ornl

ORNL/TM-11501

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES

3 4456 0348636 9

OAK RIDGE NATIONAL LABORATORY

MARTIN MARIETTA

Chemical Potentials from Integral Equations Using Scaled Particle Theory

D. M. Pfund
H. D. Cochran

OAK RIDGE NATIONAL LABORATORY
CENTRAL RESEARCH LIBRARY
CIRCULATION SECTION
4500N ROOM 175
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this report, send in name with report and the library will arrange a loan.

OPERATED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615) 576-8401, FTS 626-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.
NTIS price codes—Printed Copy: A12 Microfiche A01

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ORNL/TM-11501

Chemical Technology Division

CHEMICAL POTENTIALS FROM INTEGRAL EQUATIONS USING SCALED PARTICLE THEORY

D. M. Pfund*
H. D. Cochran

*Department of Chemical Engineering and Materials Sciences, University of Oklahoma, Norman, Oklahoma 73069.

This report was prepared as a dissertation and submitted to the faculty of the Graduate School of the University of Oklahoma in partial fulfillment of the degree of Doctor of Philosophy in Chemical Engineering. This work was supported, in part, by the Division of Chemical Sciences, USDOE, under subcontract with the University of Oklahoma. Part of the work was performed at ORNL during the summers of 1987 and 1988 under the aegis of ORAU.

Date Published–April 1990

Prepared by the
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831
operated by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES

3 4456 0348636 9

TABLE OF CONTENTS

	page
LIST OF TABLES	iv
LIST OF ILLUSTRATIONS	vii
ABSTRACT	x
CHAPTER	
I. Introduction	1
II. Theory	25
III. Results	57
IV. Conclusions and Recommendations	91
BIBLIOGRAPHY	96
ACKNOWLEDGEMENTS	99

LIST OF TABLES

TABLE		page
1	Comparison of the Proposed Method Using the HNC Theory to Known HNC Results for Pure Lennard-Jones Fluids	100
2	Comparison Between Exact and SPT Values for the Work of Inserting the Hard Point in the HNC Approximation	101
3	Comparison Between Exact and SPT Pair Correlation Functions at Contact With the Hard Point in the HNC Approximation	102
4	Upper Bounds on the HMSA Bridge Function Integrals in Lennard-Jones Fluids	103
5	The Effect of the Choice of Effective Hard Sphere Diameters on the Calculated Repulsive Contribution to the Chemical Potential	104
6	Comparison Between the Rogers-Young and Verlet-Weis Equations of State for Pure WCA Repulsive Fluids	105
7	Comparison of Free Energies From the Method Using Rogers-Young Theory to Known (Verlet-Weis) Results for Pure WCA Repulsive Fluids	106
8	Comparison Between Exact and SPT Pair Correlation Functions at Contact With the Hard Point in the Rogers-Young Approximation	107
9	Comparison of Free Energies From the Method to Thermodynamic Integration of the Rogers-Young Equation of State For Pure WCA Repulsive Fluids	108
10	Densities Required for Isobaric Formation of Some WCA Repulsive Mixture - A Comparison of Rogers-Young Densities to Simulation	109
11	Residual Chemical Potentials in Mixtures of WCA Repulsive Particles	110
12	Free Energies of Mixing WCA Repulsive Particles	111

TABLE		page
13	Comparison of the Proposed Method Using HMSA Theory to Simulation Results for Pure Lennard-Jones Fluids	112
14	Comparison Between Exact and SPT Pair Correlation Functions at Contact With the Hard Point in the HMSA Approximation	113
15	Comparison Between the HMSA Equation of State for Pure Lennard-Jones Fluids and Molecular Simulation	114
16	Comparison of Chemical Potentials From the Proposed Method Using the HMSA Theory with Molecular Simulation Results for Pure Lennard-Jones Fluids	115
17	Comparison of Chemical Potentials From the Proposed Method Using the HMSA Theory with Results From Thermodynamic Integration for Pure Lennard-Jones Fluids	116
18	Compressibilities From the Proposed Method Using The HMSA Theory Compared to Results From the Compressibility Equation for Pure Lennard-Jones Fluids	117
19	Comparison of the Proposed Method Using The HMSA Theory to Simulation Results for Chemical Potentials at Infinite Dilution and Different Energy Ratios	118
20	Comparison of the Proposed Method Using The HMSA Theory to Simulation Results for Chemical Potentials at Infinite Dilution and Different Size Ratios	119
21	Effect of Size and Energy Ratios on the Predicted Chemical Potential for Near Critical States	120
22	The Lennard-Jones Parameters Used for the Finite Concentration Mixtures	121
23	The Volumetric Properties Predicted from HMSA Theory for Mixtures of Lennard-Jones Particles at Finite Concentrations Compared to Results from Molecular Simulation	122
24	Residual Chemical Potentials Predicted by the Proposed Method in Finite Concentration Mixtures Using the HMSA Integral Equation Theory	123
25	Chemical Potentials Predicted by the Method in Finite Concentration Mixtures Compared to Simulation Results	124

TABLE		page
26	The Predicted Chemical Potential of a Large, Attractive, Dilute Solute in a Near Critical Solvent	125

LIST OF ILLUSTRATIONS

FIGURE		page
1	Kirkwood Charging Scheme	126
2	Definition of the Reference System	127
3	Multi-Step Charging Scheme	128
4	Inserting the Hard Sphere	129
5	Pair Correlation Functions About an Inserted Hard Sphere	130
6	Softening the Hard Sphere	131
7	Integrand of the Work of Softening Formula	132
8	Charging the Attractive Potential	133
9	Rate of Change of Helmholtz Energy With Change in the Attractive Coupling	134
10	HMSA Pair Correlation Functions About the Effective Hard Sphere Compared to Those About the WCA Repulsive Test Particle - *Pure Lennard-Jones bath at at supercritical conditions*	135
11	HMSA Pair Correlation Functions About the Effective Hard Sphere Compared to Those About the WCA Repulsive Test Particle - *For a large test particle immersed in a pure Lennard-Jones bath at conditions near saturated liquid*	136
12	HMSA Pair Correlation Functions About the Effective Hard Sphere Compared to Those About the WCA Repulsive Test Particle - *Pure Lennard-Jones bath at at compressed liquid conditions*	137
13	HMSA Bridge Functions About the Effective Hard Sphere Compared to Those About the WCA Repulsive Test Particle - *Pure Lennard-Jones bath at at supercritical conditions*	138
14	HMSA Bridge Functions About the Effective Hard Sphere Compared to Those About the WCA Repulsive Test Particle - *For a large test particle immersed in a pure Lennard-Jones bath at conditions near saturated liquid*	139

FIGURE		page
15	HMSA Bridge Functions About the Effective Hard Sphere Compared to Those About the WCA Repulsive Test Particle - *Pure Lennard-Jones bath at at compressed liquid conditions*	140
16	Predicted Excess Gibbs Free Energies of Mixing Softly Repulsive (WCA) Fluids	141
17	Compressibility Factors in Pure Lennard-Jones Fluids	142
18	Predicted Residual Gibbs Free Energies in Pure Lennard-Jones Fluids Compared With Simulation	143
19	Predicted Residual Gibbs Free Energies in Pure Lennard-Jones Fluids Compared With Simulation - *High Density Range*	144
20	Predicted Residual Gibbs Free Energies Compared to Thermodynamic Integration For Pure Lennard-Jones Fluids	145
21	Predicted Residual Chemical Potentials of a Dilute Lennard-Jones Solute in a Lennard-Jones Solvent versus Energy Ratio	146
22	Predicted Residual Chemical Potentials of a Dilute Lennard-Jones Solute in a Lennard-Jones Solvent versus Size Ratio	147
23	HMSA Pair Correlation Functions About a Large, Dilute, Lennard-Jones Solute in a Lennard-Jones Solvent Compared to Molecular Simulation - *For a solvent near saturated liquid conditions*	148
24	HMSA Pair Correlation Functions About a Large WCA Repulsive Test Particle in a Lennard-Jones Bath Compared to to Molecular Simulation - *For a bath near saturated liquid conditions*	149
25	HMSA Pair Correlation Functions About a Small WCA Repulsive Test Particle in a Lennard-Jones Bath Compared to to Molecular Simulation - *For a bath near saturated liquid conditions*	150
26	HMSA Pair Correlation Functions About a Small WCA Repulsive Test Particle in a Lennard-Jones Bath Compared to to Molecular Simulation - *For a bath near the critical point*	151
27	HMSA Pair Correlation Functions About a Small WCA Repulsive Test Particle in a Lennard-Jones Bath Compared to to Molecular Simulation - *For a compressed liquid bath*	152

FIGURE		page
28	HMSA Pair Correlation Functions in a Lennard-Jones Mixture Compared to Molecular Simulation - *A model of carbon dioxide and acetone*	153
29	HMSA Pair Correlation Functions in a Lennard-Jones Mixture Compared to Molecular Simulation - *A model of carbon dioxide and acetone (cont.)*	154
30	HMSA Pair Correlation Functions in a Lennard-Jones Mixture Compared to Molecular Simulation - *A model of carbon dioxide and acetone (cont.)*	155

ABSTRACT

A new method is presented for calculating chemical potentials using integral equation theories. The method uses a multi-step charging process which allows attractive and repulsive contributions to the chemical potential to be determined separately. Integral equation theories are used to provide needed correlation functions about the test particle. A novel application of particle scaling is used to determine the repulsive contribution to the chemical potential. A formal definition is given for the effective hard core diameter of a softly repulsive solute. A simple Kirkwood charging process is used to determine the attractive contribution. The method provides accurate chemical potentials in mixtures of softly repulsive WCA particles when used with the HMSA/Rogers-Young integral equation. Calculated excess Gibbs energies agreed with WCA repulsive simulations to an average of -0.67% for 2:1 diameter ratio mixtures. The method provides approximate results in Lennard-Jones mixtures when used with the HMSA integral equation. Results for supercritical isotherms reproduce simulation data to an average of -3.0%. For subcritical isotherms, vapor results are exact while liquid results are qualitatively correct. The method used with the HMSA theory correctly predicts the effect of energy ratio on the Henry's Law constant. The predicted effect of size ratio on the constant has an incorrect slope at subcritical temperatures when the solvent density is near the value for a saturated liquid. The incorrect slope reflects an inconsistency in the HMSA theory.

CHEMICAL POTENTIALS FROM INTEGRAL EQUATIONS USING SCALED PARTICLE THEORY

CHAPTER I

INTRODUCTION

The basic problem of statistical mechanics is to determine the properties of a fluid when the forces between molecules are known. Only recently have methods been devised for and applied to the calculation of chemical potentials. These approaches are based on molecular simulation or on perturbation theories and have limitations. Rigorous, though computationally intensive approaches are based on molecular simulation. Since molecular simulations can deal with only a small number of particles and generate only a sample of the population of particle configurations, the computed results have a degree of statistical uncertainty which is difficult to quantify. These uncertainties can sometimes be reduced by increasing the number of particles in the simulation or by increasing the run time. In other cases the statistical uncertainties can only be reduced by trying alternative methods designed to deliberately sample different regions of configuration space. The periodic boundary conditions used in molecular simulations to eliminate wall effects introduce unrealistic periodicities which makes the simulation of states near the critical point difficult. Perturbation theories require the similarity of the structure of the fluid to that of a reference

fluid; this similarly breaks down near the critical point or when there are very strong interparticle forces that are not present in the reference fluid. Discussed below are some of the well studied methods based on molecular simulation or on perturbation theories. Within their regions of applicability methods of these types can be used to test the accuracy of alternative techniques for estimating chemical potentials.

A method which is frequently used with molecular simulations is the test particle method of Widom[1]. The technique requires little modification of existing simulations. In this method the residual chemical potential of species i is given by:

$$\frac{\mu_i - \mu_i^*}{kT} = -\ln\left\langle \exp(-\beta\Phi_i^f)\right\rangle_{NVT} \tag{1}$$

where μ_i^* is the chemical potential of an ideal gas at the temperature, density and composition of interest and $\beta = 1/kT$. Φ_i^f is the potential energy between a "ghost" test particle and the molecules in the fluid and the angle brackets denote the average value in the canonical (constant N, V, T) ensemble. A ghost test particle is a static measuring device introduced into the simulation which has the potential energy of a molecule of species i but which does not alter the trajectories of the surrounding particles. The Widom method has a disadvantage in that it is difficult to determine the statistical accuracy of the computed result. There is also an "inverse Widom" relationship which gives the residual chemical potential in terms of the average of the potential energies Φ_i^r of the real particles in the simulation[2]:

$$\frac{\mu_i - \mu_i^*}{kT} = \ln\left\langle \exp(\beta\Phi_i^r)\right\rangle_{NVT} \tag{2}$$

By "real particles" in this context it is meant that those particles are part of the simulation of the mixture. They have trajectories which can influence and are influenced by those of the

other particles in the simulation. The inverse Widom relationship is seldom applied directly since large values of Φ_i^r are inadequately sampled by molecular simulations at high densities.

The Widom method has been applied to the calculation of residual chemical potentials in pure Lennard-Jones fluids[3] and in Lennard-Jones mixtures at infinite dilution[4,5]. Heinbuch and Fischer[3] have found that the method yielded results with a uncertainty of about 0.1 kT for pure fluids with reduced densities $\rho\sigma^3$ less than 0.7. The uncertainty was about 0.2 kT for $\rho\sigma^3$ between 0.8 and 0.85. These uncertainties were estimated by comparing the results to those obtained from a trusted perturbation theory (these theories are described below). Lotfi and Fischer[4] found that a large cut-off size, a large number of particles, and a very large number of time steps were required in order to obtain a reproducable result for large solutes in mixtures at infinite dilution. Shing, Gubbins, and Lucas[5] found that the Kirkwood method (described below) is preferable to the Widom method at moderate to high densities and for extemely non-ideal mixtures.

The method of Powles[6,7] is more complex than the Widom method but has the advantage of providing a measure of the statistical uncertainty in the computed chemical potential at the state of interest. In this method the weighting functions f and g [2] which are implicit in the Widom and inverse Widom equations are explicitly determined:

$$\left\langle \exp(-\beta\Phi_i^f) \right\rangle = \int f(\Phi_i^f) \exp(-\beta\Phi_i^f)\, d\Phi_i^f \tag{3}$$

$$\left\langle \exp(\beta\Phi_i^r) \right\rangle = \int g(\Phi_i^r) \exp(\beta\Phi_i^r)\, d\Phi_i^r \tag{4}$$

f(u) is the probability that a ghost test particle experiences a potential energy between u and u + du. g(u) is the probability that a real particle experiences a potential energy between u and u + du. Shing and Gubbins[2] noted a relationship (used by Powles, Evans, and Quirke[6])

between the temperature, the functions f and g, and the residual chemical potential:

$$L(u) \equiv \ln\left[{}^{f(u)}\!/_{g(u)}\right] = \beta u - \beta(\mu_i - \mu_i^*) \tag{5}$$

A plot of estimated L(u) values versus u should have a slope of $\beta = 1/kT$ and an intercept equal to the negative of the residual chemical potential divided by kT. Such plots are indeed very linear with the correct slope except at very large and very small values of u. The method has the disadvantage that redundant information must be accumulated which are sufficient to determine (imprecisely) the chemical potential from both the Widom and inverse Widom relationships. In addition, the values of f and g must be estimated for enough points in order to estimate the intercept to within a small confidence interval. The confidence interval on the intercept then provides a measure of the statistical uncertainty in the reported chemical potential.

Panagiotopoulos, Suter, and Reid[7] applied Powles' method to the computation of chemical potentials in pure and mixed Lennard-Jones fluids. They reported uncertainies in the computed chemical potentials which increased with density, becoming approximately 0.3 kT at $\rho\sigma^3 = 0.8$. The results for mixtures were found to be accurate to within 0.1 kT over the conditions examined. They applied the method to the determination of phase coexistence curves and found that the curves for mixtures of acetone and carbon dioxide could be qualitatively modelled using Lennard-Jones potentials.

The Kirkwood charging method is based on a technique which changes the identity of some of the particles in the simulation. For instance, a pure fluid may be converted into a mixture. The changing identity of the particles is measured by a parameter λ, referred to as a coupling parameter. Thus, the potential energy U of the system is a function of the

configuration of the system and the value of the coupling parameter:

$$U = U(\mathbf{r}^N;\lambda) \tag{6}$$

When the NVT ensemble is used the Helmholtz free energy change which occurs during this process is given by:

$$A(\lambda_1) - A(\lambda_0) = \int_{\lambda_0}^{\lambda_1} \left\langle \frac{\partial U}{\partial \lambda} \right\rangle_{NVT} d\lambda \tag{7}$$

Similarly, when the isothermal, isobaric NPT ensemble is used the Gibbs free energy change is:

$$G(\lambda_1) - G(\lambda_0) = \int_{\lambda_0}^{\lambda_1} \left\langle \frac{\partial U}{\partial \lambda} \right\rangle_{NPT} d\lambda \tag{8}$$

Shing[5] et. al. used equation (7) to compute the free energy change when one particle in a pure fluid is converted into a solute particle. The result was the difference between the residual chemical potential of the solute at infinite dilution and the residual chemical potential of the original pure fluid. Shukla and Haile[8,9] have used equation (8) in the computation of excess Gibbs free energies of mixing at constant temperature and pressure. The mixing property was obtaining by computing the free energy differences between each of the pure fluids and the mixture and mole fraction averaging the results. Kirkwood charging methods are numerically intensive because the integrations in equation (7) and (8) require a number of separate simulations to generate the integrand at points between λ_0 and λ_1. The multitude of simulations and the numerical integration make it difficult to determine the uncertainty in the results[5]. The precision of the results is obtained by these methods is often judged from comparisons with perturbation theories.

In perturbation theory, the Helmholtz free energy of a model fluid is written as an expansion about that of a reference fluid whose properties are known. The goal of perturbation theory is to choose a reference fluid with a microscopic structure that closely approximates that of the fluid of interest, allowing the expansion to be truncated after the first order. The chemical potential of a species can then be determined from the Helmholtz free energy by differentiating with respect to species mole number at constant temperature and volume. The theory of Weeks, Chandler, and Andersen[10] (WCA) involved dividing the intermolecular pair potential into a short-ranged, softly repulsive component u_{ij}^{o} and a long-ranged attractive component u_{ij}^{1}. The free energy A of the fluid was then written as an expansion about that of a softly repulsive reference fluid[11],

$$\frac{A - A^0}{NkT} = \frac{\beta\rho}{2} \sum_{i,j} x_i x_j \int_0^{+\infty} g_{ij}^0(r) u_{ij}^1(r)\, 4\pi r^2\, dr + \ldots \tag{9}$$

where A^o denotes the free energy of a fluid whose particles interact only with the repulsive component of the potential u_{ij}^{o}. The g_{ij}^{o} are the pair correlation functions (discussed in detail below) of the reference fluid at the temperature and density of interest. These functions describe the structure of the reference fluid. The first order truncation of the series in equation (9) is accurate under state conditions where the structure of the reference fluid approximates that of the fluid of interest: $g_{ij}^{o} \approx g_{ij}$. This situation prevails at high (liquid-like) densities because, as the molecules of a fluid pack closely together, their strong mutual repulsions dominate the determination of fluid structure. Under such conditions the WCA attractive potential only slightly perturbs the structure determined by the repulsive forces. The free energy A^o of the WCA repulsive fluid is in turn approximated by that of a hard sphere fluid

with appropriately chosen effective hard sphere diameters. The free energy of the hard sphere fluid is then given by the accurate equation of state due to Carnahan and Starling[12,13]. Accurate procedures for estimating A^0 and the pair correlation functions in the reference fluid were given by Verlet and Weis[14] for pure fluids and by Lee and Levesque[11] for mixtures. Modifications of these theories have been proposed which slightly improve the accuracy and thermodynamic consistency of the results[15]. A disadvantage of perturbation theories is that the truncation of the free energy expansion at the first order is inaccurate near the critical point of the fluid and when intermolecular attractions are strong. For such systems the structure of the fluid of interest as measured by g_{ij} is not approximated well by g_{ij}^0.

Recent advances in integral equation theories for molecular correlation functions and in methods for solving the equations suggest that it is possible to use them to predict chemical potentials. These theories provide a means of estimating the pair and direct correlation functions in a fluid. These functions depend on the relative positions of two molecules irrespective of the positions of the others and irrespective of molecular orientations (when the molecules are non-spherical). Thermodynamic properties can be estimated from these functions using the relationships provided by statistical mechanics. Integral equation theories combine the use of the Ornstein-Zernicke (OZ) integral equation which is an exact defining relationship between the direct and total correlation functions and a "closure" equation which is an approximate one. The OZ equation is written in terms of a convolution integral[16],

$$h_{ij}(r) - C_{ij}(r) = \rho_1 \int_V C_{i1}(\mathbf{r}_i, \mathbf{r}_1) h_{1j}(\mathbf{r}_1, \mathbf{r}_j)\, d\mathbf{r}_1 + \rho_2 \int_V C_{i2}(\mathbf{r}_i, \mathbf{r}_2) h_{2j}(\mathbf{r}_2, \mathbf{r}_j)\, d\mathbf{r}_2 \tag{10}$$

where the intermolecular separation distance is $r = \| \mathbf{r}_i - \mathbf{r}_j \|$ and the equation has been written for the case of a binary mixture. h_{ij} is called the total correlation function and is defined by $h_{ij} = g_{ij} - 1$, where g_{ij} is the pair correlation (or radial distribution) function. The pair correlation function is defined so that $\rho_i g_{ij}(\mathbf{r}_i,\mathbf{r}_j)$ is the local density of species i at position $\mathbf{r}_i$ surrounding a molecule of species j at position $\mathbf{r}_j$ [17]. Because of the attractive field which surrounds a molecule, this local density is greater than the average bulk density for separation distances in the neighborhood of the potential mininum. Ordering in the fluid (such as the ordered packing of hard spheres) also causes the local density of the nearest neighbors of a molecule to be higher that the bulk value. Thus g_{ij} is greater than 1.0 for these separation distances. For small separation distances the field becomes strongly repulsive, and the local density is reduced. The pair correlation function is less than one for small separations, becoming zero in the limit of particle coincidence. At very large separation distances the field approaches zero, the local density of species i approaches the bulk average ρ_i and g_{ij} approaches 1.0. Two special cases of interest are:

1. Ideal gases. In this case there are no forces between the particles and $g_{ij} = 1$ for all separation distances.
2. Low pressure gases. In this case the probability of more than two molecules being in the same neighborhood is very small. Then the probability of an arbitrary pair of molecules being a given distance r apart equals the Boltzmann factor, which is : $\exp[u_{ij}(r)/kT] = g_{ij}$, where u_{ij} is the intermolecular pair potential.

C_{ij} is called the direct correlation function and equation (10) can be considered as its definition. Alternatively, as described by Percus[18], the direct correlation function can be

defined in terms of the rate of variation in the required pair potential with respect to independent variations in the local density (a functional density derivative). From this alternative definition of C_{ij} the OZ equation (10) can be derived. Thus, the direct correlation function appears as part of the solution to the problem of how the local density of the fluid around a field source (such as another molecule) varies with the potential energy between the source and the molecules of the fluid. At low densities the direct correlation function approaches the Mayer factor, $\exp[-u_{ij}/kT] - 1$. Thus it approaches -1 at small separation distances where the potential is large and approaches $-u_{ij}/kT$ at large separations where the magnitude of the potential is small. The long range behavior of the direct correlation function changes little as the density is increased; the function at small separation distances becomes much more negative.

Equation (10) is solved numerically together with a closure equation. The closure equation implicitly contains all of the approximations in the theory being used. It is an approximate relation between the direct correlation function and the total correlation function. Such relationships have been created by choosing an objective (or "generating functional") which is some functional of the local density and potential energy due to a field source, and taking the functional Taylor expansion of it in powers of the difference between the local and bulk average densities[18]. In this way a relationship between the local density, the direct correlation function, and the pair potential can be obtained. Truncating the expansion after the first order yields the desired simplified closure.

Different generating functionals yield different closures, which may differ in their suitabilities for pair potentials of varying sign and steepness. One such closure is the hypernetted chain (HNC) equation[19],

$$C_{ij} = h_{ij} - \ln(y_{ij}) \tag{11}$$

where y_{ij} is called the background correlation function and is defined as $y_{ij} = g_{ij}\exp(u_{ij}/kT)$. Each of the functions in equation (11) is dependent on the intermolecular separation distance. HNC theory was commonly used at low densities and for systems containing both attractive (or long range) and repulsive (or short range) forces. Another such closure is the Percus-Yevick (PY) equation[19]:

$$C_{ij} = 1 + h_{ij} - y_{ij} \tag{12}$$

PY theory was commonly used for systems containing only short range repulsive forces such as mixtures of hard spheres. Both the PY and HNC theories become more accurate as the density is reduced; from each of them exact second and third virial coefficients can be derived[19]. They approach each other at low densities since in this case the background correlation function approaches 1. The PY equation (12) yields a direct correlation function which has a finite range if the pair potential has a finite range (since in that case, for large enough separations $g_{ij} = y_{ij}$). The HNC direct correlation function does not vanish at large separation distances even if the pair potential does[19].

One numerical method used to simultaneously solve the OZ and closure equations is that due to Labik et. al.[20]. This method is a combination of Newton and direct iterations that involves decomposing $h_{ij} - C_{ij}$ into coarse and fine parts. The coarse part is described as a series of basis functions, the coefficients of which are found by Newton's method. The fine part is found by fixed point iterations in Fourier transform space.

Thermodynamic properties can be obtained from the correlation functions by using the relations of statistical mechanics. For example, the residual (sometimes referred to as

configurational) internal energy of the fluid is given by[21]:

$$\frac{U-U^*}{NkT}=\left(\frac{\rho}{2kT}\right)\int_0^{+\infty}\left(x_1^2u_{11}g_{11}+2x_1x_2u_{12}g_{12}+x_2^2u_{22}g_{22}\right)4\pi r^2dr \tag{13}$$

Both the PY and HNC theories yield reasonably accurate predictions of the internal energy. However, for some properties thermodynamically inconsistent results can occur because the closure relation is approximate. In particular, properties obtained from the pair correlation functions tend to differ from those obtained from the direct correlation functions. If a comparison is made between the pressure computed from the virial equation[21],

$$\frac{P}{\rho kT}=1-\left(\frac{1}{6\rho kT}\right)\int_0^{+\infty}\left(\rho_1^2u_{11}'g_{11}+2\rho_1\rho_2u_{12}'g_{12}+\rho_2^2u_{22}'g_{22}\right)4\pi r^3dr \tag{14}$$

(where the prime superscript denotes a derivative with respect to r) and the pressure computed by integrating the compressibility equation,

$$\frac{1}{kT}\left(\frac{\partial P}{\partial\rho}\right)_{T,V}=1-\frac{1}{\rho}\int_0^{+\infty}\left(\rho_1^2C_{11}+2\rho_1\rho_2C_{12}+\rho_2^2C_{22}\right)4\pi r^2dr \tag{15}$$

over density, the results will not agree in general since the relationship between the total and direct correlation functions is only approximate[16]. For example, the compressibility equation (15) yields a more accurate pressure than does the virial pressure equation (14) when the PY theory is applied to hard spheres, though both are considerably in error [13](the correct pressure being nearly one third times the virial pressure plus two thirds times the compressibility pressure). The virial pressure equation (14) is derived from the canonical partition function. The compressibility equation (15) is derived from an analysis of particle number fluctuations in the grand canonical ensemble. So, it is evident that different routes

to calculating the thermodynamic properties from integral equation solutions tend to yield different results.

Newer theories improve the prediction of the correlation functions by imposing thermodynamic consistency on some property calculated from two different routes. The closure equation is then parameterized to allow such an optimization. The Rogers-Young (RY) mixed integral equation theory [22] provides a description of the properties and structures of repulsive fluids such as those composed of hard spheres or of softly repulsive particles. The RY closure is said to be "mixed" since consistency between the results of equations (14) and (15) for the pressure is obtained by using a combination of the PY and HNC closures,

$$C_{ij} = h_{ij} - \left(\frac{1}{s}\right) \ln\left[s y_{ij} - (s-1)\right] \tag{16}$$

where "s" is a switching function. The switching function varies between zero and one and is chosen so that pressure consistency is obtained. When $s = 1$ the HNC equation (11) is recovered. In the limit when s approaches zero the PY equation (12) is recovered. An arbitrary form for the switching function is used which allows interpolation between the PY closure at short interparticle distances and the HNC at large distances[23],

$$s = 1 - e^{-\alpha r} \tag{17}$$

and the mixing parameter α is varied in order to vary the switching function. In practice, the parameter α is chosen so that the derivative of the pressure with respect to density obtained from equation (15) matches the results of a numerical differentiation with respect to density of equation (14). The resulting α is state dependent. The numerical differentiation of the virial pressure is done assuming the α parameter is only weakly state dependent, therefore its derivative can be neglected - an assumption which is justified when the RY theory is

applied to repulsive fluids. This procedure is referred to as a local consistency criterion, as opposed to a global consistancy criterion which would compare a numerical integral over density of equation (15) with the pressure from equation (14). The RY theory works when applied to fluids consisting of repulsive particles because the PY and HNC components of the theory yield compressibilities (from equation 15) that bracket the correct value. The theory reproduces the pair correlation functions, pressures, and internal energies obtained for these fluids from molecular simulations with surprising accuracy[22] - though the resulting pressures are biased low for harshly repulsive fluids such as those composed of hard spheres. RY theory is not applicable to fluids with both attractive and repulsive forces because, in general, the PY and HNC components of the theory do not bracket the correct compressibility[23].

The hybrid mean spherical approximation (HMSA) integral equation theory[23] is a modification of the RY theory which can be used with realistic pair potential models and which reduces to the RY theory when the potential is purely repulsive. In the HMSA theory the intermolecular pair potential is divided into repulsive and attractive parts according to the division of Weeks, Chandler, and Andersen (WCA) [24]:

$$u_{ij} = u_{ij}^{0} + u_{ij}^{1} \tag{18}$$

The WCA repulsive potential is short ranged and is given by,

$$u_{ij}^{0} = \begin{cases} u_{ij} + \varepsilon_{ij}\,, & r \le r_{ij}^{min} \\ 0\,, & r \ge r_{ij}^{min} \end{cases} \tag{19}$$

where ε_{ij} is the depth of the potential minimum and r_{ij}^{min} is the intermolecular separation at the

minimum. The WCA attractive potential is given by:

$$u_{ij}^{1} = \begin{cases} -\varepsilon_{ij}, & r \le r_{ij}^{min} \\ u_{ij}, & r \ge r_{ij}^{min} \end{cases} \tag{20}$$

The WCA potential division has been shown to be an effective basis for perturbation theories because the pair correlation functions in dense fluids are very nearly equal to those in a fluid whose particles interact with the steep WCA repulsive potential[25]. Under such conditions the direct correlation function is assumed to be approximated by that of a WCA repulsive fluid plus a correction which is exact for large separation distances. In the HMSA the direct correlation functions are divided into attractive and repulsive parts, the repulsive part is given by the RY theory and the attractive part is set equal to the negative of the WCA attractive potential. The resulting closure equation is:

$$C_{ij} = h_{ij} - \left(\frac{1}{s}\right) \ln\left[s g_{ij} e^{\beta u_{ij}^{0}} - (s-1)\right] - \beta u_{ij}^{1} \tag{21}$$

As in the RY closure, when $s = 1$ the HNC equation is recovered. The HNC limit yields accurate pair correlation functions at low to moderate densities [23]. In the limit as s approaches zero the HMSA closure approaches the soft mean spherical approximation (SMSA) of Madden and Rice[25] - an approximation which is accurate for liquids. The SMSA limit of the theory represents fluids which have softly repulsive cores and long range attractive forces. It assumes that the pair correlation functions are determined by the strength of the repulsive forces and are independent of the attractive forces - thus, the SMSA theory applies only at high densities. The switching function used in the HMSA theory is the same as that used in RY theory and the α parameter is found in the same way as in RY theory - by applying the local consistency criterion. The local consistency criterion is less satisfactory when the

theory is applied to fluids with attractive and repulsive forces since α has a limit of positive infinity (thus forcing the switching function to approach 1.0) as the density approaches zero. In any case, HMSA pressures and internal energies exhibit excellent agreement with molecular simulations for Lennard-Jones fluids[23].

Integral equation theories have therefore progressed to the point where they can be be used to predict the volumetric properties and internal energies of model fluids with spherically symmetric, pair-wise additive potentials. One might hope that it would be an easy matter to obtain chemical potentials, Gibbs free energies, and Helmholtz free energies from these theories. Integral equation theories can be applied to systems for which simulations or perturbation theories can not be used. Unlike perturbation theories, integral equation theories can in principle be applied to systems where intermolecular attractions have a large effect on the structure of the fluid (though the accuracy of the result depends on the closure equation used). Unlike both perturbation theories and molecular simulation, integral equation theories can be applied to states relatively close to the critical point of the fluid (though the location of the critical point obtained from integral equations theories may be inaccurate). If chemical potentials can be obtained from the integral equations theories then they can become useful tools for studying phase equilibrium near the critical point, particularly when large intermolecular attractions are present.

One approach to obtaining the free energies from integral equation solutions would be to perform a thermodynamic integration over the relevant volumetric property. This approach is examined in Chapter III - Results. It has a number of disadvantages. If, as in the case of the RY results for the hard sphere system, the predicted pressure is slightly lower than simulation results for a range of densities then thermodynamic integration will accumulate

these errors and lead to poor results. In addition, the α parameter must be recomputed at some number of intermediate density steps since it is state dependent. Recomputing α can impose a large computational penalty. Finally, for systems which exhibit two phases, it can be very difficult to numerically solve the integral equations for densities which lie within the phase dome thereby making it imposible to obtain a complete integral over density. As noted by Kjellander and Sarman[26], chemical potentials determined from integral equation theories depend on the method of calculation because of the approximate nature of the correlation functions they provide. If the correlation functions were exact, every calculation method would yield the same (exact) result. Since the correlation functions are inexact, there is the possibility that results obtained some calculation scheme are close to the results obtained from molecular simulation, even if the results from a thermodynamic integration differ greatly from simulation.

In this work a calculation scheme based on a Kirkwood charging process[27] is used for obtaining chemical potentials, Gibbs free energies, and Helmholtz free energies from integral equation theories. In the charging process we pick one molecule in the fluid and imagine it is at the origin of our coordinate system[28]. This central molecule is referred to as a test particle. We consider what happens when the magnitude of the pair potential between the test particle and the surrounding molecules is reduced while all other molecules in the system interact normally. We shall refer to the surrounding molecules as the bath. Because the pair potentials for interactions with the central molecule have been perturbed, the pair correlation functions about it will also be perturbed. In effect, the test particle is a field source which induces inhomogeneity in the fluid. Integral equation theories can be used to calculate the perturbed pair correlation functions about the test particle. By reducing the test particle - bath

molecule pair potentials in a series of steps the test particle can be removed from the system. The Helmholtz free energy change for this process can be computed from the knowledge of the pair correlation functions about the test particle. The derivative of the free energy with respect to component density at constant temperature volume and densities of the other species equals the chemical potential:

$$\left(\frac{\partial A}{\partial n_j}\right)_{T,\ V,\ n_i} = A(T,V,n_1,\ldots,n_j,\ldots) - A(T,V,n_1,\ldots,n_j-1,\ldots) = \mu_j \tag{22}$$

Since the number of particles in the fluid is very large, the chemical potential equals the negative of the free energy change for removing the test particle (alternatively, it equals the free energy change for inserting a new test particle) [28]. The Kirkwood charging approach has the advantage of only requiring solutions of the integral equation at the state of interest, thereby avoiding accumulation of errors, multiple α calculations, and numerical problems in crossing the phase dome.

There is a unique analytical solution to the charging process for the case of the HNC integral equation theory [29,30]. For integral equation theories in general, the chemical potential obtained from integral equations using Kirkwood charging is not unique. This inconsistency arises from the approximate nature of integral equation theories. It has been proven by Kjellander and Sarman [26] that the calculated chemical potential obtained from the RY closure depends on the way the pair potential (or equivalently, the local density of the fluid about the test particle) is varied during the charging process and not just on its initial and final values. For the HNC closure the calculated chemical potential is independent of the charging

path. Kjellander and Sarman obtained exact results for the RY theory with a charging process which required that the total correlation function grow linearly from zero to its final value as the test particle is inserted into the fluid. The computed chemical potentials in hard sphere systems were accurate only at low densities. Slightly more accurate results were obtained by them using a modified RY closure, but the high density results were still poor.

In the work presented here a numerical approach to the charging process was taken where the test particle is inserted into the fluid in a series of steps. The multi-step procedure used is based on well-known techniques and is designed to take advantage of accurate results provided by scaled particle theory[31]. Reiss, Frisch, Helfand and Lebowitz[32], proposed dividing the residual chemical potential into attractive and repulsive contributions, the repulsive contribution being estimated as the work of inserting the hypothetical hard spherical core of a molecule into the fluid at a fixed position. The work of inserting a hard sphere test particle into the fluid was determined from a charging process provided by scaled particle theory (SPT) [32,33]. This particle scaling process has been shown to be able to provide accurate chemical potentials in hard sphere fluids. Reiss et. al. [32] were able to estimate Henry's Law constants for helium in liquid argon and in liquid benzene by choosing hard core sizes equal to the Lennard - Jones size parameters and neglecting the attractive contribution. After using empirical data to estimate the attractive contribution they were also able to estimate the heats of vaporization of inert gases, and of hydrogen, nitrogen and benzene. In this work, we eliminate both the explicit and implicit assumption that molecules have hard sphere cores. Instead, the repulsive contribution consists of the work of inserting an effective hard sphere core into the fluid plus the work of softening the hard sphere into a softly repulsive WCA sphere. This softly repulsive sphere therefore represents the repulsive

core of a real molecule. We retain the idea that the repulsive contribution to the chemical potential is given by SPT simply by choosing effective hard sphere sizes so that the work of softening is zero. Thus, we also eliminate the arbitrary specification of core sizes made in past applications of SPT to realistic fluids. Finally, we do away with any need for empirical data or approximations in the estimation of the attractive contribution by using a formally exact Kirkwood charging process to couple the WCA attractive forces between the bath and the test particle. The calculation of the work of inserting the effective hard sphere, the work of softening, and the attractive contribution all require knowledge of the correlation functions about the evolving test particle. These correlation functions are estimated using integral equation theories.

The word "work" was used freely in the above discussion of Kirkwood charging in phrases such as "work of inserting a hard sphere" and "work of softening". This is a generalized notion of work (done on the system) which equals the Helmholtz free energy change of the process. In this case the displacement of the system occurs along an abstract coordinate which is not directly related to the physical movement of particles or system boundaries (though a reconfiguration of particles in the system does occur as the work is done). We imagine that the process of changing the pair potential between the test particle (which is present at a fixed position) and the fluid is accomplished by the equivalent process of turning on an external field source at that point. This process of turning-on is accomplished by varying an external coordinate referred to as the coupling parameter, denoted by λ. The total energy of a member of the canonical ensemble is then a function of λ. A generalized force generated by this member opposing the change in λ can be defined as the negative of

the gradient of its energy with respect to λ. The macroscopic force is then the ensemble average of these forces on the ensemble members. From statistical mechanics [16], the ensemble average force <F> is related to the derivative of the canonical partition function Z,

$$\langle F \rangle = kT\left(\frac{\partial (\ln Z)}{\partial \lambda}\right)_{T,\,V,\,N} = -\left(\frac{\partial A}{\partial \lambda}\right)_{T,\,V,\,N} \tag{23}$$

which also shows the relationship between <F> and the Helmholtz free energy A. So, the generalized work done on the system during the turning on process equals the negative of the integral over λ of the ensemble average force, which in turn equals the change in the Helmholtz free energy of the system from initial to final values of the coupling parameter:

$$A(1) - A(0) = -\int_0^1 \langle F \rangle \, d\lambda = \int_0^1 \left(\frac{\partial A}{\partial \lambda}\right)_{T,\,V,\,N} d\lambda \tag{24}$$

$-$ <F> is the force exerted by the external agent; $d\lambda$ is the infinitessimal displacement over which the force is exerted. It can be proven that the integral in equation (24) depends only on the initial ($\lambda = 0$) and final ($\lambda = 1$) states of the system - it does not depend on the way in which the external field source is turned on. Thus, the integral has the mathematical properties of "work" and it can be legitimately written as the difference in scalar potential functions $A(1) - A(0)$. How this free energy change is related to the residual chemical

potential will be described in Chapter II - Theory. The Theory chapter will explain how the free energy change can be determined from the pair correlation functions for fluid molecules about a test particle (or equivalently, about the external field source). Equation (24) is path independent when the true correlation functions are used in evaluating it. As noted in reference (26), the path independence can be destroyed when approximate integral equation theories are used to estimate the correlation functions.

The multi-step charging process will introduce three different coupling parameters which take the system from its initial to its final states in a sequence of steps. In order to apply the SPT formula effective hard core diameters are needed for each species in the fluid, as described above. The effective hard sphere diameters are based on the idea[17] that the Helmholtz energy of a fluid containing a soft WCA repulsive test particle can be approximated by the Helmholtz energy of a fluid containing a hard sphere test particle. The free energy difference between these two systems is defined as the work of softening. One coupling parameter is introduced to convert the hard sphere into the WCA repulsive particle. With hard sphere diameters chosen so that the work of softening is zero, the repulsive contribution to the chemical potential equals the work of inserting the hard sphere test particle. This work of insertion equals the free energy difference between a system containing the hard sphere and a system containing an non-interacting test particle. The insertion of the effective (in the sense that it approximates a WCA repulsive particle) hard sphere is done in two steps. First a hard sphere with a diameter of zero (a "hard point") is inserted into the fluid. SPT provides a simple formula for this step which is a function of the effective packing fraction of the fluid. Second, the size of the inserted hard sphere is increased from a point up to the effective hard sphere diameter. Another coupling parameter increases

the hard sphere size. SPT provides an expression for the work of this step which utilizes the contact values of the pair correlation functions of the bath molecules with the test particle. These contact values are determined from the integral equation theory. Finally, the WCA attractive potential is charged and the test particle becomes identical to other molecules of its species in the fluid. The final coupling parameter changes the attractive component of the potential. The free energy change in this step also depends on the pair correlation functions about the test particle. The Theory chapter which follows developes the mathematics of each of the charging steps in detail and describes how the pair correlation functions about the test particle are determined. The result is an effective method for computing the chemical potential.

