since total molar properties are needed in most applications, it serves to make the work consistent with the existing literature\(^{(1,3,4)}\), and a comparison of the anisotropic contribution to the Helmholtz free energy from various sources is shown in tables 5.11 and 5.12 for dipolar and quadrupolar Lennard-Jones 12:6 fluids respectively.

For dipolar fluids, method II and the Monte Carlo perturbation calculations consistently overpredict the anisotropic contribution to the Helmholtz free energy, \(\Delta A/NkT\), whereas method I underpredicts \(\Delta A/NkT\) for \(\mu^* = 1.0\) and overpredicts for \(\mu^* = 2.0\). A direct comparison of the results for method II with molecular dynamics simulations using the full dipolar potential is reasonably good, the deviations increasing with increasing density only for \(\mu^* = 2.0\). Comparison of the Monte Carlo exact perturbation theory with molecular dynamics simulations is very consistent and indeed some of the deviations at \(\mu^* = 1\) can be attributed to computational errors in both these methods of the order of \(\pm 0.05\) in values of \(\Delta A/NkT\). For method I, deviations for \(\mu^* = 2.0\) increase when compared to molecular dynamics as the density increases.

For quadrupolar fluids all three methods underpredict the anisotropic contribution to the Helmholtz free energy. However, due to the small size of these values at the low quadrupole moment, it is difficult to make any meaningful comparisons in view of the the errors involved. A comparison of the Monte Carlo perturbation calculations with the full potential molecular dynamics simulations clearly shows the consistency of the deviations with respect to density. Further it is noted that the predictions of methods I and II are close to the MC results. For the higher quadrupole moment, method II seriously
underpredicts the results and although the results from method I and Monte Carlo perturbation calculations are comparable in magnitude with each other they too are significantly smaller than the results obtained from simulations using the full potential.

While comparisons are reasonably good for Monte Carlo exact perturbation calculations for dipolar fluids, serious underpredictions of the Helmholtz free energy have been noted for quadrupolar fluids. Wojcik and Gubbins\(^\text{(14)}\) have observed similar behavior for first-order Monte Carlo perturbation calculations of fluids of hard-dumbbells with point charge quadrupoles. It was shown that the second-order term was of similar magnitude to the first-order term and was therefore necessary for convergence of the series expansion. Calculation of the second-order term, \(A_2\), requires calculation of the triplet distribution function and this can significantly extend the computing requirements of the simulations. However, the results do clearly show the need to include a second-order term in the perturbation expansion.

The anisotropic contribution to the Helmholtz free energy predicted here has been compared with existing literature values at \(\rho^* = 0.85\) and \(T^* = 1.15\) and the results are shown in table 5.13. For dipolar fluids, the predictions of method II are very close to those of Kohler and Quirke\(^\text{(4)}\) even though the two theories are significantly different. Mo and Gubbins\(^\text{(1)}\) predict a value of \(\Delta A/NkT = -0.55\) for \(\mu^* = 1.0\), which is close to the simulation result of Verlet and Weis\(^\text{(3)}\) however no values for large dipole moments are reported since it is believed\(^\text{(15)}\) that the Bellemans expansion, used by Mo and Gubbins to obtain \(A_0\), breaks down for high values of the dipole moment. For quadrupolar fluids
<table>
<thead>
<tr>
<th>ANISOTROPY</th>
<th>SIMULATION</th>
<th>Kohler and Quirke (4)</th>
<th>METHOD I</th>
<th>METHOD II</th>
<th>MC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu^*$ = 1.00</td>
<td>-0.535 ± 0.01$^\dagger$</td>
<td>-0.60</td>
<td>-0.315</td>
<td>-0.598</td>
<td>-0.733 ± 0.05</td>
</tr>
<tr>
<td>$\mu^*$ = 2.00</td>
<td>-4.40 ± 0.02$^\dagger$</td>
<td>-5.13</td>
<td>-6.43</td>
<td>-5.16</td>
<td>-5.10 ± 0.10</td>
</tr>
<tr>
<td>$Q^*$ = 0.6985</td>
<td>-0.43 ± 0.01$^+$</td>
<td>-0.69</td>
<td>-0.229</td>
<td>-0.192</td>
<td>-0.21 ± 0.05</td>
</tr>
<tr>
<td>$Q^*$ = 1.397</td>
<td>-5.03 ± 0.10$^+$</td>
<td>-3.51</td>
<td>-2.84</td>
<td>-1.95</td>
<td>-2.87 ± 0.05</td>
</tr>
</tbody>
</table>

$^\dagger$ MC results of Verlet and Weis (3)
$^+$ MD results obtained in this study

Table 5.13 Contribution of the anisotropic potential to the Helmholtz free energy $\Delta A/NkT$, for dipolar and quadrupolar Lennard-Jones 12:6 fluids at $\rho^* = 0.85$ and $T^* = 1.15$
the predictions by Kohler and Quirke(4) are similar to methods I and II, and for this no results by Mo and Gubbins are available.

The anisotropic contribution to the configurational internal energy has also been predicted. The configurational internal energy of a bulk fluid is determined by numerical differentiation of the Helmholtz free energy $A^* = A/N\epsilon$, according to an expression given by Abascal et al. (16)

$$U^* = \frac{\partial (A^*/T^*)}{\partial (1/T^*)}V$$  \hspace{1cm} (5.6)

where $T^* = kT/\epsilon$ and $U^* = U/N\epsilon$, and the anisotropic contribution is determined by difference. Calculations have been performed for both dipolar and quadrupolar Lennard-Jones 12:6 fluids at $\rho^* = 0.80$ and $T^* = 0.719$, a point close to the triple point, for which the simulation data of Wang et al. (2) is available. The results are shown in table 5.14 together with those predicted by Mo and Gubbins (1).

The Monte Carlo simulation results of Wang et al. (2) were for 64 particles only, and as such the accuracy of their results is questionable. Therefore, for this state point 256 particle molecular dynamics simulations have been performed also using a potential truncated at 3.0\sigma and the results from these simulations, along with the estimated errors, are also given in table 5.14. It must be pointed out that while the results for the anisotropic contribution to the configurational internal energy from the simulations appear to be close, the absolute values reported by Wang et al. (2) are consistently smaller in magnitude when compared to the results obtained in this study. This is thought to be due to the smaller cut-off radius used by Wang et al. (2).
<table>
<thead>
<tr>
<th>ANISOTROPY</th>
<th>$\mu^*$</th>
<th>MC$^+$</th>
<th>Mo &amp; Gubbins$^{(1)}$</th>
<th>MD$^+$</th>
<th>METHOD I</th>
<th>METHOD II</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu^*$ = 0.7071</td>
<td>-0.34 ± 0.13</td>
<td>-0.34</td>
<td>-0.382 ± 0.03</td>
<td>-0.297</td>
<td>-0.489</td>
<td></td>
</tr>
<tr>
<td>$\mu^*$ = 1.1832</td>
<td>-1.60 ± 0.17</td>
<td>-----</td>
<td>-1.73 ± 0.05</td>
<td>-2.26</td>
<td>-1.65</td>
<td></td>
</tr>
<tr>
<td>$Q^*$ = 0.500</td>
<td>-0.313 ± 0.11</td>
<td>-0.31</td>
<td>-0.304 ± 0.03</td>
<td>-0.069</td>
<td>-0.052</td>
<td></td>
</tr>
<tr>
<td>$Q^*$ = 0.7071</td>
<td>-0.977 ± 0.12</td>
<td>-0.91</td>
<td>-1.01 ± 0.05</td>
<td>-0.278</td>
<td>-0.154</td>
<td></td>
</tr>
<tr>
<td>$Q^*$ = 0.866</td>
<td>-1.93 ± 0.16</td>
<td>-1.60</td>
<td>-1.99 ± 0.05</td>
<td>-0.718</td>
<td>-0.525</td>
<td></td>
</tr>
<tr>
<td>$Q^*$ = 1.000</td>
<td>-3.12 ± 0.20</td>
<td>-----</td>
<td>-3.40 ± 0.08</td>
<td>-1.27</td>
<td>-1.06</td>
<td></td>
</tr>
</tbody>
</table>

$^+$ MC results of Wang et al.$^{(2)}$

$^*$ MD results obtained in this study

Table 5.14 Contribution of the anisotropic potential to the configuration internal free energy $\Delta U/N_\varepsilon$, for dipolar and quadrupolar Lennard-Jones 12:6 fluids at $\rho^* = 0.80$ and $T = 0.719$
For dipolar fluids, the predictions from methods I and II are close to the simulation results except for $\mu^* = 1.18$ where method I overpredicts $\Delta U/\mathcal{N}e$ by 30%. The theory of Mo and Gubbins\(^{(1)}\) predicts the anisotropic contribution reasonably well up to $\mu^* = 0.7071$, however this theory is believed to fail\(^{(15)}\) for higher dipole moments. For quadrupolar fluids both methods I and II significantly underpredict the anisotropic contribution to the internal energy. It is interesting to note that the theory of Mo and Gubbins works substantially better than methods I and II, although this theory also shows some consistent underpredictions. Mo and Gubbins\(^{(1)}\) have not reported results for $Q^* = 1.0$ and again it is felt that the Bellemans expansion breaks down\(^{(15)}\) in the vicinity of $Q^* = 1.0$. Kohler and Quirke\(^{(4)}\) have not reported any results for the fluids discussed in table 5.14, however, based on the results shown in table 5.13, it is felt that this method would work better than methods I and II and perhaps also better than the theory of Mo and Gubbins, for quadrupolar fluids. Substantial underprediction of the anisotropic contribution may still exist for large values of the quadrupole moment, $Q^*$.

Although comparisons of the results obtained in this study with other theories are hampered by a scarcity of literature data, a clear picture definitely emerges about the use of an anisotropic reference potential in the perturbation theory of polar fluids. Methods I and II work well for dipolar fluids, and in particular method II, however neither method works very well for quadrupolar fluids. The reason for this may be in that some of the assumptions, equations (2.80), (2.84) and (2.86), utilized in the development of these methods are not applicable for quadrupolar fluids in addition to the need for a
second-order term to assure convergence of the series. The validity of
equation (2.80) for use with quadrupolar fluids has already been
questioned previously by Wang et al. (2) and also by Kohler and Quirke (4)
however the effect of this on predictions by method I, equation (2.85),
is not clear. It could be argued that values of A_O obtained using
equation (2.84) are perhaps too large for the case of quadrupolar
fluids, however a comparison with the values of A_O obtained from the
Monte Carlo exact perturbation calculations shows this not to be the
case. In the light of these results, and the results obtained by
Wojcik and Gubbins (14) on investigation of the second-order term of the
expansion is certainly warranted.

5.4 Spherical Harmonic Coefficients

In an attempt to obtain at least a qualitative understanding of the
structure of the reference fluid used in the perturbation theories
described in chapter II and, in particular, the changes in the fluid
structure that occur as a result of splitting the total interaction
potential, the coefficients of the spherical harmonic expansion, \( \ell \ell' m \)
have been determined by computer simulation. The determination of
these coefficients has been described earlier in section 2.4.1.

Figures 5.1 and 5.2 show a comparison of the center-to-center pair
distribution function, \( g_{o o o} (r) \), obtained from simulations using the full
polar potentials, simulations using the corresponding nonspherical
reference potentials and the numerical solution of the Percus-Yevick
equation applied the soft-repulsive potential, \( \Phi (r) \), given by equation
(2.81). It should be noted that \( g_{o o o} (r) \) values for the full quadrupolar
and dipolar fluids are very close as expected although a direct
comparison is not given.
A comparison of the $g_{000}(r)$ values obtained from simulations using the full potential with those using the nonspherical reference potential shows the effect of attractive forces, omitted from the Barker-Henderson reference, is to bring particles closer to each other for both dipolar and quadrupolar fluids. The same comparison also shows that the locations of the maxima in $g_{000}(r)$ are relatively unaffected by the attractive forces of the potential. Probably the most interesting point to note is the close agreement between the numerical solution of the Percus-Yevick equation and the results from simulations using the nonspherical reference potential. This demonstrates that equation (2.81) is indeed a valid approximation, at least for obtaining the angle-averaged (center-to-center) pair distribution function of the reference fluid defined by equations (2.74)a,b.

A qualitative description of the effect of the orientation-dependent electropolar potential on the structure of a Lennard-Jones 12:6 fluid can be obtained from an examination of the remaining spherical harmonics coefficients of the pair correlation function expansion. These selected coefficients, $g_{\ell \ell ' m}(r)$, for dipolar fluids ($\mu^* = 1.0$) are shown in figure 5.3-5.5 and for quadrupolar fluids ($Q^* = 1.0$) in figures 5.6-5.9. Each figure gives a comparison of the spherical harmonic coefficient, calculated during the course of the computer simulations, for the full-potential fluid and for the split-potential fluid.

Probably the most important conclusion that can be drawn from the plots of the spherical harmonic coefficients comes from a comparison of the $g_{220}(r)$ coefficients shown in figures 5.3 and figures 5.6 for dipolar and quadrupolar fluids respectively. For dipolar fluids, the
Figure 5.1  Angle-averaged pair distribution, $g(r)_*$ for a dipolar fluid with $\mu = 2.0$ at $T = 1.15$ and $\rho = 0.85$. Simulation using the full polar potential (solid line), simulation using the nonspherical reference potential (dashed line), and numerical solution of the Percus-Yevick equation for the soft-repulsive potential (dotted line).
Figure 5.2  Angle-averaged pair distribution, $g(r)$, for a quadrupolar fluid with $Q^* = 1.0$ at $T^* = 1.15$ and $\rho^* = 0.85$. Lines are same as figure 5.1.
Figure 5.3 Comparison of spherical harmonic coefficients $g_{200}(r)$ for the full potential (lines) and the nonspherical reference potential (points) for dipolar-fluids with $T = 1.15$.