Chapter III - Results, describes the testing of the method. The testing procedure is designed to examine:

1. Agreement with known (and path independent) results for the HNC closure.
2. Effectiveness of the SPT based procedure in purely repulsive systems when used with the RY theory.
3. Effectiveness of the SPT based procedure in realistic systems when used with the HMSA theory.

The method is compared to the analytical HNC result in case where $s = 1$. The HNC results allow the estimates to be made of the errors (numerical or otherwise) of each step in the charging process. In all cases these errors are negligible. The work of inserting the hard point obtained from the SPT is slightly inconsistent with the known exact HNC result. This inconsistency is shown to be smaller when the more accurate RY and HMSA integral equations are used. All other steps are consistent with the HNC when $s = 1$. The method is used with the RY integral equation theory to compute Gibbs and Helmholtz energies in pure

fluids which interact according to the WCA repulsive potential. For these fluids the attractive contribution to the chemical potential is zero. The computed Helmholtz energies agree with the accurate results of Verlet and Weis[14] for these fluids but are slightly inconsistent with thermodynamic integration. The results from the proposed method are more accurate than those of thermodynamic integration. The proposed charging process and thermodynamic integration should yield identical results. Inconsistent results occur because of errors in the correlation functions supplied by the integral equation theory. Unlike the procedure used in reference (26), the proposed method provides accurate results at high densities without modifying the RY closure. The accurate results confirm that the particle scaling procedure is appropriate for computing the repulsive contribution to the chemical potential. In mixtures of WCA repulsive particles the method accurately reproduces simulation results for the excess Gibbs free energies of mixing. These results are a strong proof of the method and of the RY theory since the free energies of mixing are the small differences between large chemical potentials and so are sensitive to small errors in the chemical potentials. The method is then used with the HMSA integral equation theory to compute Gibbs free energies in pure fluids which interact according to the Lennard-Jones potential. The results are accurate at the lowest ($\rho\sigma^3 <$ about 0.4) and highest ($\rho\sigma^3 >$ about 0.8) densities examined. At intermediate densities the chemical potentials are overpredicted and are also inconsistent with thermodynamic integration. These errors disappear at supercritical temperatures. The inaccurate results at intermediate densities are related to errors in the pair correlation functions about the test particle predicted by the HMSA theory - errors which disappear at low and high densities. The effect of varying the solvent-solute size (σ_{AB}) and energy (ε_{AB}) parameters in mixtures at infinite dilution are examined. The trend

in the residual solute chemical potential with increasing ε_{AB} is always correct - satisfying a consistency condition with the energy equation (13). The trend with increasing σ_{AB} is sometimes incorrect - a violation of a consistency condition with the pressure equation (14). This latter error also disappears at supercritical temperatures. The source of the errors with increasing σ_{AB} is traced to increased errors in the pair correlation functions about the test particle predicted by the HMSA theory. The method is then applied to Lennard - Jones mixtures of finite concentration which are intended to model the coexistence curve of carbon dioxide and acetone at a temperature above the critical temperature of carbon dioxide. Chemical potentials in the vapor phase are accurately predicted by the method with the HMSA theory. In the liquid phase the chemical potentials of the supercritical species are reasonable, those of the subcritical species are overestimated.

The method combined with the HMSA theory can always be used reliably at supercritical temperatures. In Chapter III - Results, the method is applied to the computation of chemical potentials in supercritical fluids. The method is used to determine how residual solute chemical potentials at infinite dilution in supercritical solvents depend on the fluid state and on the parameters of the intermolecular force relation. The predictions made in this section await experimental confirmation. They do show that the calculations can be performed for states near the critical point.

CHAPTER II

THEORY

1. Overall Approach

The chemical potential of a species in solution equals the derivative of the Helmholtz free energy with respect to the number density of the species at constant temperature and volume. In the Kirkwood charging process[27] this derivative is (in the thermodynamic limit) the change in the free energy which occurs upon the introduction of a test particle:

$$\left(\frac{\partial A}{\partial n_j}\right)_{T,\ V,\ n_i} = A(T,V,n_1,\ldots,n_j,\ldots) - A(T,V,n_1,\ldots,n_j-1,\ldots) = \mu_j \tag{25}$$

The ideal gas chemical potential can also be written as the free energy change in an ideal gas upon the introduction of an ideal gas particle. This free energy change also equals that which occurs upon the introduction of an ideal gas particle into a real (not an ideal gas) system,

$$\begin{aligned} &A^*(T,V,n_1,\ldots,n_j,\ldots) - A^*(T,V,n_1,\ldots,n_j-1,\ldots) \\ &= A(T,V,n_1,\ldots,n_j-1+\text{'*'},\ldots) - A(T,V,n_1,\ldots,n_j-1,\ldots) \\ &= \mu_j^* \\ &= kT\ln(\rho_j\Lambda_j^3) \end{aligned} \tag{26}$$

where the notation $n_j - 1 + '*'$ denotes a system containing $n_j - 1$ real molecules of species j and one ideal gas particle. The ideal gas particle has a mass equal to the mass of a molecule of species j (here we consider simple molecules without rotational or internal degrees of freedom). The residual chemical potential therefore equals the Helmholtz free energy change which occurs when an ideal gas particle is replaced by a real particle,

$$A(T,V,n_1,\ldots,n_j,\ldots) - A(T,V,n_1,\ldots,n_j - 1 + '*',\ldots) = \mu_j - \mu_j^* \tag{27}$$

which is the difference of equations (25) and (26).

In this report, the residual chemical potential given by equation (27) is broken up into a number of positive and negative contributions which arise due to repulsive and attractive interactions between the fluid and the test particle. As a first step the ideal gas particle is replaced by a reference particle. The reference test particle interacts with the surrounding (or "bath") molecules with specified pair potential energies. The free energy change for this first step is assumed to be known a priori. For example, the reference particle may be a hard sphere and the free energy change for the first step might then be estimated by scaled particle theory[32]. The residual chemical potential can then be computed by adding the free energy change which occurs when the reference particle is replaced by a real particle. A schematic of this multi-step process is given in Figure 1. It is hoped that by making a proper choice of the reference system the free energy changes for the remaining steps will be easier to compute. The free energy change which occurs when the reference particle is replaced by a real particle will be determined from methods which use the results of integral equation theories.

First, it is necessary to choose the reference system. It is known that the work of

inserting a hard sphere of diameter zero (or a "hard point") into a bath of hard spheres at a fixed position is given exactly in the scaled particle theory [31]. This work of insertion equals the free energy difference between a system containing a hard point and a system containing an ideal gas particle. It will be shown in Chapter III - Results, Application to Pure Lennard-Jones Fluids using Hypernetted Chain Theory, that the work of insertion into a bath of Lennard-Jones molecules is also given to high accuracy by SPT. Since the work of inserting a hard point into the fluid at a fixed position is known accurately, we choose a reference system consisting of a bath of real particles and a hard point test particle. The residual chemical potential is then equal to the sum of two free energy differences. The first is the free energy difference between the actual and reference systems. The second is the free energy difference between the reference system and the system containing the ideal gas test particle. A schematic of this process is given in Figure 2. The pair potential energy for interactions of the bath molecules of species i with the hard point is,

$$u_{ic}^{H}(r;R_i) = \begin{cases} +\infty \, , \, r \leq R_{ic} = R_i \\ 0 \, , \, r > R_{ic} \end{cases} \tag{28}$$

where R_i is the radius of the bath molecule of species i. If the bath molecules have hard cores then R_i is well defined. If the bath molecules have softly repulsive cores then an effective value of R_i must be defined which may depend on the temperature and density of the fluid. $2R_i$ then represents an effective minimum distance of closest approach between two bath molecules of species i. Therefore $2R_i = d_{ii}$ is defined as the effective diameter of species i. Also given in Figure 2 are schematics of the pair potentials for interactions with ideal gas and hard point test particles. A procedure for estimating the effective diameters will be described

below.

The free energy change which occurs when the ideal gas test particle is replaced by the hard point is given by SPT. Imagine a point test particle which can penetrate the core of a bath molecule of species i to within a center-to-center distance $R + R_i$, where R_i is the radius of the core of the bath molecule and $R \leq 0$. At larger separations the test particle does not interact with the bath molecule. Such a particle is excluded from spherical volumes of radius $R + R_i$ centered within bath molecules of species i. In the hard sphere system these volumes can not overlap, so any volume of radius $R + R_i$ can contain at most one bath molecule of species i. The probability that this volume is occupied by a molecule of species i is just $(4/3)\pi\rho_i(R+R_i)^3$. The probability $P_0(R)$ of finding a hole to contain a hard sphere test particle of radius $R \leq 0$ is:

$$\begin{aligned} P_0(R) &= 1 - P_1(R) \\ &= 1 - \frac{4\pi\rho_1}{3}(R + R_1)^3 - \frac{4\pi\rho_2}{3}(R + R_2)^3 \end{aligned} \tag{29}$$

The work W(0), needed to create such a hole for the case where R = 0 is therefore giv en by[33]:

$$\begin{aligned} \beta W(0) &= -\ln P_0(0) \\ &= -\ln\left(1 - \xi_3\right) \end{aligned} \tag{30}$$

where $\beta = 1/kT$ and ξ_3 is the packing fraction. ξ_3 for non-hard sphere fluids is an effective value based on the use of effective diameters. Since the developement of equation (30) depends on the assumption of non-overlap of molecular cores the equation will be approximate for soft-core molecules. Equation (30) will be accurate for non-hard sphere fluids if the molecular cores are in sufficiently hard. The accuracy of equation (30) for Lennard-Jones molecules will be demonstrated in Chapter III - Results with the aid of the HNC theory.

2. Review of Kirkwood Charging

The free energy difference between the actual and reference systems can be determined by integrating over a path where the test particle changes continously from a reference particle to an actual particle. Assume that the actual system contains n_1 molecules of species 1 and n_2 molecules of species 2 that interact with spherically symmetric, pair-wise additive potentials. One of these molecules is the test particle. The difference between the free energies of the reference and actual systems is denoted by $A(\lambda'=1) - A(\lambda'=0)$. $\lambda' = 0$ indicates the system where the test particle interacts with the bath according to the reference pair potentials given by equation (28). $\lambda' = 1$ indicates the system where the test particle interacts with the bath according to the real pair potentials. The parameter λ' is a coupling parameter. If Q is the configurational integral then, from the relation between the Helmholtz free energy and the canonical partition function:

$$\left(\frac{\partial A}{\partial \lambda'}\right)_{T,V,N} = -\left(\frac{kT}{Q}\right)\left(\frac{\partial Q}{\partial \lambda'}\right)_{T,V,N} \tag{31}$$

The configurational integral is defined by:

$$Q = \int \left\{ e^{\left[-\beta U(\lambda')\right]} \right\} d\mathbf{r}^N \tag{32}$$

therefore the derivative of the configurational integral with respect to the coupling parameter is,

$$\frac{\partial Q}{\partial \lambda'} = \int \left\{ e^{\left[-\beta U(\lambda')\right]} \left(\frac{\partial \left[-\beta U(\lambda')\right]}{\partial \lambda'} \right) \right\} d\mathbf{r}^N \tag{33}$$

where $U(\lambda')$ is the total potential energy of the system. $\mathbf{r}^N$ is a condensed notation denoting the position vectors of all $N = n_1 + n_2$ particles in the system. Thus, the integral is 3 N -fold.

Each of the position vectors can range over the volume of the system. The potential energy is a function of the coupling parameter - that is, it depends on the pair potential energies for interactions between the test particle and the bath molecules. Integrating between the reference and actual systems gives the required free energy difference,

$$A(1) - A(0) = \int_0^1 \left(\frac{1}{Q}\right) \left\{ \int \left\{ e^{\left[-\beta U(\lambda')\right]} \left(\frac{\partial \left[U(\lambda')\right]}{\partial \lambda'} \right) \right\} dr^N \right\} d\lambda' \tag{34}$$

A path between the reference and actual systems is specified by stating how the total potential energy of the system varies with the coupling parameter. If U(N - 1) is the sum of pair potentials which do not include the test particle then the total potential energy of the system is,

$$U(\lambda') = U(N-1) + \left(\begin{array}{c} \text{a sum of pair-wise} \\ \text{interactions with the test particle} \end{array} \right) \tag{35}$$

where the sum of interactions with the test particle (which is sometimes called the excess potential) is a function of the coupling parameter. The pair potential between a molecule of species i in the bath and a molecule of species j in the bath is assumed to be given by a Lennard-Jones type or similar (in the sense of having a short range repulsion and long range attraction) pair potential,

$$u_{ij} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right] \tag{36}$$

where r is the separation distance of the pair, σ_{ij} is the distance at which the potential is zero, and ε_{ij} is the depth of the potential minimum. The u_{ij} and thus U(N - 1) are independent of

the coupling parameter. The inside integral in equation (34) for the free energy change then becomes,

$$\frac{1}{Q}\int\left\{e^{\left[-\beta U(\lambda')\right]}\left(\frac{\partial\left[U(\lambda')\right]}{\partial\lambda'}\right)\right\}d\mathbf{r}^N=\frac{1}{Q}\int\left\{n_1 e^{\left[-\beta U(\lambda')\right]}\left(\frac{\partial u_{1c}}{\partial\lambda'}\right)\right\}d\mathbf{r}^{N-2}d\mathbf{r}_1 d\mathbf{r}_c \tag{37}$$

$$+\frac{1}{Q}\int\left\{(n_2-1)e^{\left[-\beta U(\lambda')\right]}\left(\frac{\partial u_{2c}}{\partial\lambda'}\right)\right\}d\mathbf{r}^{N-2}d\mathbf{r}_2 d\mathbf{r}_c$$

where the equation has been written for the specific case where the test particle becomes a molecule of species 2 when $\lambda' = 1$. The equation for the case where the test particle becomes a molecule of species 1 can be obtained from equation (37) by swapping species indices. The test particle "c" interacts with a molecule of species i in the bath with the reference potential when the coupling parameter is zero and with the Lennard-Jones type potential when the coupling parameter is one: (38)

$$u_{ic}(r;\lambda') = \begin{cases} u_{ic}^{H}(r;R_i)\,,\ \lambda' = 0 \\ u_{ij}(r)\,,\ \lambda' = 1 \end{cases}$$

where in the example the test particle is assumed to become a molecule of species j when $\lambda' = 1$. The parameter R_i in the reference potential is the effective distance of closest approach of the hard point to the bath molecule of species i which was illustrated in Figure 2.

The integral for the free energy difference equation (34), can be expressed in terms of the pair correlation functions for interactions of the bath with the test particle. These pair correlation functions are defined using basic statistical physics. The 3N-variate joint probability density function $P^{(N)}$ for finding the molecules in a configuration $\mathbf{r}^N$, independent

of their momenta is:

$$p^{(N)}(\mathbf{r}^N) = \left(\frac{1}{Q}\right)\left[e^{(-\beta U)}\right] \tag{39}$$

The potential energy, configurational integral, and probability density are all functions of the coupling parameter since one of the molecules in the system is the test particle. The marginal probability density for finding a specific molecule of species i at position $\mathbf{r}_i$ and the test particle "c" at position $\mathbf{r}_c$ is therefore:

$$p^{(2)}(\mathbf{r}_i, \mathbf{r}_c) = \left(\frac{1}{Q}\right)\int\left[e^{(-\beta U)}\right] d\mathbf{r}^{N-2} \tag{40}$$

where the integration has been carried out over every molecular position except those of the test particle and of the molecule of species i. The two-body generic distribution functions for finding an arbitrary bath molecule of species i at position $\mathbf{r}_i$ and the test particle at position $\mathbf{r}_c$ are therefore:

$$\rho^{(2)}_{1c}(\mathbf{r}_1, \mathbf{r}_c) = \left(\frac{n_1}{Q}\right)\int\left[e^{(-\beta U)}\right] d\mathbf{r}^{n_1-1}\, d\mathbf{r}^{n_2-1} \tag{41}$$

$$\rho^{(2)}_{2c}(\mathbf{r}_2, \mathbf{r}_c) = \left(\frac{n_2-1}{Q}\right)\int\left[e^{(-\beta U)}\right] d\mathbf{r}^{n_1}\, d\mathbf{r}^{n_2-2} \tag{42}$$

for the specific case where the test particle is considered to be a molecule of species 2 when $\lambda' = 1$. The equations for the case where the test particle becomes a molecule of species 1 can be obtained from equations (41) and (42) by swapping the species index. The two-body generic distributions functions are obtained from equation (40) by multiplying it by the number of permutations of species i which are possible. The two-body generic distribution functions $\rho^{(2)}_{ic}(\mathbf{r}_i, \mathbf{r}_c)$ are the marginal probability densities for finding an arbitrary molecule of species i at position $\mathbf{r}_i$ and the test particle at position $\mathbf{r}_c$. The 1-body generic distribution functions (or "singlet densities") $\rho^{(1)}_i(\mathbf{r}_i)$ are the marginal probability densities for finding an

arbitrary molecule of species i at position $\mathbf{r}_i$ independent of the positions of all of the other molecules. The correlation between the position of a molecule of species i and the position of the test particle can be measured by forming the pair correlation function which is defined by:

$$g_{ic}(\mathbf{r}_i, \mathbf{r}_c) = \frac{\rho^{(2)}_{ic}(\mathbf{r}_i, \mathbf{r}_c)}{\rho^{(1)}(\mathbf{r}_i)\,\rho^{(1)}(\mathbf{r}_c)} \tag{43}$$

The pair correlation functions measure how the presence of the test particle disturbs the local, microscopic structure of the fluid surrounding it. The positions of the molecules of species i and the position of the test particle are independent when the pair correlation function is 1 for all $\mathbf{r}_i$ and $\mathbf{r}_c$. This is true when u_{ic} is identically zero and the test particle is an ideal gas particle. Since the fluid is homogeneous, the singlet densities equal the ordinary bulk densities. Therefore the pair correlation functions are,

$$\begin{aligned} g_{ic}(\mathbf{r}_i, \mathbf{r}_c) &= \frac{\rho^{(2)}_{ic}(\mathbf{r}_i, \mathbf{r}_c)}{\rho_i \rho_c} \\ &= V\,\frac{\rho^{(2)}_{ic}(\mathbf{r}_i, \mathbf{r}_c)}{\rho_i} \end{aligned} \tag{44}$$

where the density of test particles is simply 1/V. Substituting equations (41) and (42) (or their equivalents for species 1) for the 2-body generic distributions yields a formal relationship between the pair correlation functions and the total potential energy of the system,

$$g_{ic}(\mathbf{r}_i, \mathbf{r}_c) = \left(\frac{V^2}{Q}\right) \int \left[e^{(-\beta U)}\right] d\mathbf{r}^{N-2} \tag{45}$$

where the integration is carried out over every position except $\mathbf{r}_i$ and $\mathbf{r}_c$. Substituting these into equation (37) yields[27],[28]:

$$\frac{1}{Q}\int\left\{e^{\left[-\beta U(\lambda')\right]}\left(\frac{\partial\left[U(\lambda')\right]}{\partial\lambda'}\right)\right\}d\mathbf{r}^N=\frac{\rho_1}{V}\int g_{1c}(\mathbf{r}_1,\mathbf{r}_c;\lambda')\frac{\partial}{\partial\lambda'}\left[u_{1c}(\mathbf{r}_1,\mathbf{r}_c;\lambda')\right]d\mathbf{r}_1 d\mathbf{r}_c$$

$$+\frac{\rho_2}{V}\int g_{2c}(\mathbf{r}_2,\mathbf{r}_c;\lambda')\frac{\partial}{\partial\lambda'}\left[u_{2c}(\mathbf{r}_2,\mathbf{r}_c;\lambda')\right]d\mathbf{r}_2 d\mathbf{r}_c$$

$$=\frac{\rho_1}{V}\int g_{1c}(\mathbf{r}_{1c};\lambda')\frac{\partial}{\partial\lambda'}\left[u_{1c}(\mathbf{r}_{1c};\lambda')\right]d\mathbf{r}_{1c}d\mathbf{r}_c$$

$$+\frac{\rho_2}{V}\int g_{2c}(\mathbf{r}_{2c};\lambda')\frac{\partial}{\partial\lambda'}\left[u_{2c}(\mathbf{r}_{2c};\lambda')\right]d\mathbf{r}_{2c}d\mathbf{r}_c$$

$$=\rho_1\int g_{1c}(\mathbf{r}_{1c};\lambda')\frac{\partial}{\partial\lambda'}\left[u_{1c}(\mathbf{r}_{1c};\lambda')\right]d\mathbf{r}_{1c}$$

$$+\rho_2\int g_{2c}(\mathbf{r}_{2c};\lambda')\frac{\partial}{\partial\lambda'}\left[u_{2c}(\mathbf{r}_{2c};\lambda')\right]d\mathbf{r}_{2c} \tag{46}$$

where $\mathbf{r}_{ic} = \mathbf{r}_c - \mathbf{r}_i$ is the center-to-center vector between the test particle and a molecule of species i. The last series of steps in equation (46) involves using the homogeneity property of the fluid in order to translate the origin of the system to the center of the test particle and to note that the result must be independent of the position $\mathbf{r}_c$. Substituting the result from equation (46) into equation (34) for the free energy difference between actual and reference systems gives:

(47)

$$A(1) - A(0) = \int_0^1 \left\{ \left[\rho_1 \int g_{1c}(\mathbf{r}_{1c};\lambda') \frac{\partial}{\partial \lambda'} \left[u_{1c}(\mathbf{r}_{1c};\lambda') \right] d\mathbf{r}_{1c} \right] + \left[\rho_2 \int g_{2c}(\mathbf{r}_{2c};\lambda') \frac{\partial}{\partial \lambda'} \left[u_{2c}(\mathbf{r}_{2c};\lambda') \right] d\mathbf{r}_{2c} \right] \right\} d\lambda'$$

Equation (47) is written in a general fashion for an arbitrary path between the reference and actual systems. It can also be applied to calculate the free energy difference between any two systems containing different types of test particles. Therefore it can be used to compute the free energy difference between the reference and actual system in a series of steps. In each step the test particle is replaced with a new type of particle, beginning the series with a hard point and ending the series with a real particle. The multi-step process allows the attractive and repulsive contributions to the chemical potential to be determined.

3.The Multi-step Charging Process

In this work the free energy difference between the actual and the reference system is determined in three steps, each step having its own coupling parameter. The three step process allows a charging path to be specified for each step which will yield an accurate result.

Suppose that the chemical potential of species j is to be calculated, where j is either 1 or 2. In the first step of the process the hard point test particle is replaced by a hard sphere of diameter d_{jj}, where d_{jj} is the effective diameter of species j. This hard sphere can approach to within a center-to-center distance d_{1j} of a molecule of species 1 and to within d_{2j} of a molecule of species 2. This step is called the particle scaling step. The Helmholtz free energy change for this step is calculated from an application of equation (47) which was given by the developers of scaled particle theory[32]. In the second step the hard sphere is replaced by a softly repulsive particle. This step is called the softening step. The softly repulsive particle repels the bath molecules with the repulsive component of the real potential. In this work the real potential is divided into repulsive and attractive components according to the method of Weeks, Chandler and Andersen (WCA)[24]. The WCA repulsive potential is relatively steep. Therefore the structure of the fluid around the softly repulsive particle is similar to the structure of the fluid around the hard sphere. So the free energy change for the second step is reletively small. Indeed, the effective diameters d_{1j} and d_{2j} will be chosen so that this free energy change is zero. The free energy change for this step is also calculated from an application of equation (47). However, a simplification can be made to the coupling parameter integration since the free energy change comes from a small perturbation in the structure. This simplification allows the integration over the coupling parameter to be done analytically. The development of the simplified equation is based on the analysis due to Lado[34]. In the third step the WCA softly repulsive test particle is replaced by a real particle. The free energy change for this step is also calculated from an application of equation (47). A schematic of the entire process for computing the free energy change which occurs when an ideal gas test particle is replaced by a real particle is given in Figure 3.

The three step charging process used is based on assumptions about the nature of the fluids of interest. The fluid is assumed to consist of spherical bodies of definable extents and locations. Otherwise, it makes little sense to try to define their diameters or to apply scaled particle theory. In other words, the molecules must be sufficiently hard in order to take advantage of the SPT formula for the work of inserting the hard point and in order to develope a simple yet accurate expression for the work of softening the effective hard sphere into a WCA repulsive test particle. The Kirkwood charging process used here provides the free energy change which occurs when a new particle is inserted into the fluid at a fixed position. That is, the partition function is assumed to be separable in translational and configurational parts and the translational part does not change during particle insertion. In non-classical situations where the particle being inserted has a very small mass the uncertainty principle makes such a process meaningless. The perspective being applied here assumes that there are two kinds of forces, an attractive force which acts at a distance and a repulsive force which acts only at contact. The procedure for determining the effective diameters defines what is meant by "contact" in the context of this work. Such a viewpoint is probably inappropriate for describing many of the situations of interest in the physics of fluids. Fluids consisting of oppositely charged point particles (with long-ranged repulsions), or particles with very soft cores which are not adequately modelled by hard spheres, or delocalized particles (such as solvated electrons or other non-classical systems) are not easily described with the three step charging process given here. These restrictions are similar to those of perturbation theory. Unlike perturbation theory, the method does not assume that intermolecular attractions cause only small changes in the structure of the fluid. The structure of the fluid is determined by integral equation theories for every value of the coupling parameter. The changes in the

structure with coupling parameter thus determined can be quite large. The accuracy of the method will depend on the ability of the chosen integral equation theory to accurately model such structural changes. Unlike perturbation theory, the effective hard sphere diameters determined by the method are influenced by the strength of the attractive force. Changing the attractive forces between the bath molecules changes the local density about the test particle, thereby changing the effective diameters.

4. Particle Scaling from a Hard Point to a Hard Sphere.

Review of Scaled Particle Theory

In the first step of the charging process for determining the chemical potential of species j the test particle grows from a hard point into a hard sphere with a diameter equal to the effective diameter of species j. This process is referred to as particle scaling in the SPT[33]. A schematic of this process is given in Figure 4. The coupling parameter is chosen to be the radius of a cavity surrounding a hard sphere test particle which has a radius of R, where $0 \leq R \leq d_{ij}/2$. In this case the total potential energy of the system as a function of the hard sphere radius is,

$$U(R) = U(N-1) + \sum_{\text{species 1}}^{n_1} u_{1c}^{H}(r_{1c}; R + R_1) + \sum_{\text{species 2}}^{n_2 - 1} u_{2c}^{H}(r_{2c}; R + R_2) \tag{48}$$

where the test particle is assumed in equation (48) to become a molecule of species 2 in the actual system. The potential energy in the case where the test particle becomes a molecule of species 1 can be obtained from equation (48) by swapping species indices. The pair potential for interactions of the bath molecules of species i with the test particle is the hard sphere pair potential:

$$u_{ic}^{H}(r_{ic}; r) = \begin{cases} +\infty\,, & r_{ic} \leq r = (R_i + R) \\ 0\,, & r_{ic} > r \end{cases} \tag{49}$$

where $r = R_i + R$ is the radius of a cavity surrounding the test particle which excludes the centers of the molecules of species i. The superscript H has been used here to denote the fact that the test particle is a hard sphere. The free energy difference between the system containing a hard sphere of radius R and the reference system is given by a version of equation

(47),

$$\beta W(R) - \beta W(0) = \beta\rho_1 \int_{R_1}^{R_1+R} \int_0^{+\infty} g_{1c}^H(r_{1c};r)\left[\frac{\partial}{\partial r} u_{1c}^H(r_{1c};r)\right] 4\pi r_{1c}^2 dr_{1c} dr$$

$$+ \beta\rho_2 \int_{R_2}^{R_2+R} \int_0^{+\infty} g_{2c}^H(r_{2c};r)\left[\frac{\partial}{\partial r} u_{2c}^H(r_{2c};r)\right] 4\pi r_{2c}^2 dr_{2c} dr \tag{50}$$

where the coupling parameter r is the cavity radius. In equation (50) the free energy difference W(R) – W(0) has been reduced by a factor of $\beta = 1/kT$. The inside integrals over intermolecular separation can be re-written with the aid of,

$$\begin{aligned} \beta g_{ic}^H(r_{ic};r)\left[\frac{\partial}{\partial r} u_{ic}^H(r_{ic};r)\right] &= -\, g_{ic}^H(r_{ic};r)\left[e^{\beta u_{ic}^H(r_{ic};r)}\right] \frac{\partial}{\partial r}\left[e^{-\beta u_{ic}^H(r_{ic};r)}\right] \\ &= -\, y_{ic}^H(r_{ic};r) \frac{\partial}{\partial r}\left[e^{-\beta u_{ic}^H(r_{ic};r)}\right] \end{aligned} \tag{51}$$

yielding,

$$\int_0^{+\infty} \beta g_{ic}^H(r_{ic};r)\left[\frac{\partial}{\partial r} u_{ic}^H(r_{ic};r)\right] 4\pi r_{ic}^2 dr_{ic} = -\int_0^{+\infty} y_{ic}^H(r_{ic};r) \frac{\partial}{\partial r}\left[e^{-\beta u_{ic}^H(r_{ic};r)}\right] 4\pi r_{ic}^2 dr_{ic} \tag{52}$$

where the background correlation function has been defined as $y_{ic}^H = g_{ic}^H \exp(\beta u_{ic}^H)$. As described in reference (33), the integration over separtion distance in equation (52) can be performed analytically by noting that the following partial derivatives are the same Dirac delta function with impulse at $r = r_{ic}$,

$$\begin{aligned} \frac{\partial}{\partial r}\left[1 - \exp(-\beta u_{ic}^H)\right] &= -\frac{\partial}{\partial r} \exp(-\beta u_{ic}^H) \\ &= \frac{\partial}{\partial r_{ic}} \exp(-\beta u_{ic}^H) \end{aligned} \tag{53}$$

where $1 - \exp(-\beta u_{ic}^{H})$ is a unit step function when plotted versus r and $\exp(-\beta u_{ic}^{H})$ is a unit step function when plotted versus r_{ic}. The delta function is positive and obeys the normalization condition:

$$-\int_0^{+\infty}\left[\frac{\partial}{\partial r}\exp(-\beta u_{ic}^{H})\right]dr_{ic} = \int_0^{+\infty}\left[\frac{\partial}{\partial r_{ic}}\exp(-\beta u_{ic}^{H})\right]dr_{ic} = 1 \tag{54}$$

That is, it is a probability density function. Therefore, the integral in equation (52) is an expected value calculation. Since the delta function is non-zero only at $r = r_{ic}$ the expected value of the integrand is:

$$-\int_0^{+\infty} y_{ic}^{H}(r_{ic};r)\frac{\partial}{\partial r}\left[e^{-\beta u_{ic}^{H}(r_{ic};r)}\right]4\pi r_{ic}^{2}dr_{ic} = y_{ic}^{H}(r;r)\,4\pi r^{2} = g_{ic}^{H}(r;r)\,4\pi r^{2} \tag{55}$$

Substituting the result for the inside integral from equation (55) into equation (50) for the free energy change gives:

$$\beta W(R) - \beta W(0) = \rho_1\int_0^{R} g_{1c}^{H}(R+R_1;R+R_1)4\pi(R+R_1)^2dR + \rho_2\int_0^{R} g_{2c}^{H}(R+R_2;R+R_2)4\pi(R+R_2)^2dR \tag{56}$$

In the above equation the integration over the radius of the cavity r has been replaced by an integration over the radius of the test particle R. $g_{ic}^{H}(R+R_i;R+R_i)$ is the contact value of the pair correlation function for a bath molecule of species i with a hard sphere test particle of radius R and $R + R_i$ is the cavity radius. An example plot of a pair correlation function

$g_{ic}^{H}(r_{ic};R+R_i)$ about a hard sphere test particle is given in Figure 5. The contact value is the height of the peak at $r_{ic} = R + R_i$. The test particle and bath molecules of species i can not get closer to each other than this distance because of their infinite mutual repulsion. The work of inserting a hard sphere of any radius can be determined by numerically integrating the equation (56) once the contact values have been determined over the range of integration. In the determination of the chemical potential of species j the upper limit of integration is $R = R_j$, where $2R_j = d_{jj}$ is the effective diameter of species j.

5. Test Particle Correlation Functions

Pair correlation functions about the test particle can be determined from the integral equation theory. The Ornstein-Zernicke (OZ) equations for a terniary mixture of species 1, species 2, plus a finite concentration of species "c" are,

$$\begin{aligned} r[h_{ij}(r) - C_{ij}(r)] = {} & \rho_1 \int_V h_{i1}(\mathbf{r}_i, \mathbf{r}_1) C_{1j}(\mathbf{r}_1, \mathbf{r}_j)\, d\mathbf{r}_1 \\ & + \rho_2 \int_V h_{i2}(\mathbf{r}_i, \mathbf{r}_2) C_{2j}(\mathbf{r}_2, \mathbf{r}_j)\, d\mathbf{r}_2 \\ & + \rho_c \int_V h_{ic}(\mathbf{r}_i, \mathbf{r}_c) C_{cj}(\mathbf{r}_c, \mathbf{r}_j)\, d\mathbf{r}_c \end{aligned} \tag{57}$$

where indices i and j can be 1, 2 or c and $r = \| \mathbf{r}_i - \mathbf{r}_j \|$. The h_{ij} are the total correlation functions, where $h_{ij} = g_{ij} - 1$. The C_{ij} equal rC_{ij} where the C_{ij} are the direct correlation functions. Since there is only a single test particle, the density ρ_c of species c is zero in the thermodynamic limit. Therefore the correlation functions for bath molecules about the test particle must satisfy the following test particle OZ equations,

$$\begin{aligned} r[h_{ic}(r) - C_{ic}(r)] = {} & \rho_1 \int_V h_{i1}(\mathbf{r}_i, \mathbf{r}_1) C_{1c}(\mathbf{r}_1, \mathbf{r}_c)\, d\mathbf{r}_1 \\ & + \rho_2 \int_V h_{i2}(\mathbf{r}_i, \mathbf{r}_2) C_{2c}(\mathbf{r}_2, \mathbf{r}_c)\, d\mathbf{r}_2 \end{aligned} \tag{58}$$

where the bath is assumed to be a binary mixture. The h_{ij}, where i and j are either 1 or 2, are

the total correlation functions for the bath molecules with each other. These are obtained independently of the determination of the test particle correlation functions using the OZ equations (10) for the bath and a closure such as (but not limited to) equation (16) or equation (21). The α parameter is obtained as described in Chapter I - Introduction. A simultaneous solution of the OZ equations (58) and approximate closure equation (21) yields results which depend on the order of convolution[16] due to the MSA contribution to the closure equation. The order shown in equation (58) is consistent with the HMSA closure used in this work. The other order of convolution $\boldsymbol{C} * h$, is un-physical since it results in a computed $h(r = 0) \neq -1$ when $s = 0$. Taking the Fourier transform of the OZ equations yields,

$$\tilde{\Gamma}_{ic} = \rho_1 \tilde{h}_{i1} \tilde{C}_{1c} + \rho_2 \tilde{h}_{i2} \tilde{C}_{2c} \tag{59}$$

where the functions with the tildes have been Fourier transformed. The notation of reference (20) has been used in writing equation (59). The function Γ_{ic} is equal to $r(h_{ic} - C_{ic})$. Alternatively,

$$\tilde{C}_{ic} = t\tilde{h}_{ic} - \tilde{\Gamma}_{ic} \tag{60}$$

where t is the transform of r. Substituting equations (60) into equations (59) gives:

$$\tilde{\Gamma}_{ic} = \rho_1 \tilde{h}_{i1}\left(t\tilde{h}_{1c} - \tilde{\Gamma}_{1c}\right) + \rho_2 \tilde{h}_{i2}\left(t\tilde{h}_{2c} - \tilde{\Gamma}_{2c}\right) \tag{61}$$

Thus, Γ_{1c} depends on Γ_{2c} and vice-versa. In a binary mixture there are two OZ equations (61), one for the correlation functions of each species about the test particle. They must be solved simulaneously to obtain the Γ_{ic}. In matrix form:

$$\begin{pmatrix} \left(1 + \rho_1 \tilde{h}_{11}\right) & \rho_2 \tilde{h}_{12} \\ \rho_1 \tilde{h}_{12} & \left(1 + \rho_2 \tilde{h}_{22}\right) \end{pmatrix} \begin{pmatrix} \tilde{\Gamma}_{1c} \\ \tilde{\Gamma}_{2c} \end{pmatrix} = \begin{pmatrix} t\left(\rho_1 \tilde{h}_{11}\tilde{h}_{1c} + \rho_2 \tilde{h}_{12}\tilde{h}_{2c}\right) \\ t\left(\rho_1 \tilde{h}_{12}\tilde{h}_{1c} + \rho_2 \tilde{h}_{22}\tilde{h}_{2c}\right) \end{pmatrix} \tag{62}$$

Solving for the transforms of Γ_{1c} and Γ_{2c} gives:

$$\tilde{\Gamma}_{1c} = \frac{t\left[\rho_1 \tilde{h}_{1c}\left(\tilde{h}_{11} + \rho_2 \tilde{h}_{11}\tilde{h}_{22} - \rho_2 \tilde{h}_{12}^2\right) + \rho_2 \tilde{h}_{2c}\tilde{h}_{12}\right]}{\left[\left(1 + \rho_1 \tilde{h}_{11}\right)\left(1 + \rho_2 \tilde{h}_{22}\right) - \rho_1 \rho_2 \tilde{h}_{12}^2\right]} \tag{63}$$

$$\tilde{\Gamma}_{2c} = \frac{t\left[\rho_2 \tilde{h}_{2c}\left(\tilde{h}_{22} + \rho_1 \tilde{h}_{11}\tilde{h}_{22} - \rho_1 \tilde{h}_{12}^2\right) + \rho_1 \tilde{h}_{1c}\tilde{h}_{12}\right]}{\left[\left(1 + \rho_1 \tilde{h}_{11}\right)\left(1 + \rho_2 \tilde{h}_{22}\right) - \rho_1 \rho_2 \tilde{h}_{12}^2\right]} \tag{64}$$

As a first step in solving equations (63) and (64), initial guesses are made for each Γ_{ic}. These are substituted into closure equations (16) or (21) (used with subscript j = c) to obtain estimates for the C_{ic}. When computing correlation functions about the test particle the α parameter is kept fixed at the value obtained during the solution for the correlation functions in the bath. The functions $rC_{ic}(r)$ are Fourier transformed and substituted into re-arranged versions of equations (59) to obtain estimates of the transforms of the total correlation functions:

$$t\tilde{h}_{ic} = \tilde{C}_{ic} + \rho_1 \tilde{h}_{i1}\tilde{C}_{1c} + \rho_2 \tilde{h}_{i2}\tilde{C}_{2c} \tag{65}$$

The transformed total correlation functions are then substituted into equations (63) and (64) to obtain the transforms of the Γ_{ic}. Inverting the transforms gives new guesses for the Γ_{ic} and the process can be repeated until convergence. Final values of the direct correlation functions C_{ic} about the test particle are obtained by substituting the converged Γ_{ic} into the closure equations (16) or (21). Final values of the background $y_{ic,}$ and pair $g_{ic,}$ correlation functions are also obtained by substituting the Γ_{ic} into either equations (16) or (21). A complete

FORTRAN program for performing these calculations is listed in Appendix A. The program uses the method of Labik et. al. [20] to simultaneously solve the OZ and closure equations.

6. Softening the Hard Sphere into a Soft Repulsive Particle

The second step determines the free energy difference between the system containing the softly repulsive test particle and the system containing the hard sphere test particle of diameter d_{ij}. A schematic of this step is given in Figure 6. The system labeled " $\delta = 0$" contains the hard sphere test particle and the system labeled "$\delta = 1$" contains the softly repulsive particle. The softly repulsive potential u_{ic}^{0} between the test particle and a molecule of species i can be written as the sum of a reference pair potential u^{H}_{ic} and a perturbation,

$$u_{ic}^{0}(r_{ic};\delta = 1) = u_{ic}^{H}(r_{ic}) + \Delta u_{ic}(r_{ic}) \tag{66}$$

where the test particle becomes a molecule of species j in the actual system and r_{ic} is the intermolecular separation distance. When the derivation has been completed we take the limit as the reference potentials approach the hard sphere potentials $u^{H}_{ic}(r_{ic};R_i + R_j)$ given by equation (49). The derivation used here is a modification (for test particles) of that by Lado [34]. In this work the softly repulsive potential used is the Weeks-Chandler-Anderson (WCA) repulsive potential[24],

$$u_{ic}^{0}(r_{ic};\delta = 1) = \begin{cases} u_{ij}(r_{ic}) + \varepsilon_{ij}\,, & r_{ic} \le r_{ij}^{min} \\ 0\,, & r_{ic} \ge r_{ij}^{min} \end{cases} \tag{67}$$

where u_{ij} is the real potential and r_{ij}^{min} is the separation distance at the potential minimum ($2^{1/6}$ times σ_{ij} in the case where u_{ij} is Lennard-Jones). By introducing a coupling parameter δ which varies between zero and one a path for the variation of the test particle pair potential can be defined by,

$$u_{ic}^{0}(\delta) = u_{ic}^{H} + \delta \Delta u_{ic} \tag{68}$$

where, to save space, the dependency on intermolecular separation has not been shown. The total potential energy of the system is then,

$$U(\delta) = U(N-1) + \sum_{\text{species 1}}^{n_1} u_{1c}^{H} + \sum_{\text{species 2}}^{n_2-1} u_{2c}^{H} + \delta \sum_{\text{species 1}}^{n_1} \Delta u_{1c} + \delta \sum_{\text{species 2}}^{n_2-1} \Delta u_{2c} \tag{69}$$

where, in this example the test particle becomes a molecule of species 2 in the actual system. The potential energy for the case where the test particle becomes a molecule of species 1 can be obtained by swapping indices. The free energy difference between a system with a softly repulsive test particle and a system with the reference test particle is given by another version of equation (47),

$$A(\delta = 1) - A(\delta = 0) = \int_0^1 \left\{ \left[\rho_1 \int g_{1c}^{0}(\mathbf{r}_{1c};\delta)\, \Delta u_{1c}(\mathbf{r}_{1c})\, d\mathbf{r}_{1c} \right] + \left[\rho_2 \int g_{2c}^{0}(\mathbf{r}_{2c};\delta)\, \Delta u_{2c}(\mathbf{r}_{2c})\, d\mathbf{r}_{2c} \right] \right\} d\delta \tag{70}$$

where the superscript "0" is used to indicate that the correlation functions are for the softly repulsive test particle.