$g_{200}(r)$ - solid line and $\bigcirc$

$g_{220}(r)$ - dashed line and $\blacktriangle$
Figure 5.4 Comparison of Spherical Harmonic Coefficients $g_{201}(r)$ and $g_{222}(r)$ for the full potential fluid (lines) and the nonspherical reference potential fluid (points) for dipolar-fluids with $T = 1.15$.
- $g_{221}(r)$ - solid line and ○
- $g_{222}(r)$ - dashed line and △
Figure 5.5  Comparison of Spherical Harmonic Coefficients $g_{400}(r)$ and $g_{440}(r)$ for the full potential fluid (lines) and the nonspherical reference potential fluid (points) for dipolar-fluids with $T = 1.15$.

$g_{400}(r)$ - solid line and $\circ$
$g_{440}(r)$ - dashed line and $\Delta$
Figure 5.6  Comparison of Spherical Harmonic Coefficients \( g_{200}(r) \) and \( g_{220}(r) \) for the full potential fluid (lines) and the nonspherical reference potential fluid (points) for dipolar-fluids with \( T^* = 1.15 \).

- \( g_{200}(r) \) - solid line and \( \bigcirc \)
- \( g_{220}(r) \) - dashed line and \( \triangle \)
Figure 5.7  Comparison of Spherical Harmonic Coefficients $g_{221}(r)$ and $g_{222}(r)$ for the full potential fluid (lines) and the nonspherical reference potential fluid (points) for dipolar-fluids with $T = 1.15$.

$g_{221}(r)$ - solid line and $\bigcirc$
$g_{222}(r)$ - dashed line and $\triangle$
Figure 5.8 Comparison of Spherical Harmonic Coefficients $g_{400}(r)$ and $g_{422}(r)$ for the full potential fluid (lines) and the nonspherical reference potential fluid (points) for dipolar-fluids with $T = 1.15$.

$g_{400}(r)$ = solid line and ∗
$g_{422}(r)$ = dashed line and △
Figure 5.9 Comparison of Spherical Harmonic Coefficients $g_{440}(r)$ and $g_{442}(r)$ for the full potential fluid (lines) and the nonspherical reference potential fluid (points) for dipolar fluids with $T = 1.15$.

- $g_{440}(r)$ - solid line and ⊙
- $g_{442}(r)$ - dashed line and △
coefficient shows a positive peak or maxima at small separations indicative of side-by-side orientations. This is directly related to the minimum in the potential for this orientation shown as line 3 in figure 2.7. In contrast the same coefficient for quadrupolar fluids shows a negative peak or minima at small separations indicating a preference for "T"-shaped orientations which is confirmed again by line 3 in the plot of quadrupolar potentials, figure 2.8. Although, as would be expected, this preference for certain orientations is diminished by splitting the potential into its repulsive and attractive parts, the effect is still certainly distinguishable.

Although not shown here, all coefficients up to \( \ell = \ell' \) \( m = 4 \) were calculated. The contributions of coefficients with \( m \neq 0 \) is small indicating that the dependence of the orientations on the azimuthal angle, \( \phi_{12} \), is small.

This information concerning the structure of the electropolar fluid, although not directly applicable to the perturbation theories derived in this work, will provide, the insight necessary for the development of any perturbation theories attempting to use a nonspherical reference fluid such as an oblate or prolate ellipsoid discussed briefly earlier.
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Chapter VI

CONCLUSIONS AND RECOMMENDATIONS

The ability of the experimental apparatus and techniques used in this study to produce accurate and reproducible values for the liquid phase compositions of high-pressure gas-water systems has been clearly demonstrated. The lower pressure results for the argon-water system are in close agreement with values found in the literature. Further the results for the three binary gas mixtures of nitrogen and methane follow trends suggested by the pure solute-water systems of these gases studied by a previous investigator\(^{(1)}\).

The pure solute solubility data obtained here has been correlated by equations described previously\(^{(1)}\) and the results compared to similar correlation of data obtained previously. A modified Krichevsky-Ilinskaya equation has been developed where the non-ideal behavior of the solute gas in solution is predicted by Wilson's equation rather than the two-suffix Margules equation. The results from the correlation of the pure solute solubility data have been explained in terms of the inter-attractions of solute and solvent. Solubility data for the ternary systems have been correlated by the modified Krichevsky-Kasarnovsky equation and the results suggest that an accurate prediction of the composition of such systems is possible by assuming that the two required parameters, the Henry's law constant, \(H_{i}^{pS}\), and the apparent partial molar volume, \(v_{i}^{\alpha\Sigma}\), of each solute are the same in the binary gas mixtures as in the pure solute systems. Predictions based on this assumption have been calculated and a comparison with the experimental values confirms this suggestion.
Two versions of a new, computationally simple perturbation theory, using a nonspherical reference potential, have been derived and values of the Helmholtz free energy and configurational internal energy for both dipolar and quadrupolar Lennard-Jones 12:6 fluids calculated. The agreement between these calculated values and existing computer simulation data is comparable with the agreement of other perturbation theories. A Monte Carlo computer simulation method has been developed and used to determine the "exact" perturbation expansion terms up to first-order of fluids described by the same reference and perturbation potentials as used in the corresponding perturbation theory calculations. These results illustrate the need to include a second-order term in the expansion, particularly for the larger electropolar moments, to obtain close agreement with computer simulation values for the full-potential fluid. Preliminary results for such calculations indicate that three and four-body potential interactions must be included in determining the total configurational potential.

The effect upon the fluid structure of separating the repulsive and attractive forces according to the suggestion of Barker and Henderson has been illustrated through the corresponding change on the distribution function \( g(r,\omega_1,\omega_2) \). For the center-to-center correlation function, \( g_{oo0}(r) \), of the reference fluid the agreement between values predicted by Monte Carlo simulation and by the Percus-Yevick equation is certainly encouraging. However, the decrease in the definition and ordering of the fluid, suggested by a decrease in the peak height of the \( g_{oo0}(r) \) plots when compared to the full-potential correlation, due to removal of the fluid attractive forces is probably a major reason for the inaccuracies in the perturbation theories. These
inaccuracies would themselves be reduced by including the second-order expansion term in the perturbation series, however this again requires evaluation of the triplet distribution function.

Further qualitative details concerning the change in the fluid structure due to the splitting of the interaction potential have been obtained by calculation of the spherical harmonic coefficients of the pair distribution expansion. These coefficients reinforce the conclusions described in the preceding paragraph.

One of the problems encountered in developing perturbation methods to predict thermodynamic properties of fluids such as those used in this study is that the nature of the reference fluid is not known unlike the case of nonspherical nonpolar molecules such as dumbbells\(^{(2-4)}\) or soft-ellipsoids\(^{(5)}\) for which the reference molecule has an obvious and clearly defined shape. One can attempt to represent the reference fluid of the perturbation theories described in chapter II by a molecule of known shape such as a prolate or oblate ellipsoid and then develop perturbation expansions based on this hard nonspherical molecule. The biggest difficulty in this approach, however would be establishing the actual size and shape of such a molecule required for calculation of the reference fluid properties. This problem can be avoided for the case of polar molecules with nonspherical cores where the reference fluid would simply be similar in shape to the core molecule with the size perhaps being determined through a zeroth-order expansion.

Recently there has been an interest in utilizing the median potential theory to predict the properties of nonpolar diatomic fluids\(^{(6-10)}\), and such attempts have enjoyed reasonable success. Work has also been done on extending this work to more complicated nonpolar
molecules (11) (e.g. benzene). It was suggested by both MacGowan et al. (6) and Gubbins (12) that the median potential theory fails for polar fluids such as dipolar hard spheres if the original procedure of MacGowan et al. (6) is used which would lead to a hard-sphere potential as the median potential. However, in a more recent approach, MacGowan (7) has studied the separation of potentials into anisotropic reference and perturbation parts. Application of the median potential theory and recombination of the sphericalized reference and perturbation terms is then used to obtain the sphericalized potential. This method successfully predicts properties of a fluid whose molecules have a nonspherical core without explicitly modeling a nonspherical hard molecule. Application of this approach to polar fluids, using a potential split according to equations (2.74)a,b would avoid some of the problems discussed earlier of having to determine the precise nature of the reference fluid and therefore ought to be worthy of investigation. Initial studies (13) are encouraging and confirm this optimism whilst providing motivation for a greater effort.

Calculation of the second-order term of Zwanzig’s perturbation expansion, from both Monte Carlo computer simulation and perturbation theory, would not only improve agreement with existing data but also provide further insight into the effect of higher-order interactions and corresponding distribution functions. Although computationally tedious and as a result costly, the improvement in the existing theories ought to far outweigh such an expense.
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APPENDIX A

Unsymmetric Activity Coefficients From Wilson's Equation

The multicomponent recursive formula for activity coefficients defined according to Wilson's equation is commonly written as

\[
\ln \gamma_i = - \ln \left( \sum_{j=1}^{m} X_{ij} \Lambda_{ij} \right) + 1 - \sum_{k=1}^{m} \frac{X_{ik}}{m} \left( \sum_{j=1}^{m} X_{kj} \Lambda_{kj} \right) \tag{A.1}
\]

where

\[
\Lambda_{ij} \neq \Lambda_{ji} \tag{A.2.a}
\]

\[
\Lambda_{ii} = \Lambda_{jj} = \ldots = 1 \tag{A.2.b}
\]

The relationship between activity coefficients defined on the unsymmetric convention, \( \gamma_i^* \), and those defined according to the symmetric convention, \( \gamma_i \), is given in the literature as

\[
\ln \gamma_i^* = \ln \gamma_i - \lim_{X_i \to 0} \ln \gamma_i \tag{A.3}
\]

\[
\begin{align*}
X_i & > 0 \\
X_j & = 0 \\
j & \neq i \\
j & \neq 1
\end{align*}
\]

Therefore, a recursive formula for \( \gamma_i^* \) based on Wilson's equation is obtained upon substituting equations (A.1) and (A.2) into equation (A.3)

\[
\ln \gamma_i = 1 - \ln \left( \sum_{j=1}^{m} \frac{X_{ij}}{m} \Lambda_{ij} \right) - \sum_{k=1}^{m} \frac{X_{ik}}{m} \left( \sum_{j=1}^{m} X_{kj} \Lambda_{kj} \right) + \ln \Lambda_{ii} + (\Lambda_{ii} - 1) \tag{A.4}
\]
A similar expression has been obtained previously for the unsymmetric activity coefficient, $Y_i^\ast$, derived from expressions for the excess Gibbs free energy given by the two-suffix Margules equation. This expression was given as

$$
\ln Y_i^\ast = -A_{i1} + \sum_{k=1}^{m} A_{ik} X_k - \frac{1}{2} \sum_{k=1}^{m} \sum_{j=1}^{m} A_{kj} X_k X_j
$$

(A.5)
APPENDIX B

Derivation of Zwanzig's Perturbation Expansion

The configurational Helmholtz free energy of a system in the canonical ensemble, $A_c$, is related to the partition function of the system, $Q_c$, by

$$A_c = -kT \ln Q_c$$  \hspace{1cm} (B.1)

where $Q_c$ is written as

$$Q_c = \frac{\lambda^{-3N}}{N!} \int \cdots \int \exp \left\{ -\beta \sum_{i<j} u_{ij}(r) \right\} dr$$  \hspace{1cm} (B.2a)

$$= \frac{\lambda^{-3N}}{N!} Z_c$$  \hspace{1cm} (B.2b)

where $Z_c$ is the configurational integral of the system.

Zwanzig, using an assumption that is basic to all perturbation theories, wrote the intermolecular pair potential for two particles as the sum of a reference term, $u_{ij}^0(r)$, and a perturbation term $u_{ij}^P(r)$.

$$u_{ij}^P(r) = u_{ij}^0(r) + \eta u_{ij}^P(r)$$  \hspace{1cm} (B.3)

Here $\eta$ is the perturbation parameter that when set equal to zero gives the reference potential and when set to one gives the actual potential $u(r)$. Zwanzig then introduced this assumption into the configurational integral, $Z_c$, to give

$$Z_c = \int \cdots \int \exp \left\{ -\beta \sum_{i<j} (u_{ij}^0(r) + \eta u_{ij}^P(r)) \right\} dr$$  \hspace{1cm} (B.4)

The configurational integral was then expanded in a Taylor series expansion about the reference (i.e. $\eta=0$) as
\[ Z_c(\eta) = Z^0 + \eta \left( \frac{\partial Z_c}{\partial \eta} \right)_{\eta=0} + \frac{1}{2} \eta^2 \left( \frac{\partial^2 Z_c}{\partial \eta^2} \right)_{\eta=0} + \ldots \]  

Substituting equation B.4 into equation B.5 gives

\[ Z_c(\eta) = Z^0 - \eta \beta \int \cdots \int \sum_{i<j} u^P_{ij}(r) \exp \left\{ -\beta \sum_{i<j} u^0_{ij}(r) \right\} dr + O(\eta^2) \]  

multiplying the top and bottom of the second term on the r.h.s. of equation (B.6) and rearranging slightly,

\[ Z_c(\eta) = Z^0 \left\{ 1 - \eta \beta \int \cdots \int \sum_{i<j} u^P_{ij}(r) \exp \left\{ -\beta \sum_{i<j} u^0_{ij}(r) \right\} dr + O(\eta^2) + \ldots \right\} \]

By definition \( Z^0 \), is the configurational integral of the reference system again in the canonical ensemble given by

\[ Z^0 = \int \cdots \int \exp \left\{ -\beta \sum_{i<j} u^0_{ij}(r) \right\} dr \]  

Therefore the second term in brackets in equation (B.7) is an ensemble average over the reference system of the perturbation potential defined as

\[ \left\langle \sum_{i<j} u^P_{ij}(r) \right\rangle_o = \frac{\int \cdots \int \sum_{i<j} u^P_{ij}(r) \exp \left\{ -\beta \sum_{i<j} u^0_{ij}(r) \right\} dr}{\int \cdots \int \exp \left\{ -\beta \sum_{i<j} u^0_{ij}(r) \right\} dr} \]  

Assuming identical contributions to the pair potential for the \( N(N-1)/2 \) unlike \((i<j)\) interactions suggests that

\[ \frac{N(N-1)}{2} \left\langle u^P_{ij}(r) \right\rangle_o = \left\langle \sum_{i<j} u^P_{ij}(r) \right\rangle_o \]
which leads to

\[
\langle U^P(r) \rangle_o = \frac{N(N-1)}{2} \frac{1}{Z^o} \int \ldots \int \exp \left\{ -\beta \sum_{i<j} u^o_{ij}(r) \right\} U^P(r) \, dr \quad (B.11)
\]

The two-body density function describes the probability of finding two particles a distance \( r_{12} \) apart and is defined by

\[
f^{(2)}(r_1, r_2) = \frac{1}{Z^{N-2}} \int \ldots \int \exp \left\{ -\beta \phi(r) \right\} \, dr \quad (B.12)
\]

and for an isotropic system of spherical particles, the radial distribution function is given in terms of the density function as

\[
g_{12}(r) = \frac{f^{(2)}(r)}{\rho^2} \quad (B.13)
\]

If the total potential in equation B.10, \( \phi(r) \), is given by the sum of the reference potentials

\[
\phi(r) = \sum_{i<j} u^o_{ij}(r) \quad (B.14)
\]

then the density and radial distribution functions given in equation (B.12) and (B.13) are for the corresponding reference fluid i.e. \( f^{(2)}_o \) and \( g^o \).

Combining equations (B.12), (B.13) and (B.14) and substituting into the expression for the ensemble average of the perturbation potentials, equation (B.11), gives

\[
\langle U^P(r) \rangle_o = \frac{N\rho}{2} \int U^P(r) g^o(r) \, dr \quad (B.15)
\]
The configurational integral can now be written from equation (B.7) as

\[ Z_c(n) = Z^0 \left( 1 - \eta\beta \frac{N\sigma}{2} \int U^0(r)g^0(r)dr + O(\eta^2) + \ldots \right) \]  \hspace{1cm} (B.16)

and the free energy expansion is obtained by substitution of equation (B.16) into equations (B.2)a and (B.1)

\[ A_c(n) = -kT \log Z_c(n) \]  \hspace{1cm} (B.17)

\[ = -kT(Z^0) - kT \ln \left\{ 1 - \eta\beta \frac{N\sigma}{2} \int U^0(r)g^0(r)dr + O(\eta^2) + \ldots \right\} \]

expanding the logarithm of the second term on the right hand side in powers of \( \eta \), and then putting \( \eta = 1 \) to obtain the original yields

\[ A = A^0 + \frac{N\sigma}{2} \int U^0(r)g^0(r)dr + O(\eta^2) \]  \hspace{1cm} (B.18)

It can be shown that the second-order term in the expansion for the Helmholtz free energy is given by

\[ A_2 = -\frac{\beta}{2} \left\{ \langle U^0(r)^2 \rangle_o - \langle U^0(r) \rangle_o^2 \right\} \]  \hspace{1cm} (B.19)
APPENDIX C

Vectorizable Fortran Code for Monte Carlo Computer Simulation
MONTE CARLO SOURCE PROGRAM FOR LENNARD-JONES FLUIDS
WITH A QUADRUPOLE-QUADRUPOLE INTERACTION
THE TRANSLATIONAL AND ORIENTATIONAL MOVEMENTS
ARE PERFORMED INDEPENDENTLY

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DECEMBER 1ST 1986

VERSION 2.1

REAL*8 TOTE, TOTU1, TOTV
REAL*8 SUME, SUMU1, SUMV, SUMA
COMMON/POS/XO(500), YO(500), ZO(500)
COMMON/DISP/DAX(500), DAY(500), DAZ(500)
COMMON/ORN/AXO(500), AYO(500), AZO(500), AQO(500)
COMMON/PROP/IDIST(300), SUME, SUMU1, SUMV, SUMA, ISUM
COMMON/PROP/RDEL, RMAX, CUBE, CUBE2, HMAX, DELTA, DOMEGA, QSQ,
A
NP, NP1, IRR, IACPTT, IACPTO

=== START SIMULATION FROM PREVIOUS (0-NO, 1-YES) ===

ISTART=0

=== SET MOVE SIZES (ADJUST FOR REASONABLE ACCEPTANCE RATE) ===

DELTA=0.06
DOMEGA=0.05

=== SET NUMBER OF PARTICLES IN PRIMARY CELL ===

NP=500
PART=NP
NP1=NP-1
NP22=NP-2

=== SET VALUES OF PHYSICAL CONSTANTS ===

SIGMA=3.405
EPSI=120.
AVO=6.0225E+23
30LZ=1.38054
WTMOL=39.994
THIRD=1./3.
PI=3.14159265

=== SET DESIRED FLUID STATE CONDITION ===
TR=1.150
DR=.850
QSQ=1.95161
QSQ=QPOLE*QPOLE
T=TR*EPSI
BETA=1./TR
VOL=PART/DR
VSCALE=THIRD/TR
VOLCC=AVO*(SIGMA*1.E-8)**3/DR

C
C === SET RUN FLAGS AND PARAMETERS
C
IRR=34567
IACPTT=0
IACPTO=0
IFLG=0
KB=0
KWRI TE=10
MAXKB=8000
KDIST=1000
KEVAL=20
HMAX=10.

C
C === SET DISTANCES FOR POTENTIAL CUT-OFF, VERLET LIST, ETC.
C
CUBE=VOL**THIRD
CUBE2=.5*CUBE
RC=CUBE2

C
C === FOR THERMODYNAMIC INTEGRATION KEEP RC=CONST
C
IF (RC.GT.4.18) RC=4.18
RMAX=RC*RC

C
C === INCREMENT FOR SAMPLING FOR G(R)
C
RDEL=0.025
NY=CUBE2/RDEL-1

C
C === CORRECTIONS FOR LONG-RANGE INTERACTIONS
C
RC3=RC**3
RC9=RC3**3
CORE=8.*PI*DR*(1./9./RC9-THIRD/RC3)
CQRV=96.*PI*DR*(.5*THIRD/RC3-1./9./RC9)
DE=CORE
DP=-VSCALE*CQRV

C
C === PRINT PARAMETERS
C
CALL PRNT(NP, EPSI, SIGMA, TR, T, DR, VOL, CUBE, RMAX, RC, RDEL, DELTA,
DOMEGA, QSQ, NY, DE, DP)
C
C === LOAD INITIAL POSITIONS OF ATOMS AND CALCULATE TOTAL P.E.
C CALL FCC(CUBE,CUBE2,NP)
IF (ISTART.NE.0) THEN
READ(11) XO,YO,ZO
READ(11) DAX,DAY,DAZ
READ(11) AXO,AYO,AZO,AQO
READ(11) IDIST,SUME,SUMU1,SUMV,SUMA,ISUM
READ(11) IRR,IACPTT,IACPTO
ENDIF
CALL EVAL(TOTE,TOTU1,TOTV,BETA)

C === ENTER MAIN LOOP OF SIMULATION
C
599 KB=KB+1
CALL PMOVET(TOTE,TOTU1,TOTV,BETA)
CALL PMOVEO(TOTE,TOTU1,TOTV,BETA)
IF(MOD(KB,KEVAL).EQ.0) CALL EVAL(TOTE,TOTU1,TOTV,BETA)

C === CALCULATE MEAN SQUARE DISPLACEMENT
C
TDIST=0.
DO 540 I=1,NP
TDIST=TDIST+DAX(I)**2+DAY(I)**2+DAZ(I)**2
540 CONTINUE
TDIST=TDIST/PART

C === PROPERTY CALCULATION & PRINT-OUT AT INTERVALS
C
IF(MOD(KB,KWRITE).NE.0) GOTO 550
FKB=FLOAT(NP)*SUMA

C === FULL-POTENTIAL CALCULATION FOR ENR AND VIR
C
ENR=(SUME/FKB+CORE)
VIR=(SUMV/FKB+CORV)/(3.*TR)

C === BARKER-HENDERSON CALCULATION FOR ENR AND VIR AND PERT
C
ENR=(SUME/FKB)
VIR=(SUMV/FKB)/(3.*TR)
PERT=(SUMU1/FKB+CORE)

PRES=TR*DR*(1.-VIR)
ACPTT=FLOAT(IACPTT)/FLOAT(KB*NP)
ACPTO=FLOAT(IACPTO)/FLOAT(KB*NP)
WRITE(6,940) KB,PRES,ENR,PERT,TDIST,ACPTT,ACPTO
940 FORMAT(1X,16,6F9.3)
IF(IFLG.LT.1) GO TO 550

C === PRINT G(R) AT INTERVALS
C
560 IF(MOD(KB,1000).EQ.0.OR.KB.EQ.MAXKB) CALL RDF(DR,RDEL,NY,
A KB, MAXKB)
C
C === DURING FIRST OF RUN, SCALE VELOCITIES FOR TEMPERATURE
C
550 IF(IFLG.LT.1) CALL EQBRAT(KDIST,IFLG,NY,KB)
   IF(KB.LT.MAXKB) GO TO 599
   WRITE(11) XO,YO,ZO
   WRITE(11) DAX,DAY,DAZ
   WRITE(11) AXO,AYO,AZO,AZO
   WRITE(11) IDIST,SUME,SUMU1,SUMV,SUMA,ISUM
   WRITE(11) IRR,IACPTT,IACPTO
   STOP
END
SUBROUTINE FCC(CUBE,CUBE2,NP)

SET-UP ALPHA-FCC LATTICE FOR INITIAL START-UP

COMMON/POS/X0(500),Y0(500),Z0(500)
COMMON/ORN/AX0(500),AY0(500),AZ0(500),AQ0(500)

=== ASSIGN LATTICE POSITIONS TO CENTERS OF MASS ===

NC=(NP/4)**(1./3.)*.1
SIDE=CUBE/FLOAT(NC)
X0(1)=0.
X0(2)=.5*SIDE
X0(3)=0.
X0(4)=.5*SIDE
Y0(1)=0.
Y0(2)=.5*SIDE
Y0(3)=.5*SIDE
Y0(4)=0.
Z0(1)=0.
Z0(2)=0.
Z0(3)=.5*SIDE
Z0(4)=.5*SIDE
M=0

=== ALPHA STRUCTURE HAS THETA = ARC(DCOS(1./DSQRT(3.)))) ===

TH2=.4777
PI4=3.141593/4.

=== LOOP OVER ALL MOLECULES ===

DO 17 I=1,NC
  DO 17 J=1,NC
    DO 17 K=1,NC
      DO 18 L=1,4
        X0(L+M)=X0(L)+SIDE*(K-1)
        Y0(L+M)=Y0(L)+SIDE*(J-1)
        Z0(L+M)=Z0(L)+SIDE*(I-1)
        IF(L.EQ.1) PH2=PI4*0.5
        IF(L.EQ.2) PH2=PI4*1.5
        IF(L.EQ.3) PH2=PI4*2.5
        IF(L.EQ.4) PH2=PI4*3.5
        AX0(L+M)=-SIN(TH2)*SIN(PH2)
        AY0(L+M)=SIN(TH2)*C0S(PH2)
        AZ0(L+M)=C0S(TH2)*SIN(PH2)
        AQ0(L+M)=C0S(TH2)*C0S(PH2)
      18 CONTINUE
      M=M+4
    17 CONTINUE
  DO 20 I = 1,NP
    X0(I)=X0(I)/CUBE2-1.
    Y0(I)=Y0(I)/CUBE2-1.
    Z0(I)=Z0(I)/CUBE2-1.
SUBROUTINE RANDOM(XX,YY,ZZ,AXX,AYY,AZZ,AQQ)

C PRODUCE RANDOM TRANSLATIONS AND ORIENTATIONS OF ATOM
C
C COMMON/PROPA/RDEL,RMAX,CUBE,CUBE2,HMAX,DELTA,DOMEGA,QSQ,
A NP,NP1,IRR,IACPTT,IACPTO
   IRR=IRR*65539
   XX=FLOAT(IRR)*.4656613E-9
   IRR=IRR*65539
   YY=FLOAT(IRR)*.4656613E-9
   IRR=IRR*65539
   ZZ=FLOAT(IRR)*.4656613E-9
   IRR=IRR*65539
   AXX=FLOAT(IRR)*.4656613E-9
   IRR=IRR*65539
   AYY=FLOAT(IRR)*.4656613E-9
   IRR=IRR*65539
   AZZ=FLOAT(IRR)*.4656613E-9
   IRR=IRR*65539
   AQQ=FLOAT(IRR)*.4656613E-9
RETURN
END
SUBROUTINE EVAL(TOTE,TOTU1,TOTV,BETA)

EVALUATE POTENTIAL USING PAIRWISE ADDITIVE LENNARD-JONES (6-12) PLUS QUADRUPOLE-QUADRUPOLE POTENTIAL

REAL*8 TOTE,TOTU1,TOTV
REAL*8 SUME,SUMU1,SUMV,SUMA
COMMON/POS/X0(500),Y0(500),Z0(500)
COMMON/ORN/AY0(500),AZ0(500),AQ0(500)
COMMON/PROP/IDIST(300),SUME,SUMU1,SUMV,SUMA,ISUM
COMMON/PROP/DEL,RMAX,CUB1,CUBE2,HMAX,D DEL,T DMEGA,RSQ,A

A = NP,NP1,IRR,IACPTT,IACPTO
DIMENSION HHX(500),HHY(500),HHZ(500)
DIMENSION HJX(500),HJY(500),HJZ(500)
DIMENSION XA(500),YA(500),ZA(500),RSQA(500)
DIMENSION X(500),Y(500),Z(500),RSQ(500)
DIMENSION LIST(500)
TOTE=0.
TOTV=0.
TOUT1=0.