The coupling parameter integral in the equation (70) can not be easily estimated numerically. An analytical approach to eliminating this integration is presented which is based on the analysis of Lado[34]. In this theory bridge functions B°_{ic} are defined by the following equation,

$$g_{ic}^{0}(\delta) = e^{\left[-\beta u_{ic}^{0}(\delta) + S_{ic}^{0}(\delta) + B_{ic}^{0}(\delta)\right]} \tag{71}$$

where the vector $\mathbf{r}_{ic}$ has not been written in order save space. S°_{ic} is the series function: $S_{ic} = h^{\circ}_{ic} - C^{\circ}_{ic}$. Following Lado we assume (and will later demonstrate for specific cases) that for an appropriate choice of molecular parameters in the reference - bath molecule pair potential the dependence of the bridge functions on the coupling parameter can be neglected. The integration over the coupling parameter can be done after applying the test particle OZ equations (58) and utilizing this approximation. This allows the free energy change to be calculated using only correlation functions about the WCA repulsive and hard sphere test particles - the final and initial states of the softening step. The coupling parameter and its limits are redefined in order to follow the notation of Lado more closely:

$$\begin{gathered} \xi = 1 - \delta \,;\, d\xi = -d\delta \\ \xi = 0 \Leftrightarrow \delta = 1 \,;\, \xi = 1 \Leftrightarrow \delta = 0 \end{gathered} \tag{72}$$

Departure variables are defined in order to analyze the variations in the pair correlation functions due to variations in the series functions and bridge functions:

$$\begin{gathered} \Delta S_{ic}^{0}(\xi) = S_{ic}^{0}(\xi) - S_{ic}^{0}(\xi = 0) \\ \Delta B_{ic}^{0}(\xi) = B_{ic}^{0}(\xi) - B_{ic}^{0}(\xi = 0) \end{gathered} \tag{73}$$

The pair correlation functions written in terms of the departure functions are,

$$g_{ic}^{0}(\xi) = g_{ic}^{0}(\xi = 0)\, e^{\left[\beta\xi\Delta u_{ic} + \Delta S_{ic}^{0}(\xi) + \Delta B_{ic}^{0}(\xi)\right]} \tag{74}$$

where Δu_{ik} was defined in equation (68). The derivatives of the pair correlation functions with respect changes in the coupling parameter are obtained by differentiating equation (74):

$$\frac{\partial g_{ic}^{0}(\xi)}{\partial \xi} = g_{ic}^{0}(\xi)\left\{ \beta \Delta u_{ic} + \frac{\partial}{\partial \xi}\left[\Delta S_{ic}^{0}(\xi) + \Delta B_{ic}^{0}(\xi)\right] \right\} \tag{75}$$

Re-arranging equation (75) yields the integrand of the coupling parameter integration,

$$\begin{aligned} g_{ic}^{0}(\xi)\beta\Delta u_{ic} = & \frac{\partial}{\partial \xi}\left\{ g_{ic}^{0}(\xi) - g_{ic}^{0}(\xi)\left[\Delta S_{ic}^{0}(\xi) + \Delta B_{ic}^{0}(\xi)\right] \right\} \\ & + \left[\Delta S_{ic}^{0}(\xi) + \Delta B_{ic}^{0}(\xi)\right]\frac{\partial g_{ic}^{0}(\xi)}{\partial \xi} \end{aligned} \tag{76}$$

where the first term on the left can be integrated immediately over the coupling parameter. From the definition of the background correlation function y_{ic} :

$$\Delta S_{ic}^{0}(\xi) + \Delta B_{ic}^{0}(\xi) = \ln\left[\frac{y_{ic}^{0}(\xi)}{y_{ic}^{0}(0)}\right] \tag{77}$$

Therefore,

$$\begin{aligned} g_{ic}^{0}(\xi)\beta\Delta u_{ic} = & \frac{\partial}{\partial \xi}\left\{ g_{ic}^{0}(\xi) - g_{ic}^{0}(\xi)\ln\left[\frac{y_{ic}^{0}(\xi)}{y_{ic}^{0}(0)}\right] \right\} \\ & + \left[\Delta S_{ic}^{0}(\xi) + \Delta B_{ic}^{0}(\xi)\right]\frac{\partial g_{ic}^{0}(\xi)}{\partial \xi} \end{aligned} \tag{78}$$

The dependence of the series function on the coupling parameter in the second term on the left can also be integrated out. The term of interest is,

$$\Delta S_{ic}^{0}\frac{\partial}{\partial \xi} g_{ic}^{0} = \left(\Delta h_{ic}^{0} - \Delta C_{ic}^{0}\right)\frac{\partial}{\partial \xi} g_{ic}^{0} \tag{79}$$

where the departures of the total and pair correlation functions are defined as:

$$\begin{aligned}\Delta h_{ic}^{0}(\xi) &= h_{ic}^{0}(\xi) - h_{ic}^{0}(\xi = 0) \\ &= g_{ic}^{0}(\xi) - g_{ic}^{0}(\xi = 0) \\ &= \Delta g_{ic}^{0}(\xi)\end{aligned} \tag{80}$$

The total correlation function can be moved inside the derivative since,

$$\begin{aligned}\left(\Delta h_{ic}^{0}\right)\frac{\partial}{\partial\xi}g_{ic}^{0} &= \left(\Delta h_{ic}^{0}\right)\frac{\partial}{\partial\xi}\Delta\, h_{ic}^{0} \\ &= \frac{1}{2}\frac{\partial}{\partial\xi}\left[\left(\Delta\, h_{ic}^{0}\right)^{2}\right]\end{aligned} \tag{81}$$

yielding a new form of the integrand:

$$\begin{aligned}g_{ic}^{0}(\xi)\beta\Delta u_{ic} = \frac{\partial}{\partial\xi}&\left\{g_{ic}^{0} - g_{ic}^{0}\ln\left[\frac{y_{ic}^{0}(\xi)}{y_{ic}^{0}(0)}\right] + \left(\frac{1}{2}\right)\left(\Delta h_{ic}^{0}\right)^{2}\right\} \\ &+ \left(\Delta B_{ic}^{0} - \Delta C_{ic}^{0}\right)\frac{\partial g_{ic}^{0}}{\partial\xi}\end{aligned} \tag{82}$$

The second term on the right still contains variations in the bridge and direct correlation functions. The product of the departure of the direct correlation and the derivative of the pair correlation function can be expressed as a derivative with the aid of the test particle OZ equations. The spatial integral of this product can be replaced by an integral in transform space with the aid of the Parseval theorem[35],

$$\int_{V}\rho_{i}\Delta C_{ic}^{0}\frac{\partial\left(\Delta g_{ic}^{0}\right)}{\partial\xi}\,d\mathbf{r}_{ic} = \frac{1}{(2\pi)^{3}}\int\rho_{i}\Delta\tilde{C}_{ic}^{0}\frac{\partial\left(\Delta\tilde{g}_{ic}^{0}\right)}{\partial\xi}\,d\mathbf{k} \tag{83}$$

where all of the functions involved are real valued. The test particle OZ equations allow the right hand side to be simplified. The OZ equations (58) in transform space are written in

departure form,

$$\begin{cases} \Delta\tilde{h}^0_{1c} - \Delta\tilde{C}^0_{1c} = \rho_1\tilde{h}_{11}\Delta\tilde{C}^0_{1c} + \rho_2\tilde{h}_{12}\Delta\tilde{C}^0_{2c} \\ \Delta\tilde{h}^0_{2c} - \Delta\tilde{C}^0_{2c} = \rho_1\tilde{h}_{12}\Delta\tilde{C}^0_{1c} + \rho_2\tilde{h}_{22}\Delta\tilde{C}^0_{2c} \end{cases} \tag{84}$$

and solved simulaneously for the direct correlation function departures in terms of total correlation functions:

$$\Delta\tilde{C}^0_{ic} = \frac{\left(\Delta\tilde{h}^0_{ic}\right)\left[\left(\rho_k\tilde{h}_{kk}\right) - 1\right] - \left(\Delta\tilde{h}^0_{kc}\right)\left(\rho_k\tilde{h}_{ik}\right)}{\left\{\left[\left(\rho_1\tilde{h}_{11}\right) - 1\right]\left[\left(\rho_2\tilde{h}_{22}\right) - 1\right] - \rho_1\rho_2\left(\tilde{h}_{12}\right)^2\right\}}, \qquad i,k=1,2\ (i\neq k) \tag{85}$$

The product of the departure function for the direct correlation function and the derivative of the pair correlation function can be written as, (86)

$$\left[\rho_1\Delta\tilde{C}^0_{1c}\frac{\partial}{\partial\xi}\left(\Delta\tilde{h}^0_{1c}\right)\right] + \left[\rho_2\Delta\tilde{C}^0_{2c}\frac{\partial}{\partial\xi}\left(\Delta\tilde{h}^0_{2c}\right)\right] = \frac{\left(\Delta\tilde{h}^0_{1c}\right)\left[\left(\rho_2\tilde{h}_{22}\right) - 1\right] - \left(\Delta\tilde{h}^0_{2c}\right)\left(\rho_2\tilde{h}_{12}\right)}{\left\{\left[\left(\rho_1\tilde{h}_{11}\right) - 1\right]\left[\left(\rho_2\tilde{h}_{22}\right) - 1\right] - \rho_1\rho_2\left(\tilde{h}_{12}\right)^2\right\}}\left[\rho_1\frac{\partial}{\partial\xi}\left(\Delta\tilde{h}^0_{1c}\right)\right]$$

$$+ \frac{\left(\Delta\tilde{h}^0_{2c}\right)\left[\left(\rho_1\tilde{h}_{11}\right) - 1\right] - \left(\Delta\tilde{h}^0_{1c}\right)\left(\rho_1\tilde{h}_{12}\right)}{\left\{\left[\left(\rho_1\tilde{h}_{11}\right) - 1\right]\left[\left(\rho_2\tilde{h}_{22}\right) - 1\right] - \rho_1\rho_2\left(\tilde{h}_{12}\right)^2\right\}}\left[\rho_2\frac{\partial}{\partial\xi}\left(\Delta\tilde{h}^0_{2c}\right)\right]$$

$$= \frac{1}{2}\frac{\partial}{\partial\xi}\left[\left(\rho_1\Delta\tilde{C}^0_{1c}\Delta\tilde{h}^0_{1c}\right) + \left(\rho_2\Delta\tilde{C}^0_{2c}\Delta\tilde{h}^0_{2c}\right)\right]$$

where the last equality results from combining the total correlation function terms inside the derivative and applying the OZ based equations for the departure of the direct correlation function again. Integrating over the coupling parameter and applying the Parseval theorem again yields: (87)

$$\int\int_0^1 \rho_1 \Delta C_{1c}^0 \frac{\partial\left(\Delta g_{1c}^0\right)}{\partial\xi} + \rho_2 \Delta C_{2c}^0 \frac{\partial\left(\Delta g_{2c}^0\right)}{\partial\xi}\, d\xi d\mathbf{r} = \frac{1}{16(\pi)^3}\int\int_0^1 \frac{\partial}{\partial\xi}\left(\rho_1 \Delta\tilde{C}_{1c}^0 \Delta\tilde{h}_{1c}^0 + \rho_2 \Delta\tilde{C}_{2c}^0 \Delta\tilde{h}_{2c}^0\right) d\xi d\mathbf{k}$$

$$= \frac{1}{16(\pi)^3}\int\left(\rho_1 \Delta\tilde{C}_{1c}^0(1)\Delta\tilde{h}_{1c}^0(1) + \rho_2 \Delta\tilde{C}_{2c}^0(1)\Delta\tilde{h}_{2c}^0(1)\right) d\mathbf{k}$$

$$= \frac{1}{2}\int_V\left(\rho_1 \Delta C_{1c}^0(1)\Delta h_{1c}^0(1) + \rho_2 \Delta C_{2c}^0(1)\Delta h_{2c}^0(1)\right) d\mathbf{r}$$

Therefore, the difference between the free energy of the system with a softly repulsive test particle and the system with a hard sphere test particle is,

$$\beta A(\xi = 0) - \beta A(\xi = 1) \tag{88}$$

$$= \int_V \left(\rho_1 \left\{\Delta g_{1c}^0(1) - g_{1c}^0(1)\ln\left[\frac{y_{1c}^0(1)}{y_{1c}^0(0)}\right] + \left(\frac{1}{2}\right)\left(\Delta g_{1c}^0(1)\right)^2 - \frac{1}{2}\Delta C_{1c}^0(1)\Delta g_{1c}^0(1)\right\}\right.$$

$$\left. + \rho_2 \left\{\Delta g_{2c}^0(1) - g_{2c}^0(1)\ln\left[\frac{y_{2c}^0(1)}{y_{2c}^0(0)}\right] + \left(\frac{1}{2}\right)\left(\Delta g_{2c}^0(1)\right)^2 - \frac{1}{2}\Delta C_{2c}^0(1)\Delta g_{2c}^0(1)\right\}\right) d\mathbf{r}$$

$$+ \int\int_0^1 \left(\rho_1 \Delta B_{1c}^0 \frac{\partial g_{1c}^0}{\partial\xi} + \rho_2 \Delta B_{2c}^0 \frac{\partial g_{2c}^0}{\partial\xi}\right) d\xi d\mathbf{r}$$

where the reference potential is now identified with the hard sphere potential of equation (49) with $R = R_j$. The dependence of the series function on the coupling parameter ξ has been integrated out. Equation (88) is the test particle analog of equation (20) of reference 34. The free energy change given by equation (88) might be referred to as the "work of softening" the hard sphere into a WCA repulsive particle.

The dependence of the free energy difference on variations in the bridge functions can be neglected with an appropriate choice of effective diameters for interactions of the bath molecules with the hard sphere test particle [36]. This assertion will be demonstrated in Chapter III - Results for the case where the diameters are chosen as described here and the fluid consists of Lennard - Jones particles. The ability to neglect the bridge function integrals stems from the fact that the WCA repulsive component of the Lennard - Jones potential is relatively hard and therefore easily modelled by an effective hard sphere potential. The goal in choosing effective diameters is to make the free energy of the system containing the hard sphere test particle equal to the free energy of the system containing the WCA repulsive test particle. That is, for intermolecular separations that are less than the effective diameter, the WCA repulsive potential is less than the hard sphere potential. These separation distances make a negative contribution to the free energy change. For intermolecular separations that are greater than the effective diameter, the WCA repulsive potential is greater than the hard sphere potential. These separation distances make a positive contribution to the free energy change. The proper choice of an effective diameter balances these two effects. The integrand of equation (88) is plotted versus separation distance in Figure 7 for an example pure fluid. For the specified choice of effective hard sphere diameter the integrand of equation (88) is non-zero over only a small range of intermolecular separation distances. The behavior of

integrand is analogous to the "blip" function of WCA perturbation theory[10]. The area under the curve to the left of the effective diameter balances the area to the right. In mixtures, an appropriate choice for a species 1 - test particle effective diameter will make first term on the left of equation (88) equal to zero. Similarly, an appropriate choice for a species 2 - test particle effective diameter will make second term on the left of equation (88) equal to zero. This choice will allow us to approximate the repulsive contribution to the chemical potential using by using scaled particle theory.

Two effective diameters are determined during each chemical potential calculation for a species in a binary mixture. There is a "like" effective diameter which is the distance of closest approach between the test particle and members of its own species. The "unlike" effective diameter is the distance of closest approach between the test particle and members of the other species. The like diameter was chosen so that its contribution to the work of softening equation (88) was 0.0001 kT or less. The step size for the integral equation solution procedure was chosen so that the like diameter falls precisely on one of the mesh points. The diameter must fall exactly on a mesh point if accurate contact values of the pair correlation functions are to be obtained. The unlike diameter is obtained by making a table of work of softening versus unlike diameter and interpolating to zero work of softening. Each unlike diameter in the table is chosen to fall exactly on a mesh point. In a binary mixture there are four effective diameters which are calculated: d_{11}, d_{12}, d_{21}, d_{22}. d_{12} is approximately equal to d_{21}, though there is some numerical difference due to the different step sizes and correlation functions used in the separate calculations and due to the interpolation technique used to find these unlike diameters. d_{12} (and d_{21}) are slightly less than $(d_{11} + d_{22})/2$.

7. Coupling of the Attractive Forces

The third step determines the free energy difference between a system containing a Lennard-Jones test particle and a system containing a WCA test particle. The Lennard-Jones potential is the sum of the WCA repulsive potential u_{ic}^0 plus an attractive term u_{ic}^1:

$$u_{ic}^1 = \begin{cases} -\varepsilon_{ij}, & r \le r_{ij}^{min} \\ u_{ij}, & r \ge r_{ij}^{min} \end{cases} \tag{89}$$

where, in this example, the test particle becomes a molecule of species j in the actual system. Plots of the WCA attractive and repulsive potentials versus separation distance are given in Figure 8. By introducing a coupling parameter λ which varies between zero and one a path for the variation of the test particle pair potential can be defined by:

$$u_{ic}(\lambda) = u_{ic}^0 + \lambda u_{ic}^1 \tag{90}$$

When $\lambda = 1$, $u_{ic} = u_{ij}$ and the actual system is recovered. This process is illustrated in Figure 8. The potential energy of the system is:

$$U(\lambda) = U(N-1) + \sum_{\text{species 1}}^{n_1} u_{1c}^0 + \sum_{\text{species 2}}^{n_2-1} u_{2c}^0 + \lambda \sum_{\text{species 1}}^{n_1} u_{1c}^1 + \lambda \sum_{\text{species 2}}^{n_2-1} u_{2c}^1 \tag{91}$$

where again, in this example, the test particle becomes a molecule of species 2. The potential energy for the case where the test particle becomes a molecule of species 1 can be obtained from equation (91) by swapping indices. The free energy difference between a system with a Lennard-Jones test particle and a system with a WCA repulsive test particle is given by another version of equation (47),

$$A(\lambda = 1) - A(\lambda = 0) = \int_0^1 \left\{ \left[\rho_1 \int g_{1c}(\mathbf{r}_{1c})\, u_{1c}^1(\mathbf{r}_{1c})\, d\mathbf{r}_{1c} \right] + \left[\rho_2 \int g_{2c}(\mathbf{r}_{2c})\, u_{2c}^1(\mathbf{r}_{2c})\, d\mathbf{r}_{2c} \right] \right\} d\lambda \tag{92}$$

The WCA division of the pair potential into attractive and repulsive contributions is efficient since it nearly linearizes the variation in the free energy with respect to variations of the coupling parameter λ. This property makes the numerical evaluation the outside integral over the coupling parameter efficient. No furthur analytical simplifications are required. The integrand of equation (92) for an example solute at infinite dilution is plotted versus separation distance in Figure 9. The plot is nearly linear.

8. Summary of Charging Steps

In summary, the residual chemical potential has been expressed as the sum of an approximately determined work of inserting a hard point plus formally exact contributions due to particle scaling, softening the hard sphere, and adding attractive potentials. Errors in the computed chemical potential can result from three sources:

1. The SPT equation (30) for the work of inserting the hard point, which is inexact when applied to fluids with soft cores.
2. Neglecting the integrals over the bridge functions in the work of softening equation (88).
3. Errors in the correlation functions predicted by the integral equation (in this case the HMSA) theory being used.

The chemical potential of species j can be computed from the sum of the above free energy changes. A clockwise path is taken around Figure 3 beginning with the actual system. First, the correlation functions in the actual system are obtained from the integral equation theory by using OZ equations (10) and either closure equations (16) or (21). Next, the free energy difference between the actual system and a system containing a WCA repulsive test

particle is determined from equation (92). By trial and error, effective diameters for an equivalent hard sphere are determined from equation (88); the diameters being chosen so that the free energy change is small (10^{-4} kT or less). The free energy difference between the reference system containing the hard point and a system containing a hard sphere of diameter $d_{jj} = 2\,R_j$ is determined from equation (56). Finally, the packing fraction based on the effective diameters is computed and used to obtain the work of inserting the hard point from equation (30). The total free energy change equals the configurational contribution to the chemical potential of species j.

CHAPTER III

RESULTS

1. Application to Pure Lennard-Jones Fluids Using Hypernetted Chain Theory

The procedure was first validated by applying it to the HNC integral equation theory. The RY and HMSA integral equation theories reduce to HNC when $s = 1$ in either equation (16) or equation (21). Comparing the method with known results for the chemical potential in the HNC allows inconsistencies and numerical errors to be identified and reduced to a negligible level. In this comparison there can be no error in the method due to the correlation functions or due to neglecting the integrals over the bridge functions in equation (88). In addition, there is no path dependence to chemical potentials obtained from Kirkwood charging in the HNC theory[26]. Therefore, the HNC test reveals the accuracy of the SPT formula for the work of inserting the hard point, combined with the numerical accuracy of the implementation. Morita derived an exact expression for the Gibbs free energy in a pure fluid whose correlation functions are described by the HNC theory. The result involves only spatial integrals of the correlation functions for the fluid[29]:

$$\frac{G - G^*}{NkT} = \rho \int_0^{+\infty} \left\{ \left(\frac{1}{2}\right)[h(r)]^2 - C(r) \right\} 4\pi r^2 dr - \left(\frac{1}{2}\right)[h(r=0) - C(r=0)] \tag{93}$$

where the notation used follows reference (30). The subscripts have been omitted since the correlation functions are those in a pure fluid. The Morita equation can be obtained from

equation (88) by letting $\xi = 0$ represent a system containing a real test particle and letting $\xi = 1$ represent a system containing an ideal gas test particle. In the HNC theory the bridge functions are identically zero so equation (71) becomes,

$$g^0_{ic}(\delta) = e^{\left[-\beta u^0_{ic}(\delta) + S^0_{ic}(\delta)\right]} \tag{94}$$

therefore the integrals over the bridge functions in equation (88) are identically zero for any chosen effective diameters. Since equations (56), (88) (with $\Delta B_{ic} \equiv 0$), and (92) are all exact in the HNC approximation, any inconsistency between the proposed method and Morita's equation stems from the work of inserting the hard point as given by equation (30) plus any numerical error. It was found that $(G - G^*)/NkT$ obtained from the method agrees with known HNC results from equation (93) to within -0.014. The work determined from SPT equation (30) for inserting the hard point test particle was inconsistent with the approximate HNC theory. This inconsitency was found to account for most of the disagreement with the Morita equation under most conditions.

HNC correlation functions for a pure Lennard-Jones fluid were calculated at three conditions: $T^* = kT/\varepsilon = 1.5$, $\rho^* = \rho\sigma^3 = 0.4$ and $T^* = 1.2$, $\rho^* = 0.7$ and 0.85. Effective diameters for the fluid at each set of conditions were computed by setting the right hand side of equation (88) to zero. The effective diameters for each state are listed in Table 1. The Gibbs free energy of the fluid equals the work required to insert a hard sphere with the chosen effective diameter into the fluid plus the work of coupling the test particle attractive forces; the former being given by the sum of equations (30) and (56), the latter being given by equation (92). The work of coupling the attractive forces will be referred to as the attractive contribution. Summing the results from equations (30), (56) and (92) for each set of conditions gave estimates of the Gibbs free energies of the fluid. The results are compared to those from Morita's equation

(93) in Table 1. The magnitude of the inconsitency is acceptably small and increases with density. Because of the accurate HNC results it is reasonable to assert that, aside from neglecting the bridge function term in equation (88), the method will yield correct results when applied to other integral equation theories. The exact attractive and repulsive contributions to the HNC chemical potential are compared to those from the proposed method in Table 1.

Listed in Table 2 are the values for the work of inserting the hard point from the SPT equation (30). The exact HNC values for the work of insertion can be obtained from the following specialization of equation (88):

$$\beta W(0)_{HNC} = \int_V \left\{ \rho_1 \left[\left(\frac{1}{2}\right)\left(h_{1c}^{HP}\right)^2 - C_{1c}^{HP} - \frac{1}{2} C_{1c}^{HP} h_{1c}^{HP} \right] + \rho_2 \left[\left(\frac{1}{2}\right)\left(h_{2c}^{HP}\right)^2 - C_{2c}^{HP} - \frac{1}{2} C_{2c}^{HP} h_{2c}^{HP} \right] \right\} d\mathbf{r} \tag{95}$$

where the superscript HP denotes the HNC correlation functions about the hard point. The difference between the SPT formula and equation (95) accounts for most of the inconsitency between the proposed method and the Morita equation. The difference between the formulas is zero at low densities and increases in magnitude with density. In the worst case, at $T^* = 1.2$ and $\rho^* = 0.85$, the difference between the HNC and SPT formulas for the work of insertion is -0.0065 kT - a relatively small error.

Both the HNC and SPT formulas for the work of inserting the hard point were approximate in this application. As was discussed in Chapter II - Theory, the SPT formula is exact only when the cores of the molecules do not overlap - in other cases equation

(30) must be taken to be an approximation. In the application to Lennard-Jones fluids the cores of the molecules are soft and therefore do overlap. The HNC theory is an approximate theory for the Lennard - Jones fluid, therefore equation (95) derived from it is also approximate.

The purely numerical error in the implimentation of the method also increases with in magnitude with density, being -0.0074 at $T^* = 1.2$, $\rho^* = 0.85$. Similar numerical errors can be expected when the method is used with the RY or HMSA closures. The numerical errors for each of the three states examined are also listed in Table 2. The numerical errors shown were based on the the following choices of parameters in the numerical algorithm. The OZ equations were solved at 2048 mesh points spaced at a nominal distance apart of $\Delta r = 0.00625$ times the smallest value of σ_{ij}. As noted in Chapter II - Theory, the precise value of the step size Δr used depended on the value of the effective hard sphere diameters. A small step size was necessary for accurate contact values of the bath molecule - hard sphere pair correlation functions used in equation (56). The procedure for calculating the contact values was valided by setting the switching function s equal to zero and comparing the results for hard sphere fluids to the analytical solution of the PY theory due to Leibowitz [37]. At the upper integration limit of approximately $2048 \cdot \Delta r$ the pair correlation functions were found to have all decayed to unity for all of the fluids examined in this work. Tail corrections were added to the computed chemical potentials which were based on the homogeneity of the fluid outside of the upper integration limit. The work of particle scaling equation (56) was calculated with a simple trapazoidal rule integration using a step size of $2 \cdot \Delta r$. An additional decimal place of accuracy (units as in Table 2) in the calculated repulsive contribution can be gained at the

highest densities by furthur reducing the step size to $1^{*}\Delta r$. If only one decimal place of accuracy is required in the repulsive contribution a step size of $20^{*}\Delta r$ can be used in evaluating equation (56). The work of softening equation (88) was evaluated using the trapazoidal rule with step size equal to $1^{*}\Delta r$ and with one Romberg extrapolation step. The left and right halves of the integrand shown in Figure 7 were integrated separately and the results added to give the total work of softening. The limits of the integrand from the left and right at the contact point were determined from quadratic polynomials passed through the adjacent mesh points. Equation (92) for the attractive contribution to the chemical potential was also integrated with the trapazoidal rule using one Romberg extrapolation step. A large step size of $\Delta\lambda = 0.25$ gave results accurate to the fifth decimal place because of the linearity of the integrand (as shown in Figure 9).

Furthur evidence for the inconsistency between HNC and the SPT equation (30) for the work of insertion can be found by examining the contact values of the pair correlation functions with the hard point. An exact relationship[33] for the derivative with respect to hard sphere radius of the work of inserting a hard sphere follows from equation (56):

$$\beta\frac{\partial}{\partial R}W = \rho_1 4\pi(R+R_1)^2 g^H_{1c}(R+R_1;R+R_1) + \rho_2 4\pi(R+R_2)^2 g^H_{2c}(R+R_2;R+R_2) \tag{96}$$

From equations (29) and (30) this derivative is known in the limit as R approaches zero from $R < 0$,

$$\beta\left(\frac{\partial W}{\partial R}\right)_{R=0^-} = -\left(\frac{1}{P_0}\frac{\partial P_0}{\partial R}\right)_{R=0^-} = \frac{1}{(1-\xi_3)}\left[\pi(2R_1)^3 + \pi(2R_2)^3\right] \tag{97}$$

which implies for pure fluids that the contact value of the hard point pair correlation function is[31]:

$$g^H_{ic}(R_i;R_i) = \frac{1}{(1-\xi_3)} \tag{98}$$

The SPT equation (98) yields predictions for the contact values which disagree with the results from the HNC theory. The HNC contact values are result of taking the limit as r approaches zero from $r > 0$ of the integral equation theory solution. Contact values from SPT and from HNC are listed in Table 3. The average percent difference between the SPT and HNC contact values is -3.65%. The largest magnitude difference occured at $T^* = 1.2$, $\rho^* = 0.85$ - the error being -5.20%. The HNC contact values lie above the SPT results for every choice of effective diameters. The difference declines as the chosen effective diameters are made smaller. In order for both the SPT and HNC contact values to be correct, $g_{ic}^{H}(R + R_i; R + R_i)$ would have to be discontinuous at $R = 0$ - a hypothesis which is disproven in the reference (31). The difference between the HNC and SPT contact values suggests that the work of inserting the hard point in the HNC is not given by equation (30). For theories other than the HNC it will not be possible to directly determine the accuracy of the SPT formula for the work of insertion. However, the formula can be judged to be consistent with the theory if the contact values obtained from the theory agree with those obtained from SPT. The HNC calculations illustrate that the SPT formula for the work of insertion can be expected to be accurate even when the theory and the SPT are inconsistent.

2. Effective Hard Sphere Diameters in Non-HNC Applications

In the application to the HNC theory discussed above, the bridge function integrals in equation (88) were identically zero. Thus, the work of softening was given exactly by the equation for every choice of effective diameters. In applying the method to other integral equation theories the bridge function integrals can also be neglected when the effective hard sphere diameters are chosen according to the zero work of softening criterion. This allows

the work of softening to be determined using only correlation functions about the effective hard sphere and about the WCA repulsive test particle.

The ability to neglect the double integral in equation (88) stems from two facts about the integrand which combine to make it nearly zero for all intermolecular separation distances. The behavior of the integrand was examined by comparing correlation functions for bath molecules about a WCA repulsive test particle with the correlation functions about a hard sphere test particle with effective diameters chosen to give a zero work of softening. Computations were made with the HMSA theory for supercritical dense fluid and subcritical liquid states in pure Lennard-Jones fluids and for a large Lennard-Jones solute dissolved in a Lennard-Jones liquid. The first fact is that pair correlation functions $g_{ic}^{o}(r_{ic};\xi)$ are independent of the coupling parameter ξ except for a small range of separation distances between 0.9 and 1.2 times d_{ij}, thus their derivative with respect to ξ is zero except over this interval. These pair correlation functions are plotted versus separation distance in Figures 10, 11 and 12. Secondly, over this interval where the derivative of the pair correlation functions is non-zero the bridge functions are nearly independent of ξ, thus ΔB_{ic}^{o} is nearly zero. These bridge functions are plotted versus separation distance in Figures 13, 14 and 15. So for this choice of effective diameters the double integral involving the bridge functions in equation (88) can be neglected. In neglecting the double integral we are neglecting the effect of the potential perturbations Δu_{ic} given by equation (68) on the bridge functions in equation (71) for the pair correlation functions - we are not neglecting the bridge functions themselves[34].

For a given choice of effective diameter, the magnitude of the bridge function integral

in equation (88) is bounded above by a simpler integral:

$$\left|\int\int_0^1\left(\rho_1\Delta B_{1c}^0\frac{\partial g_{1c}^0}{\partial\xi}+\rho_2\Delta B_{2c}^0\frac{\partial g_{2c}^0}{\partial\xi}\right)d\xi dr\right| \le \int\left(\rho_1\left|\Delta B_{1c}^0(1)\right|\left|\Delta g_{1c}^0(1)\right|+\rho_2\left|\Delta B_{2c}^0(1)\right|\left|\Delta g_{2c}^0(1)\right|\right)dr \tag{99}$$

Values of this upper bound for the conditions of Figures 10, 11 and 12 are listed in Table 4. The correlation functions used in the calculations were supplied by the HMSA theory. Also listed in the Table are the effective diameters used and resulting works of softening (less the bridge function integrals). Equation (99) gives a conservative upper bound since the departures in the pair correlation functions are negative for separations less than the effective diameters and are positive for separations greater than the diameters. These upper bounds are less than about 0.05 - this value is the maximum error in the residual chemical potential which would occur due to neglecting the bridge function integrals. Errors of this magnitude can be ignored.

The sum of equation (30) for the work of inserting the hard point, equation (56) for the work of particle scaling, and equation (88) for the work of softening is the repulsive contribution to the chemical potential. These three components of the repulsive contribution are listed in Table 5 for an example pure Lennard-Jones fluid. The HMSA theory was again used to give the correlation functions about the test particle. The three repulsive components are listed for a number of choices of the hard sphere test particle diameter, ranging between $0.9625 \le d/\sigma \le 1.0375$. For the conditions shown in the Table, the optimum d/σ (which gives a zero work of softening) is 1.00741. The double integral involving the bridge functions was dropped in calculating the work of softening, as discussed above. The estimated total repulsive contribution to the chemical has the desirable property of being nearly independent

of the choice of hard sphere diameter. The total would have been exactly independent of the choice if it were true that the bridge function integrals in equation (88) were exactly zero for all possible diameters. In addition, the derivative of the repulsive contribution with respect to diameter is nearly zero for the optimum d/σ, since the repulsive contribution is nearly equal to its maximum value. Therefore the total repulsive contribution is insensitive to the choice of effective diameter. These results show that an alternative criteria for the effective diameter, which conceivably might yield bridge function integrals which are even closer to zero, would give very nearly the same result for the repulsive contribution as does the zero work of softening criterion.

3. Application to Softly Repulsive Fluids Using Rogers-Young Theory

Pure Fluids

The tests described above show that the SPT can be applied to fluids without hard cores; there are only mild inconsistencies that arise when softly repulsive cores are replaced by effective hard sphere cores. The tests with the HNC theory show that the SPT formula for the work of inserting the hard point can be used in spite of the overlap of molecular cores. The use of the SPT formula (30) reduces the amount of effort needed to compute the repulsive contribution to the chemical potential. Another advantage of the SPT-based approach (which replaces the real soft core of a molecule with a hard sphere core) was revealed during the discussion of the bridge function integral - that the work of softening can be expressed only in terms of the difference between the correlation functions about the hard sphere and those about a softly repulsive WCA particle. It remains to be shown how accurate the SPT-based

charging path is when applied to inexact correlation functions obtained from the HMSA theory. Results obtained for WCA repulsive fluids show that the method successfully extends the SPT to softly repulsive fluids.

The method can be used with more exact theories than the HNC, provided that the choice of effective diameters allows the second integral in equation (88) to be neglected. As described above, calculations suggest that this integral can be neglected for a choice of diameters which give a work of softening equal to zero. It is useful to check the method for systems that have a purely repulsive pair potential since all of the simplifications are made in development of the repulsive contributions given by equations (30) and (88) (after neglecting the bridge function integrals). The RY integral equation has been shown to be very accurate for such systems[22]. If the method can accurately describe softly repulsive systems when used with the accurate theory, then the simplifications will be supported. Systems which interact with the WCA repulsive potential given by equation (19) are useful to examine since their repulsive interactions are those of the Lennard-Jones system and since the pair correlation functions in these systems are close to those in Lennard-Jones systems at high densities. In addition, the thermodynamic properties of these systems are known and are accurately predicted by theory of Verlet and Weis[14]. The first simplification has already been justified by the HNC calculations described above: that the SPT equation (30) for the work of inserting the hard point can be used. The second simplification, that second integral in equation (88) can be neglected, can be tested for fluids which are structurally similar to realistic model fluids at high densities.

RY correlation functions for pure WCA repulsive fluids were calculated at three

condtions: $T^* = kT/\varepsilon = 1.5$, $\rho^* = \rho\sigma^3 = 0.4$ and $T^* = 1.2$, $\rho^* = 0.7$ and 0.85. The compressibility factors predicted by the RY theory are slightly lower than those of the VW theory. The amount of the difference increases with density. The RY and VW compressibility factors are listed in Table 6. The slight error in the RY equation of state for the WCA repulsive fluid can be expected to produce some error in the computed chemical potentials. Effective diameters for the fluid at each set of conditions were computed by setting the right hand side of equation (88) to zero, after neglecting the integrals over the bridge functions. The effective diameters for each state are listed in Table 7. The effective diameters differed from those specified by the Verlet-Weis theory by at most 0.027%. Summing the results from equations (30) and (56) for each set of conditions gave estimates of the Gibbs free energies of the fluid. Equation (92) is identically zero since there is no attractive component in the pair potential. Predicted Helmholtz free energies were obtained by adding one minus the RY compressibility factor to the Gibbs energies. The predicted residual Helmholtz energies agree with the results of the Verlet-Weis procedure to within an average of 1.2%, the error increasing with the density. The error in the residual Helmholtz energy range between 0.004 and 0.0806 kT. Predicted Gibbs energies are low by an amount approximately equal to the error in the RY compressibility factor, suggesting that the accuracy of the method is being limited by the accuracy of the RY equation of state. The inaccurate RY compressibility factor does not reduce the accuracy of the predicted Helmholtz free energy. The relationship,

$$\frac{A - A^*}{NkT} = \frac{G - G^*}{NkT} - \left(\frac{P}{\rho kT} - 1\right) \tag{100}$$

shows how errors from this source on the right hand side approximately cancel those in the residual Gibbs energy. The average error in the predicted residual Gibbs energies is -1.5%

(the error ranging between ranging -0.0105 and -0.3002 kT) the error increasing in magnitude with the density. The Gibbs and Helmholtz free energies from the proposed method as well as those from the VW theory are also listed in Table 7. The differences between the method and the VW theory are to be expected considering the errors in the RY equation of state, as will be described below. The accurate results which have been obtained for WCA repulsive fluids support the assertion that the approximations made to the repulsive contribution to the chemical potential are accurate.

The contact values of the bath - hard point pair correlation functions obtained from the RY solutions were consistent with the use of SPT equation (30) for the work of inserting the hard point. The contact values obtained from the RY solutions for the pure WCA fluid agreed with those obtained from equation (98) to within 0.006. The average percentage difference between the SPT and RY contact values was 0.15%. Therefore $g_{ic}^{H}(R + R_i; R + R_i)$ exhibits the required continuity at $R = 0$. The agreement suggests that the SPT formula for the work of insertion can be used reliably in this application. The RY and SPT contact values for each of the three conditions are listed in Table 8.

As noted by Rogers and Young[22], their integral equation tends to underpredict the compressibility factor of harshly repulsive fluids by an amount which increases with increasing density. The error in the RY properties are a result of minor errors in the RY pair correlation functions which are amplified by the very steep WCA repulsive potential in virial pressure equation (14). The proposed method gives more accurate results than does the thermodynamic integration,

$$\frac{G - G^*}{NkT} = \int_0^{\rho} \left[\frac{1}{KT} \left(\frac{\partial P}{\partial \rho} \right)_{T,V} - 1 \right] d\rho \qquad (101)$$

a process which accumulates the errors in the RY properties as does the alternative thermodynamic path:

$$\frac{G-G^*}{NkT} = \int_0^{\rho} (Z-1)\frac{d\rho}{\rho} + (Z-1) \tag{102}$$

Equation (101) yielded residual Gibbs energies that averaged -2.5% lower than VW results for the three states examined. The error from equation (101) ranged between -0.0206 and -0.5009 kT. The results from equation (102) averaged -2.3% lower than VW. For equation (102) the error ranged between -0.0185 and -0.4673 kT. The thermodynamic integrations underestimate the Gibbs and Helmholtz energies because the pressures are consistently underestimated over the range of densities. The proposed method yields results that are different (and better) than either thermodynamic integration because it relies only on properties of the fluid at the state of interest. The predicted properties given by the proposed method are listed in Table 9. Also listed in Table 9 are the results obtained from the Verlet-Weis procedure and from each thermodynamic integration of RY solutions. The results from the two thermodynamic integrations are nearly equal because of the imposition of pressure consistency in the RY method. The small difference between them results from the use of the local consistency criterion which neglects the density dependence of the switching function. This criterion works well for the WCA repulsive fluid.

Mixtures

The method was also applied to mixtures of WCA particles. Haile [8] has simulated the excess Gibbs free energy of mixing WCA particles with equal ε parameters and unequal σ parameters. The proposed method was used to reproduce these data for the cases σ_{22}/σ_{11} =

1.125 and σ_{22}/σ_{11} =2.0 at a reduced temperature of kT/ε_{11} = 1.0 and a reduced pressure of $P\sigma_{11}^3/\varepsilon_{11}$ = 0.5. Since the particles differ only in size and have no attractive forces these mixtures exhibit only small deviations from ideal solution behavior. Thus, the excess Gibbs free energies of mixing determined by the method provide a stringent test of the accuracy of the RY theory, the approximations made to the repulsive contribution, and the numerical accuracy of the application. The properties of the pure fluids and of mixtures of 25%, 50%, and 75% were calculated under isobaric conditions. The densities needed in the RY theory to meet the specified pressure of $P\sigma_{11}^3/\varepsilon_{11}$ = 0.5 were determined for each mixture. These densities agree to within an average of 0.35% of the simulation results. The required densities are listed in Table 10 as are those obtained from Haile's simulations. The RY densities are higher than simulation because of the tendency of the theory to underestimate the pressure.