DO 405 I=1,NP

=== DETERMINE SPACE FIXED ORIENTATIONS OF EACH MOLECULE

HHX(I)= 2.*(AY0(I)*AZ0(I)-AX0(I)*AQ0(I))
HHY(I)=-2.*(AX0(I)*AZ0(I)+AY0(I)*AQ0(I))
HHZ(I)=-AX0(I)**2-AY0(I)**2+AZ0(I)**2+AQ0(I)**2

405 CONTINUE

=== OUTER LOOP OVER MOLECULES

DO 490 I=1,NP1
MGATHR=0
JBEGIN=I+1
JEND=NP

=== STORE POSITION OF MOLECULE I

XIT=X0(I)
YIT=Y0(I)
ZIT=Z0(I)

=== STORE ORIENTATIONS OF MOLECULE I

HIX=HHX(I)
HIY=HHY(I)
HIZ=HHZ(I)

=== INNER LOOP OVER ATOMS

DO 495 J=JBEGIN,JEND

C
C === DISTANCE BETWEEN C.O.M. OF J MOLECULES AND MOLECULE I

\[ X(J) = \text{CUBE2}(XIT - XO(J) - 2 \cdot \text{INT}(XIT - XO(J))) \]
\[ Y(J) = \text{CUBE2}(YIT - YO(J) - 2 \cdot \text{INT}(YIT - YO(J))) \]
\[ Z(J) = \text{CUBE2}(ZIT - ZO(J) - 2 \cdot \text{INT}(ZIT - ZO(J))) \]
\[ RSQ(J) = X(J) \cdot X(J) + Y(J) \cdot Y(J) + Z(J) \cdot Z(J) \]
\[ RCTR = \sqrt{RSQ(J)} \]
\[ \text{IF} (RSQ(J) < RMAX) \text{ MGATHR} = \text{MGATHR} + 1 \]
\[ \text{IF} (RSQ(J) < RMAX) \text{ LIST(MGATHR)} = J \]

C === INCREMENT COUNTER FOR G(R) & UPDATE LIST AT INTERVALS

\[ \text{IF} (RSQ(J) < RMAX) IJ = RCTR / RDEL + 0.5 \]
\[ \text{IF} (RSQ(J) < RMAX) \text{ IDIST(IJ)} = \text{IDIST(IJ)} + 1 \]

495 CONTINUE

C === GATHER LOCATION AND ORIENTATION OF J MOLECULES

\[ \text{IF} (\text{MGATHR} < 1) \text{ GOTO 490} \]

DO 500 J = 1, MGATHR
   JLIST = LIST(J)
   XA(J) = X(JLIST)
   YA(J) = Y(JLIST)
   ZA(J) = Z(JLIST)
   HJXA(J) = HHX(JLIST)
   HJYA(J) = HHY(JLIST)
   HJZA(J) = HHZ(JLIST)
   RSQA(J) = RSQ(JLIST)
500 CONTINUE

C === EVALUATE POTENTIAL AND VIRIAL VALUES

DO 505 J = 1, MGATHR
   RSI = 1 / RSQA(J)
   R6 = RSI ** 3
   RPL = 48 * R6 * (R6 - 0.5)
   RCCI = SQRT(RSI)

C === CALCULATE AND STORE ORIENTATION OF RCC

   HX = XA(J) * RCCI
   HY = YA(J) * RCCI
   HZ = ZA(J) * RCCI
   HJX = HJXA(J)
   HJY = HJYA(J)
   HJZ = HJZA(J)

C === CALCULATE QUADRUPOLE CONTRIBUTION TO THE POTENTIAL

   CI = HIX * HX + HIY * HY + HIZ * HZ
   CJ = HJX * HX + HJY * HY + HJZ * HZ
   CG = HIX * HJX + HIY * HJY + HIZ * HJZ
   CI2 = CI * CI
   CJ2 = CJ * CJ
TM = CG - 5. * CI * CJ
COEF = .75 * SQ * RCCI ** 5
ULJ = 4. * R6 * (R6 - 1.)
ULJQQ = ULJ + UQQ
VIRIAL = RPL - 5. * UQQ
UREF = ULJQQ
UPERT = 0.

C
C === BARKER-HENDERSON SPLIT OF POTENTIAL
C
IF (ULJQQ .LT. 0.0) THEN
  VIRIAL = 0.
  UREF = 0.
  UPERT = ULJQQ
ENDIF

C
TOTE = TOTE + UREF
TOTV = TOTV + VIRIAL
TOTU1 = TOTU1 + UPERT
505 CONTINUE
490 CONTINUE
ISUM = ISUM + NP
RETURN
END
SUBROUTINE PMOVET(TOTE,TOTU1,TOTV,BETA)
C - RANDOMLY CHANGE LOCATION OF EACH PARTICLE IN TURN AND
C DECIDE WHETHER TO ACCEPT OR REJECT THE MOVE
C -
REAL*8 DELU,DELU1,DELV
REAL*8 TOTE,TOTU1,TOTV
REAL*8 SUME,SUMU1,SUMV,SUMA
REAL*8 TSUME,TSUMU1,TSUMV,TSUMA
COMMON/DISP/DAX(500),DAY(500),DAZ(500)
COMMON/POS/XO(500),YO(500),ZO(500)
COMMON/ORN/AX0(500),AY0(500),AZ0(500),AQ0(500)
COMMON/PROP/IDIST(300),SUME,SUMU1,SUMV,SUMA,ISUM
COMMON/PROP/RDEL,RMAX,CUBE,CUBE2,HMAX,DELTA,DOMEGA,QS,Q,
A NP,NP1,IRR,IACP1,ACP2
TSUMA =0.000
TSUME =0.000
TSUMV =0.000
TSUMU1=0.000
C
C === OUTER LOOP OVER ATOMS
C DO 400 I=1,NP
C
C === STORE POSITION OF ATOM I
C XI=X0(I)
YI=YO(I)
ZI=ZO(I)
C
C === STORE ORIENTATION OF "ATOM" I
C AXI=AX0(I)
AYI=AY0(I)
AZI=AZ0(I)
AQI=AQ0(I)
C
C === EVALUATE OLD ENERGY AND VIRIAL TERMS
C CALL PEVAL(POTOLD,U1OLD,VIROLD,XI,YI,DI,AXI,AYI,AZI,AQI,I)
C
C === RANDOM NUMBERS FOR MOVE (TRANSLATIONAL)
C CALL RANDOM(XX,YY,ZZ,XX,YY,XX,YY,AAZ,AQQ)
XINEW = XO(I) + XX*DELTA/CUBE2
YINEW = Y0(I) + YY*DELTA/CUBE2
ZINEW = Z0(I) + ZZ*DELTA/CUBE2
C
C === CHECK FOR CONSERVATION OF PARTICLES IN PRIMARY CELL (P.B.C.)
C IF(XINEW.LE.-1.) XINEW=XINEW+2.
IF(XINEW.GE.1.) XINEW=XINEW-2.
IF(YINEW.LE.-1.) YINEW=YINEW+2.
IF(YINEW.GE.1.) YINEW=YINEW-2.
IF(ZINEW.LE.-1.) ZINEW=ZINEW+2.
IF(ZINEW.GE.1.) ZINEW=ZINEW-2.

C
C === CALCULATE THE PROPOSED ENERGY AND PROPERTY CHANGES
C
CALL PEVAL(POTNEW,U1NEW,VIRNEW,XINEW,YINEW,ZINEW,
          AXI,AYI,AZI,AQI,I)
DELU = POTNEW - POTOLD
DELV = VIRNEW - VIROLD
DELU1= U1NEW - U1OLD

C
C === REJECT OR ACCEPT MOVE
C
BETAU = DELU*BETA
IF(BETAU.LT.HMAX) PROBL=EXP(-BETAU)
IF(DELU.LT.0.0) PROBL=1.0
IF(BETAU.GT.HMAX) GO TO 410
CALL RANDOM(PX,PY,PZ,PAX,PAY,PAZ,PAQ)
PZ=ABS(PZ)
IF(PROBL.LT.PZ) GO TO 410

C
C === IF MOVE ACCEPTED, PROPOSED LOCATION BECOMES THE NEW ONE
C
IACPTT = IACPTT + 1
X0(I)  = XINEW
Y0(I)  = YINEW
Z0(I)  = ZINEW
TOTE = TOTE + DELU
TOTV = TOTV + DELV
TOTU1= TOTU1+ DELU1
TSUMA = TSUMA + PROBL
TSUME = TSUME + PROBL*TOTE
TSUMV = TSUMV + PROBL*TOTV
TSUMU1= TSUMU1+ PROBL*TOTU1
DAX(I) = DAX(I) - XX*DELTA
DAY(I) = DAY(I) - YY*DELTA
DAZ(I) = DAZ(I) - ZZ*DELTA
GO TO 400

C
C === IF MOVE REJECTED, OLD LOCATION BECOMES NEW LOCATION
C
410 TSUME = TSUME + TOTE
TSUMV = TSUMV + TOTV
TSUMA = TSUMA + 1.
TSUMU1= TSUMU1+ TOTU1
400 CONTINUE

C
C === UPDATE SUM ACCUMULATORS
C
SUME = SUME + TSUME
SUMV = SUMV + TSUMV
SUMA = SUMA + TSUMA
SUMU1= SUMU1+ TSUMU1
RETURN
END
SUBROUTINE PMOVEO(TOTE,TOTU1,TOTV,BETA)
C - ----------------------------------------
C RANDOMLY CHANGE ORIENTATION OF EACH PARTICLE IN TURN AND
C DECIDE WHETHER TO ACCEPT OR REJECT THE CHANGE
C - ----------------------------------------
C REAL*8 DELU,DELU1,DELV
C REAL*8 TOTE,TOTU1,TOTV
C REAL*8 SUME,SUMU1,SUMV,SUMA
C REAL*8 TSUME,TSUMU1,TSUMV,TSUMA
C COMMON/DISP/DAX(500),DAY(500),DAZ(500)
C COMMON/POS/X0(500),Y0(500),Z0(500)
C COMMON/ORN/AX0(500),AY0(500),AZ0(500),AQ0(500)
C COMMON/PROP/IDIST(300),SUME,SUMU1,SUMV,SUMA,ISUM
C COMMON/PROPA/RDEL,RMAX,CUBE,CUBE2,HMAX,DELTA,DOMEGA,QSQ,
C A NP,NP1,IRR,IACPTT,IACPTO
TSUMA = 0.
TSUME = 0.
TSUMV = 0.
TSUMU1 = 0.
C === OUTER LOOP OVER ATOMS
C DO 400 I=1,NP
C === STORE POSITION OF ATOM I
C XI=X0(I)
YI=Y0(I)
ZI=Z0(I)
C === STORE ORIENTATION OF "ATOM" I
C AXI=AX0(I)
AYI=AY0(I)
AZI=AZ0(I)
AQI=AQ0(I)
C === EVALUATE OLD ENERGY AND VIRIAL TERMS
C CALL PEVAL(POTOLD,UIOLD,VIROLD,XI,YI,ZI,AXI,AYI,AZI,AQI,I)
C === RANDOM NUMBERS FOR MOVE (ORIENTATION)
C CALL RANDOM(XX,YY,ZZ,AXX,AYY,AZZ,AQQ)
AXNEW = AX0(I) + AXX*DOMEGA
AYNEW = AYO(I) + AYY*DOMEGA
AZNEW = AZ0(I) + AZZ*DOMEGA
AQNEW = AQ0(I) + AQQ*DOMEGA
C === NORMALIZE NEW ORIENTATIONS
C CSC=SORT(AXNEW**2+AYNEW**2+AZNEW**2+AQNEW**2)
AXNEW=AXNEW/CSC
AYNEW=AYNEW/CSC
AZNEW=AZNEW/CSC
AQNEW=AQNEW/CSC

C
C === CALCULATE THE PROPOSED ENERGY AND PROPERTY CHANGES
C
CALL PEVAL(POTNEW,U1NEW,VIRNEW,XI,YI,ZI,
A
AXNEW,AYPEW,AZNEW,AQNEW,I)
DELU = POTNEW - POTOLD
DELV = VIRNEW - VIROLD
DELU1= U1NEW - U1OLD

C
C === REJECT OR ACCEPT MOVE
C
BETAU = DELU*BETA
IF(BETAU.LT.HMAX) PROBL=EXP(-BETAU)
IF(DELU.LT.0.0) PROBL=1.0
IF(BETAU.GT.HMAX) GO TO 410
CALL RANDOM(PX, PY, PZ, PAX, PAY, PAZ, PAQ)
PZ = ABS(PZ)
IF(PROBL.LT.PZ) GO TO 410

C
C === IF MOVE ACCEPTED, PROPOSED CONFIGURATION BECOMES THE NEW ONE
C
IACPTO = IACPTO + 1
AXO(I)=AXNEW
AYO(I)=AYNEW
AZO(I)=AZNEW
AQO(I)=AQNEW
TOTE = TOTE + DELU
TOTV = TOTV + DELV
TOTU1= TOTU1+ DELU1
TSUMA = TSUMA + PROBL
TSUME = TSUME + PROBL*TOTE
TSMV = TSMV + PROBL*TOTV
TSUMU1= TSUMU1+ PROBL*TOTU1
GO TO 400

C
C === IF MOVE REJECTED, OLD CONFIGURATION BECOMES NEW CONFIGURATION
C
410
TSUME = TSUME + TOTE
TSMV = TSMV + TOTV
TSUMA = TSUMA + 1.
TSUMU1= TSUMU1+ TOTU1
400 CONTINUE

C
C === UPDATE SUM ACCUMULATORS
C
SUME = SUME + TSUME
SUMV = SUMV + TSMV
SUMA = SUMA + TSMU1
SUMU1= SUMU1 + TSMU1
RETURN
END

SUBROUTINE PEVAL(POT, U1, VIR, XI, YI, ZI, AXI, AYI, AZI, AQI, I)
EVALUATE POTENTIAL USING PAIRWISE ADDITIVE LENNARD-JONES PLUS QUADRUPOLE-QUADRUPOLE POTENTIAL FOR SINGLE PARTICLE

COMMON/POS/X0(500),Y0(500),Z0(500)
COMMON/ORN/AX0(500),AY0(500),AZ0(500),AQ0(500)
COMMON/PROP/RDEL,RMAX,CUBE,CUBE2,HMAX,DELTA,DOMEGA,QSQ,
A
NP, NP1, IRR, IACPTT, IACPTO
DIMENSION AXOA(500),AYOA(500),AZOA(500),AQOA(500)
DIMENSION XA(500),YA(500),ZA(500),RSQA(500)
DIMENSION X(500),Y(500),Z(500),RSQ(500)

U1 = 0.
POT = 0.
VIR = 0.
MGATHR=0
RLARGE=RMAX+100.