The chemical potentials were calculated for each species at the required densities and compositions. The effective diameters and residual chemical potentials in each mixture are listed in Table 11. The excess Gibbs free energies of mixing at constant temperature and pressure were then determined from:

$$\frac{\Delta G^E}{NkT} = x_1\left\{\left[\left(\frac{\mu_1-\mu_1^*}{kT}\right)-\left(\frac{\mu_1-\mu_1^*}{kT}\right)^{Pure}\right]+\ln\left(\frac{\rho}{\rho_1^{Pure}}\right)\right\} + x_2\left\{\left[\left(\frac{\mu_2-\mu_2^*}{kT}\right)-\left(\frac{\mu_2-\mu_2^*}{kT}\right)^{Pure}\right]+\ln\left(\frac{\rho}{\rho_2^{Pure}}\right)\right\} \tag{103}$$

where ρ is the mixture density at the specified temperature and pressure and the superscript "Pure" denotes a property of the pure fluid of the indicated species. The terms involving the

residual chemical potentials sum to equal the configurational part of the free energy change. The remaining terms involving the fluid densities sum to equal the free energy change of mixing ideal gases starting from pure fluids with the indicated densities and compressing to the mixture density. Therefore the accuracy of total is a reflection of both the accuracy of the proposed method and the accuracy of the RY equation of state. The results from the method agree with simulation data for the 2:1 diameter ratio mixture to an average of -0.67%. For the 1.25:1 diameter ratio mixture the method was in error by an average of -5.8%. This latter percentage is the result of small errors in the third or fourth decimal place in the very small result for $\Delta G^E/NkT$. The agreement of the method with simulation is remarkable when it is considered that small errors in the RY computed density can have a large influence on the accuracy of the ideal gas part. The results from the method and those from simulation are listed in Table 12. Also included in the Table are configurational and ideal gas parts of the excess free energy change. The excess free energies are plotted versus the mole fraction of the small species in Figure 16 as are those obtained from simulation. These mixtures are nearly ideal - the excess free energies of mixing are small and negative. The smooth curves are the Redlich-Kister expansions which exactly go through the points obtained from the method. The proposed method reproduces the known[8] asymmetry in composition of the σ_{22}/σ_{11} =2.0 curve, where the minimum in the curve is shifted toward an increased concentration of the small species. The success of the method for mixtures of WCA repulsive particles furthur validates the simplifications made to the repulsive contribution and validates the implimention of the method for mixtures.

4. Application to Lennard-Jones Fluids Using the Hybrid Mean Spherical Approximation

Pure Fluids

Applying the method to WCA repulsive fluids is straightforward in comparsion to applying it to realistic fluid models such as the Lennard-Jones model. In repulsive fluids, the residual chemical potentials always increase with increasing density along an isotherm. In Lennard - Jones fluids the attractive and repulsive contributions are nearly equal and opposite in sign under many conditions. This partial cancellation leads to residual chemical potentials along an isotherm which have a negative minimum when plotted versus density and which become positive at very high densities. In addition, the work of inserting a hard sphere into a repulsive fluid is a strictly monotonic increasing function of the radius. For Lennard - Jones fluids there are (metastable) conditions where the pressure is negative and the work of inserting a hard sphere is not a monotonic function of the radius of the sphere. These complications make the results for Lennard-Jones fluids a stringent test of both the method and the HMSA theory. Given that the errors caused by using equation (30) for the work of inserting the hard point and by neglecting the bridge functions integral in equation (88) are small, the only significant source of errors are the HMSA correlation functions about the test particle. The accuracy of the method when applied to Lennard-Jones fluids was diminished by errors in the correlation functions about the test particle determined by the HMSA theory. There were no such errors at very low and very high densities and at supercritical temperatures.

HMSA correlation functions for pure Lennard-Jones fluids were first calculated at the

three example conditions: $T^* = 1.5$, $\rho^* = 0.4$ and $T^* = 1.2$, $\rho^* = 0.7$ and 0.85. Effective diameters for the fluid at each set of conditions were computed by setting the right hand side of equation (88) to zero (after neglecting the bridge function integrals). Summing the results from equations (30), (56) and (92) for each set of condtions gave estimates of the Gibbs free energies of the fluid. These results were compared to those obtained from molecular simulation. Simulation results at $T^* = 1.5$ were obtained from Shing, Gubbins and Lucas[5], results at $T^* = 1.2$ were obtained from Heinbuch and Fischer[3]. At each state the proposed method overpredicted the Gibbs energy. The smallest error was at the highest density, lowest temperature condition; the percentage error in this case was 4.5%. The error was the largest (12.8%) at $T^* = 1.2$, $\rho^* = 0.7$. The predicted results and those obtained from simulations are listed in Table 13. Also listed in Table 13 are the available perturbation theory results and the results from the Nicolas' equation of state for the Lennard - Jones fluid[38]. This small sample of results suggests that the method is reliable at very high and very low densities. The larger sample of results described below will confirm this observation. The small sample of results also suggests that the derivatives of the predicted chemical potentials with respect to density are incorrect since the error is small at low and at high densities. Thermodynamic consistency tests were used to determine the size of this latter error.

The contact values of the bath - hard point pair correlation functions obtained from the HMSA solutions were consistent with the use of SPT equation (30) for the work of inserting the point hard sphere. The contact values obtained from the HMSA solutions for the pure Lennard-Jones fluid agreed with those obtained from equation (98) to an average of 0.13%. The largest difference was 0.54% at $T^* = 1.2$, $\rho^* = 0.85$. Therefore $g_{ic}^{H}(R+R_i; R+R_i)$ exhibits the required continuity at $R = 0$. The HMSA and SPT contact values for each of the three

example conditions are listed in Table 14. The agreement suggests that the SPT formula for the work of insertion can be used reliably in this application.

In order to gauge the state dependence of the errors, the method was used to estimate the residual Gibbs free energies in pure Lennard-Jones fluids along isotherms at reduced temperatures of $T^* = kT/\varepsilon = 1.556$, 1.15, and 0.928. The $T^* = 1.556$ isotherm is supercritical, the others are subcritical; the critical temperature being approximately $T^* = 1.35$. The results were compared to the simulations of Panagiotopoulos, Suter, and Reid[7]. Fourteen sets of conditions were examined covering a reduced density range of $\rho^* = \rho\sigma^3 = 0.025$ to $\rho\sigma^3 = 0.8$. The two lower temperature isotherms did not include any points in the reduced density range of 0.05 to 0.6 (which mostly lies within the two phase region). The HMSA theory accurately represented the pressure and internal energy of the fluid over the range of conditions examined. Compressiblity factors were predicted to within an average absolute error of 2.7% and configurational internal energies to within an average absolute error of 0.49%. Therefore, errors in the HMSA equation of state are small and can be expected to contribute little to errors in the results from the method. Also, the accurate predictions of pressure and energy indicate the pair correlation functions up to and including the first peak, which determines the larger part of the equation of state, are accurate (results for mixtures, discussed below, will include a direct comparision of the pair correlation functions from HMSA with simulation). The conditions examined and the compressiblity factors and internal energies obtained from simulations and from the HMSA theory are listed in Table 15. The compressibility factors obtained from the HMSA theory are plotted versus density for the three isotherms in Figure 17 as are the simulation results. Additional simulation results from Hansen and Verlet[39] are also displayed for the $T^* = 1.15$ isotherm. These results indicate that

the HMSA equation of state for the Lennard-Jones fluid is qualitatively correct.

The predicted residual chemical potentials were in error by an average of 0.08 kT for the supercritical isotherm and 0.2 kT for both of the subcritical isotherms. In general, the maximum errors occurred at reduced densities of about $\rho^* = 0.6$ on each isotherm, the errors declining at higher and lower densities. The chemical potentials obtained from the method and from simulation are listed in Table 16. Figure 18 is a plot of residual chemical potential divided by $\rho^* kT$ versus reduced density for the three isotherms. Also shown are the simulation results and the exact low density limit obtained from second virial coefficients. The intercept of each isotherm is $2\sigma^3 B(T^*)$, where $B(T^*)$ is the second virial coefficient for the isotherm. The method is exact at low densities, since under these conditions the HMSA theory reduces to the exact (in the low density limit) HNC theory. The high density results are also plotted versus density in Figure 19. Included in Figure 19 are the results at $T^* = 1.2$. There appears to be an inconsistency between the simulation results of Heinbuch and Fischer[3] at $T^* = 1.2$ and of Panagiotopoulos[7] et. al. at $T^* = 1.15$ since the chemical potentials quoted for each of these isotherms a t $\rho^* = 0.7$ is nearly the same. The proposed method agrees more closely with the results of Heinbuch and Fischer. The method correctly reproduces the increase in chemical potential with increasing temperature and yields accurate results at high densities. The slope of the chemical potential versus density curves are incorrect. The inaccurate results at intermediate densities suggests that there is a thermodynamic inconsistency in the proposed method This problem disappears at low densities and high temperatures where the closure approaches the HNC theory or at high densities where the fluid structure approaches that of a WCA repulsive fluid.

The thermodynamic consistency of the method was examined by comparing the results to those from thermodynamic integration. Residual Gibbs free energies were calculated using thermodynamic integration at $T^* = 1.556$ and ρ^* between 0.05 and 0.8. The free energies were calculated using both the integration over the compressibility, equation (101), and the integration over the compressibility factor, equation (102). Equation (101) had an average absolute percent error of 6.2% and yielded results greater than simulation for $\rho^* \geq 0.4$. Equation (102) had an average absolute percent error of 4.9% and yielded results less than simulation. The proposed method had an average absolute percent error of 8.4% and yielded results that were generally higher than simulation. The two thermodynamic integrations yield different results because of the slight failure of the local consistency criterion (which neglects the density dependence of the switching function). The results from the two thermodynamic integrations are listed in Table 17 as are those from obtained from simulation and from the proposed method. The results from the proposed method are larger than either thermodynamic integration, being between them only at the lowest reduced density of 0.05 and highest reduced density of 0.8. The residual Gibbs free energies obtained from each procedure divided by $\rho^* kT$ are plotted versus reduced density in Figure 20. It is apparent that the slope of the chemical potential with respect to density obtained from the proposed method is inconsistent not only with simulation but also with the bulk phase properties obtained from the HMSA solution. Such inconsistencies probably develope in the repulsive contribution, as will be discussed below.

For subcritical isotherms the thermodynamic integration could not be performed because the integral equation solution procedure would not always converge for states within

the phase envelope. An alternative consistency test is based on the Gibbs-Duhem equation:

$$\beta\left(\frac{\partial P}{\partial \rho}\right)_{T,V,x_1,x_2} = \rho_1\left(\frac{\partial \beta\mu_1}{\partial \rho}\right)_{T,V,x_1,x_2} + \rho_2\left(\frac{\partial \beta\mu_2}{\partial \rho}\right)_{T,V,x_1,x_2} \qquad (104)$$

The derivatives with respect to density can be evaluated with the aid of the local consistency criterion described in the Chapter I - Introduction. That is, the derivatives are evaluated under the assumption that the derivative of the α parameter in equation (17) with respect to density can be neglected. Under this assumption the derivatives of the chemical potential can be evaluated numerically. The derivatives of the effective diameters with respect to density can also be neglected - however, when a finite step is taken in the density in the numerical differentiation, the right hand side of equation (88) for the work of softening is non-zero and this contribution must be added to the chemical potential. The thermodynamic consistency of the method combined with the HMSA theory can be evaluated by comparing the left hand side of equation (104) as evaluated from the compressibility equation (15) to the right hand side as evaluated from chemical potentials obtained from the proposed method. Again it was found that the chemical potentials were not consistent with the bulk phase properties and correlation functions. The Gibbs-Duhem test was performed at each of the three example conditions: $T^* = 1.5$, $\rho^* = 0.4$ and $T^* = 1.2$, $\rho^* = 0.7$ and 0.85. The left and right hand sides of equation (104) are listed in Table 18 for each of three states examined. At the lowest density the rate of change in the chemical potential with density is overestimated by the method, at the higher densities it is underestimated. This result is consistent with the previous observation that the error in the chemical potential is maximum at a reduced density between 0.4 and 0.6 and declines as density is increased furthur.

Infinitely Dilute Mixtures

A direct test of the consistency of the method with the energy equation (13) and the virial pressure equation (14) can be made by examining the accuracy of calculated chemical potentials in infinitely dilute solutions. Lotfi and Fischer [4] have simulated chemical potentials of infinitely dilute Lennard-Jones solutes in a Lennard-Jones solvent at $T^* = 1.2$, $\rho^* = 0.7$. Residual chemical potentials at infinite dilution were obtained for a range of solvent-solute size and energy parameters. In addition, exact expressions were given for the derivatives of the chemical potential with respect to changes in these parameters. The derivatives of the infinite dilution solute chemical potentials with respect to solute-solvent size and energy ratios are given by[4],

$$\frac{\partial}{\partial\left(\frac{\sigma_{AB}}{\sigma_{BB}}\right)}\left(\frac{\mu_A-\mu_A^*}{kT}\right)\Bigg|_{\frac{\varepsilon_{AB}}{\varepsilon_{AB}}=\frac{\sigma_{AB}}{\sigma_{BB}}=1} = 6(Z-1) \tag{105}$$

and,

$$\frac{\partial}{\partial\left(\frac{\varepsilon_{AB}}{\varepsilon_{BB}}\right)}\left(\frac{\mu_A-\mu_A^*}{kT}\right)\Bigg|_{\frac{\varepsilon_{AB}}{\varepsilon_{BB}}=\frac{\sigma_{AB}}{\sigma_{BB}}=1} = \frac{2(U-U^*)}{NkT} \tag{106}$$

where species A is the solute, B is the solvent, and the derivatives are taken at constant solvent temperature and density and are evaluated at $\sigma_{AB}/\sigma_{BB} = \varepsilon_{AB}/\varepsilon_{BB} = 1$. Z and $(U - U^*)/NkT$ are the compressibility factor and the residual internal energy, respectively, of the pure solvent. Equation (105) can be obtained from the Kirkwood charging equation (47) by using σ_{AB} as a coupling parameter and using the Fundamental Theorem to evaluate the derivative of the integral with respect to σ_{AB}. Equation (106) can be derived similarly. They provide a measure of consistency of the method with the virial pressure and energy equations.

The results from the proposed method were compared to simulation and to equations (105) and (106) for the cases,

1. $\sigma_{AB}/\sigma_{BB} = 1$ and $\varepsilon_{AB}/\varepsilon_{BB} = 0.75, 0.875, 1.0, 1.125, 1.5$, and 2.0.
2. $\varepsilon_{AB}/\varepsilon_{BB} = 1$ and $(\sigma_{AB}/\sigma_{BB})^3 = 0.75, 1.0, 1.5$, and 2.0.

of a Lennard - Jones solute present at infinite dilution in a Lennard - Jones solvent at $T^* = 1.2$, $\rho^* = 0.7$. The results discussed below show that the chemical potentials for the dilute species had the correct trend as the ε - ratio was varied. The trend in the chemical potential as the σ - ratio was varied was incorrect. This later error disappeared at higher solvent temperatures and lower densities.

The chemical potentials obtained from the proposed method decreased with increasing ε - ratio at constant $\sigma_{AB}/\sigma_{BB} = 1$ in agreement with simulation and the energy consistency equation (106). The procedure described in Chapter II - Theory for computing effective diameters provides no way to determine the solvent-solvent diameter, and therefore the packing fraction, when computing the chemical potential of an infinitely dilute solute. However, the packing fraction is the same as that obtained during a pure solvent chemical potential calculation; it was this packing fraction which was used in determining the work of inserting the hard point in all of the infinite dilution cases. The method was constrained so that the packing fraction was the same as for each case. At $T^* = 1.2$, $\rho^* = 0.7$ the HMSA internal energy for the solvent was $U^c/kT = -3.9639$, therefore the slope of the residual chemical potential with ε - ratio should be, from equation (106), -7.9278. The proposed method yielded chemical potentials with a slope of -7.8108 - reasonably consistent with the internal energy of the solvent. The slope obtained from the simulation data was -7.929. The solute residual chemical potentials are plotted versus ε - ratio in Figure 21. Also shown in the Figure are

the simulation results. The calculated chemical potentials decrease as required as the epsilon ratio increases, being in error only by the amount of the error in the pure solvent chemical potential. The results are listed in Table 19 as are those from simulation. Also listed in Table 19 are the effective diameters for the solvent-solute interaction and the repulsive and attractive contributions to the chemical potentials. The repulsive part of the solute-solvent pair potential becomes steeper as the ε - ratio is increased; thus the effective diameters and repulsive contributions to the chemical potentials increase with epsilon ratio, though the effect is relatively small. Some portion of this increase in the repulsive contribution is also due to an increase in local solvent density about the solute. The increase in local solvent density increases the contact values of the correlation functions in equation (56), leading to a slight increase in the repulsive contribution. The change in the chemical potential is dominated by the reduction (toward more negative values) in the attractive contribution as ε_{AB} is increased. This reduction is in turn caused by an increased aggregation of solvent about the solute. A measure of solvent aggregation is the Kirkwood fluctuation integral[40] G_{AB}, the magnitude of which is an average volume surrounding a solute molecule within which the positions of solvent molecules are correlated with that of the solute,

$$G_{AB} = \int_0^{+\infty} \left[g_{AB}(r) - 1\right] 4\pi r^2 dr \tag{107}$$

where g_{AB} is the pair correlation function for solvent about the solute. The above equation for G_{AB} has not been made dimensionless, so the size of the result depends on the size of the

solvent molecules. $G_{AB} > 0$ implies that, within this volume, there is a larger number of solvent molecules than in an equal amount of bulk fluid. $G_{AB} < 0$ implies that, within this volume, there is a smaller number of solvent molecules than in an equal amount of bulk fluid. Thus, a positive G_{AB} indicates an excess of solvent about the solute, and a negative G_{AB} indicates a deficiency. When $\varepsilon_{AB}/\varepsilon_{BB} = 1$, $G_{AB} = -57.6$ cu. Angstroms and when $\varepsilon_{AB}/\varepsilon_{BB} = 2$, $G_{AB} = +5.4$ cu. Angstroms, based on a solvent size of $\sigma_{BB} = 3.8$ Angstroms. Thus, when the ε - ratio is increased, an excess of solvent collects around the solute, decreasing the attractive contribution to the chemical potential. As a partial compensation, the increase in local solvent density about the test particle caused by increasing with ε - ratio acts to increase solvent-solute effective diameter and to increase the repulsive contribution to the chemical potential.

The chemical potentials obtained from the proposed method increased with increasing σ - ratio at constant $\varepsilon_{AB}/\varepsilon_{BB} = 1$ in disagreement with simulation and virial pressure consistency equation (105). At $T^* = 1.2$, $\rho^* = 0.7$ the HMSA compressibility factor for the solvent was $Z = 0.77117$, therefore the slope of the chemical potential with σ-ratio should be, from equation (105), -1.373. The proposed method yielded chemical potentials with a slope of +1.356 - inconsistent with the bulk properties of the solvent. The slope obtained from the simulation data was -0.934. The solute residual chemical potentials are plotted versus σ - ratio in Figure 22. Also shown in the Figure are the simulation results from reference (4). The effective diameters, repulsive and attractive contributions, and the residual chemical potentials obtained from the method are listed in Table 20. Also listed are the residual chemical potentials obtained from simulation. The HMSA solvent-solute pair correlation functions are nearly scaled versions of solvent-solvent function, therefore the repulsive and

attractive contributions obtained from the method both grow in magnitude nearly in proportion to $(\sigma_{AB}/\sigma_{BB})^3$. However, the repulsive contribution rises faster than the attractive contribution can decrease, leading to an increase in the chemical potential with σ-ratio.

Inaccurate HMSA correlation functions about the test particle cause the errors noted in the predicted solute chemical potentials at the solvent conditions of $kT/\varepsilon_{BB} = 1.2$ and $\rho\sigma_{BB}^3 = 0.7$. The solvent-solute pair correlation functions in the bulk fluid obtained from the HMSA and from new simulations are plotted versus reduced separation distance in Figure 23 for the case where $(\sigma_{AB}/\sigma_{BB})^3 = 2$. These new molecular dynamics results are for a mixture of 1 atom of solute in 255 atoms of solvent. The two curves are nearly identical. When the attractive component of the pair potential is decoupled however, the first peak of the HMSA correlation function about the WCA repulsive particle is significantly larger (about 0.25) than the simulation result. Plotted in Figure 24 are the pair correlation functions about the WCA repulsive particle obtained from the HMSA and from simulation. The large first peak in the HMSA result for correlation functions causes the predicted work of inserting a WCA repulsive test particle to be larger than the true value. It also causes an reduction in the predicted attractive contribution which, in this particular case, does not offset the increase in the repulsive. When the solute size is reduced to that of the solvent so that $(\sigma_{AB}/\sigma_{BB})^3 = 1$ the error in the first peak of predicted correlation functions about the WCA repulsive test particle remains large (about 0.25). Pair correlation functions for this case are plotted in Figure 25. When the temperature is increased to supercritical values and the density reduced, the HMSA makes an accurate prediction of the structure about the WCA repulsive particle, as is shown in Figure 26. The proposed method yields accurate chemical potentials under such

conditions. At subcritical temperatures and high densities the HMSA theory (which approaches SMSA in such cases) once again accurately predicts the pair correlation function about the WCA repulsive particle, as shown in Figure 27. The simulation results for these liquid-like conditions show the independence of the fluid structure on the attractive part of the pair potential which is the basis of perturbation theories. The correlation functions predicted by the HMSA theory also change little as a attractive force is decoupled - a behavior which is a built into the SMSA part of the closure. In these cases the chemical potential is also accurately predicted by the method.

The solvent is near saturated liquid conditions at a reduced temperature of $T^* = 1.2$ and a reduced density of $\rho^* = 0.7$. As noted by Shing et. al. [2] the local solvent structure is flexible in some sense under such conditions. The meaning of this statement is revealed by the molecular dynamics results discussed above for the pair correlation functions about repulsive test particles. The simulation results show that when a repulsive particle is inserted into such fluids it actually has to push aside fewer solvent molecules than the number predicted by simple theories. Under these conditions the HMSA, HNC, PY, and simple hydrostatic theories (using a local compressiblity equal to the bulk phase value) yield nearly the same inaccurate correlation functions about the WCA repulsive test particle when the bulk phase is described by the HMSA theory.

At higher temperatures and lower densities the method correctly predicts both a decrease in residual chemical potential with increasing σ - ratio and a decrease with increasing ε - ratio. At $T^* = 1.4$, $\rho^* = 0.35$ the HMSA internal energy for the solvent was $U^c/kT = -1.7353$, therefore the slope of the chemical potential with ε - ratio should be, from

equation (106), -3.471. The slope obtained from the proposed method was approximately –3.487. At $T^* = 1.4$, $\rho^* = 0.35$ the HMSA compressibility factor for the solvent was $Z = 0.3457$, therefore the slope of the chemical potential with σ - ratio should be, from equation (105), -3.926. The slope obtained from the proposed method was approximately -3.659. Therefore, under these conditions the method yields chemical potentials which are reasonably consistent with the energy and pressure of the bulk fluid. At $\sigma_{AB}/\sigma_{BB} = 1$ and $\varepsilon_{AB}/\varepsilon_{BB} = 1$ the method yielded a residual chemical potential divided by kT of -1.3808 - in agreement with the result of -1.362 from Nicolas' equation of state[38] at equal $P\sigma^3/\varepsilon = 0.1694$. The effective diameters, atttractive and repulsive contributions for this condition and for,

1. $\sigma_{AB}/\sigma_{BB} = 1$ and $\varepsilon_{AB}/\varepsilon_{BB} = 1.125$
2. $(\sigma_{AB}/\sigma_{BB})^3 = 1.25$ and $\varepsilon_{AB}/\varepsilon_{BB} = 1.0$

are listed in Table 21. The reduction in the chemical potential with increasing σ - ratio and with increasing ε - ratio was acompanied by an increase in solvent-solute aggregation. When $\sigma_{AB}/\sigma_{BB} = \varepsilon_{AB}/\varepsilon_{BB} = 1$, $G_{AB} = 432.8$ cu. Angstroms (based on $\sigma_{BB} = 3.8$ Angstroms). Increasing the σ - ratio to $(\sigma_{AB}/\sigma_{BB})^3 = 1.25$ caused the fluctuation integral to increase to 495.2 cu. Angstroms. Increasing the ε - ratio to $\varepsilon_{AB}/\varepsilon_{BB} = 1.125$ caused the fluctuation integral to increase to 662.3 cu. Angstroms. In each case the increased aggregation of solvent about the solute decreases the attractive contribution to the chemical potential. The increased local solvent density also acts to slightly increase the repulsive contribution and the effective solvent-solute diameter. For the case where $\sigma_{AB}/\sigma_{BB} = \varepsilon_{AB}/\varepsilon_{BB} = 1$, the effective diameter divided by σ_{AB} was 1.00367. Increasing the σ - ratio to $(\sigma_{AB}/\sigma_{BB})^3 = 1.25$ caused the diameter divided by σ_{AB} to increase to 1.00400.

Finite Concentration Mixtures

The method was also applied to seven finite concentration mixtures. The results were compared to the simulations of Panagiotopolous[7]. The simulations were intended to be a simple model of carbon dioxide - acetone mictures above the critical temperature of carbon dioxide. The Lennard-Jones parameters given in the original reference were obtained from the critical properties of the real fluids and are listed in Table 22. The Lorenz-Berthelot combining rules were used for the unlike parameters. The simulations gave the coexistence curve at a temperature of 350 K. A subsequent study[41] confirmed the properties of the coexisting phases given in reference (7) by directly simulating vapor-liquid equilibrium. In particular, the latest study confirmed the simulated chemical potentials in the liquid phase, since those in the equilibrium (and low density) vapor are easily calculated. The compositions and densities of these mixtures are listed in Table 23. Also given in the Table are the compressibility factors obtained from the simulations and from the HMSA theory. The HMSA theory predicted the compressibility factors to within an average of 0.0238, indicating that the HMSA equation of state is accurate for these mixtures. The pair correlation functions for a equimolar liquid mixture obtained from the HMSA are plotted in Figures 28, 29 and 30. The symbols are results from a new molecular dynamics simulation. The correlation functions from HMSA are in excellent agreement with simulation. Therefore, any errors in the results from the proposed method are not due to errors in the pair correlation functions for or properties of the bulk fluid obtained from the HMSA theory.

The effective diameters and residual chemical potentials obtained from the proposed method are listed in Table 24. The chemical potentials are converted to the standard state of

reference (7) and are compared with the simulation results in Table 25. The results for the vapor phase were very accurate due to the low densities involved. The average absolute percent error in the chemical potentials for both species was 0.514%. The method was also in agreement with the chemical potentials obtained from the second virial coefficients. For the liquid phase the method overpredicted the chemical potentials of each species, which is consistent with previous observations for pure fluids. For the supercritical (carbon dioxide) species the method overpredicted the chemical potential by an average of 10.15% (based on Panagiotopolous' choice of standard state). For the subcritical (acetone) species the error averaged 10.49%. At least half of the observed error must be attributed to the calculated repulsive contribution. The calculated attractive contibution has a greatest lower bound equal to the rate of change in the Helmholtz energy with respect to the attractive coupling parameter for the fully coupled test particle. That is, the attractive contribution is bounded below by the integrand of equation (92) evaluated at $\lambda = 1.0$. Since the HMSA correlation functions for the bulk fluid are accurate, this lower bound is known for each of the liquid mixtures. These lower bounds are so close to the calculated attractive contribution that the attractive contribution can not be the sole source of error in these cases. It must also be true that the calculated repulsive contribution is too large. This observation is consistent with the results obtained for the infinite dilution mixtures (where it was observed that the work of inserting a WCA repulsive test particle was overpredicted for near saturated liquid states where the fluid structure is flexible).

5. Application to Supercritical Fluids

The results for pure Lennard - Jones fluids were accurate at supercritical conditions, as were the variations of the residual chemical potentials at infinite dilution with respect to variations in the molecular parameters. Therefore, the method can be legitimately used as a tool to study how these chemical potentials depend on the fluid state and on the parameters of the intermolecular force relation.

In near ideal and attractive[42] supercritical fluid mixtures the attractive contribution to the chemical potential grows roughly in proportion to the bulk density. The repulsive contribution grows more rapidly. For a solute at infinite dilution with $\sigma_{AB}/\sigma_{BB} = 1.0772$ and $\varepsilon_{AB}/\varepsilon_{BB} = 1.125$ in a solvent at reduced temperature $kT/\varepsilon_{BB} = 1.4$ some predicted residual chemical potentials are:

Case	Reduced Density $\rho\sigma_{BB}^3$	Repulsive Contribution	Attractive Contribution	$(\mu_A - \mu_A^\circ)/kT$
Below CP	0.5	4.4949	-6.8811	-2.3862
Near CP	0.35	2.4265	-4.6297	-2.2032
Above CP	0.5	4.4949	-6.8811	-2.3862

When the solute is large and attractive, the attractive contribution to the chemical potential is dominant. For an attractive solute at infinite dilution with $\sigma_{AB}/\sigma_{BB} = 1.2175$ and $\varepsilon_{AB}/\varepsilon_{BB} = 2.6533$ in a solvent at reduced temperature $kT/\varepsilon_{BB} = 1.4$ some residual chemical potentials are:

Case	Reduced Density $\rho\sigma_{BB}^3$	Repulsive Contribution	Attractive Contribution	$(\mu_A - \mu_A^\circ)/kT$
Low density	0.025	0.2117	-1.6980	-1.4864
Near CP	0.35	3.6953	-18.9897	-15.2944

For large attractive solutes the solute residual chemical potential is roughly proportional to the bulk density and therefore its derivative with respect to pressure along an isotherm is

roughly proportional to the derivative of the density with respect to pressure. This behavior was present in earlier models of supercritical mixtures[40].

For a given solvent density near the critical value the "attractive" and "repulsive" mixtures described by Debenedetti and Petsche[42] have large negative and slightly positive residual chemical potentials, respectively. These cases differ primarily in the size of the attractive contribution to the chemical potential. Using the same solvent as in "Near CP" case ($kT/\varepsilon_{BB} = 1.4$ and $\rho\sigma_{BB}^3 = 0.35$) yields the following residual chemical potentials at infinite dilution:

Case	σ_{AB}/σ_{BB}	$\varepsilon_{AB}/\varepsilon_{BB}$	Repulsive Contribution	Attractive Contribution	$(\mu_A - \mu_A^*)/kT$
Attractive	1.2175	2.6533	3.6953	-18.9897	-15.2944
Near ideal	1.0772	1.125	2.4265	-4.6297	-2.2032
Pure	1.0	1.0	1.9314	-3.3122	-1.3808
Repulsive	0.8484	0.3769	1.0390	-0.7616	0.2774

Thus the repulsive case might be more descriptively, if more clumsily, termed "non-attractive."

It is interesting to consider furthur the attractive and repulsive cases discussed above. The repulsive case consists of a small solute in a bath of large solvent molecules and the second being a large solute in a bath of small solvent molecules. The conditions and Lennard-Jones parameters are chosen so that the reduced temperature and density of the solvent is the same in both cases and so that the solvent-solute intermolecular pair potential is the same in both cases. Under these conditions the repulsive case has a large positive chemical potential and the attractive case has a large negative chemical potential, in spite of the equality of the solvent-solute pair potential. The effective diameters, and attractive and repulsive contributions to the chemical potentials for both cases are listed in Table 26. The difference

in the residual chemical potentials for the two cases is the result of large deviations in the solvent-solute pair correlation functions from the low density limit (which is the same in each case). In the repulsive case this deviation results in a low in solvent-solute aggregation: $G_{AB} \bullet \sigma_{AB}^{-3} = -9.675$. In the attractive case there is a high solvent-solute aggregation: $G_{AB} \bullet \sigma_{AB}^{-3} = +83.166$. In the repulsive case the low aggregation yields a low local solvent density and a high (toward less negative values) attractive contribution, resulting in a positive chemical potential. The repulsive contribution is also low in the "repulsive" case, due to both the reduction in solute size and to the reduction in local solvent density, but not low enough to yield a net negative chemical potential. The exact opposite situation prevails in the attractive case. The high aggregation of solvent about the solute greatly lowers the attractive contribution and slightly increases the repulsive contribution leaving a very negative chemical potential. It is this behavior which causes the high solubility of large solutes in supercritical fluids.

The attractive contribution and its approximate proportionality to the bulk density are thus seen to be important factors in describing supercritical chemical potentials and therefore, solubilities in supercritical fluids. The above examples show that the proposed method can be used to make useful estimates of chemical potentials at near critical conditions from fluid structural data obtained from the HMSA theory.

It is tempting to try to analyze how enhanced solvent aggregation in the different coordination shells surrounding a solute contribute to the very negative chemical potentials determined from the Kirkwood charging process. Unfortunately, the resulting function of intermolecular separation depends on the path of the coupling parameter integration. This

lack of path independence makes it impossible to uniquely assign the observed reduction in the solute chemical potential near the solvent critical point to either enhanced nearest neighbor or to enhanced long-ranged solvent-solute interactions. The residual chemical potential's independence of the path of the coupling parameter integration comes about only after averaging the positions of the test particle and all of the bath molecules over the entire volume of the fluid. Thus the entire volume of the fluid is important in determining the solute chemical potential. Care must be taken when making micro-structural interpretations of bulk phase thermodynamic properties.

CHAPTER IV

CONCLUSIONS AND RECOMMENDATIONS

In this work a Kirkwood charging procedure was introduced for calculating chemical potentials from integral equation theories which used the particle scaling from SPT to calculate the repulsive contribution. The multi-step charging procedure was particularly effective at high densities. A summary of the results obtained with the RY and HMSA theories follows:

- When used with the RY theory, the method reproduced the Gibbs free energies of pure WCA repulsive fluids to within the error of the RY compressibility factor. The residual Helmholtz free energies were reproduced to within 0.081 kT.
- It also reproduced the excess Gibbs free energies of mixing WCA repulsive particles at constant pressure to within 0.0009 kT at the moderate conditions examined.
- When used with the HMSA theory, the method reproduced the residual Gibbs free energies of pure Lennard - Jones fluids to within 0.2 kT except within the reduced density range of about $0.6 \leq \rho\sigma^3 \leq 0.75$, (where errors reached as much as 0.4 kT). The large errors at these intermediate densities disappeared for reduced temperatures kT/ε greater than about 1.5.

- It reproduced the correct change in the chemical potential with changes in the solvent-solute energy parameter in infinitely dilute mixtures - satisfying a consistency condition with the energy equation.
- It did not predict the change in the chemical potential with changes in the solvent-solute size parameter in infinitely dilute mixtures under some conditions - violating a consistency condition with the pressure equation. This error also disappeared for reduced temperatures kT/ε greater than about 1.5.
- Residual chemical potentials in vapor phase mixtures of dissimilar Lennard - Jones particles were predicted to within experimental error (which was 0.1 kT).
- Residual chemical potentials of supercritical components in liquid phase mixtures of Lennard - Jones particles were predicted only to within 0.2 - 0.3 kT.
- Residual chemical potentials of subcritical components in liquid phase mixtures of dissimilar Lennard - Jones particles were predicted poorly - to within 0.4 - 0.6 kT.

The errors in the results for Lennard - Jones systems are due to inaccurate predictions of the correlation functions about the repulsive test particles by the HMSA theory for near saturated liquid states. They were not caused by the approximations used in the method. The errors caused by the approximations used were:

1. Error caused by using the SPT equation (30) for the work of inserting the hard point. The error in the residual chemical potential from this source was less than 0.007 kT (as estimated from the HNC results, see Table 3).
2. Numerical errors due to the procedure for solving the integral equations and to the

numerical integrations of the correlation functions. This error was also estimated to be less than 0.007 kT (as estimated from the HNC results, see Table 3). Of course, this figure is implimentation dependent.

3. Errors due to neglecting the integral over the bridge functions in equation (88) for the work of softening. A conservative upper bound on this error when using the HMSA theory was 0.056 kT (see Table 4).

Therefore, errors in the predicted chemical potential which were not due to errors in the HMSA correlation functions were at most 0.07 kT. The overestimation of pure fluid chemical potentials at intermediate densities was caused by overestimates by the HMSA of the first peak of the pair correlation functions about the WCA repulsive test particle. The overestimate of the first peak caused an overestimate of the work required to insert the effective hard sphere. The HMSA correlation functions for such a case were compared to simulation results in Figure 25. The increasing error in the residual chemical potential at infinite dilution with increasing size parameter was also caused by an overestimate of the first peak of pair correlation functions about the repulsive test particle. The predicted correlation functions for such a case were compared to simulation results in Figure 24. The HMSA yields accurate test particle correlation functions at low densities or supercritical temperatures (Figure 26) and at high densities (Figure 27), therefore the method yields accurate chemical potentials under these conditions. The ability to calculate chemical potentials of attractive solutes in supercritical fluids makes the method a useful suppliment to existing techniques based on molecular dynamics and perturbation theories which cannot be used under these conditions.

More accurate results for Lennard - Jones fluids will require an integral equation theory that can predict the correlation functions about the WCA repulsive test particle under a broader range of conditions. It is impossible to determine if a theory qualifies for this short of trying it. One theory worth trying is the reference hypernetted chain theory[36,43] (RHNC). The method is suitable for application to the RHNC theory since the implimentation of the method is then greatly simplified. The theory is based on the following definition of the bridge functions B:

$$C_{ij} = h_{ij} - \ln(y_{ij}) + B_{ij} \tag{108}$$

Thus, the bridge functions represent the error in the HNC closure equation (11). If the bridge functions were known exactly, an exact theory would result. However, bridge functions are known (approximately) for only the hard sphere system. In the RHNC theory the bridge functions of the system of interest are modeled by those of a reference system of hard spheres,

$$C_{ij} = h_{ij} - \ln(y_{ij}) + B_{ij}^{H}(\{d_k'\}) \tag{109}$$

where d_i' is the diameter of the hard sphere which represents species i in the reference system of hard spheres. The hard sphere system is taken at the same temperature, density and relative composition as in the system of interest. The diameters are chosen in a way that minimizes the Helmholtz free energy of the system of interest[36] as determined from the RHNC correlation functions, under the assumption that the bridge functions do not vary as all of the particles are tranformed from hard spheres into real particles. In this case we divide the residual chemical potential of species j into hard sphere and non-hard parts. The non-hard part is given by equation (88) with $\xi = 0$ representing a system containing a Lennard - Jones

test particle of species j and $\xi = 1$ representing a system containing a hard sphere with diameter d_j'. The integral over the bridge functions is identically zero in the RHNC. The test particle correlation functions in equation (88) are calculated using closure equation (109) with j = c and with the bridge functions being independent of the coupling parameter ξ of the non-hard forces. The hard sphere part is then given by the sum of equations (30) and (56). Equation (30) is evaluated with a packing fractio n ξ_3 determined from $\{d_k'\}$. Equation (56) is evaluated with an upper limit of integration $R = d_j'/2$. The correlation functions $g^H_{ic}(R + R_i ; R + R_i)$ in equation (56) are determined from closure equation (109) using the bridge function for a hard sphere of diameter $R + R_i$ in a bath of hard spheres with diameters $\{d_k'\}$. So, the determination of effective diameters and the evaluation of equation (92) is eliminated when applying the method to the RHNC theory. The major difficulty is the determination of the $\{d_k'\}$. The fact that the integral over the bridge functions in equation (88) is identically zero (rather than being neglected) should slightly improve the thermodynamic consistency of the method's results. In addition, the RHNC produces correlation functions which yield consistent Helmholtz free energies, virial pressures and internal energies. The consistency between the Helmholtz energy and virial pressure may enhance the consistency between the chemical potentials and the virial pressure.

BIBLIOGRAPHY

1. Widom, B., "Some topics in the theory of fluids," J. Chem. Phys. 39 p. 2808 (1963).
2. Shing, K.S. and K.E. Gubbins, "The chemical potential in dense fluids and fluid mixtures via computer simulation," Mol. Phys. 46(5) pp. 1109-1128 (1982).
3. Heinbuch, U. and J. Fischer, "On the application of Widom's test particle method to inhomogeneous fluids," Mol. Sim. 1 pp. 109-120 (1987).
4. Lotfi, A. and J. Fischer, "Chemical potentials of model and real dense fluid mixtures from perturbation theory and simulations," Mol. Phys. 66(1) pp. 199-219 (1989).
5. Shing, K.S., K.E. Gubbins and K. Lucas, "Henry constants in non-ideal mixtures, Computer simulation and theory," Mol. Phys. 65(5) pp. 1235-1252 (1988).
6. Powles, J.G., W.A. Evans and N. Quirke, "Non-destructive molecular-dynamics simulation of the chemical potential of a fluid," Mol. Phys. 46(6) pp. 1347-1370 (1982).
7. Panagiotopoulos, A.Z., U.W. Suter and R.C. Reid, "Phase diagrams of nonideal fluid mixtures from Monte Carlo simulation," Ind. Eng. Chem. Fundam. 25(4) pp. 525-535 (1986).
8. Haile, J.M., "On the use of computer simulation to determine the excess free energy in fluid mixtures," Fluid Phase Equilib. 26 pp. 103-127 (1986).
9. Shukla, K.P. and J.M. Haile, "Computer simulation results for thermodynamic excess properties in fluid mixtures," Mol. Phys. 62(3) pp. 617-636 (1987).
10. Andersen, H.C., J.D. Weeks and D. Chandler, "Relationship between the hard sphere fluid and fluids with realistic repulsive forces," Phys. Rev. A 4(4) pp. 1597-1607 (1971).
11. Lee, L.L. and D. Levesque, "Perturbation theory for mixtures of simple fluids," Mol. Phys. 26(6) pp. 1351-1370 (1973).
12. Carnahan, N.F. and K.E. Starling, "Equation of state for nonattracting rigid spheres," J. Chem. Phys. 51(2) pp. 635-636 (1969).

13. Mansoori, G.A., N.F. Carnahan, K.E. Starling and T.W. Leland, "Equilibrium thermodynamic properties of the mixture of hard spheres," J. Chem. Phys. 54(4) pp. 1523-1525 (1971).
14. Verlet, L. and J. Weis, "Equilibrium theory of simple liquids," Phys. Rev. A 5(2) pp. 939-952 (1972).
15. Bohn, M., J. Fischer and F. Kohler, "Prediction of excess properties for liquid mixtures," Fluid Phase Equilib. 31 pp. 233-252 (1986).
16. Lee, L.L., Molecular Thermodynamics of Non-Ideal Fluids, Butterworths, Boston (1988).
17. Chandler, D., "Equilibrium structure and molecular motion in liquids," Accnts. of Chem. Res. 7 pp. 246-248 (1974).
18. Percus, J.K., "The pair correlation function in classical statistical mechanics," in The Equilibrium Theory of Classical Fluids, H.L. Frisch and J.L. Lebowitz eds., W.A. Benjamin Inc., New York (1964).
19. Barker, J.A. and D. Henderson, "What is 'liquid'?" Rev. Mod. Phys. 48(4) pp. 587-665 (1976).
20. Labik, S., A. Malijevsky and P. Vonka, "A rapidly convergent method of solving the OZ equation," Mol. Phys. 56(3) pp. 709-715 (1985).
21. Reed, T.M. and K.E. Gubbins, Applied Statistical Mechanics, p. 189 New York (1973).
22. Rogers, F.J. and D.A. Young, "New, thermodynamically consistent, integral equation for simple fluids," Phys. Rev. A 30(2) pp. 999-1007 (1984).
23. Zerah, G. and J. Hansen, "Self-consistent integral equations for fluid pair distribution functions: Another attempt," J. Chem. Phys. 84(4) pp. 2336-2343 (1986).
24. Weeks, J.D., D. Chandler and H.C. Andersen, "Role of repulsive forces in determining the equilibrium structure of simple liquids," J. Chem. Phys. 54(12) pp. 5237-5245 (1971).
25. Madden, W.G. and S.A. Rice, "The mean spherical approximation and effective pair potentials in liquids," J. Chem. Phys. 72(7) pp. 4208-4215 (1980).
26. Kjellander, R. and S. Sarmen, "The chemical potentials of simple fluids in a common class of integral equation closures," J. Chem. Phys. 90(5) pp. 2768-2775 (1989).
27. Kirkwood, J.G., "Statistical Mechanics of Fluid Mixtures", J. Chem. Phys. 3(5), pp. 300-313 (1935).
28. Hill, T.L., An Introduction to Statistical Thermodynamics, p. 307, Addison-Wesley, Reading Mass. (1960).
29. Morita, T., Prog. Theor. Phys. 23 p. 829 (1960).
30. Lee, L.L., "Correlation functions of classical fluids. III. The method of partition function variation applied to the chemical potential: Cases of PY and HNC2," J. Chem. Phys. 60(4) pp. 1197-1206 (1974).
31. Reiss, H., H.L. Frisch and J.L. Lebowitz, "Statistical mechanics of rigid spheres," J. Chem. Phys. 31(2) pp. 369-380 (1959).

32. Reiss, H., H.L. Frisch, E. Helfand and J.L. Lebowitz, "Aspects of the statistical thermodynamics of real fluids," J. Chem. Phys. 32(1) pp. 119-124 (1960).
33. Lebowitz, J.L., E. Helfand and E. Praestgaard, "Scaled particle theory of fluid mixtures," J. Chem. Phys. 43(3) pp. 774-779 (1965).
34. Lado, F., "Perturbation correction for the free energy and structure of simple fluids," Phys. Rev. A 8(5) pp. 2548-2552 (1973).
35. Champeney, D.C., Fourier Transforms and their Physical Applications, p. 221
36. Lado, F., S.M. Foiles and N.W. Ashcroft, "Solutions of the reference-hypernetted chain equation with minimized free energy," Phys. Rev. A 28(4) p. 2374 (1983).
37. Lebowitz, J.L., "Exact Solution of Generalized Percus-Yevick Equation for a Mixture of Hard Spheres", Phys. Rev., 133(4A), p. A895 (1964).
38. Nicolas, J.J., K.E. Gubbins, W.B. Street and D.J. Tildesley, "Equation of state for the Lennard-Jones fluid," Mol. Phys. 37(5) pp. 1429-1454 (1979).
39. Hansen, J.P. and L. Verlet, Phys. Rev. 184 pp. 151-161 (1969).
40. Pfund, D.M., L.L. Lee and H.D. Cochran, "Application of the Kirkwood-Buff theory of solutions to dilute supercritical mixtures. II. The excluded volume and local composition models," Fluid Phase Equilib. 39 pp. 161-192 (1988).
41. Panagiotopoulos, A.Z., N. Quirke, M. Stapleton and D.J. Tildesley, "Phase equilibria by simulation in the Gibbs ensemble. Alternative derivation, generalization and application to mixture and membrane equilibria," Mol. Phys. 63(4) pp. 527-545 (1988).
42. Petsche, I.B. and P.G. Debenedetti, "Solute-solvent interactions in infinitely dilute mixtures, a molecular dynamics investigation," submitted J. Chem. Phys. (1989).
43. Enciso, E., F. Lado, M. Lombardero, J.L.F. Abascal and S. Lago, "Extension of the optimized RHNC equation to multicomponent liquids," J. Chem. Phys. 87(4) pp. 2249-2256 (1987).

ACKNOWLEDGEMENTS

This work has been supported in part by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc., and subcontract with the University of Oklahoma.

Table 1

Comparision of the Proposed Method Using the HNC Theory to

Known HNC Results For Pure Lennard-Jones Fluids

Case	Effective Diameter, d/σ	Repulsive Contribution This Work	Repulsive Contribution HNC	Attractive Contribution This Work	Attractive Contribution HNC	Total $(G - G^*)/NkT$ This Work	Total $(G - G^*)/NkT$ HNC(1)
1	1.00057	2.3855	2.3867	-3.5786	-3.5786	-1.1931	-1.1919
2	1.00537	7.8419	7.8476	-8.5562	-8.5562	-0.7144	-0.7086
3	1.00166	13.6559	13.6698	-10.7773	-10.7773	2.8786	2.8925

The conditions examined were:

Case	Reduced Temperature, kT/ε	Reduced Density, $\rho\sigma^3$
1	1.5	0.4
2	1.2	0.7
3	1.2	0.85

(1) HNC results for the residual Gibbs free energies were obtained from equation (93). The HNC repulsive and attractive contributions were obtained from modified versions of equation (88), with the bridge function integrals being identically zero in this (HNC) case. The results from the SPT-based charging process used in this work are in agreement with the known results from HNC theory.

Table 2

Comparision Between Exact and SPT Values for the

Work of Inserting the Hard Point In the HNC Approximation

Case	Repulsive Contribution: This Work	Repulsive Contribution: HNC	Repulsive Contribution: Error	Work of Inserting the Hard Point: SPT	Work of Inserting the Hard Point: HNC(1)	Work of Inserting the Hard Point: Error	Residual Numerical Error
1	2.3855	2.3867	-0.0012	0.2355	0.2367	-0.0012	0.0000
2	7.8419	7.8476	-0.0057	0.4659	0.4706	-0.0047	-0.0010
3	13.6559	13.6698	-0.0139	0.5929	0.5994	-0.0065	-0.0074

Pure Lennard-Jones fluids were examined under the following conditions:

Case	Reduced Temperature, kT/ε	Reduced Density, $\rho\sigma^3$
1	1.5	0.4
2	1.2	0.7
3	1.2	0.85

(1) HNC results for the work of inserting the hard point were obtained from equation (95). The corresponding SPT values were obtained from equation (30). The repulsive contributions shown were taken from Table 1. The SPT formula equation (30) provides a good estimate of the work of inserting the hard point even though it is based on the false assumption of the non-overlap of molecular cores.

Table 3

Comparision Between Exact and SPT Pair Correlation

Functions at Contact With the Hard Point In the HNC Approximation

Contact Values of the Pair Correlation Function With the Hard Point, $g^H(d/2;d/2)$

Case	SPT	HNC	Error
1	1.26550	1.28706	-0.02156
2	1.59352	1.66131	-0.06779
3	1.80923	1.90846	-0.09923

Pure Lennard-Jones fluids were examined at the following conditions:

Case	Reduced Temperature, kT/ε	Reduced Density, $\rho\sigma^3$
1	1.5	0.4
2	1.2	0.7
3	1.2	0.85

The contact values of the pair correlation functions shown are those for bath molecules in contact with a hard point. The effective diameters used are those shown in Table 1. The SPT contact values from equation (98) do not agree with the HNC results, indicating an inconsistency between the SPT equation (30) for the work of inserting the hard point and the HNC equation (95). It is expected that, for a given integral equation theory, a small difference between the SPT and integral equation contact values implies consistency between the SPT equation (30) for the work of inserting the hard point and the integral equation theory. As shown in Table 2, the effect of this inconsistency on the accuracy of the work of insertion is very small.

Table 4

Upper Bounds on the HMSA Bridge

Function Integrals in Lennard - Jones Fluids

Case	Trial Effective Diameter, d_{AB}/σ_{BB}	Soft Repulsive Contribution	Upper Bound on Bridge Function Integral
A	1.00071	2.6439×10^{-6}	7.7152×10^{-5}
B	1.26556	0.12844	0.0083191
C	1.27186	-0.17363	0.055611
D	1.00570	-4.4102×10^{-6}	0.041039

The cases are for mixtures of an infinitely dilute species A in a solvent species B:

Case	Reduced Temperature, kT/ε_{BB}	Reduced Density, $\rho\sigma_{BB}^3$	$(\sigma_{AB}/\sigma_{BB})^3$	$\varepsilon_{AB}/\varepsilon_{BB}$
A	1.5	0.4	1.0	1.0
B	1.2	0.7	2.0	1.0
C	1.2	0.7	2.0	1.0
D	1.2	0.85	1.0	1.0

Cases A and D are pure fluids. The trial diameters shown for cases B and C are not the optimal value (which gives a work of softening equal to zero) for these conditions. The sub-optimal values are shown in order to make the case that the bridge function integrals in equation (88) are small even when the diameters are not perfectly chosen. The soft repulsive contributions shown were obtained from equation (88) with the bridge function integrals neglected and the upper bounds on the neglected integrals were obtained from equation (99).

Table 5
The Effect of the Choice of Effective Hard Sphere Diameter
on the Calculated Repulsive Contribution to the Chemical Potential

Trial Effective Diameter, d/σ	Work of inserting the hard sphere/kT	Work of softening the hard sphere to WCA/kT	Total Repulsive Contribution/kT
0.9625	5.9921	1.0151	7.0072
0.9750	6.2768	0.7555	7.0323
0.9875	6.5698	0.4784	7.0482
1.0000	6.8712	0.1835	7.0547
1.00741	7.0620	0.0000	7.0620
1.0125	7.1920	-0.1295	7.0625
1.0250	7.5122	-0.4608	7.0514
1.0375	7.8417	-0.8106	7.0311

The work of inserting the hard sphere is the sum of results from equations (30) and (56). The work of softening was obtained from equation (88) with the bridge function integrals neglected. Calculations were performed for a test particle in a pure Lennard - Jones solvent bath at a reduced temperature of $kT/\varepsilon = 1.2$ and a reduced density of $\rho\sigma^3 = 0.7$. If the test particle/bath molecule bridge functions were actually invarient during the softening process, then the numbers in the last column would have been all the same. The fact that they are nearly so for the whole range of reasonable choices of hard sphere size suggests that it is reasonable to assume that the bridge functions are invarient during softening. Note that the work of inserting the hard sphere includes the work of inserting the hard point, which is also changing (over a range of 0.3957 to 0.5265) with changes in the choice of effective diameter. The proper accounting of each of these variations leaves the balance in the final column unchanged. The resulting repulsive contribution is insensitive to the choice of effective hard sphere diameters. For these conditions the effective diameter for a WCA repulsive reference fluid determined by Verlet - Weis perturbation theory is $d/\sigma = 1.00693$. The presence of attractive forces in this case acts to increase the effective diameter.

Table 6

Comparision Between the Rogers - Young and Verlet - Weis

Equations of State for Pure WCA Repulsive Fluids

Compressibility Factor, $P/\rho kT$

Case	Rogers - Young	Verlet - Weis	Error
1	2.5064	2.5209	-0.0145
2	5.7548	5.9109	-0.1561
3	8.8577	9.2385	-0.3808

Pure WCA repulsive fluids were examined at the following conditions:

Case	Reduced Temperature, kT/ε	Reduced Density, $\rho\sigma^3$
1	1.5	0.4
2	1.2	0.7
3	1.2	0.85

Table 7

Comparision of Free Energies From the Method Using the Rogers - Young Theory to Known (Verlet - Weis) Results For Pure WCA Repulsive Fluids

	Effective Diameter, d/σ		Residual Gibbs Energy, $(G - G^*)/NkT$		Residual Helmholtz Energy, $(A - A^*)/NkT$	
Case	This Work	VW	This Work	VW	This Work	VW
1	1.00068	1.00066	2.6461	2.6566	1.1396	1.1357
2	1.00706	1.00693	7.5556	7.6773	2.8009	2.7664
3	1.00516	1.00490	11.9459	12.2461	4.0882	4.0076

Pure WCA repulsive fluids were examined at the following conditions:

Case	Reduced Temperature, kT/ε	Reduced Density, $\rho\sigma^3$
1	1.5	0.4
2	1.2	0.7
3	1.2	0.85

Helmholtz free energies are accurately predicted by the proposed method. The accuracy of the predicted Gibbs energies is reduced by errors in the RY equation of state for the WCA repulsive fluid. The errors in the Gibbs free energies roughly equal the errors in the compressibility factors predicted by the RY theory (see Table 6). Errors in the compressibility are related to errors in the Gibbs energy through equation (100). For the WCA repulsive fluid the effective diameters obtained from the proposed method agree with those obtained from VW perturbation theory.

Table 8

Comparision Between Exact and SPT Pair Correlation Functions at Contact With the Hard Point In the Rogers - Young Approximation

Contact Values of the Pair Correlation Function With the Hard Point, $g^H(d/2;d/2)$

Case	SPT	RY	Error
1	1.26561	1.26512	0.00049
2	1.59830	1.59669	0.00161
3	1.82478	1.81923	0.00555

Pure WCA repulsive fluids were examined at the following conditions:

Case	Reduced Temperature, kT/ε	Reduced Density, $\rho\sigma^3$
1	1.5	0.4
2	1.2	0.7
3	1.2	0.85

The contact values of the pair correlation functions are for bath molecules in contact with a hard point. The effective diameters used are those shown in Table 7. The consistency between the SPT contact values from equation (98) the RY values suggest that the work of inserting the hard point can be reliably obtained from SPT equation (30).

Table 9

Comparision of Free Energies From the Method to Thermodynamic Integration of the Rogers - Young Equation of State For Pure WCA Repulsive Fluids

	Residual Gibbs Energy, $(G - G^*)/NkT$				Residual Helmholtz Energy, $(A - A^*)/NkT$			
		Thermo. Integration				Thermo. Integration		
Case	This Work	(1)	(2)	VW	This Work	(1)	(2)	VW
1	2.6461	2.6381	2.6360	2.6566	1.1397	1.1316	1.1296	1.1357
2	7.5556	7.4844	7.4657	7.6773	2.8009	2.7296	2.7109	2.7664
3	11.9459	11.7788	11.7452	12.2461	4.0882	3.9211	3.8875	4.0076

(1) From integration of the virial pressure, using equation (102).
(2) From integration of the compressibility, using equation (101).

Pure WCA repulsive fluids were examined at the following conditions:

Case	Reduced Temperature, kT/ε	Reduced Density, $\rho\sigma^3$
1	1.5	0.4
2	1.2	0.7
3	1.2	0.85

Results from the proposed method (which uses an SPT-based Kirkwood charging process) are more accurate than either thermodynamic integration. The thermodynamic integrations accumulate the errors in the pressure predicted by the RY theory. The errors in the RY pressure were illustrated in Table 6.

Table 10

Densities Required for Isobaric Formation of Some WCA Repulsive Mixtures - A Comparison of Rogers - Young Densities to Simulation

Mole % Small	Density Required, $\rho\sigma_{11}^3$ to Give $P\sigma_{11}^3/\varepsilon_{11} = 0.5$ RY	Simulation	Error	Configurational Internal Energy, U^c/kT RY	Simulation
$\sigma_{22}/\sigma_{11} = 1.25$:					
0	0.19746	0.1964	0.00106	0.1644	0.1664
25	0.21136	0.2111	0.00026	0.1463	0.1469
50	0.22726	0.2274	-0.00014	0.1284	0.1280
75	0.24561	0.2447	0.00091	0.1106	0.1116
100	0.26698	0.2665	0.00048	0.0930	0.0930
$\sigma_{22}/\sigma_{11} = 2.0$:					
0	0.086048	0.0855	0.000548	0.5322	0.5402
25	0.10375	0.1035	0.00025	0.4202	0.4222
50	0.13053	0.1301	0.00043	0.3091	0.3116
75	0.17567	0.1743	0.00137	0.1996	0.2030
100	0.26698	0.2665	0.00048	0.0930	0.0930

For all mixtures, $\varepsilon_{11} = \varepsilon_{12} = \varepsilon_{22}$, $\sigma_{12} = 0.5(\sigma_{11} + \sigma_{22})$ and $kT/\varepsilon_{11} = 1.0$.

Simulation results were obtained from reference 8. The densities are used in the calculation of the excess Gibbs free energy of mixing at constant pressure. At the pressure used here the RY equation of state for the WCA repulsive fluid is accurate.

Table 11

Residual Chemical Potentials in Mixtures of WCA Repulsive Particles

Mole %	Effective Diameters, d_{ij}/σ_{11}				Residual Chemical Potentials	
Small	1-1	2-1	1-2	2-2	$(\mu_1 - \mu_1^*)/kT$	$(\mu_2 - \mu_2^*)/kT$
$\sigma_{22}/\sigma_{11} = 1.24993$:						
0	-	-	-	1.26999	-	2.68560
25	1.01645	1.14353	1.14340	1.27004	1.81231	2.61460
50	1.01648	1.14357	1.14343	1.27008	1.74789	2.53496
75	1.01650	1.14361	1.14347	1.27013	1.67526	2.44109
100	1.01653	-	-	-	1.59306	-
$\sigma_{22}/\sigma_{11} = 2.0$:						
0	-	-	-	2.02798	-	7.62915
25	1.01628	1.52419	1.52379	2.02825	2.36914	7.41658
50	1.01633	1.52435	1.52395	2.02858	2.21617	7.11854
75	1.01641	1.52458	1.52418	2.02907	1.98403	6.67466
100	1.01653	-	-	-	1.59306	-

The chemical potentials were calculated for the compositions, temperatures and densities specified in Table 10. The 1-1 and 2-1 effective diameters were determined during the calculation of μ_1 and the 1-2 and 2-2 diameters were determined during the (separate) calculation of μ_2. The 1-2 and 2-1 effective diameters differ because their calculation is only accurate to the third decimal place.

Table 12

Free Energies of Mixing WCA Repulsive Particles

Excess Gibbs Free Energies of Mixing $\Delta G^E/NkT$, at Constant Pressure

Mole % Small	This Work with RY Theory Configurational	Ideal Gas	Total	Simulation
$\sigma_{22}/\sigma_{11} = 1.24993$:				
25	0.00156	-0.00737	-0.00581	-0.0064
50	0.00209	-0.01026	-0.00817	-0.0085
75	0.00052	-0.00802	-0.00750	-0.0072
$\sigma_{22}/\sigma_{11} = 2.0$:				
25	0.03459	-0.09601	-0.06142	-0.0623
50	0.05625	-0.14948	-0.09323	-0.0937
75	0.05461	-0.13552	-0.08091	-0.0810

The mixtures used were those specified in Table 10. The computed excess Gibbs energies were calculated from the residual chemical potentials given in Table 11 and the densities given in Table 10 using equation (103). The configurational parts shown consist of those terms in equation (103) involving the residual chemical potentials.

Simulation results were obtained from reference 8.

Table 13

Comparision of the Proposed Method Using the HMSA Theory to

Simulation Results For Pure Lennard-Jones Fluids

Case	Effective Diameter, d/σ	Repulsive Contribution	Attractive Contribution	$(G - G^*)/NkT$ Total	EOS(1)	PT(2)	Simulation
1	1.00071	2.3857	-3.5978	-1.2121	-1.3395	-	-1.33 (3)
2	1.00741	7.0620	-8.6782	-1.6166	-1.9865	-1.94	-1.854 (4)
3	1.00570	11.4482	-10.9466	0.5016	0.3346	0.68	0.48 (5)

The conditions examined were:

Case	Reduced Temperature, kT/ε	Reduced Density, $\rho\sigma^3$
1	1.5	0.4
2	1.2	0.7
3	1.2	0.85

Notes:

(1) Equation of state for pure Lennard-Jones fluids due to Nicolas, Gubbins, Streett, and Tildesley, reference (38).
(2) Perturbation theory due to Fischer from reference (3).
(3) Result of Shing, Gubbins, and Lucas, reference (5).
(4) Average of -1.86 (Heinbuch and Fischer, reference 3) and -1.848 (Lotfi and Fischer, reference 4).
(5) Result of Heinbuch and Fischer, reference (3).

For the Lennard - Jones fluid the effective diameters obtained from the proposed method disagree with those obtained from VW perturbation theory (which were listed in column 3 of Table 7). Unlike perturbation theory, in this work the presence of attractive forces influences the choice of effective hard sphere diameters.

Table 14

Comparision Between Exact and SPT Pair Correlation

Functions at Contact With the Hard Point In the HMSA Approximation

Contact Values of the Pair Correlation Function With the Hard Point, $g^H(d/2;d/2)$

Case	SPT	HMSA	Error
1	1.26564	1.27047	-0.00483
2	1.59931	1.59586	0.00345
3	1.82721	1.81737	0.00984

Pure Lennard-Jones fluids were examined at the following conditions:

Case	Reduced Temperature, kT/ε	Reduced Density, $\rho\sigma^3$
1	1.5	0.4
2	1.2	0.7
3	1.2	0.85

The contact values of the pair correlation functions are for bath molecules in contact with a hard point. The effective diameters used are those shown in Table 13. The consistency between the SPT contact values from equation (98) the HMSA values suggest that the work of inserting the hard point can be reliably obtained from equation (30).

Table 15

Comparision Between the HMSA Equation of State for Pure

Lennard - Jones Fluids and Molecular Simulation

Reduced Temp., kT/ε	Reduced Density, $\rho\sigma^3$	Compressibility Factor, $P/\rho kT$			Configurational Internal Energy, U^c/kT		
		HMSA	Sim.	Error	HMSA	Sim.	Error
0.928	0.025	0.8488	0.8487 (1)	0.0001	-0.2691	-0.2619 (1)	-0.0072
0.928	0.6	-0.8485	-0.819	-0.0295	-4.5650	-4.596	0.031
0.928	0.7	-0.3694	-0.385	0.0156	-5.3099	-5.322	0.0121
0.928	0.75	0.1477	0.0661	0.0816	-5.6806	-5.698	0.0174
0.928	0.8	0.8965	0.843	0.0535	-6.0334	-6.037	0.0036
1.15	0.05	0.7982	0.802	-0.0038	-0.3755	-0.375	-0.0005
1.15	0.6	0.0109	0.0	0.0109	-3.5778	-3.581	0.0032
1.15	0.7	0.6075	0.596	0.0115	-4.1626	-4.167	0.0044
1.15	0.8	1.8555	1.857	-0.0015	-4.7057	-4.701	-0.0047
1.556	0.05	0.8894	0.888	0.0014	-0.2378	-0.236	-0.0018
1.556	0.2	0.6321	0.646	-0.0139	-0.9102	-0.903	-0.0072
1.556	0.4	0.5034	0.553	-0.0496	-1.7112	-1.724	0.0128
1.556	0.6	0.9164	0.955	-0.0386	-2.5255	-2.527	0.0015
1.556	0.8	2.7762	2.768	0.0082	-3.2742	-3.273	-0.0012

Notes:

(1) The simulation values for this state of 0.866 for the compressibility factor and 0.238 for the internal energy are apparently in error. The values shown are the second virial coefficient results, where $P/\rho kT = 1 + B\rho$, $U^c/kT = -\rho T\,(dB/dT)$, and B is the second virial coefficient at a reduced temperature of 0.928.

Simulation results were obtained from reference 7.

Table 16

Comparision of Chemical Potentials From the Proposed Method using the HMSA Theory with Molecular Simulation Results for Pure Lennard - Jones Fluids

Reduced Temp., kT/ε	Reduced Density, $\rho\sigma^3$	Effective Diameter d/σ	Residual Gibbs Free Energy, $(G - G^*)/NkT$ Rep.	Attract.	Total	Sim.	Error
0.928	0.025	1.01987	0.1104	-0.4127	-0.3023	-0.3026 (1)	0.0003
0.928	0.6	1.01768	5.1364	-9.1003	-3.9639	-4.360	0.3961
0.928	0.7	1.01700	7.3830	-11.1679	-3.7849	-3.964	0.1791
0.928	0.75	1.01657	8.7637	-12.1880	-3.4243	-3.732	0.3077
0.928	0.8	1.01604	10.3776	-13.1973	-2.8197	-2.923	0.1033
1.15	0.05	1.01210	0.2183	-0.6234	-0.4051	-0.413	0.0079
1.15	0.6	1.00978	5.0715	-7.4649	-2.3934	-2.689	0.2956
1.15	0.7	1.00904	7.1183	-9.0506	-1.9323	-1.835	-0.0973
1.15	0.8	1.00800	9.8605	-10.6433	-0.7828	-0.327	-0.4558
1.556	0.05	1.00060	0.2141	-0.4385	-0.2244	-0.218	-0.0064
1.556	0.2	1.00017	0.9412	-1.7073	-0.7661	-0.775	0.0089
1.556	0.4	0.99926	2.3857	-3.4775	-1.0918	-1.192	0.1002
1.556	0.6	0.99804	4.8698	-5.5770	-0.7072	-0.871	0.1638
1.556	0.8	0.99611	9.1244	-7.8528	1.2716	1.149	0.1226

Notes:

(1) The simulation value for this state of -0.266 for the residual Gibbs energy is apparently in error. The value shown is the second virial coefficient result, where $(G - G^*)/NkT = 2\,B\rho$, and B is the second virial coefficient at a reduced temperature of 0.928.

Simulation results were obtained from reference 7.

Table 17

Comparision of Chemical Potentials From the Proposed Method using the HMSA Theory with Results From Thermodynamic Integration for Pure Lennard - Jones Fluids

Reduced Temp., kT/ε	Reduced Density, $\rho\sigma^3$	Residual Gibbs Free Energy, $(G - G^*)/NkT$ Thermo. Integration (1)	(2)	This Work	Simulation
1.556	0.05	-0.2243	-0.2245	-0.2244	-0.218
1.556	0.2	-0.7864	-0.7786	-0.7661	-0.775
1.556	0.4	-1.2260	-1.1595	-1.0918	-1.192
1.556	0.6	-0.9661	-0.7810	-0.7072	-0.871
1.556	0.8	1.0751	1.3163	1.2716	1.149

(1) From integration of the virial pressure, using equation (102).
(2) From integration of the compressibility, using equation (101).

Simulation results were obtained from reference 7. The charging process used in this work with the HMSA theory tends to be overestimate the residual Gibbs energy except at low and high densities. At the supercritical temperature used in preparing this table the error is small.

Table 18

Compressibilities From the Proposed Method Using the HMSA Theory Compared to Results From the Compressibility Equation For Pure Lennard-Jones Fluids

Case	$\beta(\partial P/\partial \rho)_{T,V}$ From Compressibility Equation	$\beta(\partial P/\partial \rho)_{T,V}$ From the Chemical Potential
1	0.6724	0.8145
2	7.3503	6.7802
3	20.5357	19.1750

The conditions examined were:

Case	Reduced Temperature, kT/ε	Reduced Density, $\rho\sigma^3$
1	1.5	0.4
2	1.2	0.7
3	1.2	0.85

The compressibility equation results were obtained from the HMSA theory using equation (15). The results in the chemical potential column were obtained by numerically differentiating chemical potentials obtained from the proposed method and applying the isothermal, non-isobaric Gibbs-Duhem equation. The underestimated values obtained from the chemical potentials indicate that the test particle sees a local environment (predicted by the HMSA theory) that is reletively incompressible; this results in an overestimate in the repulsive contribution to the chemical potential.

Table 19

Comparision of the Proposed Method Using the HMSA Theory to Simulation Results For Chemical Potentials at Infinite Dilution and Different Energy Ratios

$\varepsilon_{AB}/\varepsilon_{BB}$	Solvent-Solute Effective Diameter, d_{AB}/σ_{AB}	Repulsive Contribution	Attractive Contribution	$(\mu_A - \mu_A^*)/kT$ Total	Simulation	Error
0.75	0.99619	6.7854	-6.4927	0.2927	0.067	0.2257
0.875	1.00281	6.9479	-7.5829	-0.6350	-0.865	0.2300
1.0	1.00741	7.0620	-8.6786	-1.6166	-1.848	0.2314
1.125	1.01265	7.1940	-9.7803	-2.5863	-2.826	0.2397
1.25	1.01629	7.2865	-10.8884	-3.6019	-3.861	0.2591
1.5	1.02279	7.4534	-13.1244	-5.6710	-5.949	0.2780
2.0	1.03224	7.7004	-17.6814	-9.9810	-10.304	0.3230

In each case the Lennard - Jones solute properties at infinite dilution were calculated for a Lennard - Jones solvent at a reduced temperature $kT/\varepsilon_{BB} = 1.2$ and a reduced density of $\rho\sigma_{BB}^3 = 0.7$, where the subscript B denotes the solvent. Equal size ratios were used: $\sigma_{AA} = \sigma_{BB} = \sigma_{AB}$. Each calculation of the work of inserting the hard point was done at an effective packing fraction of $\xi_3 = 0.37473$. The estimated slope at $\varepsilon_{AA} = \varepsilon_{BB} = \varepsilon_{AB}$ of the residual chemical potential compared to the required slope from the energy equation is,

$d[(\mu_A - \mu_A^*)/kT]/\, d[\,\varepsilon_{AB}/\varepsilon_{BB}\,]$		
This Work	Simulation	$2(U - U^*)/kT$
-7.811	-7.929	-7.928

where $(U - U^*)/kT$ was obtained from the HMSA theory using equation (13). Thus, the variation in solute chemical potential with variations in the solvent-solute energy parameter agrees with simulation and meets the consistency condition with the internal energy given by equation (106).

Simulation results were obtained from reference 4.

Table 20

Comparision of the Proposed Method Using the HMSA Theory to Simulation Results For Chemical Potentials at Infinite Dilution and Different Size Ratios

$(\sigma_{AB}/\sigma_{BB})^3$	Solvent-Solute Effective Diameter, d_{AB}/σ_{AB}	Repulsive Contribution	Attractive Contribution	$(\mu_A - \mu_A^*)/kT$ Total	Simulation	Error
0.75	1.00799	5.0028	-6.6699	-1.6671	-1.761	0.0939
1.0	1.00741	7.0620	-8.6786	-1.6166	-1.848	0.2314
1.5	1.00740	11.3315	-12.5677	-1.2362	-1.979	0.7428
2.0	1.00660	15.6709	-16.3577	-0.6868	-2.144	1.4572

In each case the Lennard -Jones solute properties at infinite dilution were calculated for a Lennard - Jones solvent at a reduced temperature $kT/\varepsilon_{BB} = 1.2$ and a reduced density of $\rho\sigma_{BB}^3 = 0.7$, where the subscript B denotes the solvent. Equal energy ratios were used: $\varepsilon_{AA} = \varepsilon_{BB} = \varepsilon_{AB}$. Each calculation of the work of inserting the hard point was done at an effective packing fraction of $\xi_3 = 0.37473$. The estimated slope at $\sigma_{AA} = \sigma_{BB} = \sigma_{AB}$ of the residual chemical potential compared to the required slope from the pressure equation is,

$d[(\mu_A - \mu_A^*)/kT]/\, d[\,\sigma_{AB}/\sigma_{BB}\,]$		
This Work	Simulation	$6(Z-1)$
1.356	-0.934	-1.373

where $Z = P/\rho kT$ was obtained from the HMSA theory using equation (14). Thus, the variation in solute chemical potential with variations in the solvent-solute size parameter disagrees with simulation and violates the consistency condition with the virial pressure given by equation (105).

Simulation results were obtained from reference 4.

Table 21

Effect of Size and Energy Ratios on the

Predicted Chemical Potential for Near Critical States

$\varepsilon_{AB}/\varepsilon_{BB}$	$(\sigma_{AB}/\sigma_{BB})^3$	Solvent-Solute Effective Diameter, d_{AB}/σ_{AB}	Repulsive Contribution	Attractive Contribution	$(\mu_A - \mu_A^*)/kT$
1.0	1.0	1.00367	1.9314	-3.3122	-1.3808
1.125	1.0	1.00898	1.9612	-3.7778	-1.8166
1.0	1.25	1.00400	2.3938	-4.0571	-1.6633

In each case the Lennard - Jones solute properties at infinite dilution were calculated for a Lennard - Jones solvent at a reduced temperature $kT/\varepsilon_{BB} = 1.4$ and a reduced density of $\rho\sigma_{BB}^3 = 0.35$, where the subscript B denotes the solvent. Each calculation of the work of inserting the hard point was done at an effective packing fraction of $\xi_3 = 0.18528$. The estimated slopes of the residual chemical potentials at $\varepsilon_{AA} = \varepsilon_{AB} = \varepsilon_{BB}$ and $\sigma_{AA} = \sigma_{AB} = \sigma_{BB}$ compared to the required slopes from the energy and pressure equation are:

$d[(\mu_A - \mu_A^*)/kT]/d[\varepsilon_{AB}/\varepsilon_{BB}]$	$2(U-U^*)kT$	$d[(\mu_A - \mu_A^*)/kT]/d[\sigma_{AB}/\sigma_{BB}]$	$6(Z-1)$
-3.487	-3.4705	-3.659	-3.9257

where $(U-U^*)/kT$ and $Z = P/\rho kT$ were obtained from the HMSA theory using equations (13) and (14), respectively. Thus, the variation in solute chemical potential with variations in the solvent-solute energy and size parameters meets the conditions for consistency with the internal energy (equation 106) and with the virial pressure (equation 105). The inconsitency noted in Table 20 disappears at supercritical temperatures.

Table 22
The Lennard - Jones Parameters Used
For the Finite Concentration Mixtures

Interaction pair, i-j	Size σ_{ij}, Angstroms	Energy ε_{ij}/k, Kelvin
1-1	3.800	225.000
1-2	4.375	291.247
2-2	4.950	377.000

Table 23

The Volumetric Properties Predicted From the HMSA Theory For Mixtures of Lennard - Jones Particles at Finite Concentration Compared to Results From Molecular Simulation

Mole % Large, x_2	Reduced Density, $\rho\sigma_{22}^3$	Compressibility Factor, $P/\rho kT$ HMSA	Simulation	Error
Vapor Phase				
0.19	0.09	0.8504	0.862	-0.0116
0.12	0.13	0.8201	0.829	-0.0089
0.1	0.24	0.7010	0.732	-0.031
Liquid Phase				
0.625	0.86	0.1246	0.090	0.0346
0.5	0.88	0.0829	0.122	-0.0391
0.375	0.92	0.1671	0.191	-0.0239
0.25	0.91	0.2148	0.232	-0.0172

All mixtures were at a reduced temperature of $kT/\varepsilon_{22} = 0.928$, where the index 2 denotes the large species. The Lennard - Jones parameters for each species are listed in Table 22.

Simulation results were obtained from reference 7.

Table 24

Residual Chemical Potentials Predicted by the Proposed Method in Finite Concentration Mixtures Using the HMSA Integral Equation Theory

	Effective Diameters, d_{ij}/σ_{11}				Residual Chemical Potentials $(\mu_1 - \mu_1^*)/kT$			$(\mu_2 - \mu_2^*)/kT$		
Case	1-1	2-1	1-2	2-2	Rep.	Attract.	Tot.	Rep.	Attract.	Tot.
Vapor Phase										
1	1.00064	1.16338	1.16365	1.32845	0.1925	-0.4287	-0.2362	0.2953	-0.8744	-0.5791
2	1.00060	1.16332	1.16361	1.32892	0.2702	-0.5785	-0.3083	0.4158	-1.1816	-0.7658
3	1.00046	1.16311	1.16347	1.32821	0.5063	-1.0336	-0.5273	0.7736	-2.1042	-1.3306
Liquid Phase										
4	0.99823	1.16021	1.16061	1.32457	4.7627	-6.0796	-1.3169	7.7473	-11.1946	-3.4473
5	0.99842	1.16043	1.16087	1.32485	4.2998	-5.6340	-1.3342	6.9438	-10.4386	-3.4948
6	0.99852	1.16054	1.16100	1.32499	4.0327	-5.3202	-1.2875	6.4922	-9.9300	-3.4378
7	0.99880	1.16086	1.16138	1.32542	3.3752	-4.6444	-1.2692	5.3635	-8.7591	-3.3956

The temperatures, densities, and compositions for the cases listed above are given in Table 23. The Lennard - Jones parameters used are given in Table 22. The 1-1 and 2-1 effective diameters were determined during the calculation of μ_1 and the 1-2 and 2-2 diameters were determined during the (separate) calculation of μ_2. The 1-2 and 2-1 effective diameters differ slightly since these values are accurate to only three decimal places.

Table 25
Chemical Potentials Predicted by the Method in Finite
Concentration Mixtures Compared to Simulation Results

Chemical Potentials (1)

	Supercritical Species, μ_1			Subcritical Species, μ_2		
Case	Method	Sim.	Error	Method	Sim.	Error
Vapor Phase						
1	-2.649	-2.657 (2)	0.008	-4.313	-4.3 [1]	-0.013
2	-2.298	-2.303 (3)	0.005	-4.572	-4.5 [1]	-0.072
3	-1.911	-1.90 [5]	-0.011	-4.696	-4.7 [1]	0.004
Liquid Phase						
4	-2.272	-2.55 [5]	0.278	-3.775	-4.3 [1]	0.525
5	-2.000	-2.19 [5]	0.190	-4.005	-4.5 [1]	0.495
6	-1.708	-1.90 [5]	0.192	-4.178	-4.7 [1]	0.522
7	-1.532	-1.72 [5]	0.188	-4.525	-4.9 [1]	0.375

The temperatures, densities, and compositions for the cases listed above are given in Table 23. The Lennard - Jones parameters used are given in Table 22. The figures in square brackets indicate the estimated (by the original authors) error in the last digit of the simulation results. Results for the vapor phase are in agreement with simulation. Results for the saturated liquid are poor.

Notes:

(1) The chemical potentials presented in this Table are,

$$\mu_i = \left\{ \left[\frac{(\text{residual chemical potential of i})}{kT} \right] + \ln(x_i \rho \sigma_{22}^3) \right\} \frac{kT}{\varepsilon_{22}}$$

where the residual chemical potentials divided by kT are given in Table 24 and the reduced densities and compositions are given in Table 23. These units are used in the Table since the quoted error bounds on the simulation results include unknown errors in density and composition and they can not be converted with certainty to a residual basis.

(2) The value shown is the result obtained from second virial coefficients. The simulation result was -2.55 [5].

(3) The value shown is the result obtained from second virial coefficients. The simulation result was -2.19 [5].

Simulation results were obtained from reference 7.

Table 26

The Predicted Chemical Potential of a Large,
Attractive, Dilute Solute in a Near Critical Solvent

$\rho\sigma_{BB}^3$	**Solvent-Solute Effective Diameter,** d_{AB}/σ_{AB}	**Repulsive Contribution**	**Attractive Contribution**	$(\mu_A - \mu_A^*)/kT$
0.35	1.03809	3.6953	-18.9897	-15.2944

The Lennard - Jones solute properties at infinite dilution were calculated for a Lennard - Jones solvent at a reduced temperature $kT/\varepsilon_{BB} = 1.4$, where the subscript B denotes the solvent. The work of inserting the hard point was done at an effective packing fraction of $\xi_3 = 0.18528$ (as in Table 21).