=== DETERMINE ORIENTATION OF MOLECULE I ===

HIX= 2.*(AYI*AZI-AXI*AQT)
HIY=-2.*(AXI*AZI-AQI*AYI)
HIZ=-AXI**2-AQI**2+AZI**2

JBEGIN=1
JEND=NP
DO 495 J=JBEGIN,JEND

=== DISTANCE BETWEEN C.O.M. OF I AND J WITH MINIMUM IMAGE ===

X(J)=CUBE2*(XI-X0(J)-2.*INT(XI-X0(J)))
Y(J)=CUBE2*(YI-Y0(J)-2.*INT(YI-Y0(J)))
Z(J)=CUBE2*(ZI-Z0(J)-2.*INT(ZI-Z0(J)))
RSQ(J)=X(J)**2+Y(J)**2+Z(J)**2
IF(I.EQ.J) RSQ(J)=RLARGE
IF(RSQ(J).LT.RMAX) MGATHR=MGATHR+1
IF(RSQ(J).LT.RMAX) LIST(MGATHR)=J
495 CONTINUE

=== RETRIEVE LOCATION AND ORIENTATION FROM GATHERING LIST ===

DO 500 J = 1,MGATHR
JLIST=LIST(J)
XA(J)=X(JLIST)
YA(J)=Y(JLIST)
ZA(J)=Z(JLIST)
AXOA(J)=AX0(JLIST)
AYOA(J)=AY0(JLIST)
AZOA(J)=AZ0(JLIST)
AQOA(J)=AQ0(JLIST)
RSQA(J)=RSQ(JLIST)
500 CONTINUE
DO 510 J = 1, MGATHR
RSI = 1./RSQA(J)
R6 = RSI**3
RPL = 48.*R6*(R6-.5)
RCCI = SQRT(RSI)

CALCULATE ORIENTATION OF RCC
HX = XA(J)*RCCI
HY = YA(J)*RCCI
HZ = ZA(J)*RCCI
HJX = 2.*(AYOA(J)*AZOA(J)-AXOA(J)*AQOA(J))
HJY = -2.*(AXOA(J)*AZOA(J)+AYOA(J)*AQOA(J))
HJZ = -AXOA(J)**2-AZOA(J)**2+AYOA(J)**2+AQOA(J)**2

CALCULATE QUADRUPOLE CONTRIBUTION TO THE POTENTIAL
CI = HIX*HX+HIY*HY+HIZ*HZ
CJ = HJX*HX+HJY*HY+HJZ*HZ
CG = HIX*HJX+HIY*HJY+HIZ*HJZ
C12 = CI*CI
CJ2 = CJ*CJ
TM = CG-5.*CI*CJ
COEF = 0.75*QSQ*RCCI**5
UQQ = COEF*(1.-5.*C12-15.*CJ2+2.*TM*TM)
ULJ = 4.*R6*(R6-1.)
ULJJQ = ULJ+UQQ
VIRIAL = -RPL-5.*UQQ
UREF = ULJJQ
UPERT = 0.

BARKER-HENDERSON SPLIT OF POTENTIAL
IF(ULJJQ.LT.0.0) THEN
VIRIAL = 0.
UREF = 0.
UPERT = ULJJQ
ENDIF

U1 = U1+UPERT
POT = POT+UREF
VIR = VIR+VIRIAL
CONTINUE
RETURN
END
SUBROUTINE EQBRAT(KDIST, KG, LG, NY, KB)

- reset sum accumulators after equilibration -

REAL*8 TOTE, TOTU1, TOTV
REAL*8 SUME, SUMU1, SUMV, SUMA
COMMON/DISP/DAX(500), DAY(500), DAZ(500)
COMMON/PROP/IDIST(300), SUME, SUMU1, SUMV, SUMA, ISUM
COMMON/PROPA/RDEL, RMAX, CUBE, CUBE2, HMAX, DELTA, DOMEGA, QSQ,
A NP, NP1, IRR, IACPTT, IACPTO

C

C === AT END OF EQUILIBRATION STAGE, SET PROPERTY SUMS TO ZERO
C
IF (KB .LT. KDIST) RETURN
IFLG = 1
KB = 0
ISUM = 0
SUME = 0.
SUMV = 0.
SUMA = 0.
SUMU1 = 0.
IACPTT = 0
IACPTO = 0
DO 740 I = 1, NY
740 IDIST(I) = 0
DO 745 I = 1, NP
DAX(I) = 0.
DAY(I) = 0.
745 DAZ(I) = 0.
WRITE(6, 777)
777 FORMAT (/10X, '****EQUILIBRATION COMPLETE ****' //)
WRITE(6, 930)
930 FORMAT (1H1, //4X, 'KB', 5X, 'PRES', 5X, 'ENRG', 5X, 'PERT', 5X, 'DIST',
A 5X, 'ACPTT', 4X, 'ACPTO' //)
RETURN
END
SUBROUTINE RDF(DR,RDEL,NY,KB,MAXKB)
C --------------- ---------------------- --------------- ---------------
C             NORMALIZE COUNTERS FOR RADIAL DISTRIBUTION FUNCTION
C --------------- ---------------------- --------------- ---------------
REAL*8 SUME,SUMU1,SUMV,SUMA
COMMON/PROP/IDIST(300),SUME,SUMU1,SUMV,SUMA,ISUM
DIMENSION RRR(200),GR(200)
Y=ISUM
Y=0.5*Y
NM=0
PDEN=DR*(RDEL**3)
WRITE(6,968)
DO 780 J = 1, NY
    IF(IDIST(J).EQ.0) GOTO 780
    NM=NM+1
    V=(4.*3.14159/3.)*(3.*FLOAT(J)**2+.25)
    X=IDIST(J)
    GR(NM)=X/V/Y/PDEN
    RRR(NM)=RDEL*FLOAT(J)
    WRITE(6,972) J,RRR(NM),IDIST(J),GR(NM)
780 CONTINUE
WRITE(6,970)
970 FORMAT(1H1///)
RETURN
END
SUBROUTINE PRNT(NP, EPSI, SIGMA, TR, T, DR, VOL, CUBE, RMAX, RC, RDEL, 
A DELTA, DOMEGA, QSQ, NY, DE, DP) 

C ------ print input and output parameters ------ 

WRITE(6,900) 
900 FORMAT(1H1///) 
WRITE(6,902) 
902 FORMAT(7X,49('**')) 
WRITE(6,904) 
904 FORMAT(7X,'*',T56,'**') 
WRITE(6,906) NP 
906 FORMAT(7X,'%',8X,'MONTE CARLO FOR','I4,' PARTICLES','T56','**') 
WRITE(6,904) 
WRITE(6,902) 
WRITE(6,904) 
WRITE(6,908) EPSI, SIGMA 
908 FORMAT(7X,'**',2X,'EPSI/K = ','F7.3,T36,'SIGMA = ','F7.3,T56','**') 
WRITE(6,910) TR, T 
910 FORMAT(7X,'**',2X,'TR = ','F7.3,T36,' T = ','F7.3,T56','**') 
WRITE(6,912) DR, VOL 
912 FORMAT(7X,'**',2X,'DR = ','F7.3,T36,'VOL = ','F7.3,T56','**') 
WRITE(6,914) CUBE, RMAX 
914 FORMAT(7X,'**',2X,'CUBE = ','F7.3,T36,'RMAX = ','F7.3,T56','**') 
WRITE(6,916) RC, RDEL 
916 FORMAT(7X,'**',2X,'RC = ','F7.3,T36,'DELR = ','F7.3,T56','**') 
WRITE(6,920) DELTA, NY 
920 FORMAT(7X,'**',2X,'DELTA = ','F7.3,T36,'NY = ','I3,T56','**') 
WRITE(6,922) DOMEGA, QSQ 
922 FORMAT(7X,'**',2X,'DOMEGA = ','F7.3,T36,'QSQ = ','F8.4,T56','**') 
WRITE(6,904) 
WRITE(6,902) 
C === print run-table heading === 

WRITE(6,926) DE 
926 FORMAT(7X,'**',2X,'ENERGY CORRECTION = ','F7.3,T56','**') 
WRITE(6,928) DP 
928 FORMAT(7X,'**',2X,'PRESSURE CORRECTION = ','F7.3,T56','**') 
WRITE(6,904) 
WRITE(6,902) 

C RETURN 

END
BLOCK DATA
REAL*8 SUME, SUMU1, SUMV, SUMA
COMMON/DISP/DAX(500), DAY(500), DAZ(500)
COMMON/PROP/IDIST(300), SUME, SUMU1, SUMV, SUMA, ISUM
DATA DAX, DAY, DAZ/1500*0./
DATA IDIST/300*0/
DATA ISUM/0/
DATA SUME, SUMU1, SUMV, SUMA/4*0.000/
END
APPENDIX D

Reprint of "Solubility of Aromatic Hydrocarbons in Mixtures of Benzene and Cyclohexane"

By kind permission of Journal of Chemical and Engineering Data
February 1587

Mr. C. P. Williams
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Dear Mr. Williams:

This is in reply to your letter of January 22, in which you requested permission to re-microfilm a reprint of your paper (J. Chem. Eng. Data, 1985, 30, 40) to comply with your graduate school's regulations to include reprints in Ph.D. dissertations.

It’s our standard policy to grant free permission to include an author's article in his/her Ph.D. thesis provided that the required ACS copyright credit line is typed or printed on the first page of the article. I'm somewhat confused why your 1985 reprint must be re-microfilmed. Is there a problem with the original? Will the microfilming be done by Louisiana State University or by an outside organization?

I would appreciate if you would give me more information concerning your request. I look forward to your reply.

Sincerely,

Barbara F. Polansky
Copyright Administrator
SOLUBILITY OF AROMATIC HYDROCARBON SOLIDS IN MIXTURES OF
BENZENE AND CYCLOHEXANE

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Short Title: Solubility of Aromatic Hydrocarbon Solids

*To whom proofs should be sent.
Abstract

The solubilities of five solutes, biphenyl, naphthalene, fluorene, phenanthrene and acenaphthene, in pure benzene and cyclohexane and in mixtures of benzene and cyclohexane, have been determined. The activity coefficients of the five solutes in cyclohexane are correlated to within an average of 0.6% by Wilson's equation compared to 9.3% by the Scatchard-Hildebrand expression. Similarly for the solutes in benzene, the activity coefficients were correlated to within an average of 0.5% and 1.2% respectively by the same two methods. For the ternary mixtures Wilson's method correlates the activity coefficients for the 78 measured data points within 1.4% compared to 2.6% by the Scatchard-Hildebrand expression. As expected, when the solution exhibits a significant deviation from ideal behavior, regular solution theory becomes inadequate and Wilson's equation is proposed as a more appropriate correlation. The solubility data can also be correlated as functions of reduced temperature $T_m/T$ where $T_m$ is the melting point temperature.
1. Introduction

The correlation of equilibrium solubility behavior of aromatic hydrocarbon solutes in binary mixtures of benzene and cyclohexane by both Scatchard-Hildebrand regular solution theory and Wilson's equation requires four sets of experimental data: solubilities of the aromatic hydrocarbons in pure benzene and pure cyclohexane, and VLE data for the benzene-cyclohexane system are necessary to determine the parameters of the chosen activity coefficient model, and solubilities of the aromatic hydrocarbons in the three binary solvent mixtures.

In the present study, the solubilities of the five aromatic hydrocarbons, biphenyl, naphthalene, fluorene, phenanthrene andacenaphthene have been determined, (from around room temperature to near the melting points of the solids) in both pure and mixed solvents for use with the extensive VLE data for the benzene-cyclohexane system that has been compiled by Gmehling et al.\(^{(1)}\). Experimental activity coefficients of solutes in ternary systems are evaluated using these data and compared with values predicted from theory.
Biphenyl and naphthalene were purchased from Eastman Kodak, phenanthrene and fluorene from Eastern Chemical, and acenaphthene from British Drug Houses. All samples, except acenaphthene, were purified further by liquid chromatography on activated alumina using toluene as eluant. The solids were then recrystallized and toluene removed by evaporation in a vacuum. After recrystallization, fluorene was batch distilled to remove low boiling impurities and acenaphthene was zone refined.

The purified samples were analysed on a G.C. Mass Spectrometer, and their melting points determined. The results were as follows: biphenyl 99.67 wt% (342.6 K), naphthalene 99.21 wt% (352.8 K), fluorene 97.85 wt% (387.6 K), phenanthrene 98.67 wt% (372.8 K) and acenaphthene 99.2 wt% (366.5 K). The liquid samples of benzene and cyclohexane were "gold label" Aldrich products and were used without further purification.

Mixtures of pre-determined composition of single solids with the pure and mixed solvents were made in glass ampoules, and sealed while they were frozen in a Dewar bottle containing dry ice. The ampoules were then placed in a constant temperature bath, and the temperature at which the last trace of solid disappeared was visually determined, while the bath temperature was increased at a rate of 0.1 K every 1200 seconds near the expected melting temperature, with the ampoules rotated at a speed of 0.25 rps. Measurements were made at least twice for each ampoule. The experimental system and techniques were similar to that of McLaughlin and Zainal (2,3). The solubility data taken in this study are listed in columns 1 and 2 of tables 1, 2 and 3.
3. Correlation and Discussion

Equations for the Solubility of Solids

The solubility of a solid in a liquid can be used to evaluate the activity coefficient of the solute component in the solution by equation (1). This equation is valid if no phase transition takes place in the solid phase between the system temperature $T$ and the solute melting temperature $T_m$, and if the Poynting correction is neglected.

$$\ln X_2 = \frac{\Delta S^f_2}{R} \left\{ \frac{T_m}{T} - 1 \right\} - \frac{\Delta C^f}{P^2} \left\{ \frac{T_m}{T} - 1 \right\}$$

$$+ \frac{\Delta C^f}{P^2} \ln \frac{T_m}{T} + \ln \gamma_2 \quad (1)$$

When a phase transition does take place between $T$ and $T_m$, equation (1) must be modified to include the effect of the transition on solubility at solution temperatures below the transition point. For a first order phase transition, as given for example by Weimer and Prausnitz (4),

$$\ln X_2 = \frac{\Delta S^f_2}{R} \left\{ \frac{T_m}{T} - 1 \right\} - \frac{\Delta C^f}{P^2} \left\{ \frac{T_m}{T} - 1 \right\}$$

$$+ \frac{\Delta C^f}{P^2} \ln \frac{T_m}{T} + \frac{\Delta S^p_2}{R} \left\{ \frac{T_p}{T} - 1 \right\} + \ln \gamma_2 \quad (2)$$

And for a lambda point transition equation (1) is modified to equation (3), as discussed by Choi and McLaughlin (5).

$$\ln X_2 = \frac{\Delta S^f_2}{R} \left\{ \frac{T_m}{T} - 1 \right\} - \frac{\Delta C^f}{P^2} \left\{ \frac{T_m}{T} - 1 \right\}$$

$$+ \frac{\Delta C^f}{P^2} \ln \frac{T_m}{T} + \ln \gamma_2 + \lambda \quad (3)$$

where $\lambda$, the additional effect of the lambda point transition, is given by
In equation (4), $C_{p1}$ represents the specific heat of the solid during a lambda point transition from temperature $T_a$ to $T_b$ and $C^B_{p1}$ the base line specific heat as if no phase transition occurred. Experimental $X_2$ vs. $T$ data therefore permit evaluation of the activity coefficients of the solute $Y_2$ by using one of the above equations provided the necessary physical properties of the solid are available. For the five solids used in this study, the necessary physical properties are available and are given in table 4. It should be noted that the solubility equations to be used do not contain properties of the solvent and can therefore be used directly to obtain the solute activity coefficient in mixed as well as single solvents.
Solubility in Multicomponent Systems

Scatchard-Hildebrand Regular Solution Theory

Of the various theories that can be used to correlate the solute activity coefficients of the systems investigated, the Scatchard-Hildebrand regular solution theory has so far been the only one we have investigated extensively for our work in single solvents (6).

For this model, the activity coefficient of the rth component in a multicomponent mixture of C components is given by Malesinski (7) as

\[
RT \ln \gamma_r = V_r^0 \frac{1}{2} \sum \sum [A_{ri} + A_{rj} - A_{ij}] \Phi_i \Phi_j 
\]

with \( A_{ii} = A_{jj} = 0 \), \( A_{ij} = A_{ji} \), and \( r = 1, 2, \ldots, C \). The \( A_{ij} \)'s are themselves related to the solubility parameters \( \delta_i \) by the equations

\[
A_{ij} = (\delta_i - \delta_j)^2 + 2 \psi_{ij} \delta_i \delta_j
\]

where

\[
\delta_i = \sqrt{\frac{\Delta E_i^{vap}}{V_i}}^{1/2}
\]

and

\[
\Phi_i = \frac{X_i \sqrt{\psi_i}}{\sum X_i \sqrt{\psi_i}}
\]

It has already been shown by Choi and McLaughlin (b) that for the present solutes in thiophene and pyridine \( \psi_{ij} \neq 0 \) and so the accuracy of prediction can be greatly enhanced if \( \psi_{ij} \)'s are indeed used, which are currently only available by fitting the equations to experimental data.

When equation (5) is expanded for a ternary mixture of a single solute 2 in solvents 1 and 3 we get

\[
RT \ln \gamma_2 = v_2^0 \left[ A_{12} \Phi_1^2 + A_{23} \Phi_3^2 + (A_{12} + A_{23} - A_{13}) \Phi_1 \Phi_3 \right]
\]

(9)
For a solute 2 in a single solvent 1 equation (9) further reduces to
\[
RT \ln \gamma_2 = \frac{V^L}{2} A_{12} \phi_1^2 \tag{10}
\]
and in the absence of experimental data, \( A_{1j} \) may be assumed zero, then using equation (6) for \( A_{12} \)
\[
RT \ln \gamma_2 = \frac{V^L}{2} \phi_1^2 (\delta_1 - \delta_2)^2 \tag{11}
\]
For the solvent mixtures, values of \( z_{13} \) representing the solvent-solvent interaction were evaluated from three sets of isothermal data giving 18 experimental activity coefficients, which were fitted to equation (10) using the solubility parameters and liquid molar volumes listed in table 5 for each particular system for which \( z_{13} \) is required.
Wilson's Equation

The use of Wilson's equation to predict the activity coefficient of a solute in both a pure and a mixed solvent system ought to show a marked improvement over regular solution theory for systems exhibiting a significant deviation from ideal behavior.

Wilson's equation for $g_i^E$, of a C component mixture, is given by (8)

$$\frac{\delta_i}{RT} = (-) \sum_{i \neq 1} C \frac{X_i}{\prod_{j \neq i} \Lambda_{ij}} \ln \left\{ \sum_{j \neq i} \Lambda_{ij} X_j \right\}$$  \hspace{1cm} (12)

where

$$\Lambda_{i,j} = \frac{\Lambda_{ji}}{\Lambda_{ij}} \exp \left\{ \frac{-\lambda_{i,j} - \lambda_{j,i}}{RT} \right\}$$  \hspace{1cm} (13)

$$\Delta \Lambda_{i,j} = \Lambda_{i,j} - \Lambda_{j,i}
\Lambda_{i,j} \neq \Lambda_{j,i} \hspace{1cm} \Lambda_{ii} = \Lambda_{i,i} = 1$$

The resulting expression for the activity coefficient of the $i$th component in a mixture of C components is given by (8)

$$\ln \gamma_i = 1 - \ln \left\{ \sum_{j \neq i} \frac{X_j}{\prod_{k \neq 1} \Lambda_{i,k}} \right\} - \sum_{k=1}^{C} \frac{X_k}{\sum_{j=1}^{C} \Lambda_{i,j} X_j} \ln \left\{ \sum_{j \neq i} \Lambda_{i,j} X_j \right\} \hspace{1cm} (14)$$

When equation (14) is expanded for the activity coefficient of solute 2 in mixed solvents of 1 and 3 we get

$$\ln \gamma_2 = 1 - \ln \left\{ \sum_{k=1}^{C} \frac{X_k}{\Lambda_{21} + \Lambda_{22} + \Lambda_{23}} \right\} - \left\{ \frac{X_1 \Lambda_{21}}{X_1 + X_2 \Lambda_{12} + X_3 \Lambda_{13}} + \frac{X_2 \Lambda_{22}}{X_1 + X_2 \Lambda_{12} + X_3 \Lambda_{13}} + \frac{X_3 \Lambda_{23}}{X_1 + X_2 \Lambda_{12} + X_3 \Lambda_{13}} \right\} \hspace{1cm} (15)$$

Equation (15) contains 6 adjustable parameters, two from each of the three binary mixtures. Recommended values of the solvent-solvent binary
interaction parameters $\Lambda_{13}$ and $\Lambda_{31}$ are given by Gmehling et al.\(^{(1)}\), in the form of $\Delta\Lambda_{13}$ and $\Delta\Lambda_{31}$, from VLE data for the benzene-cyclohexane system.

Equation (14) may be rewritten for a binary solute-2, solvent-1 mixture as

$$\ln \gamma_2 = -\ln \left( X_2 + \Lambda_{21} X_1 \right) - X_1 \left\{ \frac{\Lambda_{12}}{X_1 + X_2 \Lambda_{12}} + \frac{\Lambda_{21}}{X_1 \Lambda_{21} X_2} \right\}$$

Taking note of the fact that the differences in the characteristic energies ($\Lambda_{1j} - \Lambda_{i1}$), $\Delta\Lambda_{ij}$, in equation (13), are approximately independent of temperature over modest temperature ranges, then equation (16) can be solved iteratively for both $\Delta\Lambda_{1j}$ and $\Delta\Lambda_{ji}$ by comparing the results of equation (16) determined for two different experimental data points and corresponding activity coefficients.

Values of $\Delta\Lambda_{1j}$ and $\Delta\Lambda_{ji}$ were determined using the lowest experimental solubility data point and each of the other experimental binary data points in sequence, on approaching the melting temperature. Arithmetic averages were then taken to obtain overall values of the characteristic energy difference. The lowest solubility data point, and hence the largest deviation from ideality, was always used in these determinations, as it was felt that the corresponding value of $\gamma$, the activity coefficient, would likely be more accurate for the calculations due to its magnitude. If side-by-side data points were used this produced instabilities in the iterative calculations. This procedure was repeated for all 10 solute-solvent binary mixtures.
Discussion

Experimental activity coefficients of biphenyl, naphthalene, fluorene and acenaphthene in the mixed solvents were calculated using equation (1) and for phenanthrene using equation (3) for temperatures below the end of the lambda point transition and equation (1) above the end of the transition. In the calculations, the observed melting points of the solutes were used so that the condition \( \ln X_2 \rightarrow 0 \) as \( T_m / T \rightarrow 1 \) was satisfied. For biphenyl, values of \( \Delta S_2^f \) and \( \Delta G_{p2}^f \) were taken as listed in a previous study on the solubility in thiophene and pyridine\(^{(6)}\).

These values of experimental activity coefficients are compared to those correlated by the methods discussed earlier with the differences defined by \( \Delta \), given by

\[
\Delta = \frac{(Y_2)_\text{exp} - (Y_2)_\text{pred}}{(Y_2)_\text{exp}} \times 100
\]

**Binary Mixtures**

As can be seen from tables 2 and 3 for solutes with either pure benzene or cyclohexane and with \( \ell_{12} = 0 \), and the floating datum point method applied to the Scatchard-Hildebrand regular solution theory, equation (11) predicts the experimental activity coefficient for the five solutes in benzene within 1.2 percent for the 32 data points given in table 2 and within 9.3 percent for the 38 data points of table 3 for the solutes in cyclohexane. This difference in accuracy is not surprising as solutions in cyclohexane are considerably more non-ideal than in benzene and the model therefore expected to be less successful.

If equation (10) is used with \( \ell_{12} \) of equation (6) evaluated at the lowest temperature at which solubility measurements were taken, then as seen from tables 2 and 3, the results for benzene are within 0.6 percent
and for cyclohexane within 4.0 percent. The $\delta_{ij}$'s used are given in table 6.

The additional parameter of the Wilson equation should allow a further improvement in the correlation of the activity coefficient. Using equation (16) and evaluating the binary parameters as discussed earlier, the results for benzene are within 0.5 percent and for cyclohexane within 0.6 percent. The values of the characteristic energy differences, $\Delta A_{ij}$, of the binary Wilson parameters are given in table 7.

In order to test these methods with solubilities at other than saturation conditions a comparison can be made of the calculated and experimental activity coefficients of benzene (1) at infinite dilution with phenanthrene (2), $\gamma_1^{x2} = 1.444$ at 393K compared with the experimental value of 1.41 at 393K and $3.31 \times 10^5 \text{ N m}^{-2}$ determined by Turek et al. (9) using gas-liquid chromatography.

**Tenary Mixtures**

Table 1 gives a comparison of experimental activity coefficients and values produced by both Scatchard-Hildebrand regular solution theory and Wilson's equation for the five solutes in three solvent mixtures. The activity coefficients, calculated with the floating datum point method of Choi and McLaughlin (6) with the $\delta_{ij}$'s = 0, show an average reproducibility of 2.6 percent for 78 data points. On the other hand, when the activity coefficients are calculated with the $\delta_{ij}$'s ≠ 0, the average reproducibility improved to 2.2 percent. However the extent of improvement depended upon the solute being considered and the composition of the solvent mixture. Indeed for solutes, particularly biphenyl, the reproducibility decreased. In general however,
improvement was more noticeable for solvent mixtures with a higher proportion of cyclohexane.

The activity coefficients correlated by the Wilson equation had an average reproducibility of 1.4 percent and the improvement above the Scatchard-Hildebrand regular solution theory is readily seen in table 1. Again this improvement is more noticeable for solvent mixtures with a higher proportion of cyclohexane which exhibit a greater deviation from ideal behavior.