Figure 1

Kirkwood Charging Scheme

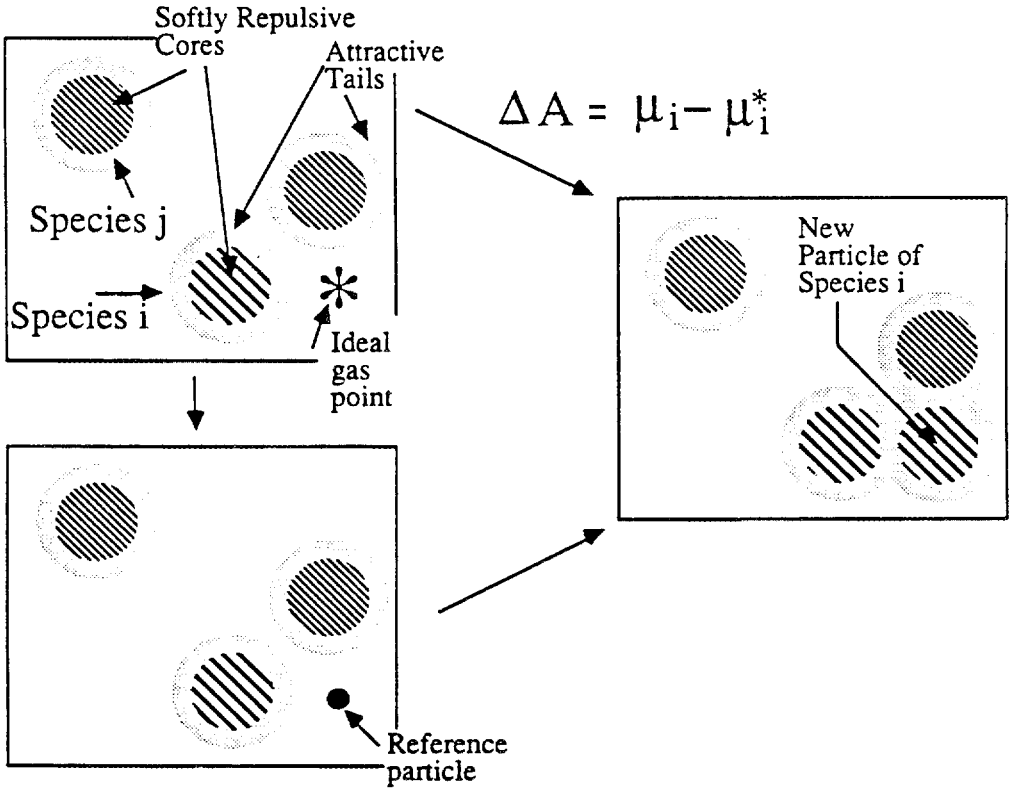


Figure 2

Definition of the Reference System

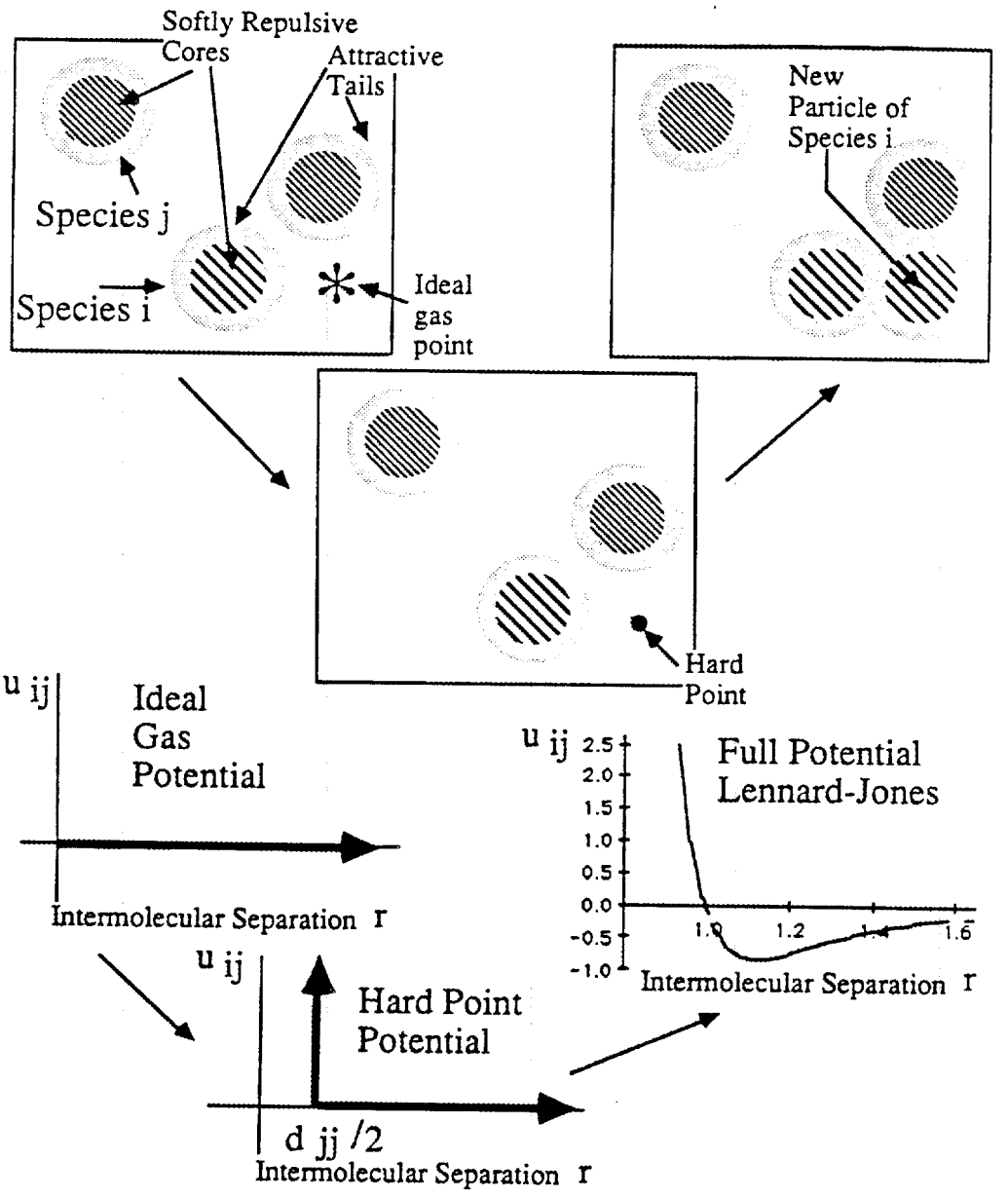


Figure 3

Multi-step Charging Scheme

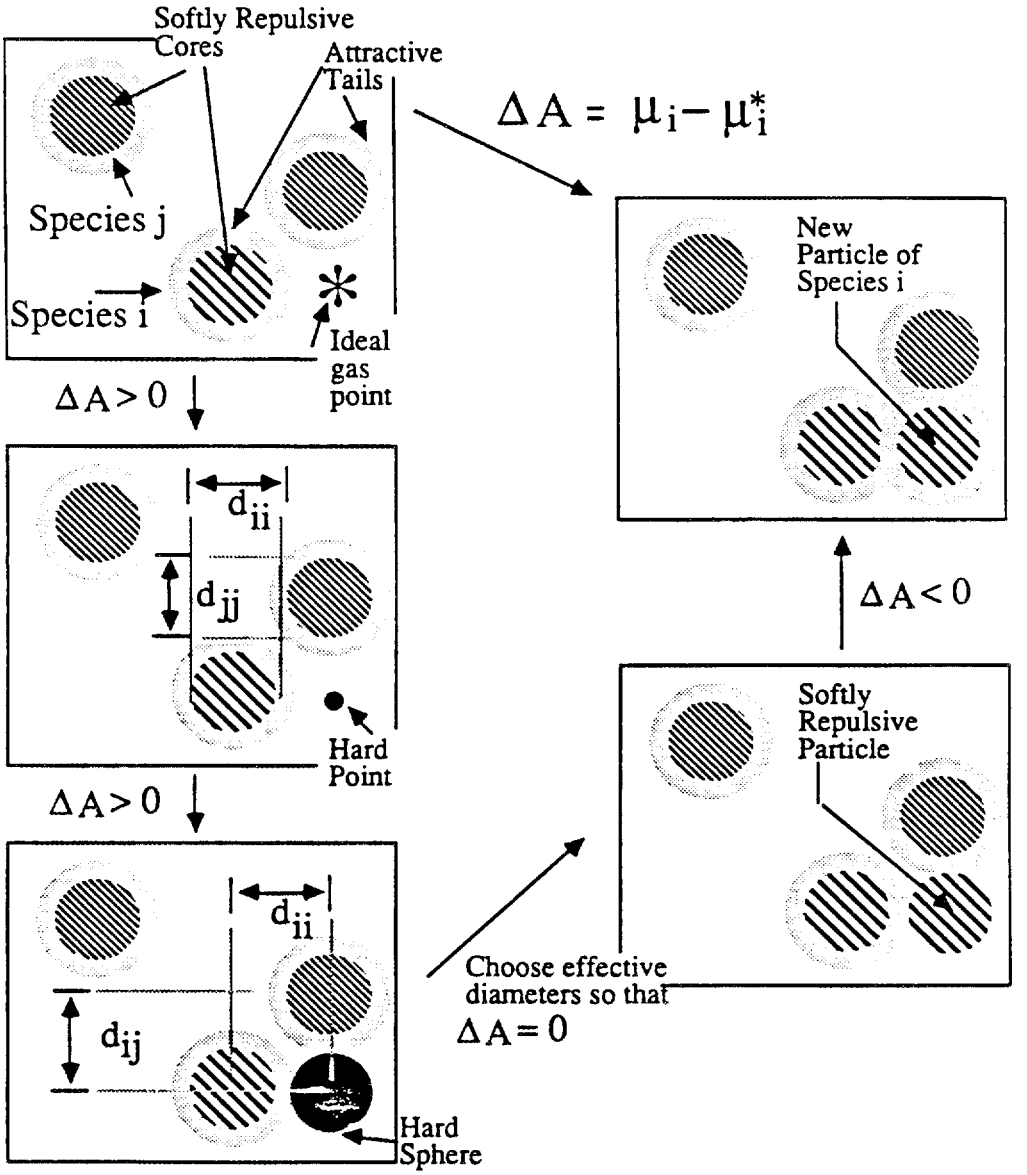


Figure 4

Inserting the Hard Sphere

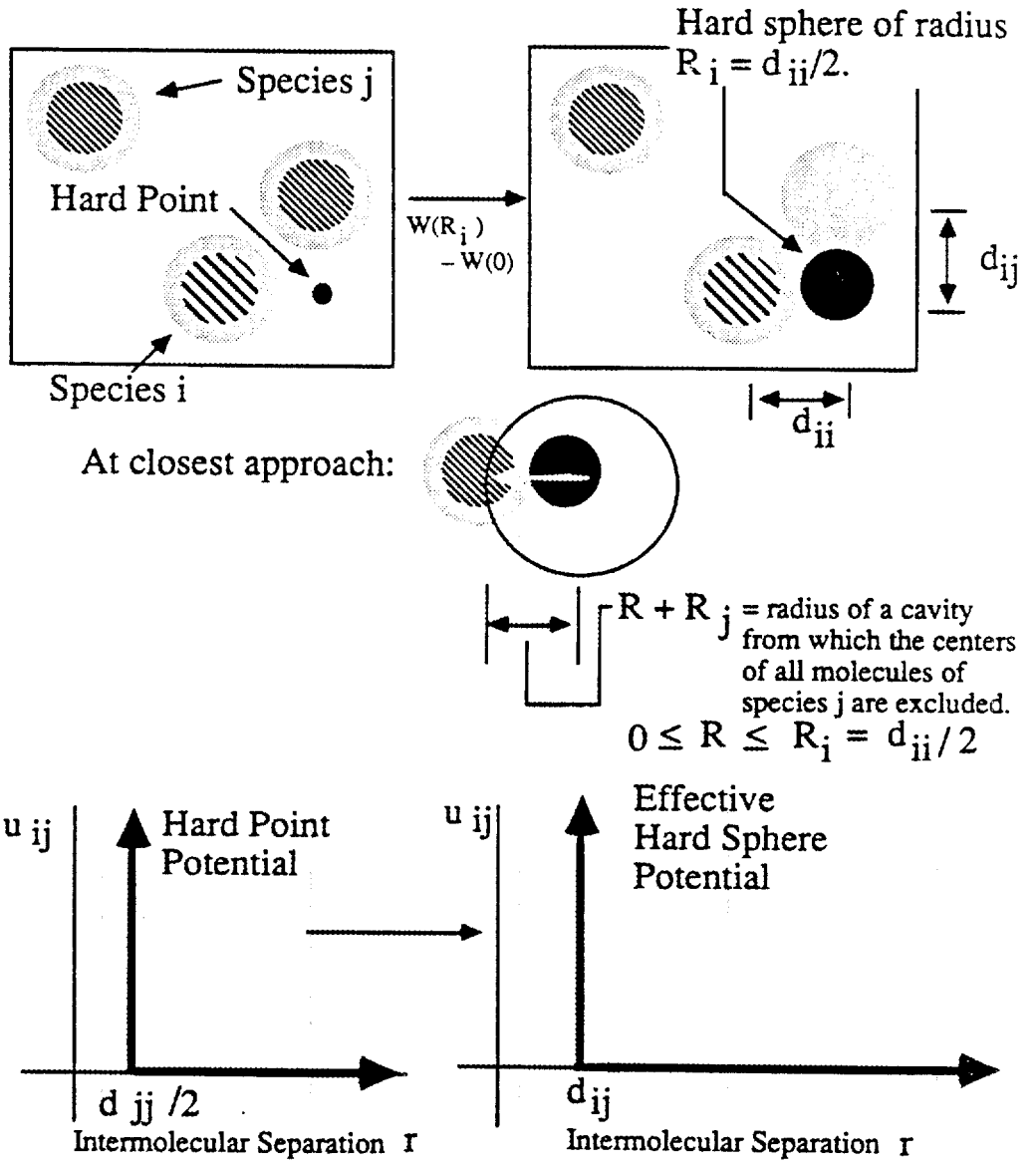
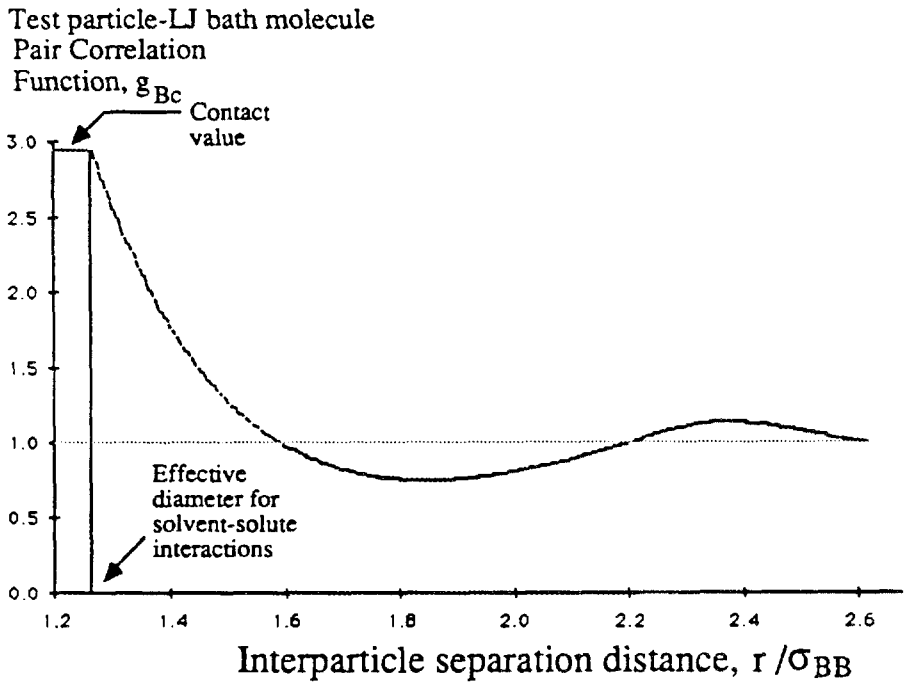


Figure 5

Pair Correlation Functions About an Inserted Hard Sphere



An example of the pair correlation functions for a pure Lennard - Jones (denoted by B) fluid about an inserted hard sphere. The diameter of the hard sphere equals some specified minimum distance of closest approach between the inserted particle and the Lennard - Jones particles; for small separations the pair correlation function is zero. The contact value of the pair correlation function is used in the calculation of the work required to insert the hard sphere into the fluid. The larger the contact value is the more molecules will be in contact with the hard sphere and the larger the work of insertion will be. The correlation function shown was determined with the HMSA integral equation theory.

Figure 6

Softening the Hard Sphere

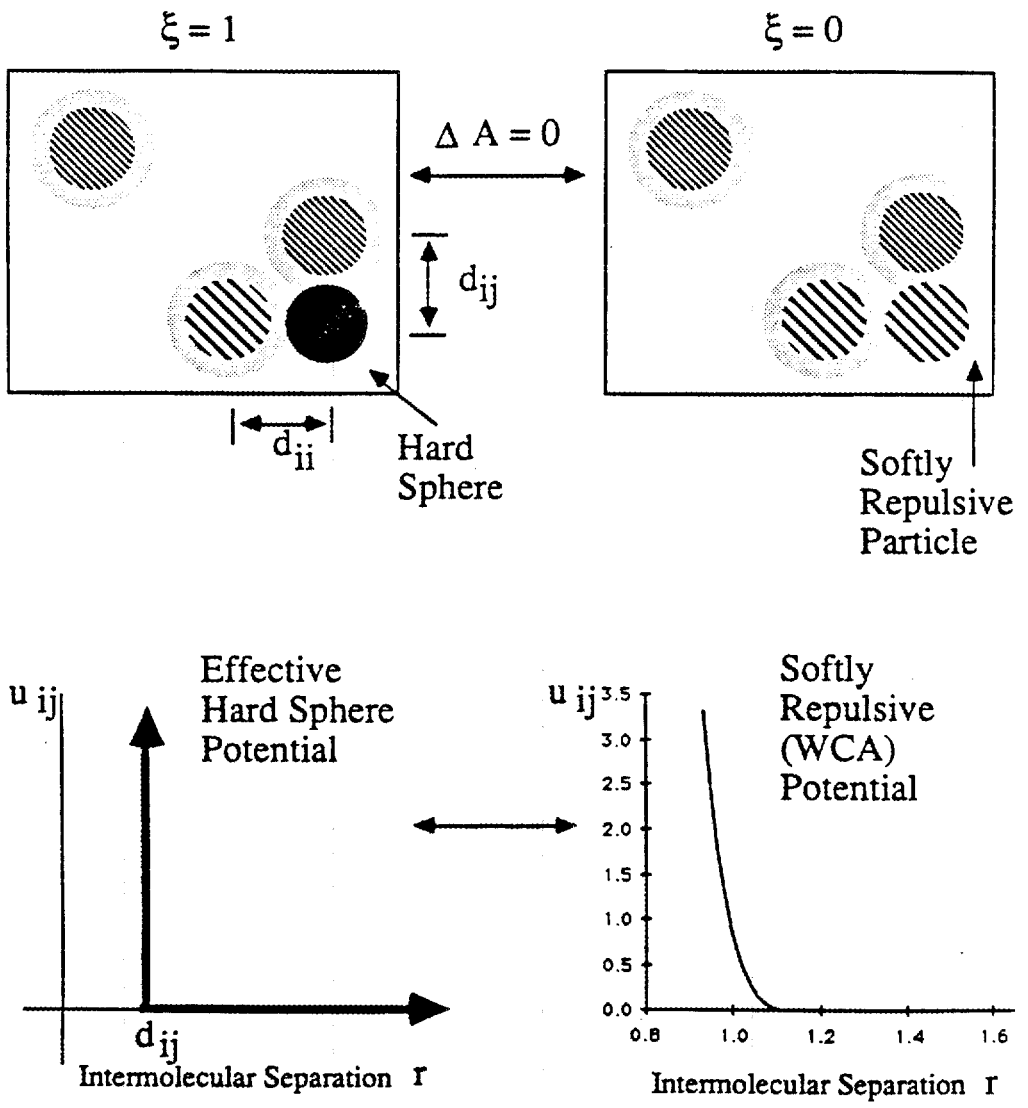
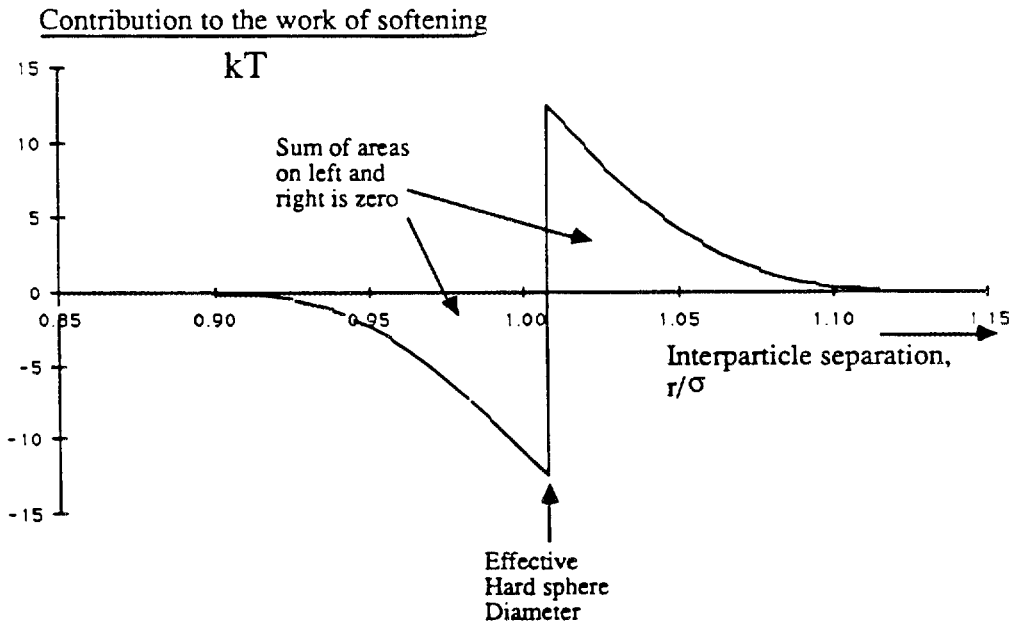


Figure 7

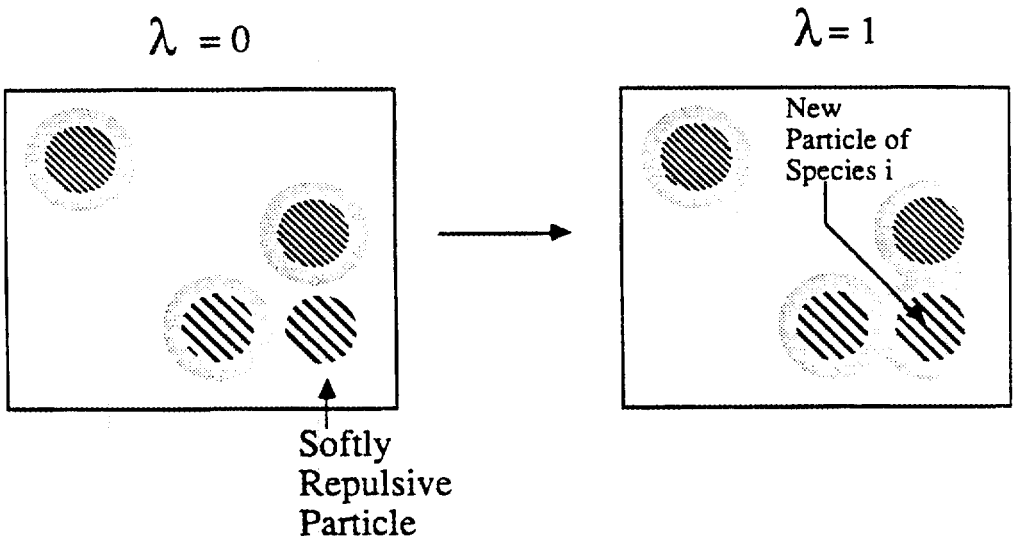
Integrand of the Work of Softening Formula



The integral of the above function gives the work required to change a hard sphere test particle into a softly repulsive WCA test particle. The function is the integrand of equation (88), neglecting the integrals over the bridge functions. The effective hard sphere diameter has been chosen so that the work of softening is zero. The shape of the function is similar to that of the "blip" function used in perturbation theories. However, for fluids which are not purely repulsive the effective diameter differs slightly from that of perturbation theory, since the function includes the effects of attractions between the bath molecules. The diameters determined by the method depend on the attractive forces in a way which is different from perturbation theories.

Figure 8

Charging the Attractive Potential



Split the potential into two components:

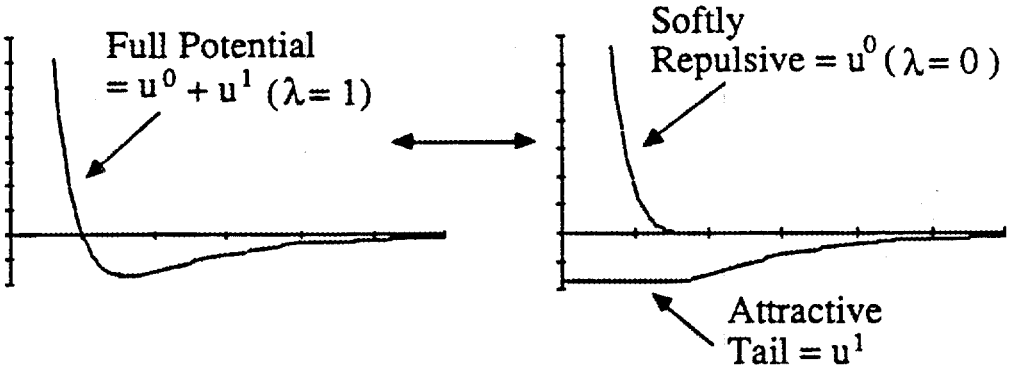
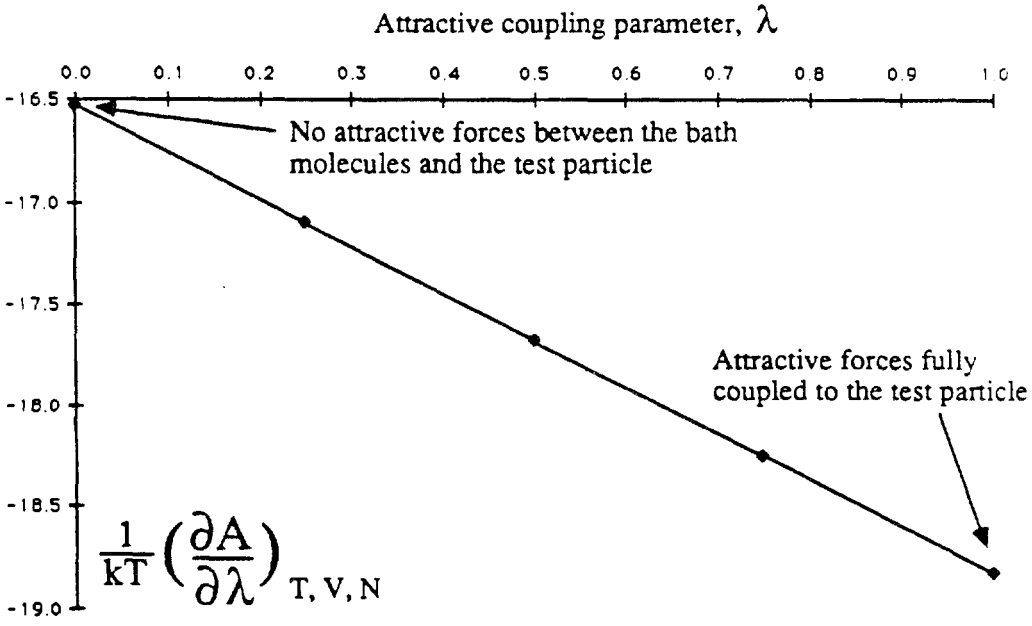


Figure 9

Rate of change of Helmholtz Energy With Change in the Attractive Coupling

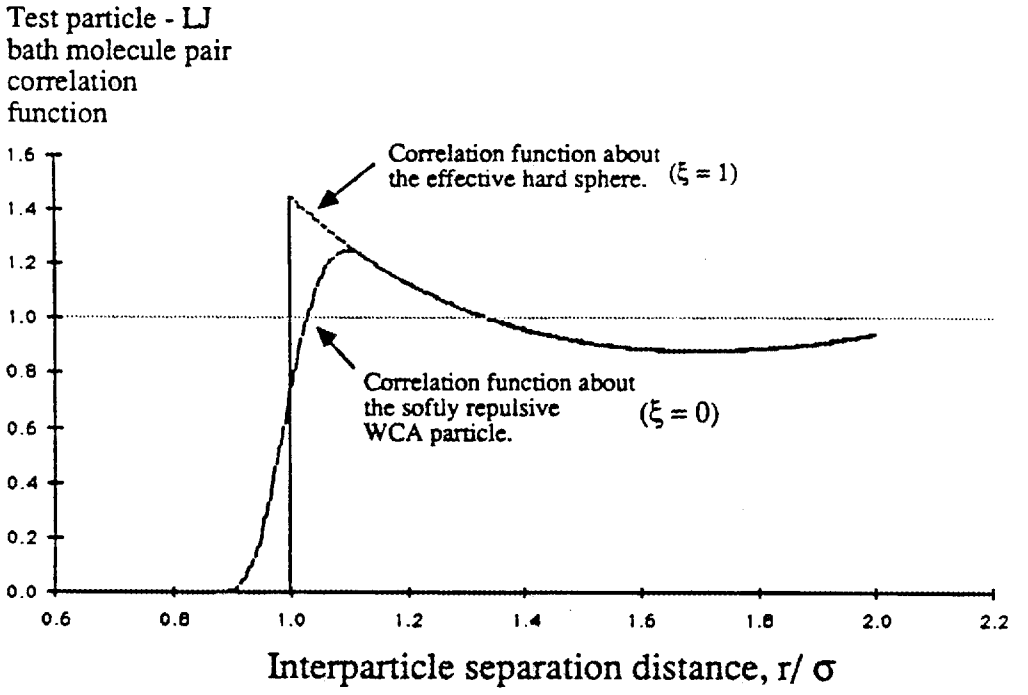


Integrand of equation 92 for the case of a Lennard-Jones solute present at infinite dilution in a Lennard-Jones solvent. The solvent conditions were $kT/\varepsilon_{BB} = 1.2$ and $\rho\sigma_{BB}^3 = 0.7$, where the subscript B denotes the Lennard-Jones parameters for the solvent. The solvent-solute parameters were, $\sigma_{AB} = \sigma_{BB}$ and $\varepsilon_{AB} = 2\varepsilon_{BB}$ The linearity of the function simplifies the numerical integration needed to determine the attractive contribution to the chemical potential. The integral over the coupling parameter gives the attractive contribution, which is in this case -17.6814.

Figure 10

HMSA Pair Correlation Functions About the Effective Hard Sphere Compared to Those About the WCA Repulsive Test Particle

Pure Lennard-Jones bath at supercritical conditions

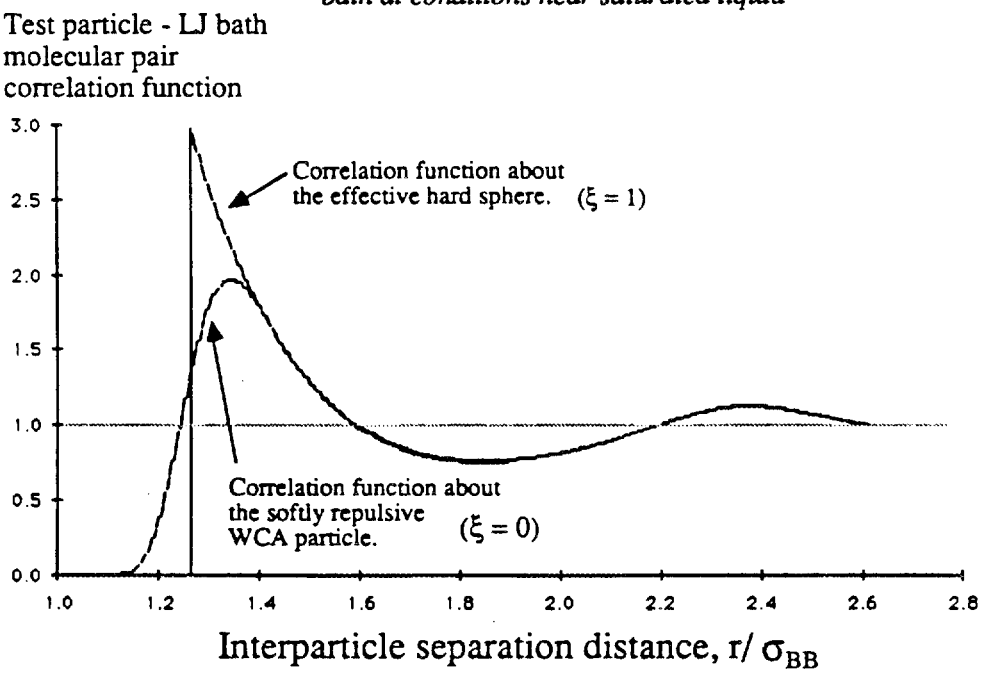


The pair correlation functions of a pure Lennard - Jones fluid about a WCA repulsive particle with the same size and energy parameters are compared to those about the effective hard sphere. In the case shown the fluid is at a reduced temperature of $kT/\varepsilon = 1.5$ and a reduced density of $\rho\sigma^3 = 0.4$. For an effective hard sphere size determined as described in Figure 7, the structure about the hard sphere accurately represents that about the WCA repulsive particle. They differ only within are narrow range of separation distances about the contact point. Intuition requires that an appropriate hard sphere model of a softly repulsive test particle will exhibit a hard sphere - bath molecule pair correlation function which mimicks the soft sphere - bath molecule function.

Figure 11

HMSA Pair Correlation Functions About the Effective Hard Sphere Compared to Those About the WCA Repulsive Test Particle

For a large test particle immersed in a pure Lennard - Jones bath at conditions near saturated liquid

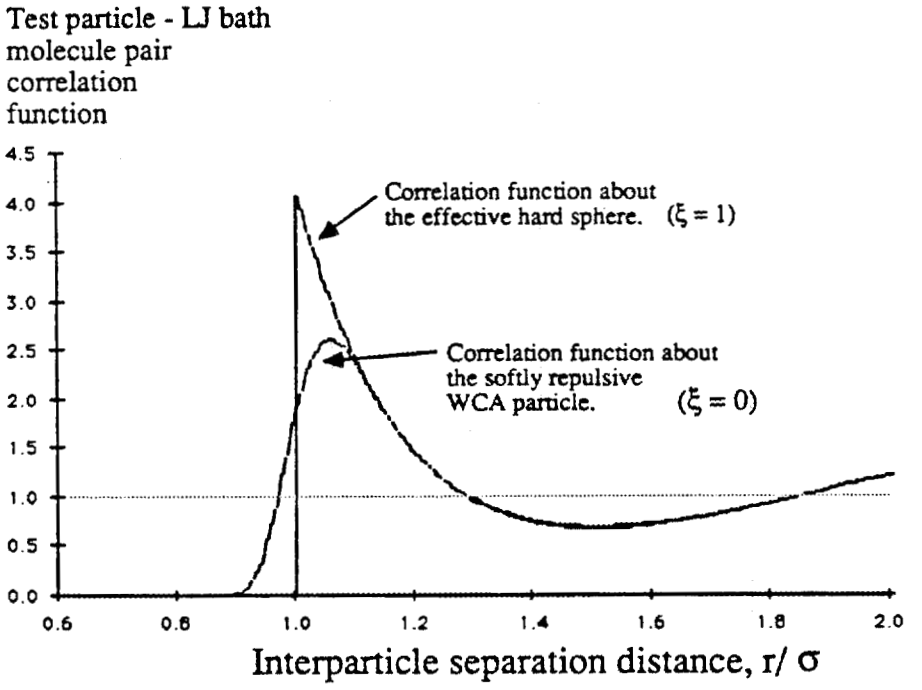


The pair correlation function about a large WCA repulsive solute in a pure Lennard - Jones bath is compared to that of its effective hard sphere. The fluid is at a reduced temperature of $kT/\varepsilon_{BB} = 1.2$ and a reduced density of $\rho\sigma_{BB}^3 = 0.7$, where the subscript B denotes the Lennard - Jones parameters of the solvent bath. The bath and solute have equal energy parameters and the size parameters are given by $(\sigma_{AB}/\sigma_{BB})^3 = 2$. In this case the choice of effective solvent - solute diameter also allows the structure about the large WCA repulsive particle to be approximated by the structure about the effective hard sphere, except for separation distances in the neighborhood of the contact point.

Figure 12

HMSA Pair Correlation Functions About the Effective Hard Sphere Compared to Those About the WCA Repulsive Test Particle

Pure Lennard - Jones bath at compressed liquid conditions

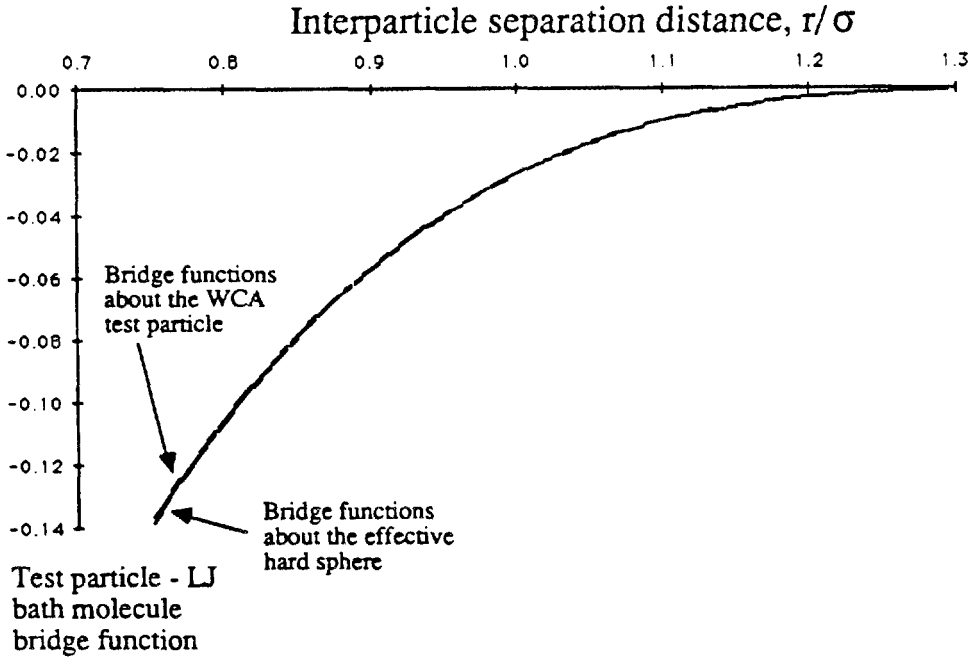


The pair correlation functions of a pure Lennard - Jones fluid about a WCA repulsive particle with the same size and energy parameters are compared to those about the effective hard sphere. In the case shown the fluid is at a reduced temperature of $kT/\varepsilon = 1.2$ and a reduced density of $\rho\sigma^3 = 0.85$. For an effective hard sphere size determined as described in Figure 7, the structure about the hard sphere accurately represents that about the WCA repulsive particle. They differ only within are narrow range of separation distances about the contact point. Figures 10, 11 and 12 show that method of specifying the effective diameters yields structures about the hard spheres which always approximate those about the WCA repulsive particles.

Figure 13

HMSA Bridge Functions About the Effective Hard Sphere Compared to Those About the WCA Repulsive Test Particle

Pure Lennard-Jones bath at supercritical conditions

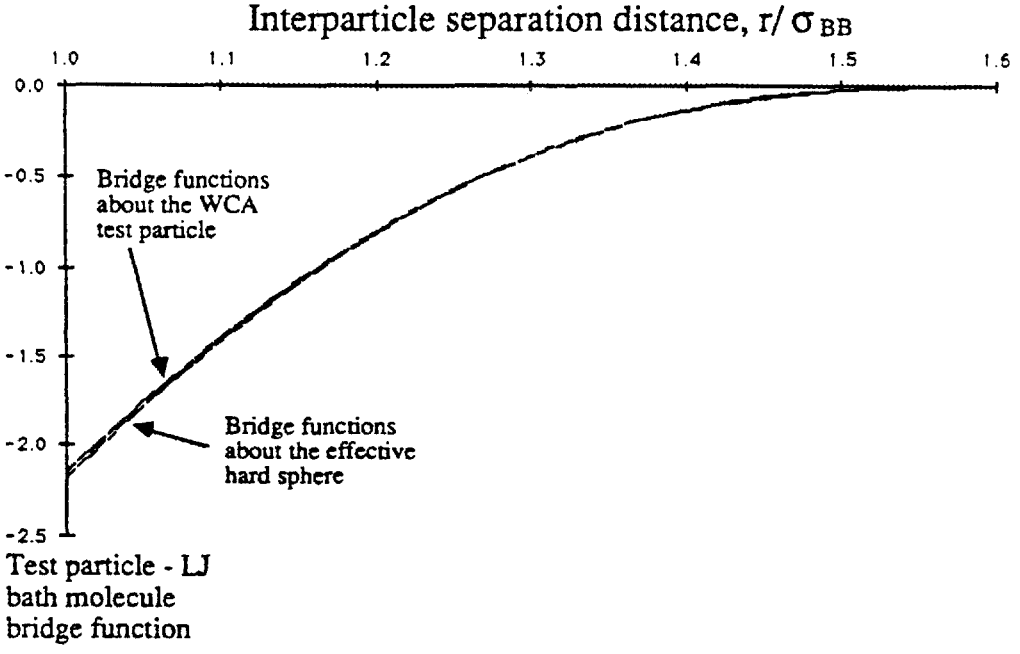


Bridge functions about the WCA repulsive and hard sphere test particles for the conditions of Figure 10. The bridge functions for the two cases are nearly identical, implying that the integral over their difference in equation (88) can be neglected. This allows the work of softening to be determined using only correlation functions from the initial and final states of the softening process. Without such a simplifiction in the work of softening there would be little incentive to using a charging path which proceeds through the hard sphere particle and which applies the scaled particle theory.

Figure 14

HMSA Bridge Functions About the Effective Hard Sphere Compared to Those About the WCA Repulsive Test Particle

For a large test particle immersed in a pure Lennard - Jones bath at conditions near saturated liquid

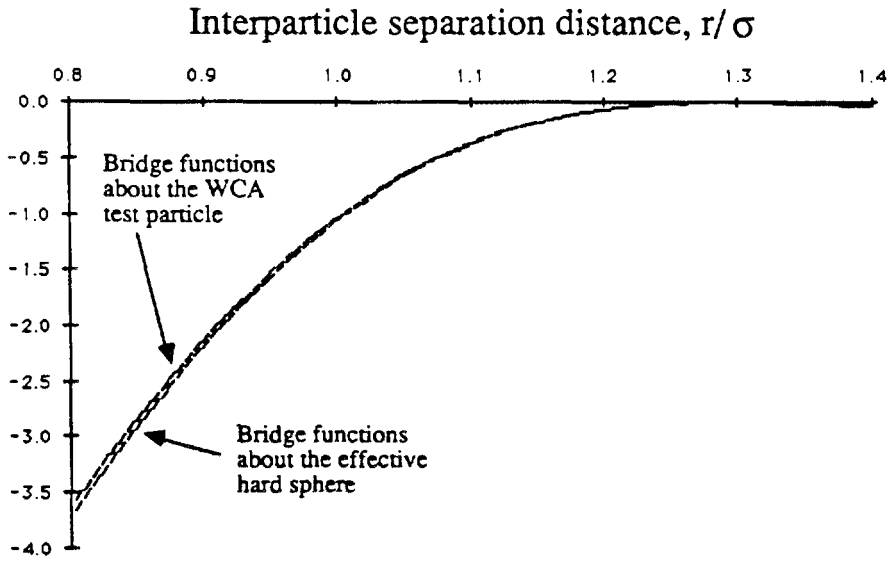


Bridge functions about the WCA repulsive and hard sphere test particles for the conditions of Figure 11. Once again, the bridge functions for the two cases are nearly identical, implying that the integral over their difference in equation (88) can be neglected. Therefore, the conclusions of Figure 13 also apply here. The large asymmetry of the components in the mixture does not reduce the accuracy of the assumption that the bridge functions are invarient during the softening process.