Generalization of the Solubility of Solids

It was shown by McLaughlin and Zainal\(^{1,2}\) and Choi and McLaughlin\(^4\) that the solubility of solids in binary systems can be generalized when \(-\log X_s\) was plotted as a function of \((T_m/\ell)\). Similar plots have been made for the five solids in each of the three mixed solutions, 70, 59 and 30 mole percent benzene, each showing a straight line trend with correlation coefficients of 0.993, 0.994 and 0.995 respectively.

The equation of the straight line, which was obtained by a least squares fit of the solubility data for each solvent, can be represented by equation (18).

\[
-\log X_s = \frac{\Delta S_s^g}{2.303R} \left( \frac{T_m}{\ell} - 1 \right)
\]

The value of \(\Delta S_s^g\) in equation (18) can be used to compare the average non-ideality of the solutes in each solution. \(\Delta S_s^g\), for example, becomes 60.833, 65.719 and 74.492 J.mol\(^{-1}\).K\(^{-1}\) for the solutions with the three mixed solvents 70, 50 and 30 mole percent benzene, respectively. McLaughlin and Zainal\(^{2,3}\) obtained 57.778 and 101.739 J.mol\(^{-1}\).K\(^{-1}\) for
Non-ideality of solutes in the three solutions thus lies between that in benzene and in cyclohexane solutions with increasing departure from ideality for increasing concentrations of cyclohexane.

This result can be expected, however, if one examines equation (19), another form of equation (9) with $\psi_{ij} = 0$, we have

$$RT \ln \gamma_2 = V_2^q \phi_0^2 (\delta_2 - \delta_0)^2$$

where

$$\delta_0 = \frac{\phi_1 \delta_1 + \phi_3 \delta_3}{\phi_1 + \phi_3}$$

and

$$\phi_0 = \phi_1 + \phi_3$$

For a given value of $\phi_0$, $\delta_0$ approaches $\delta_3$ as the volume fraction of cyclohexane $\phi_3$ increases in equation (20). Accordingly, $\gamma_2$ of the ternary solution approaches $\gamma_2$ of the cyclohexane solution while the concentration of cyclohexane in the solvent mixture increases.

Generalization is possible due to the fact that $\Delta S^f_2$ and $\delta_2$ of the five solids are similar in magnitude. Accordingly, the solubility of a different solute in a ternary solution of the three mixtures of solvents can be predicted approximately if $\Delta S^f_2$ and $\delta_2$ of the new solute are similar to those of the five solutes used in this study.
Nomenclature

$\Delta C_p^f$ - difference of molar specific heat between those of liquid and solid at fusion temperature, J/mol-K

$\Delta E^V$ - molar energy of vaporization, J/mol

$g^E$ - excess molar Gibbs free energy, J/mol

$\Delta h_P^f$ - molar enthalpy change of phase transition, J/mol

$\Delta h_V^f$ - molar enthalpy of vaporization, J/mol

$g^E_{ij}$ - binary parameter

$R$ - gas constant

$\Delta S^E$ - excess molar entropy of mixing, J/mol-K

$\Delta S^f_2$ - molar entropy change of fusion, J/mol-K

$\Delta S^g_2$ - least-squares-fitted value, J/mol-K

$\Delta S^p_2$ - molar entropy change of phase transition, J/mol-K

$T$ - system temperature, K

$T_m$ - melting temperature, K

$T_P$ - temperature of first-order phase transition, K

$V^L$ - molar liquid volume, m$^3$/mol

$X$ - mole fraction

Greek Letters

$\Lambda_{ij}$ - binary interaction parameter-Wilson equation

$\gamma$ - activity coefficient

$\delta$ - solubility parameter

$\phi$ - volume fraction

$\lambda$ - characteristic energy, J/mol

Subscripts

1, 2 - solvent

2 - solute (solid)
Literature Cited


TABLE 1

Comparison of the Experimental and Predicted Activity Coefficients of Aromatic Hydrocarbon Solids in three mixed solvents

<table>
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<tr>
<th>K (%)</th>
<th>X%</th>
<th>(Y)exp</th>
<th>(Y)cal</th>
<th>Δ%</th>
<th>(Y)cal</th>
<th>Δ%</th>
<th>Wilson’s Eq.</th>
<th>Δ%</th>
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### TABLE 4

Physical Properties of Five Aromatic Hydrocarbon Solids

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<td>Phenanthrene</td>
<td>372.4(^{\text{(c)}})</td>
<td>16.474×10(^3)(^{\text{(c)}})</td>
<td>44.254</td>
<td>12.586(^{\text{(c)}})</td>
<td>1.307×10(^3)(^{\text{(c)}})</td>
<td>3.853(^{\text{(c)}})</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>366.6(^{\text{(c)}})</td>
<td>21.476×10(^3)(^{\text{(c)}})</td>
<td>58.573</td>
<td>14.855(^{\text{(c)}})</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{\text{(a)}}\) According to Spaght et al.\(^\text{(10)}\).

\(^{\text{(b)}}\) According to Timmermans\(^\text{(11)}\).

\(^{\text{(c)}}\) According to Finke et al.\(^\text{(12)}\).

$T_m$, $\Delta h_f^\text{m}$, $\Delta S_f^\text{m}$ and $\Delta C_p^\text{l}$ are values at the triple point.
TABLE 5

Solubility Parameters and Molar Liquid Volumes of Solids and Liquids at the Melting Points of the Solids

<table>
<thead>
<tr>
<th>Solids</th>
<th>$T_m$ K</th>
<th>$10^{-4} \delta_2$</th>
<th>$10^6 V^l_2$</th>
<th>$10^{-4} \delta_1$</th>
<th>$10^6 V^l_1$</th>
<th>$10^{-4} \delta_3$</th>
<th>$10^6 V^l_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$(J \cdot m^{-3})^{1/2}$</td>
<td>$(m^3 \cdot mol^{-1})$</td>
<td>$(J \cdot m^{-3})^{1/2}$</td>
<td>$(m^3 \cdot mol^{-1})$</td>
<td>$(J \cdot m^{-3})^{1/2}$</td>
<td>$(m^3 \cdot mol^{-1})$</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>342.6</td>
<td>1.9304(a)</td>
<td>155.16(b)</td>
<td>1.7274(h)</td>
<td>94.57(i)</td>
<td>1.5473(h)</td>
<td>114.82(i)</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>352.8</td>
<td>1.9662(a)</td>
<td>130.86(c)</td>
<td>1.6959(h)</td>
<td>95.96(i)</td>
<td>1.5203(h)</td>
<td>116.89(i)</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>372.8</td>
<td>1.9772(a)</td>
<td>168.05(d)</td>
<td>1.6283(h)</td>
<td>98.65(i)</td>
<td>1.4501(h)</td>
<td>120.23(i)</td>
</tr>
<tr>
<td>Fluorene</td>
<td>37.6</td>
<td>1.8508(e)</td>
<td>163.70(f)</td>
<td>1.5817(h)</td>
<td>100.40(i)</td>
<td>1.4117(h)</td>
<td>122.33(i)</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>366.5</td>
<td>1.8930(e)</td>
<td>149.80(g)</td>
<td>1.6607(h)</td>
<td>99.64(h)</td>
<td>1.4845(h)</td>
<td>118.54(i)</td>
</tr>
</tbody>
</table>

(a) Enthalpy of vaporization was evaluated using the Clausius-Clapeyron equation with Antoine equation constants given by Reid et al.\(^{(13)}\)

(b) According to Timmermans\(^{(11)}\)

(c) According to Weast et al\(^{(14)}\), Reid et al\(^{(13)}\), and Dean\(^{(15)}\)

(d) Int. Crit. Tables\(^{(16)}\). Extrapolated by using equation 12-3.2 of Reid et al\(^{(13)}\)

(e) Antoine equation constants given by Dean\(^{(15)}\)

(f) According to McLaughlin and Ubbelohde\(^{(17)}\)

(g) According to Lange and Farkas\(^{(18)}\)

(h) From ref. 19.

(i) From ref. 20.
### TABLE 6
Binary Parameters Used in Equation (6)

<table>
<thead>
<tr>
<th>Solvent (1)</th>
<th>Solvent (2)</th>
<th>Solvent (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>Cyclohexane</td>
<td>Benzene</td>
</tr>
<tr>
<td>Solute (2)</td>
<td>Solute (2)</td>
<td>Solute (2)</td>
</tr>
<tr>
<td>£12</td>
<td>£23</td>
<td>£13</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>-.0005</td>
<td>.0004</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>.0036</td>
<td>-.0005</td>
</tr>
<tr>
<td>Fluorene</td>
<td>.0020</td>
<td>-.0020</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>-.0036</td>
<td>.0036</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>.0005</td>
<td>.0005</td>
</tr>
</tbody>
</table>
TABLE 7
Characteristic Energy Differences Used in Equation (13)

<table>
<thead>
<tr>
<th>Solute-(2)</th>
<th>Benzene-(1) $\Delta \lambda_{12}$ (J/mol)</th>
<th>Benzene-(1) $\Delta \lambda_{21}$ (J/mol)</th>
<th>Cyclohexane-(3) $\Delta \lambda_{32}$ (J/mol)</th>
<th>Cyclohexane-(3) $\Delta \lambda_{23}$ (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biphenyl</td>
<td>1,786.4</td>
<td>-1,270.7</td>
<td>2,139.0</td>
<td>1,449.7</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>2,436.8</td>
<td>-1,607.6</td>
<td>1,990.4</td>
<td>1,158.6</td>
</tr>
<tr>
<td>Fluorene</td>
<td>1,287.1</td>
<td>-412.1</td>
<td>3,605.9</td>
<td>1,190.4</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>494.8</td>
<td>397.5</td>
<td>2,942.5</td>
<td>780.4</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>1,680.2</td>
<td>-348.5</td>
<td>3,785.3</td>
<td>2,041.3</td>
</tr>
</tbody>
</table>

Benzene-(1) $\Delta \lambda_{14}$ (J/mol) = 771.4
Cyclohexane-(3) $\Delta \lambda_{31}$ (J/mol) = 417.5
APPENDIX E

Reprint of "Perturbation Theory of Liquids"

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Perturbation Theory of Liquids

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Department of Chemical Engineering
Louisiana State University
Baton Rouge, Louisiana 70803

†Supported by NSF grant #CPE-81-811287.

∗Supported by a postdoctoral fellowship from LSU - Baton Rouge.
Recently, Abascal and coworkers have developed an extended perturbation theory for diatomic liquids which combines the Weeks-Chandler-Andersen choice of reference potential with the Barker-Henderson choice of hard sphere diameter. Here we report results for the case of atomic liquids. This theory is shown to work well for atomic liquids at moderate densities, for \( \rho < 0.75 \). At higher densities, this theory is less accurate than the first order Barker-Henderson theory. Implications for perturbation theories involving molecular liquids are discussed.
Perturbation theories of Barker and Henderson\(^1\) (BH) and Weeks-Chandler-Andersen\(^2\) (WCA) are well established for atomic liquids and have also been extended to molecular fluids\(^3\)\(^-\)\(^6\) modeled by site-site potentials. Recently, Abascal et al.\(^6\) have proposed and tested a so-called BH-WCA theory, originally suggested by Gubbins et al.\(^7\), for diatomic liquids. The BH-WCA theory overpredicts the pressure at higher densities in these liquids and it is suggested\(^6\) that errors in the hard convex body equation of state of Boublik and Nezbeda\(^8\) may be the reason. Further, it is unclear whether the elongation ratio \(l/d\) for the hard diatomics should be the same as \(l/a\) for the soft diatomics\(^4\)\(^,\)\(^6\). Such uncertainties can be avoided by testing this theory for atomic liquids.

In the WCA theory\(^2\) the reference potential, \(U_o\), is given by

\[
U_o(r) = \begin{cases} 
U(r) + \epsilon & \text{for } r < r_{\text{min}} \\
0 & \text{for } r > r_{\text{min}} 
\end{cases}
\]

(1)

where \(U(r)\) is the full Lennard-Jones \((12\text{:}6)\) potential \(r_{\text{min}}\) is the pair separation at which \(U(r)\) is a minimum \((r_{\text{min}} = (2)^{1/6}\sigma)\) and \(\epsilon\) and \(\sigma\) are the usual Lennard-Jones parameters. Zwanzig’s first order expansion for the Helmholtz free energy, \(A\), leads to\(^9\)

\[
A = A_o + \frac{N\phi}{2} \int p(r) g_o(r) \, dr
\]

(2)

where \(p(r) = U(r) - U_o(r)\) is the perturbation potential.
In the case of atomic fluids the reference fluid is further approximated by a hard sphere fluid to obtain \( A_0 \) and \( g_0(r) \) to be used in (2). In the WCA theory the hard sphere diameter of such a fluid is obtained by solving a blip-function which requires a trial-and-error solution and involves multiple evaluations of the background correlation \( y_{HS}(r) \). To avoid this time consuming procedure Abascal et al. use the Barker-Henderson choice of the hard sphere diameter in conjunction with (1) and (2)

\[
d_{BH} = \frac{r_{\text{min}}}{\int_0^{r_{\text{min}}} |1 - e^{-\beta U_0(r)}| \, dr}
\]

Actually (3) is the zeroth order result of the WCA choice of diameter. In our tests for this theory we have used an equation of state for the hard sphere fluid given by Carnahan and Starling (the equation of Boublik and Nezbeda reduces to this) to obtain the Helmholtz free energy, \( A_0 = A_{HS} \). In addition, we have used the \( g(r) \) obtained from the solution of the Percus-Yevick equation for a hard sphere fluid and corrected by Verlet and Weis before using in (2). Figure 1 shows a comparison between the Helmholtz free energy from various perturbation theories and computer simulations at \( T^* = 1.35 \). Figure 2 shows a similar comparison for the compressibility factor. The BH-WCA theory shows agreement with simulation as good as the WCA theory at low densities, \( \rho^* < 0.7 \). However, as the density is increased, \( \rho^* < 0.7 \), the BH-WCA theory clearly deviates from simulation. In fact, for \( T^* = 2.74 \) (not shown) the first order BH theory (BH1) is better than the BH-WCA theory for \( \rho^* > 0.65 \).