Figure 15

HMSA Bridge Functions About the Effective Hard Sphere Compared to Those About the WCA Repulsive Test Particle

Pure Lennard - Jones bath at compressed liquid conditions

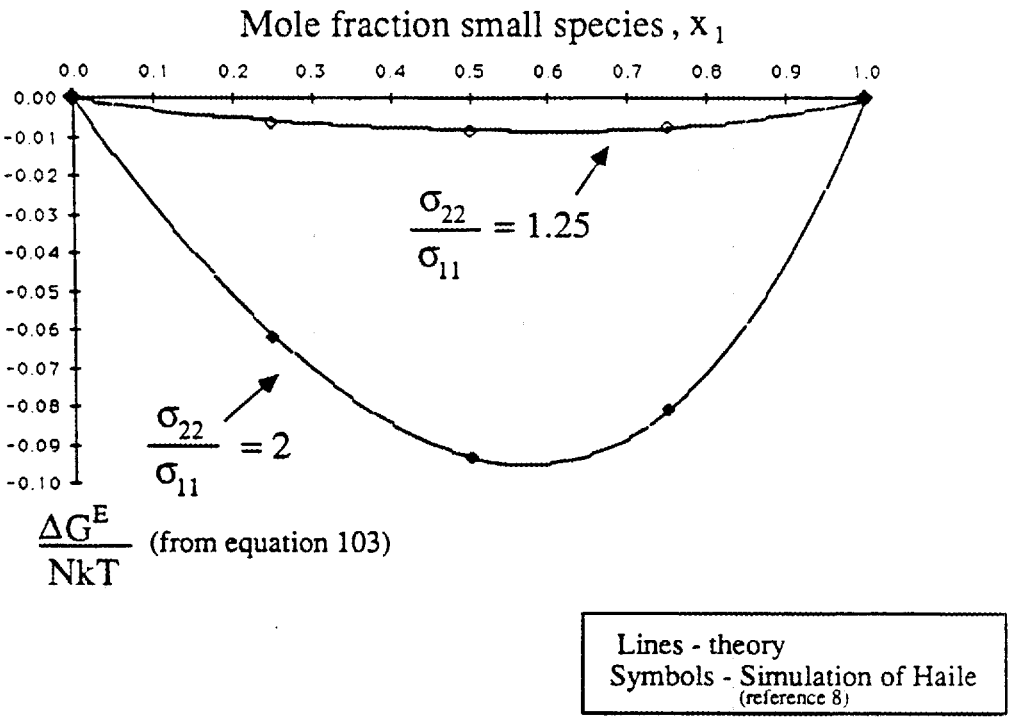


Test particle - LJ bath molecule bridge function

Bridge functions about the WCA repulsive and hard sphere test particles for the conditions of Figure 12. Once again, the bridge functions for the two cases are nearly identical, implying that the integral over their difference in equation (88) can be neglected. Therefore, the conclusions of Figure 13 also apply here. In this case, the assumption of the invarience of the bridge functions remains accurate even though their magnitude is large. Figures 13, 14 and 15 together show that the bridge function integrals can be neglected under all conditions.

Figure 16

Predicted Excess Gibbs Free Energies of Mixing in Softly Repulsive (WCA) Fluids

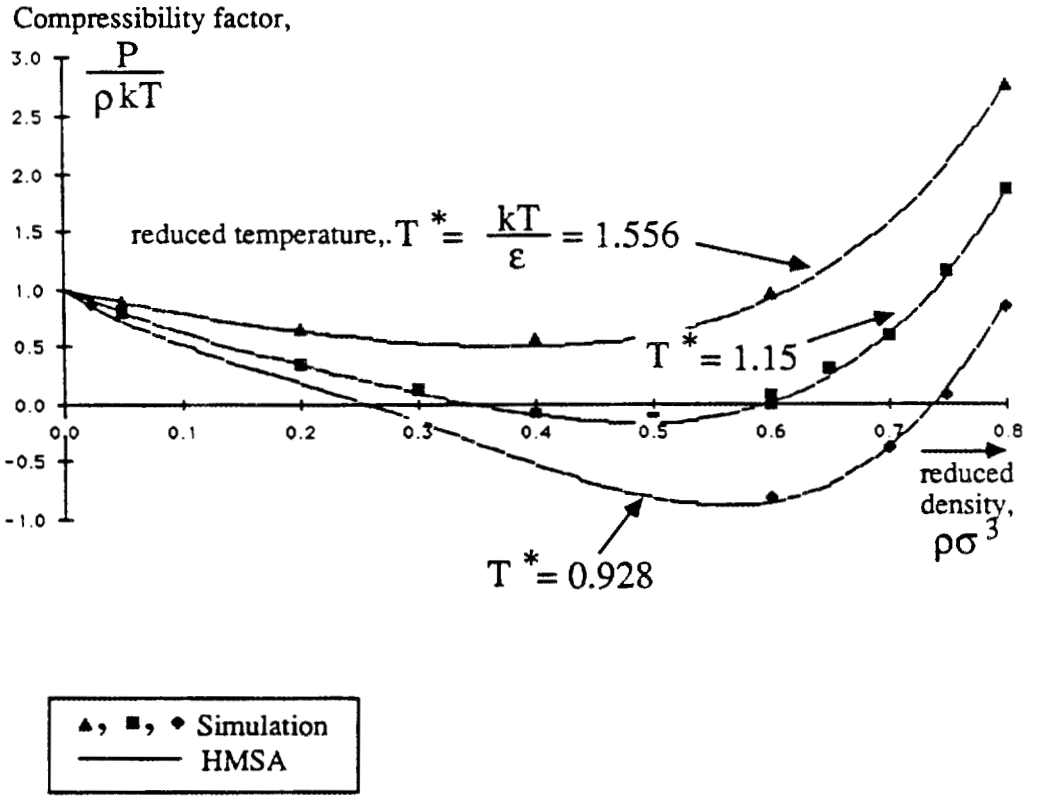


Excess Gibbs free energies of mixing WCA repulsive fluids at constant pressure $P\sigma_{11}^3/\varepsilon_{11} = 0.5$ and temperature $kT/\varepsilon_{11} = 1.0$. The fluids being mixed have equal energy parameters and unequal size parameters. The proposed method accurately predicts the free energies of mixing of these nearly ideal mixtures; qualitative features such as the asymmetry of the bottom curve are predicted correctly.

Figure 17

Compressibility Factors in Pure Lennard-Jones Fluids

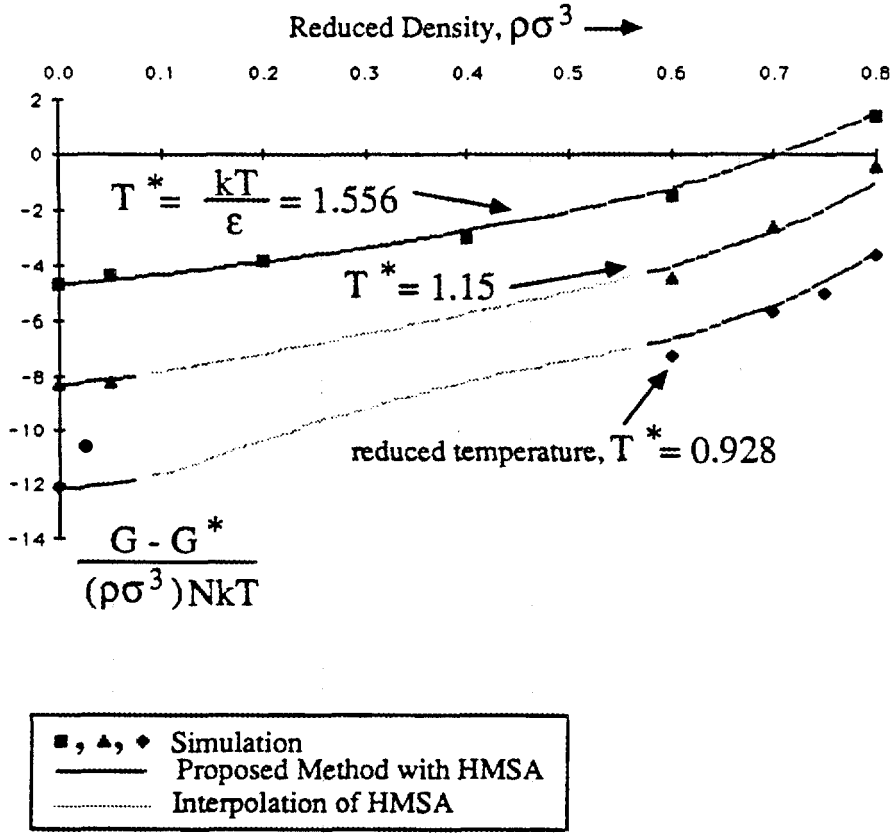
Comparision of HMSA results to molecular simulation



A comparison of compressibility factors for pure Lennard-Jones fluids obtained with the HMSA theory with simulation results from references (7) and (39). Results for three isotherms are plotted versus reduced density. The highest temperature isotherm is supercritical, the others are subcritical. The HMSA theory accurately describe the P-V-T properties of Lennard-Jones fluids. Thus, it should be possible to obtain accurate chemical potentials using it.

Figure 18

Predicted Residual Gibbs Free Energies in Pure Lennard-Jones Fluids Compared With Simulation

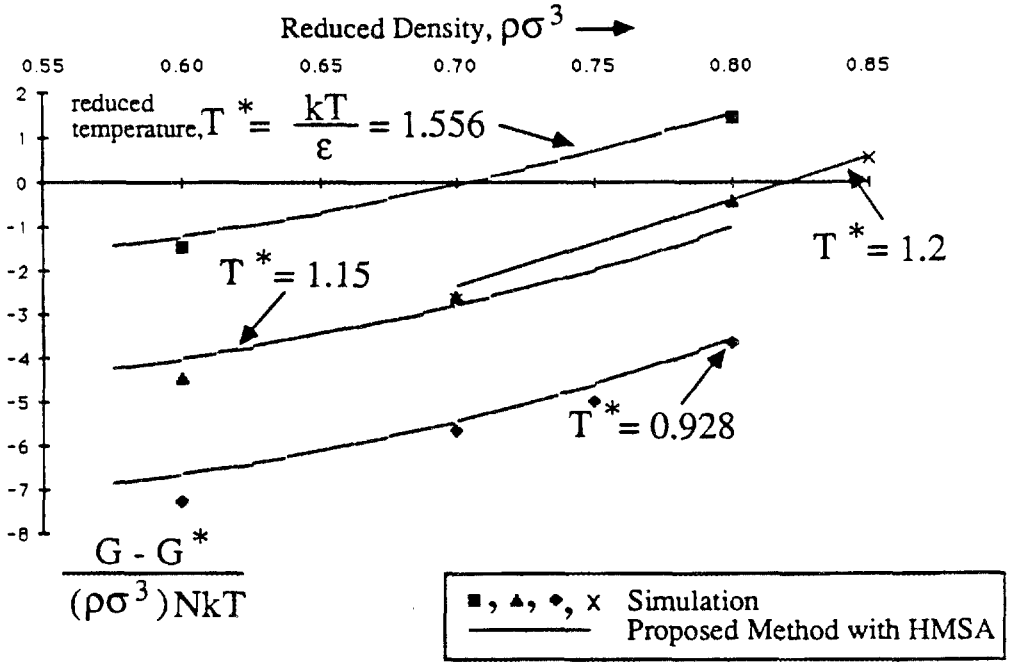


The residual chemical potentials divided by the reduced density are plotted versus reduced density for three different isotherms, as are those obtained from simulation. Simulation results are from reference (7). The intercept of each isotherm is twice the reduced second virial coefficient. The highest temperature isotherm, which is supercritical, is well described by the method. For the two subcritical isotherms the method yields accurate results at the lowest and highest densities.

Figure 19

Predicted Residual Gibbs Free Energies in Pure Lennard-Jones Fluids Compared With Simulation

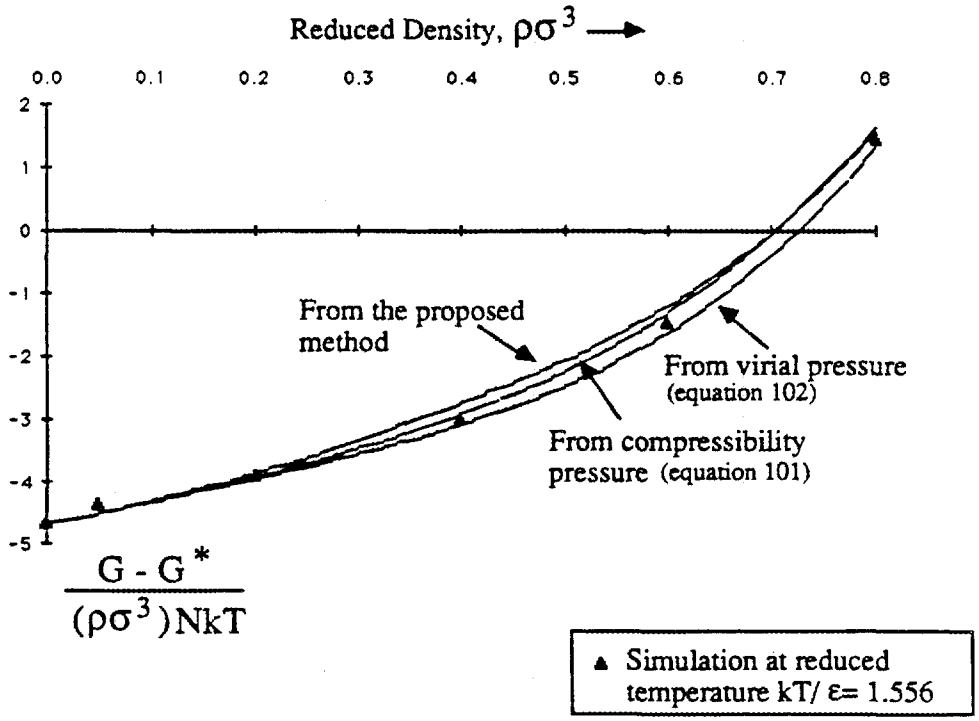
high density range



The residual chemical potentials divided by reduced density are plotted versus reduced density for the high density range, as are those obtained from simulation. Simulation results are from references (7) and (3). This figure shows the high density range of Figure 18 and includes an additional isotherm at a reduced temperature of 1.2. The proposed method yields very accurate results at the highest densities. The temperature dependence of the method's results is also very good. The slope of the method's results with respect to density is less than that of the simulation data for the density range shown.

Figure 20

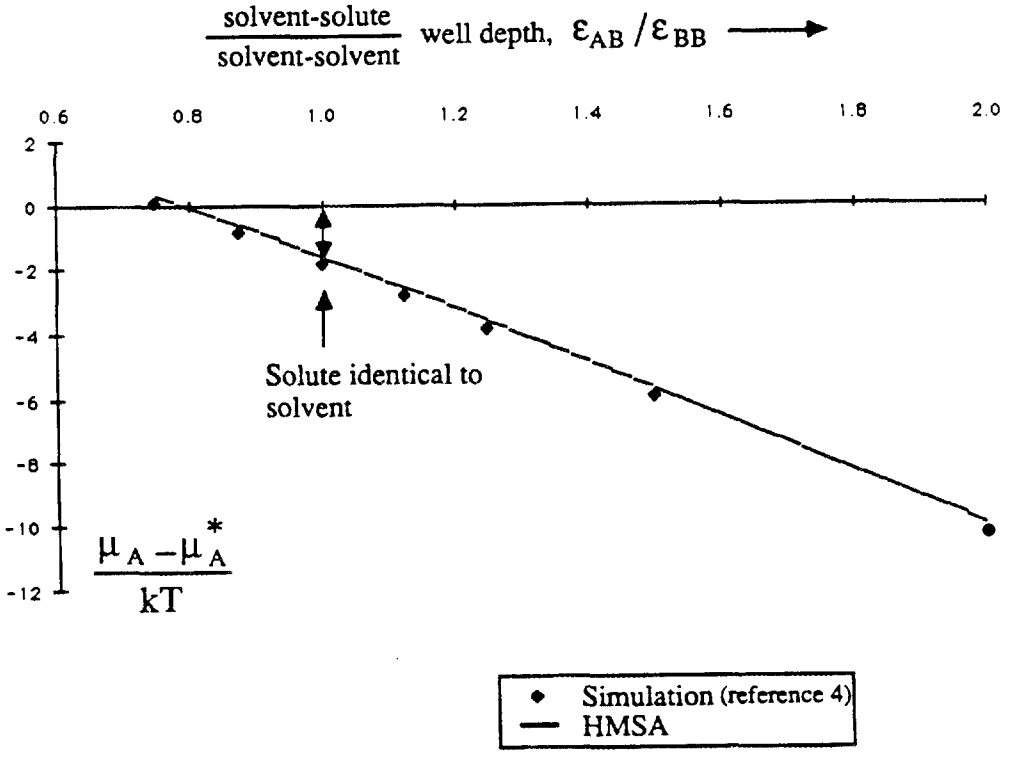
Predicted Residual Gibbs Free Energies Compared to Thermodynamic Integration For Pure Lennard - Jones Fluids



The residual chemical potentials divided by reduced density are plotted versus reduced density at a reduced temperature of 1.556, as are those obtained from simulation. Simulation results are from reference (7). Also plotted are results from two different thermodynamic integrations of HMSA properties (which yield different results due to failure of the local consistency criterion). There is a slight thermodynamic inconsistency between the method and the P-V-T properties of the bulk fluid. The inconsistency disappears at the highest and lowest densities.

Figure 21

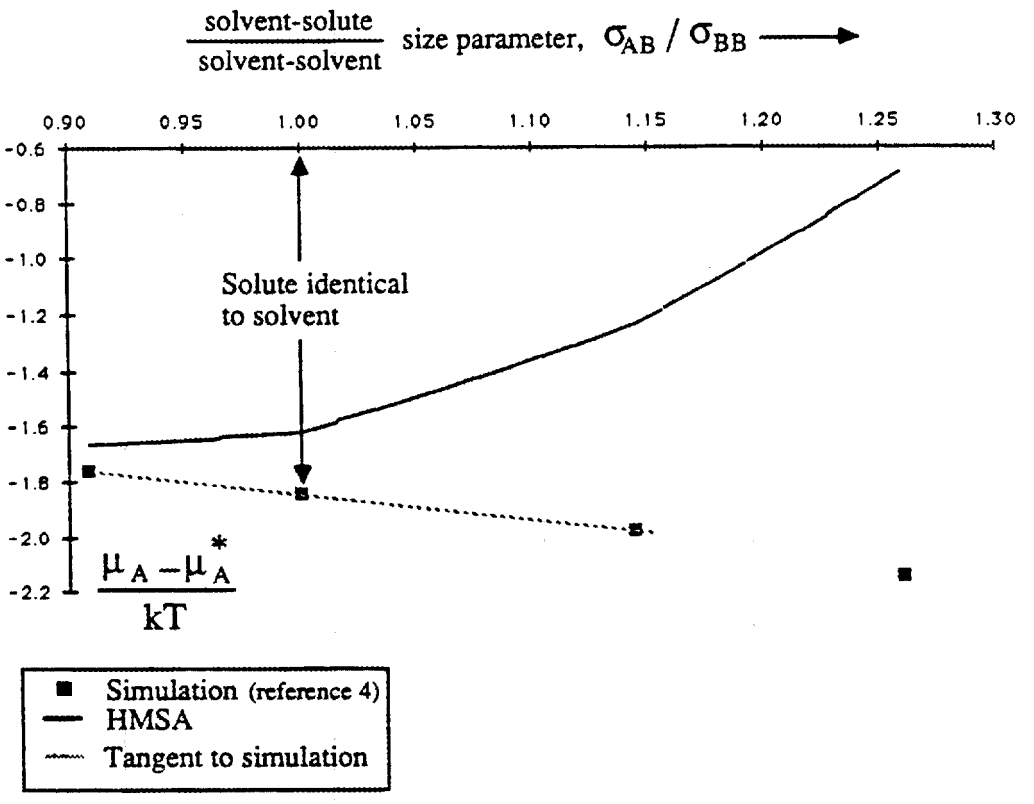
Predicted Residual Chemical Potentials of a Dilute Lennard - Jones Solute in a Lennard - Jones Solvent versus Energy Ratio



The residual chemical potential of an infinitely dilute solute is plotted versus the ratio of Lennard-Jones well depths. The solvent is at a reduced temperature of 1.2 and a reduced density of 0.7. The solvent and solute have equal Lennard - Jones size parameters. The method exhibits the correct trend in the chemical potential as the energy ratio is varied, the chemical potential declining nearly linearly as the solvent-solute attraction is increased. The correct slope indicates consistency with the energy equation, meeting the test of equation (106).

Figure 22

Predicted Residual Chemical Potentials of a Dilute Lennard - Jones Solute in a Lennard - Jones Solvent versus Size Ratio

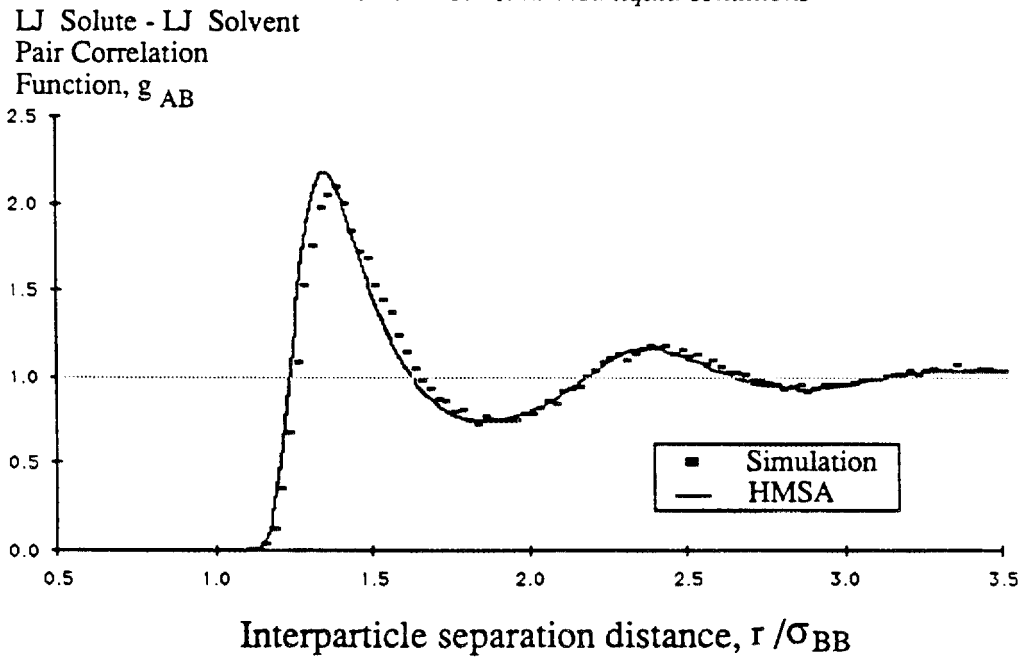


The residual chemical potential of an infinitely dilute solute is plotted versus the ratio of Lennard-Jones size parameters. The solvent is at a reduced temperature of 1.2 and a reduced density of 0.7. The solvent and solute have equal Lennard - Jones energy parameters. The method exhibits the wrong trend in the chemical potential as the size ratio is varied, the predicted chemical potential increasing rather than decreasing as the solvent-solute size is increased. The incorrect slope indicates inconsistency with the virial pressure equation; the method fails to meet the test of equation (105) under these conditions.

Figure 23

HMSA Pair Correlation Functions About a Large, Dilute Lennard - Jones Solute in a Lennard - Jones Solvent Compared to Molecular Simulation

For a solvent near saturated liquid conditions

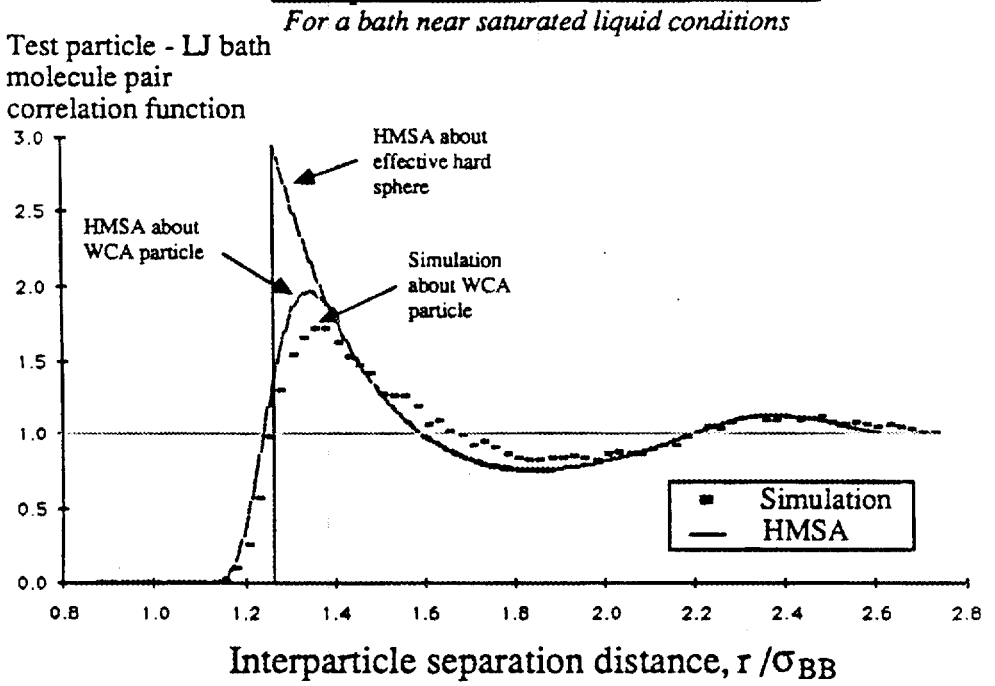


The pair correlation function for the case of a solute present at infinite dilution in a Lennard-Jones solvent. The solvent conditions were $kT/\varepsilon_{BB} = 1.2$ and $\rho\sigma_{BB}^3 = 0.7$, where the subscript B denotes the Lennard-Jones parameters for the solvent. The solvent-solute parameters were, $(\sigma_{AB}/\sigma_{BB})^3 = 2$ and $\varepsilon_{AB} = \varepsilon_{BB}$ The HMSA theory accurately predicts the structure of the solvent about the infinitely dilute solute, except for a small descrepancy in the neighborhood of the first peak.

Figure 24

HMSA Pair Correlation Functions About a Large WCA Repulsive Test Particle in a Lennard - Jones Bath Compared to Molecular Simulation

For a bath near saturated liquid conditions

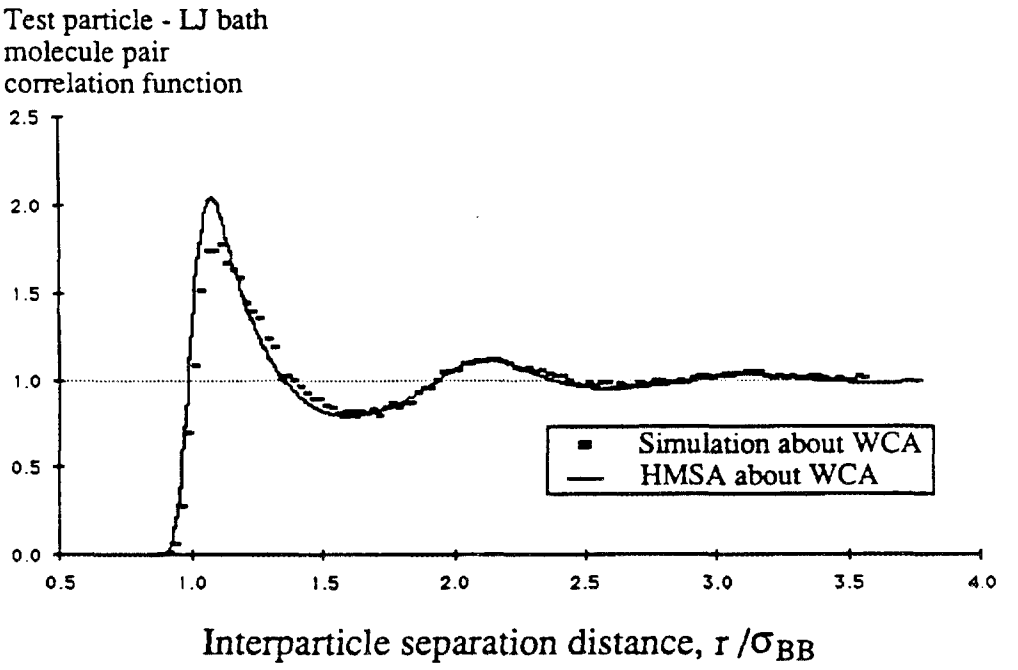


The pair correlation function for the case of a WCA repulsive test particle in a Lennard - Jones bath. The bath is identical to the solvent used in Figure 23 and the test particle has molecular parameters identical to those of the solute in Figure 23. Thus, the WCA repulsive test particle represents a solute molecule with the attractive force de-coupled. Also shown is the HMSA correlation function about the effective hard sphere. The HMSA correlation function about the WCA repulsive particle is considerably steeper than simulation; it can be expected that the correlation function about the hard sphere is also too steep at contact. This latter error causes the repulsive contribution to the chemical potential to be overestimated. That is, the overprediction of the first peak height made by the HMSA theory results in an overestimate of the work required to insert a WCA repulsive test particle.

Figure 25

HMSA Pair Correlation Functions About a Small WCA Repulsive Test Particle in a Lennard - Jones Bath Compared to Molecular Simulation

For a bath near saturated liquid conditions

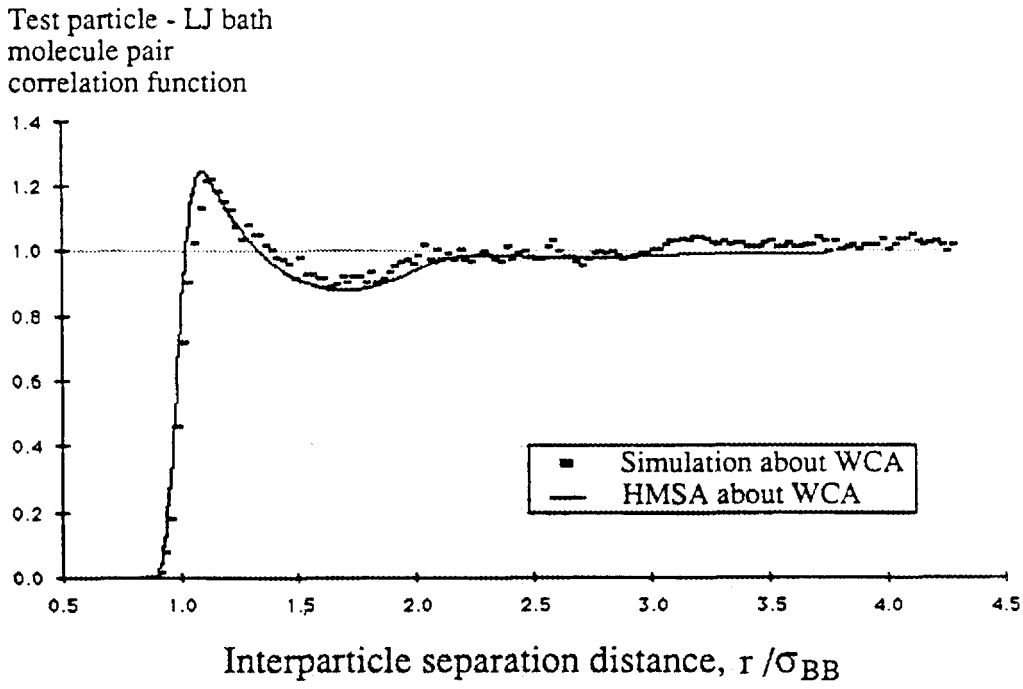


The pair correlation function for the case of a WCA repulsive test particle in a Lennard - Jones bath. The bath is identical to the solvent used in Figure 23. The test particle has molecular parameters identical to those of the solvent. Thus, the WCA repulsive test particle represents a solvent molecule with the attractive force de-coupled. As in Figure 24, the first peak of the HMSA correlation function about the WCA repulsive particle is considerably higher than simulation, resulting in an overprediction of the repulsive contribution to the chemical potential.

Figure 26

HMSA Pair Correlation Functions About a Small WCA Repulsive Test Particle in a Lennard - Jones Bath Compared to Molecular Simulation

For a bath near the critical point

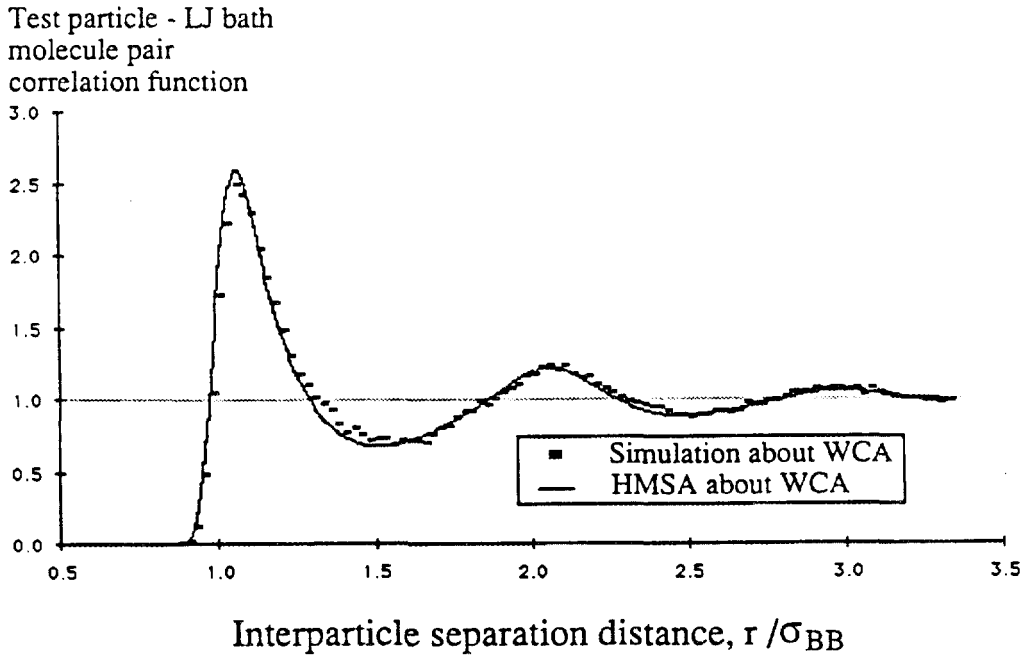


The pair correlation function about a WCA repulsive particle immersed in a pure solvent is plotted versus separation distance divided by the solvent size parameter. In this case the solute size and energy parameters are identical to those of the solvent. The solvent is at a reduced temperature of 1.5 and a reduced density of 0.4. Under these conditions the HMSA theory accurately represents the correlation functions abour the test particle for every value of the attractive coupling parameter. The proposed method for calculating chemical potentials works well in this case.

Figure 27

HMSA Pair Correlation Functions About a Small WCA Repulsive Test Particle in a Lennard - Jones Bath Compared to Molecular Simulation

For a compressed liquid bath

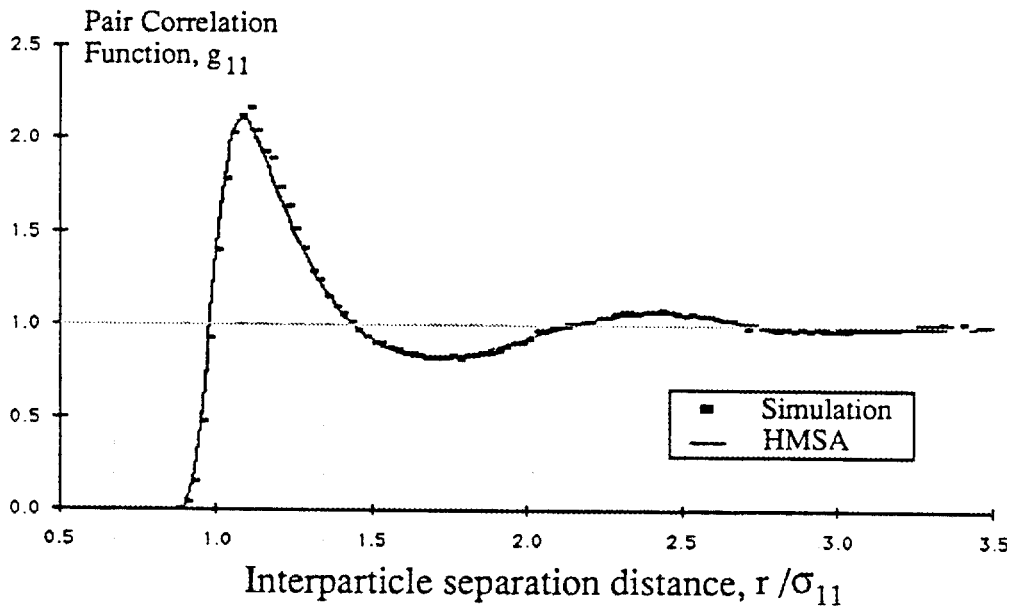


The pair correlation function about a WCA repulsive particle immersed in a pure solvent is plotted versus separation distance divided by the solvent size parameter. In this case the solute size and energy parameters are identical to those of the solvent. The solvent is at a reduced temperature of 1.2 and a reduced density of 0.85. Under these conditions the HMSA theory accurately predicts the correlation function about the WCA repulsive test particle. The HMSA pair correlations change little with the attractive coupling parameter - this lack of change is a consequence of the fact that the closure approaches the SMSA limit in this case (α =0.208). The method accurately predicts the chemical potential for this fluid since the correlation functions are accurately predicted for every value of the coupling parameter.

Figure 28

HMSA Pair Correlation Functions in a Lennard - Jones Mixture Compared to Molecular Simulation

A model of carbon dioxide and acetone



The '1 - 1' pair correlation function in a mixture consisting of the following Lennard - Jones species:

$\sigma_{11} = 3.8$ Å $\quad \sigma_{12} = 4.375$ Å $\quad \sigma_{22} = 4.95$ Å

$\varepsilon_{11}/k = 225$ K $\quad \varepsilon_{12}/k = 291.247$ K $\quad \varepsilon_{22}/k = 377$ K

The conditions were:

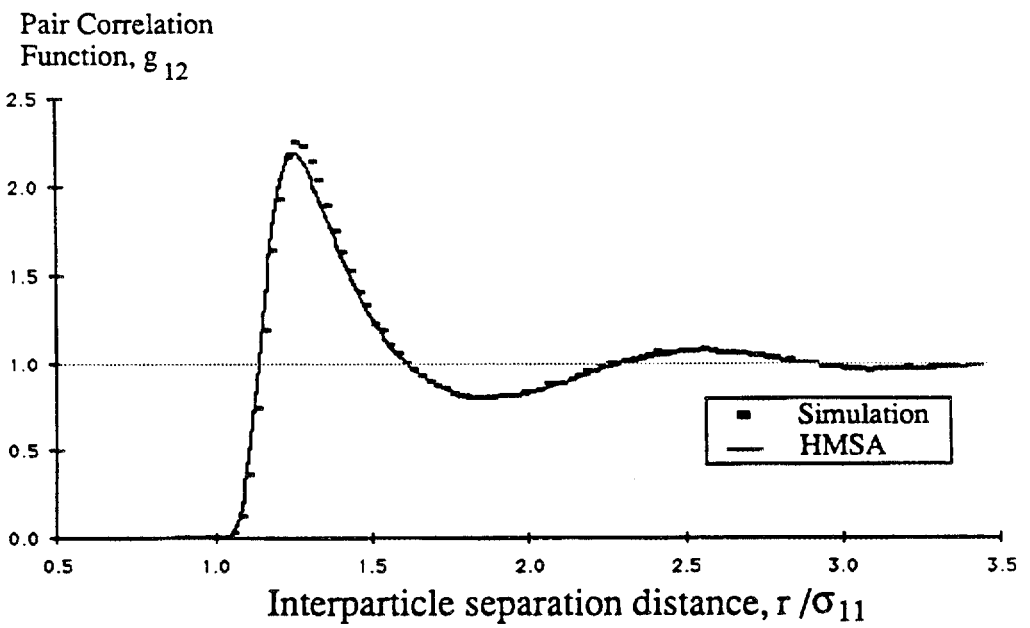
$kT/\varepsilon_{11} = 1.5549 \quad \rho\,\sigma_{11}^3 = 0.39812 \quad x_1 = 0.5$

The HMSA theory accurately reproduces the pair correlation function obtained from molecular simulation. The accurate structural results obtained from the HMSA theory imply a low error in the attractive contribution to the chemical potentials determined from the proposed method. Therefore the large positive error in the predicted chemical potentials must be due, at least in part, to errors in the repulsive contribution.

Figure 29

HMSA Pair Correlation Functions in a Lennard - Jones Mixture Compared to Molecular Simulation

A model of carbon dioxide and acetone (cont.)

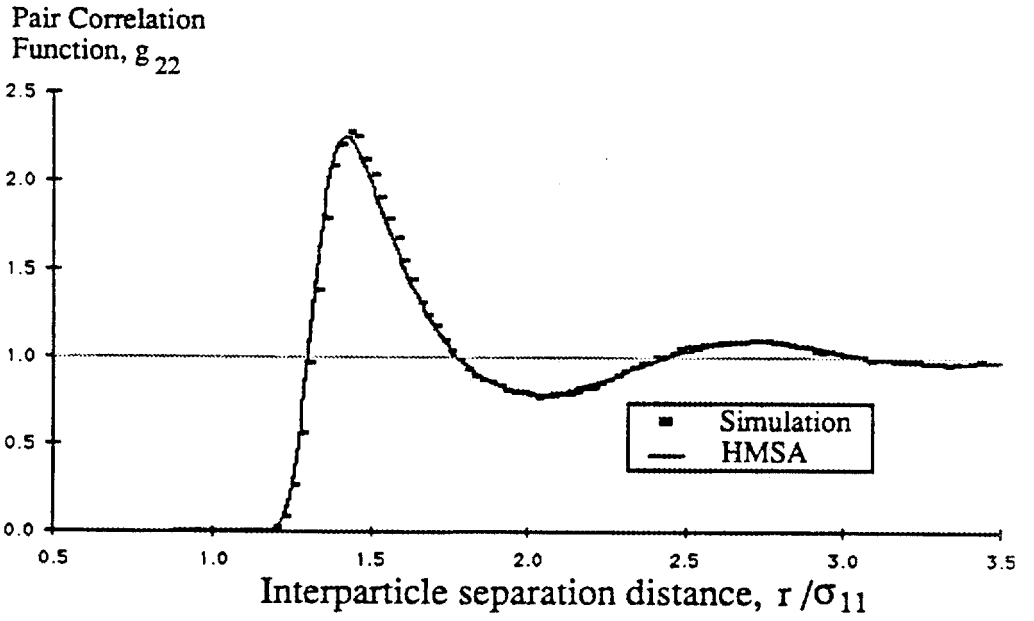


The '1 - 2' pair correlation function for the same conditions as in Figure 28. Again, the agreement of the HMSA theory with simulation data is good.

Figure 30

HMSA Pair Correlation Functions in a Lennard - Jones Mixture Compared to Molecular Simulation

A model of carbon dioxide and acetone (cont.)



The '2 - 2' pair correlation function for the same conditions as in Figure 28. Again, the agreement of the HMSA theory with simulation data is good.