Error bars in both these figures show the difference between the computer simulation results of Alder and Wainwright and the Carnahan-
Starling EOS\(^{11}\) for a hard sphere fluid. For the free energy this difference has a small contribution to the total error. For the pressure although this difference is now significant, it is by no means the major source of error; especially at high temperatures (\(T^* > 1.35\)).

Predictions for the pressure by Abascal et al\(^{6}\) for Lennard-Jones diatomics using the BH-WCA theory show similar trends. It is suggested that inaccuracies in the Boublik-Nezbeda EOS\(^{8}\) may be responsible for this problem. At least for atomic liquids this is not the case. One can expect that the use of an equation more accurate than the Boublik-Nezbeda equation\(^{8}\) coupled with the BH-WCA theory for molecular liquids would lead to results similar to atomic liquids. Thus one may prefer to use a BH type theory which has worked well\(^{6}\) for Lennard-Jones diatomics.

The theory of Fischer\(^{4}\) provides an interesting alternative. In this theory, the background correlation function obtained from the numerical solution of the Percus-Yevick equation for the soft-reference fluid is used in the solution of the blip function. The disadvantage of numerically solving the PY equation is offset by the fact that only one solution is required. This idea can be easily extended to perturbation theories based upon site-site distribution functions. Recently, Monson\(^{15}\) has solved the site-site type Percus-Yevick equation for diatomics using Gillan's method\(^{16}\). Abascal et al\(^{6}\) have already given the blip function needed to evaluate \(A_0\) for such theories.
Figure 1: Comparison of the BH-WCA theory (triangles) with the BH1 theory (circles), the WCA theory (squares), and computer simulations (line) for the Helmholtz free energy at $kT/\varepsilon = 1.35$. 
Figure 2: Comparison of the BH-WCA theory (triangles) with the BH1 theory (circles), the WCA theory (squares), and computer simulations (line) for the compressibility factor at $kT/\varepsilon = 1.35$. 
APPENDIX F

Preliminary Experimental Vapor Phase Studies

An attempt has been made to experimentally determine the vapor phase composition of both pure and mixed solute systems, and the preliminary results obtained for the methane-water system are presented here.

Two of the many problems that have to be overcome are to minimize the effect of withdrawing a sample on the equilibrium conditions of the system and the possibility of adsorption of solvent from the sample and the corresponding experimental uncertainties. However, by far the biggest difficulty was found in determining the response factor of the gas sample. To a first approximation the solvent concentration decreases in proportion to the reciprocal of the system pressure, therefore, at the highest pressures used in this study the concentration of solvent in the gaseous phase will be approximately three orders of magnitude less than the concentration of the same system at standard conditions. For this reason determining the G.C. response factor using standard solutions was prohibitively difficult and an alternative method had to be found.

Vapor Phase Sampling Procedure

The vapor phase is sampled by a procedure somewhat similar to that for the liquid phase. The equilibrium cell is evacuated and filled with fresh distilled water, degassed and the solute gas compressed to the desired conditions as described previously. However, instead of rocking the cell and risking entrainment of liquid on the internal vapor
sampling line, the cell is left to stand for at least 24 hours in the near-vertical position. After this time all gas sampling lines from V-13 to V-19 and from V-13A to V-27 are evacuated. These lines are also heated by heat-tracing to a temperature greater than that of the equilibrium cell to prevent condensation of any solvent during sampling. The equilibrium cell is then opened to the gas sampling line through V-13 and a vapor sample trapped between V-13 and V-19. This procedure causes a drop in pressure of the system, which together with the elevated temperatures of the sampling lines ensures that the partial pressure of water in the gas phase is always lower than its equilibrium saturation pressure and thus prevents water vapor from condensing in the gas sampling line. The vapor sample is then released into the teflon gas buret system (see figure F.1) through the 3-way valve V-13A and the composition determined directly by gas chromatography. A teflon system was used as opposed to glass systems of previous investigators, to reduce (if not remove) the problem of adsorption of water from the vapor onto the surface of the glassware, which can result in uncertainty of the measured water content in the vapor sample.

Table F.1 gives the G.C. reported area % values, $a_1$, for a series of pressures of the methane-water vapor phase system at 323k. These values are plotted in figure F.2 and do indeed follow, to some degree, the proportionality with respect to pressure discussed earlier. In figure F.3 these results are plotted as $a_1 P/P^s_1$, where $P^s_1$ is the solvent vapor pressure at the system temperature of 323k, and compared to the literature values of Rigby and Prausnitz\(^{(1)}\) plotted as $y_1 P/P^s_1$.

Extrapolating the data shown in figure F.3 to coincide with the value corresponding to that for Raoult's Law given by equation F.1
TABLE F.1

$T = 323k$

<table>
<thead>
<tr>
<th>Pressure /MPa</th>
<th>G.C. Area, $a_1$ /%</th>
<th>$(a_1 P/P_S)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.76</td>
<td>0.092</td>
<td>0.206</td>
</tr>
<tr>
<td>4.14</td>
<td>0.068</td>
<td>0.228</td>
</tr>
<tr>
<td>5.51</td>
<td>0.053</td>
<td>0.237</td>
</tr>
<tr>
<td>6.89</td>
<td>0.044</td>
<td>0.246</td>
</tr>
<tr>
<td>8.27</td>
<td>0.036</td>
<td>0.242</td>
</tr>
<tr>
<td>9.65</td>
<td>0.030</td>
<td>0.235</td>
</tr>
<tr>
<td>11.03</td>
<td>0.025</td>
<td>0.224</td>
</tr>
<tr>
<td>12.41</td>
<td>0.021</td>
<td>0.224</td>
</tr>
<tr>
<td>13.79</td>
<td>0.018</td>
<td>0.201</td>
</tr>
</tbody>
</table>
Figure F.1  Vapor Phase Sample Analysis
\[
\frac{y_1^p}{p^s_1 P^0} = 1.0 \tag{F.1}
\]

indicates that a value for the response factor, R.F, defined according to equation F.2,

\[
R.F. = \frac{a_1}{y_1} \tag{F.2}
\]
of approximately 6 is required. It is understood that this procedure does not provide an 'a priori' value for the response factor, and further it requires independent experimental data. However, as in the case of Rigby and Prausnitz\(^{(1)}\), this data may be obtained using apparatus and procedures avoiding the need for the calibration of analytical equipment.

Preliminary results, in terms of the G.C. reported area-percent of the vapor phase compositions for the three gas mixtures with water are given in tables F.2 to F.4. Once the uncertainty in the determination and values of the response factor of water in the vapor phase has been resolved, the corresponding vapor phase compositions may be calculated.
Figure F.2  G.C. Reported Area Percent Versus Pressure
Figure F.3  Uncorrected G.C. Reported Concentrations (circles) Compared to Literature Mole Fraction Values (triangles)
### Table F.2

**Vapor Phase Compositions (Area %) for 25% CH\(_4\) - 75% N\(_2\)/H\(_2\)O System**

\(T = 323\text{K}\)

<table>
<thead>
<tr>
<th>Pressure /MPa</th>
<th>H(_2)O Area %</th>
<th>CH(_4) Area %</th>
<th>N(_2) Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.50</td>
<td>0.059</td>
<td>19.969</td>
<td>79.971</td>
</tr>
<tr>
<td>21.85</td>
<td>0.048</td>
<td>19.965</td>
<td>79.978</td>
</tr>
<tr>
<td>21.64</td>
<td>0.047</td>
<td>19.988</td>
<td>79.965</td>
</tr>
<tr>
<td>42.25</td>
<td>0.032</td>
<td>19.997</td>
<td>79.970</td>
</tr>
<tr>
<td>42.32</td>
<td>0.028</td>
<td>20.011</td>
<td>79.959</td>
</tr>
<tr>
<td>43.63</td>
<td>0.040</td>
<td>19.981</td>
<td>79.977</td>
</tr>
<tr>
<td>63.21</td>
<td>0.033</td>
<td>20.013</td>
<td>79.952</td>
</tr>
<tr>
<td>63.69</td>
<td>0.038</td>
<td>20.015</td>
<td>79.946</td>
</tr>
<tr>
<td>63.21</td>
<td>0.048</td>
<td>20.053</td>
<td>79.921</td>
</tr>
<tr>
<td>84.64</td>
<td>0.042</td>
<td>20.027</td>
<td>79.931</td>
</tr>
<tr>
<td>84.02</td>
<td>0.044</td>
<td>20.026</td>
<td>79.929</td>
</tr>
<tr>
<td>83.95</td>
<td>0.054</td>
<td>20.030</td>
<td>79.914</td>
</tr>
<tr>
<td>104.70</td>
<td>0.048</td>
<td>20.034</td>
<td>79.916</td>
</tr>
<tr>
<td>104.77</td>
<td>0.050</td>
<td>20.044</td>
<td>79.905</td>
</tr>
<tr>
<td>104.56</td>
<td>0.048</td>
<td>20.049</td>
<td>79.905</td>
</tr>
<tr>
<td>124.34</td>
<td>0.050</td>
<td>20.032</td>
<td>79.916</td>
</tr>
<tr>
<td>126.96</td>
<td>0.043</td>
<td>20.046</td>
<td>79.909</td>
</tr>
<tr>
<td>125.17</td>
<td>0.046</td>
<td>20.045</td>
<td>79.908</td>
</tr>
</tbody>
</table>
### Table F.3

**Vapor Phase Compositions (Area %) for 50% CH₄ - 50% N₂/H₂O System**

\[ T = 323k \]

<table>
<thead>
<tr>
<th>Pressure /MPa</th>
<th>H₂O</th>
<th>CH₄</th>
<th>N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>22.13</td>
<td>0.096</td>
<td>42.695</td>
<td>57.209</td>
</tr>
<tr>
<td>22.47</td>
<td>0.077</td>
<td>42.672</td>
<td>57.251</td>
</tr>
<tr>
<td>21.50</td>
<td>0.092</td>
<td>42.686</td>
<td>57.222</td>
</tr>
<tr>
<td>41.98</td>
<td>0.042</td>
<td>42.710</td>
<td>57.249</td>
</tr>
<tr>
<td>42.87</td>
<td>0.042</td>
<td>42.683</td>
<td>57.275</td>
</tr>
<tr>
<td>43.42</td>
<td>0.055</td>
<td>42.700</td>
<td>57.245</td>
</tr>
<tr>
<td>62.79</td>
<td>0.034</td>
<td>43.052</td>
<td>56.914</td>
</tr>
<tr>
<td>59.21</td>
<td>0.026</td>
<td>43.018</td>
<td>56.954</td>
</tr>
<tr>
<td>60.52</td>
<td>0.026</td>
<td>43.020</td>
<td>56.946</td>
</tr>
<tr>
<td>79.68</td>
<td>0.024</td>
<td>43.064</td>
<td>56.910</td>
</tr>
<tr>
<td>82.85</td>
<td>0.022</td>
<td>43.031</td>
<td>56.944</td>
</tr>
<tr>
<td>83.88</td>
<td>0.023</td>
<td>43.059</td>
<td>56.916</td>
</tr>
<tr>
<td>103.80</td>
<td>0.038</td>
<td>43.109</td>
<td>56.851</td>
</tr>
<tr>
<td>102.49</td>
<td>0.042</td>
<td>43.110</td>
<td>56.855</td>
</tr>
<tr>
<td>102.01</td>
<td>0.029</td>
<td>43.126</td>
<td>56.842</td>
</tr>
<tr>
<td>128.48</td>
<td>0.032</td>
<td>43.139</td>
<td>56.825</td>
</tr>
<tr>
<td>126.55</td>
<td>0.030</td>
<td>43.132</td>
<td>56.845</td>
</tr>
<tr>
<td>126.34</td>
<td>0.035</td>
<td>43.110</td>
<td>56.853</td>
</tr>
</tbody>
</table>
Table F.4

Vapor Phase Composition (Area %) for 75% CH₄ - 25% N₂/H₂O System

\( T = 323K \)

<table>
<thead>
<tr>
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<th>CH₄ (Area %)</th>
<th>N₂ (Area %)</th>
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References

(1) Rigby, M. and J.M. Prausnitz,
"Solubility of Water in Compressed Nitrogen, Argon and Methane"
Christopher Paul Williams was born in Willenhall, England on the fifteenth day of July 1960, the second son of Alec and Emily Joyce Williams. He attended Queen Mary's Grammar School for Boys in Walsall, England for seven years before leaving in 1978 with four A-levels. He entered the Department of Chemical Engineering at the University of Exeter in the beautiful county of Devon, England in October 1978 and graduated in June of 1981 with a first class Bachelor of Science Honours degree and was awarded the department prize. In August of 1981, he crossed the Atlantic Ocean and joined the Department of Chemical Engineering at Louisiana State University, Baton Rouge, Louisiana, as a graduate student. He received a Master of Science degree in Chemical Engineering in the summer of 1984 and is presently a candidate for the degree of Doctor of Philosophy again in Chemical Engineering.

The author has accepted a position as a research engineer at the Royal Dutch Shell Laboratories (KSLA) in Amsterdam, The Netherlands.
DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Christopher Paul Williams

Major Field: Chemical Engineering

Title of Dissertation: Classical and Statistical Thermodynamics of Gas Solubility in Polar Fluids

Approved:

[Signatures]

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination:

March 16, 1987