APPENDIX A

FORTRAN PROGRAM

CHEMICAL POTENTIAL PREDICTIONS IN LENNARD-JONES FLUIDS USING HMSA THEORY

```
C ******************************************************************
C        PROGRAM SPT
C        PURPOSE- CALCULATES THE CHEMICAL POTENTIAL OF A SOLUTE
C                 IN A FLUID USING A TEST PARTICLE METHOD.
C
C        DATE 6/16/87
C        REVISED 9/20/87 -TO USE DISTRIBUTION FUNCTIONS OBTAINED
C                         FROM INTEGRAL EQUATION THEORIES.
C                10/21/88 -TO ALLOW MULTIPLE TEST PARTICLE CALCS
C                         FOR EACH CALCULATION OF THE BATH MOLECULE
C                         DISTRIBUTION FUNCTIONS.
C        MAIN PROGRAM BY DAVID PFUND
C        (SOURCE CODE, DOCUMENTATION, EXAMPLE INPUT AND OUTPUT ARE
C         AVAILABLE UPON REQUEST)
C
C        THIS ROUTINE CALLS: SUBROUTINE FILES-TO SET I/O DEVICE
C                            NUMBERS.
C                            SUBROUTINE PARMS-DETERMINES THE
C                            INTERACTION POTENTIAL THE USER DESIRES
C                            AND READS THE PARAMETERS.
C                            SUBROUTINE STATE-READS THE DESIRED
C                            CONDITIONS OF TEMPERATURE AND DENSITY.
C                            SUBROUTINE REDUC-CALCULATES REDUCED
C                            POTENTIAL PARAMETERS FROM THE ABSOLUTE
C                            ONES.
C                            SUBROUTINE FINDA-CALCULATES THE RADIAL
C                            DISTRIBUTION FUNCTIONS FOR THE MIXTURE
C                            USING THE HMSA CLOSURE.
C                            SUBROUTINE PRINTR-PRINTS THE RESULTS
C                            FOR THE BULK PHASE PROPERTIES AND
C                            DISTRIBUTION FUNCTIONS.
C                            SUBROUTINE GOOF-PRINTS ERROR MESSAGES
C                            WHEN "FINDA" FAILS TO COMPUTE THE BULK
C                            PHASE PROPERTIES.
C                            SUBROUTINE TPARMS-READS THE DESIRED
C                            (TRIAL) CAVITY DIAMETERS.
C                            ALSO READS COMPONENT MOLECULAR WEIGHT.
C                            SUBROUTINE MUDRVR-CALCULATES THE
C                            CHEMICAL POTENTIAL OF THE SOLUTE.
C                            SUBROUTINE PRNTMU-PRINTS THE RESULTS
C                            OF THE CHEMICAL POTENTIAL CALCULATIONS.
C                            SUBROUTINE MUGOOF-PRINTS ERROR MESSAGES
C                            WHEN "MUDRVR" FAILS TO COMPUTE THE TEST
C                            PARTICLE PROPERTIES.
C ******************************************************************
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 G(2048,3),PAIR(2048,3),DIRECT(2048,3)
      REAL*8 TOTAL(2048,3),BATH(2048,3)
      REAL*8 AFFINS(2,2)
      REAL*8 ASIGMA(3),KEPSI(3)
      REAL*8 SOFTD(3)
      REAL*8 SIGMA(3),EPSI(3)
      REAL*8 RSOFTD(3)
      REAL*8 RO(3)
      REAL*8 TEMP,X1
      REAL*8 YU,YUIDL,ENERGY,ALPHA,COMPC
      REAL*8 MW
      REAL*8 PRESSV,CERROR,YUHS
```

```
      REAL*8 INT1,INT2
      REAL*8 E1,E2
      INTEGER ERROR,COUNT
      INTEGER DOIT
      LOGICAL OKPAR,OKCON,OKTP
      LOGICAL LOTS
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C                INITIALIZE I/O DEVICE NUMBERS.
C
      CALL FILES
      CALL DETAIL(LOTS)
C
C                GET DESIRED POTENTIAL AND PARAMETERS.
C
      CALL PARMS(OKPAR,KEPSI,SOFTD)
C
C                   GET DESIRED STATE CONDITIONS.
C
      JP=2
      IF(OKPAR) THEN
 200     CONTINUE
            E11=KEPSI(1)
            CALL STATE(OKCON,E11,RO,TEMP,X1,DOIT)
            IF(OKCON) THEN
C
C FIND THE BULK PHASE PROPERTIES AND THE DISTRIBUTION FUNCTIONS FOR
C THE BATH MOLECULES.
C
               CALL REDUC(KEPSI,SOFTD,EPSI,RSOFTD)
               TRED=TEMP/KEPSI(1)
               ERROR=0
               CALL FINDA(NBIG,NM,DR,JP,RSOFTD,EPSI,RO,TRED,G,
     $                    PAIR,DIRECT,TOTAL,BATH,ALPHA,
     $                    PRESSU,ENERGY,TCORR,COMPC,CERROR,COUNT,
     $                    ERROR,AFFINS)
               IF(ERROR.EQ.0) THEN
C PRINT BULK PHASE PROPERTIES AND DISTRIBUTION FUNCTIONS.
                  CALL PRINTR(LOTS,DR,PAIR,DIRECT,TOTAL,BATH,
     $                      KEPSI,SOFTD,TEMP,RO,X1,G,COUNT,
     $                      ALPHA,PRESSU,ENERGY,CERROR,COMPC,AFFINS)
               ELSE
                  CALL GOOF(ERROR,KEPSI,SOFTD,TEMP,RO,X1)
                  JP=2
               END IF
               IF((ERROR.EQ.0).AND.(DOIT.EQ.1)) THEN
C
C DOIT = 1:
C WANT TO DO A CHEMICAL POTENTIAL CALCULATION.
C READ IN ASSUMED EFFECTIVE DIAMETERS FOR THE CAVITIES (DIMENSIONLESS).
C ALSO READS IN A SWITCH WHICH INDICATES WHICH SPECIES THE TEST
C PARTICLE IS.
                  CALL TPARMS(OKTP,IPOT,MW,DRNEW,DLIKE,DUNLKE)
                  IF(OKTP) THEN
 300                 CONTINUE
C CALCULATE CHEMICAL POTENTIAL.
                        CALL MUDRVR(NBIG,NM,DR,DRNEW,IPOT,KEPSI,SOFTD,
     $                    EPSI,RSOFTD,TEMP,TRED,RO,X1,JP,ALPHA,
     $                    PRESSU,COMPC,DLIKE,DUNLKE,MW,G,
```

```
     $                    ASIGMA,YU,YUIDL,YUHS,INT1,INT2,E1,E2,
     $                    DMUDRO,ERROR)
                        IF(ERROR.EQ.0) THEN
C PRINT CHEMICAL POTENTIAL AND ANALYSIS OF ATTRACTIVE, REPLUSIVE,
C AND IDEAL TERMS.
                          CALL PRNTMU(IPOT,DRNEW,DLIKE,DUNLKE,
     $                         INT1,INT2,E1,E2,YU,YUIDL,YUHS,MW,
     $                         DMUDRO)
                        ELSE
                          CALL MUGOOF(ERROR,DLIKE,DUNLKE)
                        END IF
                     CALL TPARMS(OKTP,IPOT,MW,DRNEW,DLIKE,DUNLKE)
                      IF(OKTP) GOTO 300
                    END IF
                 END IF
              ELSE
                    CALL PARMS(OKPAR,KEPSI,SOFTD)
                    JP=2
C                   JP=1
              END IF
           IF(OKPAR) GO TO 200
C IPOT NEGATIVE IMPLIES USER WANTS TO QUIT.
        END IF
        END
C ******************************************************************
C          SUBROUTINE SMOOTH
C          PURPOSE-SILLY SUBROUTINE TO MAKE UP AN INTIAL GUESS FOR THE
C                  TEST PARTICLE GAMMA FUNCTIONS FROM THOSE OBTAINED
C                  FROM THE BATH. AN INTERPOLATION ROUTINE.
C
C          DATE 11/01/88
C          CODED BY DAVID PFUND
C
C          THIS ROUTINE CALLS:-
C ******************************************************************
        SUBROUTINE SMOOTH(N,DROLD,DR,GOLD,G)
        IMPLICIT REAL*8(A-H,O-Z)
        REAL*8 GOLD(N,3),G(N,3)
        REAL*8 DROLD,DR
        REAL*8 REALK,REALI,RAD
        REAL*8 R0,R1
        INTEGER I,K
        COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C SUBROUTINE SMOOTH INTERPOLATES BETWEEN THE GAMMA FUNCTIONS FOR THE
C BATH "GOLD" (WHICH ARE SPACED AT "DROLD") TO OBTAIN INTIAL GUESSES
C FOR "G" (WHICH ARE SPACED AT "DR").
        DO 100 K=1,N
           REALK=K
           RAD=REALK*DR
           I=RAD/DROLD
           IF(I.EQ.0) THEN
              REALI=1.0D0+I
              R1=REALI*DROLD
              G(K,1)=((GOLD(I+2,1)-GOLD(I+1,1))/DROLD)*(RAD-R1)
              G(K,1)=G(K,1)+GOLD(I+1,1)
              G(K,2)=((GOLD(I+2,2)-GOLD(I+1,2))/DROLD)*(RAD-R1)
              G(K,2)=G(K,2)+GOLD(I+1,2)
              G(K,3)=((GOLD(I+2,3)-GOLD(I+1,3))/DROLD)*(RAD-R1)
```

```
            G(K,3)=G(K,3)+GOLD(I+1,3)
         END IF
         IF((I.GT.0).AND.(I.LE.(N-1))) THEN
            REALI=I
            RO=REALI*DROLD
            G(K,1)=((GOLD(I+1,1)-GOLD(I,1))/DROLD)*(RAD-RO)
            G(K,1)=G(K,1)+GOLD(I,1)
            G(K,2)=((GOLD(I+1,2)-GOLD(I,2))/DROLD)*(RAD-RO)
            G(K,2)=G(K,2)+GOLD(I,2)
            G(K,3)=((GOLD(I+1,3)-GOLD(I,3))/DROLD)*(RAD-RO)
            G(K,3)=G(K,3)+GOLD(I,3)
         END IF
         IF(I.GT.(N-1)) THEN
            G(K,1)=0.0D0
            G(K,2)=0.0D0
            G(K,3)=0.0D0
         END IF
  100 CONTINUE
C     DO 200 I=2000,2048
C        WRITE(NOUT2,*)GOLD(I,1),G(I,1)
C 200 CONTINUE
C     STOP
      RETURN
      END
C ***********************************************************************
C        SUBROUTINE RHODMU
C        PURPOSE-COMPUTES THE DENSITY DERIVATIVE OF THE CHEMICAL
C                POTENTIAL OF THE SPECIES OF INTEREST TIMES THE DENSITY
C                OF THAT SPECIES.
C
C        DATE 10/31/88
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS: FUNCTION DERIV- NUMERICALLY DIFFERENTIATES
C                            THE CHEMICAL POTENTIAL W.R.T. DENSITY.
C ***********************************************************************
      SUBROUTINE RHODMU(IPOT,DELTA,X1,COMPC,RO,ASIGMA,SOFTD,GAAC3,
     $GAAC2,GAAC,GABC3,GABC2,GABC,SOFT3,SOFT2,SOFTO,
     $YU,YUHS,YUSTR,DMUDRO)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 RO(3),RHO(3)
      REAL*8 SOFTD(3),ASIGMA(3)
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C     WRITE(NOUT2,*)DELTA,RO(1),RO(2),RO(3)
C     WRITE(NOUT2,*)SOFT3,SOFT2,SOFT1,SOFTO
C     WRITE(NOUT2,*)GAAC3,GAAC2,GAAC1,GAAC
C     WRITE(NOUT2,*)GABC3,GABC2,GABC1,GABC
C     WRITE(NOUT2,*)YU,YUHS
      SOFT=DERIV2(SOFT3,SOFT2,SOFTO,DELTA,RO)
C 'AA' => LIKE-LIKE
C 'AB' => UNLIKE
      ROH=RO(1)+RO(2)
      IF(IPOT.EQ.0) THEN
C SPECIES 2 IS SOLUTE
C 'AA' => 2-2
C 'AB' => 1-2
         XJ=1.0D0-X1
      END IF
```

```
      IF(IPOT.EQ.1) THEN
C SPECIES 1 IS SOLUTE
C 'AA' => 1-1
C 'AB' => 1-2
         XJ=X1
      END IF
      SAVE=XJ*(1.0D0+YU-YUSTR)+(XJ*ROH*ROH*SOFT)
      DMUDRO=SAVE
C     WRITE(NOUT2,*)DMUDRO
      RETURN
      END
C ***********************************************************************
C        SUBROUTINE PARMS
C        PURPOSE-READS IN INTERACTION POTENTIAL PARAMETERS. INPUT
C        OF PARAMETERS THAT ARE LESS THAN OR EQUAL TO ZERO
C        ZERO MEANS USER WANTS TO QUIT (OKPAR=.FALSE. IN
C        THIS CASE).
C
C        DATE 6/9/87
C        REVISED 10/21/88 -REMOVED THE INPUT OF VARIABLES NEEDED
C                          FOR CHEMICAL POTENTIAL CALCULATION FROM
C                          THIS SUBROUTINE.
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS:-
C ***********************************************************************
      SUBROUTINE PARMS(OKPAR,KEPSI,SOFTD)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 SOFTD(3),KEPSI(3)
      REAL*8 MW
      INTEGER IPOT
      LOGICAL OKPAR
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
      OKPAR=.TRUE.
C NOT TIME TO QUIT. GET NEW POTENTIAL PARAMETERS.
175       CONTINUE
             IF(NIN.EQ.5) THEN
                WRITE(NOUT1,200)
200   FORMAT(/1X,'ENTER LJ SMALL DIAMETER, LJ LARGE DIAMETER, AND')
                WRITE(NOUT1,300)
300   FORMAT(1X,' LJ CROSS DIAMETER IN ANGSTROMS, WHERE SMALL<LARGE.')
                WRITE(NOUT1,320)
320   FORMAT(1X,'ENTER ZERO FOR CROSS DIAMETER TO USE DEFAULT.')
             END IF
             READ(NIN,*)SOFTD(1),SOFTD(2),SOFTD(3)
C        IF((SOFTD(1).GT.SOFTD(2)).AND.(NIN.EQ.5)) GO TO 175
C        IF((SOFTD(1).GT.SOFTD(2)).AND.(NIN.NE.5)) THEN
C           OKPAR=.FALSE.
C        END IF
C        IF(((SOFTD(1).LT.0.0).OR.((SOFTD(2).LT.0.0).OR.(
C    $SOFTD(3).LT.0.0))).AND.(NIN.EQ.5)) GO TO 175
         IF(((SOFTD(1).LE.0.0).OR.((SOFTD(2).LE.0.0).OR.(
     $SOFTD(3).LT.0.0)))) THEN
C    $SOFTD(3).LT.0.0))).AND.(NIN.NE.5)) THEN
            OKPAR=.FALSE.
         END IF
         IF(OKPAR) THEN
            IF(SOFTD(3).EQ.0.0) THEN
```

```
C USE DEFAULT MIXING RULE (ARITHMATIC MEAN) FOR THE LJ CROSS DIAMETER.
              SOFTD(3)=0.5D0*(SOFTD(1)+SOFTD(2))
           END IF
        ELSE
           WRITE(NOUT2,402)
402   FORMAT(/1X,'INVALID CHOICE OF MOLECULAR DIAMETERS WAS MADE.')
           WRITE(NOUT2,404)
404   FORMAT(1X,'EACH DIAMETER MUST BE GREATER THAN OR EQUAL TO ')
           WRITE(NOUT2,406)
406   FORMAT(1X,'ZERO AND THE SECOND DIAMETER ENTERED MUST BE ')
           WRITE(NOUT2,408)
408   FORMAT(1X,'LARGER THAN THE FIRST. DIAMETERS ARE IN ANGSTROMS')
           WRITE(NOUT2,410)
410   FORMAT(1X,'THIS RUN IS TERMINATED')
        END IF
        IF(OKPAR) THEN
500        CONTINUE
              IF(NIN.EQ.5) THEN
                 WRITE(NOUT1,600)
600   FORMAT(/1X,'ENTER ENERGY FOR SMALL, ENERGY FOR LARGE AND')
                 WRITE(NOUT1,700)
700   FORMAT(1X,' CROSS ENERGY IN KELVIN.')
               WRITE(NOUT1,800)
800   FORMAT(1X,'ENTER ZERO FOR CROSS ENERGY TO USE DEFAULT.')
              END IF
              READ(NIN,*)KEPSI(1),KEPSI(2),KEPSI(3)
C          IF(((KEPSI(1).LT.0.0).OR.(KEPSI(2).LT.0.0).OR.(
C    $          KEPSI(3).LT.0.0)).AND.(NIN.EQ.5)) GO TO 500
           IF(((KEPSI(1).LE.0.0).OR.(KEPSI(2).LE.0.0).OR.(
     $          KEPSI(3).LT.0.0))) THEN
C    $          KEPSI(3).LT.0.0)).AND.(NIN.NE.5)) THEN
              OKPAR=.FALSE.
           END IF
           IF(OKPAR) THEN
C USE DEFAULT MIXING RULE (GEOMETRIC MEAN) FOR THE CROSS ENERGY.
              IF(KEPSI(3).EQ.0.0) THEN
                 KEPSI(3)=DSQRT(KEPSI(1)*KEPSI(2))
              END IF
           ELSE
           WRITE(NOUT2,802)
802   FORMAT(/1X,'INVALID CHOICE OF MINIMUM PAIR POTENTIALS WAS ')
           WRITE(NOUT2,804)
804   FORMAT(1X,'MADE. EACH ENTRY MUST BE GREATER THAN OR EQUAL ')
           WRITE(NOUT2,806)
806   FORMAT(1X,'TO ZERO. THE ENTRIES ARE TO BE IN KELVIN, SO ')
           WRITE(NOUT2,808)
808   FORMAT(1X,'THEY MUST BE REDUCED BY BOLTZMANN CONSTANT. ')
           WRITE(NOUT2,810)
810   FORMAT(1X,'THIS RUN IS TERMINATED')
           ENDIF
        END IF
C (I DON'T KNOW HOW TO TRAP ERRORS INVOLVING TOO LITTLE INPUT ON A
C LINE. OH WELL.)
      RETURN
      END
C ***********************************************************************
C        SUBROUTINE STATE
C        PURPOSE-READS IN TEMPERATURE, DENSITY, AND COMPOSITION
```

```
C        ALSO READS A PARAMETER WHICH INDICATES WHETHER OR NOT A
C        CHEMICAL POTENTIAL CALCULATION IS DESIRED.
C
C        DATE 6/9/87
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS:-
C ******************************************************************
      SUBROUTINE STATE(OKCON,E11,RO,TEMP,X1,DOIT)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 RO(3)
      REAL*8 E11
      REAL*8 TEMP,X1
      INTEGER DOIT
      LOGICAL OKCON
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
      OKCON=.TRUE.
      DOIT=0
      IF(NIN.EQ.5) THEN
         WRITE(NOUT1,100)
100   FORMAT(/1X,'ENTER THE TEMPERATURE (KELVIN), REDUCED')
         WRITE(NOUT1,200)
200   FORMAT(1X,'DENSITY (RHO*SIGMA11**3), AND MOLE FRACTION')
         WRITE(NOUT1,300)
300   FORMAT(1X,'OF THE SMALL COMPONENT.  ENTER ZEROS OR ')
         WRITE(NOUT1,400)
400   FORMAT(1X,'NEGATIVE NUMBERS TO CHANGE THE POTENTIAL OR ')
         WRITE(NOUT1,500)
500   FORMAT(1X,'TO QUIT. ')
         WRITE(NOUT1,600)
600   FORMAT(1X,'ON THE SAME LINE ENTER 1 IF YOU WANT THE ')
         WRITE(NOUT1,700)
700   FORMAT(1X,'CHEMICAL POTENTIAL. ENTER ANOTHER NUMBER IF')
         WRITE(NOUT1,800)
800   FORMAT(1X,'YOU DON''T WANT IT.')
      END IF
      READ(NIN,*)TEMP,RO(1),X1,DOIT
C I'VE GIVEN UP ON ERROR TRAPPING- IF YOU CAN'T GET THIS MUCH
C RIGHT, TOO BAD.
      IF((TEMP.LE.0.0).OR.((RO(1).LE.0.0).OR.((X1.LE.0.0).OR.(
     $X1.GE.1.0)))) THEN
         OKCON=.FALSE.
      ELSE
         RO(2)=RO(1)*(1.0D0-X1)
         RO(1)=RO(1)*X1
         RO(3)=RO(1)
      END IF
      RETURN
      END
C ******************************************************************
C        SUBROUTINE TPARMS
C        PURPOSE-READS IN (TRIAL) EFFECTIVE HARD CORE DIAMETERS.
C        ALSO READS IN A PARAMETER WHICH
C        INDICATES WHICH SPECIES IS THE TEST PARTICLE AND THE MOLECULAR
C        WEIGHT OF THAT SPECIES.
C
C        DATE 10/21/88
C        CODED BY DAVID PFUND
```

```
C
C        THIS ROUTINE CALLS:-
C ***********************************************************************
      SUBROUTINE TPARMS(OKTP,IPOT,MW,DRNEW,DLIKE,DUNLKE)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 MW
      REAL*8 DLIKE,DUNLKE
      INTEGER IPOT
      LOGICAL OKTP
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
      OKTP=.TRUE.
      IF(NIN.EQ.5) THEN
         WRITE(NOUT1,100)
100   FORMAT(/1X,'ENTER 0 IF YOU WANT THE CHEMICAL POTENTIAL')
         WRITE(NOUT1,200)
200   FORMAT(1X,'OF SPECIES 2, ENTER 1 IF YOU WANT THE CHEMICAL')
         WRITE(NOUT1,300)
300   FORMAT(1X,'POTENTIAL OF SPECIES 1.  ON THE SAME LINE')
         WRITE(NOUT1,310)
310   FORMAT(1X,'ENTER THE MOLECULAR WEIGHT OF THAT SPECIES,')
         WRITE(NOUT1,315)
315   FORMAT(1X,'THE DESIRED STEP SIZE FOR TEST PARTICLE CALCS.,')
         WRITE(NOUT1,320)
320   FORMAT(1X,'THE LIKE-LIKE AND THE LIKE-UNLIKE CORE SIZES,')
         WRITE(NOUT1,330)
330   FORMAT(1X,'AND THE THERMO CONSISTANCY PARAMETER FOR THE')
         WRITE(NOUT1,340)
340   FORMAT(1X,'TEST PARTICLE DISTRIBUTION FUNCTIONS.')
         WRITE(NOUT1,390)
390   FORMAT(1X,'ENTER ZEROS OR NEGATIVE NUMBERS TO CHANGE THE')
         WRITE(NOUT1,400)
400   FORMAT(1X,'THE STATE OR TO QUIT.')
      END IF
C DRNEW=STEP SIZE FOR THE CHEMICAL POTENTIAL CALCULATION.  DRNEW SHOULD
C BE OF THE ORDER OF 0.00625 TO GET GOOD CONTACT VALUES OF THE RDF'S
C WITH THE HARD SPHERE TEST PARTICLE.
C DUNLKE=UNLIKE EFFECTIVE HARD SPHERE DIAMETER. MUST BE DIVISIBLE
C BY DRNEW.
C DLIKE=LIKE EFFECTIVE HARD SPHERE DIAMETER. MUST BE EVENLY DIVISIBLE
C BY DRNEW.
C DRNEW, DLIKE AND DUNLKE ARE DIMENSIONLESS, HAVING BEEN REDUCED
C BY THE 1-1 LENNARD-JONES SIZE PARAMETER ASIGMA(1).
C IPOT=0 => YOU WANT THE CHEMICAL POTENTIAL OF SPECIES 2 (THE TEST
C PARTICLE BECOMES A MOLECULE OF SPECIES 2 WHEN FULLY CHARGED).  IN
C THIS CASE DLIKE=SPECIES 2 - SPECIES 2 EFFECTIVE DIAMETER AND DUNLKE=
C THE SPECIES 2 - SPECIES 1 EFFECTIVE DIAMETER.
C IPOT=1 => YOU WANT THE CHEMICAL POTENTIAL OF SPECIES 1 (THE TEST
C PARTICLE BECOMES A MOLECULE OF SPECIES 1 WHEN FULLY CHARGED).  IN
C THIS CASE DLIKE=SPECIES 1 - SPECIES 1 EFFECTIVE DIAMETER AND DUNLKE=
C THE SPECIES 1 - SPECIES 2 EFFECTIVE DIAMETER.
      READ(NIN,*)IPOT,MW,DRNEW,DLIKE,DUNLKE
      IF((IPOT.NE.0).AND.(IPOT.NE.1)) THEN
         OKTP=.FALSE.
      END IF
      IF((MW.LE.0.0).OR.((DLIKE.LE.0.0).OR.((DUNLKE.LE.0.0)
     $))) THEN
         OKTP=.FALSE.
      END IF
```

```
      IF(DRNEW.LE.0.0) THEN
         OKTP=.FALSE.
      END IF
      RETURN
      END
C ******************************************************************
C        SUBROUTINE REDUC
C        PURPOSE-CALCULATES REDUCED POTENTIAL PARAMETERS.
C
C        DATE 9/20/87
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS:-
C ******************************************************************
      SUBROUTINE REDUC(KEPSI,SOFTD,EPSI,RSOFTD)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 KEPSI(3)
      REAL*8 SOFTD(3)
      REAL*8 EPSI(3)
      REAL*8 RSOFTD(3)
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
      RSOFTD(1)=1.0D0
      RSOFTD(2)=SOFTD(2)/SOFTD(1)
      RSOFTD(3)=SOFTD(3)/SOFTD(1)
      EPSI(1)=1.0D0
      EPSI(2)=KEPSI(2)/KEPSI(1)
      EPSI(3)=KEPSI(3)/KEPSI(1)
      RETURN
      END
C ******************************************************************
C        SUBROUTINE FINDA
C        PURPOSE-COMPUTES THE VALUE OF THE HMSA MIXING PARAMETER
C                "ALPHA" NEED TO MATCH DERIVATIVES OF THE VIRIAL
C                AND COMPRESSIBILITY PRESSURES WITH RESPECT TO
C                THE TOTAL DENSITY OF THE MIXTURE. NEW GUESSES
C                OF ALPHA ARE MADE BY SOLVING A QUADRATIC FIT
C                OF COMPRESSIBILITIES VS. ALPHA FOR THE VALUE THAT
C                GIVES ZERO ERROR.
C                THE ALPHA THAT IS FOUND OBEYS ZERAH AND HANSEN'S
C                "LOCAL CRITERION".
C                SUBROUTINE FINDA ALSO RETURNS THE DISTRIBUTION
C                FUNCTIONS AND THE VIRIAL PRESSURE DIVIDED BY KT
C                AND MULTIPLIED BY THE (SMALL LJ SIZE PARM**3),
C                AND THE CONFIGURATIONAL INTERNAL ENERGY DIVIDED
C                BY KT.
C                (C.F. ZERAH AND HANSEN, J. CHEM. PHYS.,
C                 VOL. 84, NO 4, P. 2336, FEBRUARY 1986)
C
C        DATE 8/14/87
C        REVISED 10/23/87 TO USE A MODIFIED LINEAR INTERPOLATION
C                         METHOD TO FIND THE ALPHA.
C                         ALSO CHANGED THE CONVERGENCE TEST TO A
C                         TWO-WAY TEST.
C                 2/18/88 TO USE A QUADRATIC INTERPOLATION METHOD.
C        CODED BY DAVID PFUND
C        THIS ROUTINE CALLS: SUBROUTINE GUESSA-PROVIDES TWO INITIAL
C                            GUESSES OF THE HMSA PARAMETER.
C                            FUNCTION MAYER-CALCULATES A VECTOR OF
```

```
C                           MAYER FACTORS FOR THE DESIRED
C                           INTERACTION POTENTIAL WHICH IS USED IN
C                           THE DISTRIBUTION FUNC. CALCS. ALSO
C                           CALCULATES A VECTOR OF PAIR POTENTIAL
C                           DERIVATIVES WHICH ARE USED IN VIRIAL
C                           PRESSURE CALCS.
C                           SUBROUTINE DO3D-COMPUTES THE OBJECTIVE
C                           FUNCTION OF THE INTERPOLATION METHOD FOR
C                           A GIVEN VALUE OF THE ALPHA.
C                           FUNCTION CONFIG- CALCULATES THE
C                           CONFIGURATIONAL INTERNAL ENERGY DIVIDED
C                           BY KT.
C                           SUBROUTINE POLY-FINDS THE COEFFICIENTS
C                           OF THE QUADRATIC FIT.
C                           SUBROUTINE NEWALF-SOLVES THE QUADRATIC
C                           FOR THE NEW ALPHA.
C ***********************************************************************
      SUBROUTINE FINDA(NBIG,NM,DR,JP,SIGMA,EPSI,RO,TRED,G,
     $     PAIR,DIRECT,TOTAL,BATH,ALPHA,
     $     PRESSU,ENERGY,TCORR,COMPC,SAVEFN,COUNT,
     $     ERROR,AFFINS)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 G(2048,3)
      REAL*8 PAIR(2048,3),DIRECT(2048,3),TOTAL(2048,3),BATH(2048,3)
      REAL*8 F(2048,3)
      REAL*8 UPRIME(2048,3)
      REAL*8 BUIJ(2048,3)
      REAL*8 SIGMA(3),RO(3),EPSI(3)
      REAL*8 CORE(3)
      REAL*8 ALPHO,ALPH1,ALPHA
      REAL*8 CC0,CC1,CC2
      REAL*8 CV0,CV1,CV2
      REAL*8 PRESSU,ENERGY
      REAL*8 TRED,DR
      REAL*8 TCORR
      REAL*8 AFFINS(2,2)
      INTEGER IPOT,IE,JP,NM,N
      INTEGER COUNT,MAX
      INTEGER ERROR
      LOGICAL BADMAT,BADALF
      LOGICAL DONE
      LOGICAL LOTS
      COMMON/TYP/JT,N
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
      DATA FTOL,ATOL/0.001D0,0.00001D0/
C     DATA FTOL,ATOL/1.000001D0,1.01D0/
      DATA MAX/20/
      DONE=.FALSE.
      BADALF=.FALSE.
      CORE(1)=0.0D0
      CORE(2)=0.0D0
      CORE(3)=0.0D0
C
C SET STEP SIZE AND NUMBER OF GRID POINTS.
C
      NBIG=2048
      NM=11
      DR=0.00625D0
```

```
      COUNT=0
C NOTE: FOR SUBCRITICAL MIXTURES MULTIPLE ALPHA ROOTS EXIST AT
C INTERMEDIATE DENSITIES. THE PROGRAM DOES ALLWAYS FUNCTION
C WELL UNDER THESE CONDITIONS. SOME OF THESE ROOTS MAY NOT BE
C PHYSICALLY SIGNIFICANT. MAY ALSO HAPPEN FOR PURES, BUT I HAVEN'T
C DISCOVERED THIS YET. BAD ANSWERS MAY ALSO OCCUR WHERE THE PRESSURE
C VERSUS ALPHA CURVE GOES THROUGH ZERO, WITH ALPHA ANSWERS POSSIBLE
C ON EACH SIDE OF THE ZERO.
      N=NBIG
      COMPC=0.0D0
C GET TWO INITIAL GUESSES OF THE HMSA PARAMETER "ALPHA" WHICH BRACKET
C THE OPTIMUM VALUE.
      CALL GUESSA(TRED,RO,SIGMA,EPSI,ALPHO,ALPH1)
C DEFINE THE MAYER FUNCTION F(R). RADIAL DISTANCES ARE IN
C REDUCED UNITS. UPRIME IS A VECTOR OF DERIVATIVES OF
C PAIR POTENTIALS/KT W.R.T. REDUCED SEPARATION DISTANCE R/ASIGMA(1).
C BUIJ IS A VECTOR OF PAIR POTENTIALS/KT.
      CALL MAYER(DR,SIGMA,EPSI,CORE,TRED,F,BUIJ,UPRIME,IPOT,N)
C     DO 10 I=30,80
C        WRITE(NOUT2,*)F(I,1),F(I,3),F(I,2)
C  10 CONTINUE
C "DO3D" CALCULATES THE DISTRIBUTION FUNCTIONS
C  AT FOUR DENSITIES. FROM THESE IT ESTIMATES
C THE DERIVATIVE OF THE VIRIAL PRESSURE WITH RESPECT TO DENSITY
C DIVIDED BY KT.
C IT ALSO CALCULATES THE DERIVATIVE OF THE
C COMPRESSIBILITY PRESSURE W.R.T. DENSITY DIVIDED BY KT
C THE DIFFERENCE BETWEEN THE TWO DERIVATIVES IS THE OBJECTIVE
C FUNCTION OF THE ALPHA ITERATION. THE INTERPOLATION METHOD TRIES TO
C FORCE THIS DIFFERENCE TO ZERO.
      CALL DO3D(ALPHO,IPOT,SIGMA,EPSI,CORE,RO,TRED,G,BUIJ,UPRIME,F,
     $PAIR,DIRECT,TOTAL,BATH,IE,BADMAT,DR,JP,NM,PRESSV,CVO,CCO)
      IF((IE.GT.0).AND.(.NOT.BADMAT)) THEN
C
         CALL DO3D(ALPH1,IPOT,SIGMA,EPSI,CORE,RO,TRED,G,BUIJ,UPRIME,F,
     $PAIR,DIRECT,TOTAL,BATH,IE,BADMAT,DR,JP,NM,PRESSV,CV1,CC1)
         CV2=0.0D0
         CC2=0.0D0
         SAVEFN=CC1-CV1
         COMPC=CC1
C        ALPHA=ALPH1
  100 CONTINUE
            IF((IE.GT.0).AND.(.NOT.BADMAT)) THEN
C              WRITE(NOUT2,*)ALPH1
               IF(COUNT.NE.0) THEN
C FIT COMPRESSIBILITIES TO A QUADRATIC
                  CALL POLY(COUNT,ALPHO,ALPH1,ALPHA,CVO,CV1,CV2,
     $CCO,CC1,CC2,BO,B1,B2)
                  ALPHO=ALPH1
                  ALPH1=ALPHA
                  CVO=CV1
                  CV1=CV2
                  CCO=CC1
                  CC1=CC2
C SOLVE QUADRATIC FOR ALPHA S.T. CV=CC:
                  CALL NEWALF(COUNT,BO,B1,B2,ALPHA)
               ELSE
C IF COUNT=0 (FIRST TIME THROUGH LOOP) TAKE THE MIDPOINT OF THE
```

```
C THE INTERVAL.
                  ALPHA=0.5D0*(ALPH0+ALPH1)
               END IF
C
C              WRITE(NOUT2,*)ALPHA
      IF((DABS(SAVEFN).LE.FTOL).OR.(DABS(ALPHA-ALPH1).LE.ATOL)) THEN
C ALL DONE, THING WORKED.
                  DONE=.TRUE.
C CALCULATE INTERNAL ENERGY/KT:
                  ENERGY=CONFIG(DR,IPOT,RO,BUIJ,PAIR,
     $                          TRED,EPSI,SIGMA,TCORR)
C TCORR=TAIL CORRECTION TO THE INTERNAL ENERGY OVER KT.
C CALCULATE FLUCTUATION INTEGRALS.
                  CALL KIRKWD(DR,TOTAL,AFFINS)
               ELSE
C NOT DONE, NOT FAILED.
                     COUNT=COUNT+1
         CALL DO3D(ALPHA,IPOT,SIGMA,EPSI,CORE,RO,TRED,G,BUIJ,UPRIME,F,
     $PAIR,DIRECT,TOTAL,BATH,IE,BADMAT,DR,JP,NM,PRESSU,CU2,CC2)
C                    WRITE(NOUT2,110)COUNT
C 110                FORMAT(/1X,'AFTER ',I3,' TRIALS:')
C                    WRITE(NOUT2,120)ALPH0,ALPH1,ALPHA
C 120   FORMAT(1X,'A0=',D13.6,' A1=',D13.6,' A=',D13.6)
C                    WRITE(NOUT2,130)F0,F1
C 130   FORMAT(1X,'F0=',D13.6,' F1=',D13.6)
                  SAVEFN=CC2-CU2
                  COMPC=CC2
               END IF
            ELSE
C DISTRIBUTION FUNCTION CALCS FAILED.
               DONE=.TRUE.
            END IF
      IF((.NOT.DONE).AND.(COUNT.LE.MAX)) GO TO 100
      END IF
C ALPHA CARRIES A FACTOR OF ASIGMA(1) (I.E. THE SMALL LJ DIAMETER) AND
C SO IS DIMENSIONLESS.
      IF(COUNT.GT.MAX) THEN
C ALPHA DIDN'T CONVERGE, BAD NEWS.
         BADALF=.TRUE.
      END IF
      ERROR=0
      IF(BADMAT) THEN
         ERROR=1
      END IF
      IF(IE.LT.0) THEN
         ERROR=2
      END IF
      IF(BADALF) THEN
         ERROR=3
      END IF
      RETURN
      END
C ***********************************************************************
C        SUBROUTINE DETAIL
C        PURPOSE-DETERMINES IF THE USER WANTS LONG OR SHORT OUTPUT.
C
C        DATE 6/9/87
C        CODED BY DAVID PFUND
```

```
C
C        THIS ROUTINE CALLS:-
C
C ******************************************************************
      SUBROUTINE DETAIL(LOTS)
      IMPLICIT REAL*8(A-H,O-Z)
      LOGICAL LOTS
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
      INTEGER ICODE
      LOTS=.FALSE.
 50   CONTINUE
        IF(NIN.EQ.5) THEN
           WRITE(NOUT1,100)
100        FORMAT(/1X,'DO YOU WANT DETAILED OUTPUT (1/0)?')
        END IF
        READ(NIN,*)ICODE
      IF((NIN.EQ.5).AND.((ICODE.NE.0).AND.(ICODE.NE.1))) GO TO 50
      IF((NIN.NE.5).AND.((ICODE.NE.0).AND.(ICODE.NE.1))) THEN
C USER FOULED UP FILE INPUT. CHOOSE RESTRICTED OUTPUT AND
C KEEP GOING.
         ICODE=0
      WRITE(NOUT2,150)
150   FORMAT(/1X,'AN INVALID CHOICE FOR PRINT OPTION WAS MADE.')
         WRITE(NOUT2,160)
160   FORMAT(1X,'VALID CHOICES ARE: ')
         WRITE(NOUT2,170)
170   FORMAT(1X,'   1- DETAILED OUTPUT')
         WRITE(NOUT2,180)
180   FORMAT(1X,'   0- SHORT OUTPUT (RDF ONLY)')
         WRITE(NOUT2,190)
190   FORMAT(1X,'I HAVE CHOSEN OPTION 0 FOR YOU.')
      END IF
      IF(ICODE.EQ.1) THEN
         LOTS=.TRUE.
      END IF
      RETURN
      END
C ******************************************************************
C        SUBROUTINE FILES
C        PURPOSE-SETS DEVICE NUMBERS FOR INPUT AND OUTPUT.
C                DEVICE NUMBERS ARE CONTAINED IN COMMON BLOCK
C                /DEVICE/. READS ARE FROM DEVICE 'NIN'. WRITES ARE
C                TO DEVICES 'NOUT1' AND 'NOUT2'.
C                NOUT1 IS FOR DIALOG, NOUT2 IS FOR ANSWERS.
C
C        DATE 1/23/86
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS:-
C ******************************************************************
      SUBROUTINE FILES
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C
C READ CODE FROM SCRATCH UNIT FT25F001
C FT25F001 WAS SET UP IN CLIST AND PASSED TO THE PROGRAM
C CODE CAN HAVE THE FOLLOWING VALUES:
C    -1 OR 1  CONVERSATIONAL INPUT;TERMINAL OUTPUT
C    -2 OR 2  FILE INPUT; TERMINAL OUTPUT
```

```
C    -3 OR 3  FILE INPUT; FILE OUTPUT
C    -4 OR 4  CONVERSATIONAL INPUT; FILE OUTPUT
C END OF FILE INDICATES A BATCH RUN.
C
C POSITIVE INTEGER INDICATES A CRT IS BEING USED
C NEGATIVE INTEGER INDICATES A TELETYPE TYPE OF DEVICE IS BEING USED.
C
      REWIND 25
      READ(25,*,END=500) INOPT
C     INOPT=3
      INABS=IABS(INOPT)
      GO TO (100,200,300,400),INABS
      WRITE(6,5)
    5 FORMAT(//'  INVALID INPUT/OUTPUT CODE.  JOB TERMINATED.')
      STOP
C
C CONVERSATIONAL INPUT; TERMINAL OUTPUT
C
  100 CONTINUE
      NIN=5
      NOUT1=6
      NOUT2=6
      GO TO 600
C
C FILE INPUT; TERMINAL OUTPUT
C
  200 CONTINUE
      NIN=4
      NOUT1=6
      NOUT2=6
      GO TO 600
C
C FILE INPUT; FILE OUTPUT
C
  300 CONTINUE
      NIN=4
      NOUT1=6
      NOUT2=7
      GO TO 600
C
C CONVERSATIONAL INPUT; FILE OUTPUT
C
  400 CONTINUE
      NIN=5
      NOUT1=6
      NOUT2=7
      GO TO 600
C
C END OF FILE - BATCH EXECUTION
C
  500 CONTINUE
      NIN=4
      NOUT1=6
      NOUT2=6
C     NOUT1=17
C     NOUT2=17
C
  600 CONTINUE
```

```
      RETURN
      END
C ***********************************************************************
C        SUBROUTINE GOOF
C
C        PURPOSE-PRINTS A NASTY MESSAGE WHEN HMSA CALCULATIONS FOR
C                THE BULK PHASE FAIL.
C
C        DATE 7/23/87
C        REVISED 10/24/88
C
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS:-
C ***********************************************************************
      SUBROUTINE GOOF(ERROR,KEPSI,SOFTD,TEMP,RO,X1)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 SOFTD(3),KEPSI(3)
      REAL*8 TEMP,X1
      REAL*8 RO(3)
      INTEGER ERROR
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
      WRITE(NOUT2,3)
  3   FORMAT(/1X,'HMSA CALCULATIONS FAILED FOR THE FOLLOWING
     $CONDITIONS')
      WRITE(NOUT2,5)
  5   FORMAT(/1X,'INPUT PARAMETERS FOR THE LENNARD-JONES POTENTIAL:')
      WRITE(NOUT2,10)SOFTD(1),KEPSI(1)
 10   FORMAT(3X,'SIGMA11: ',D11.4,' ANGSTROMS,  EPSILON11: ',
     $D11.4,' KELVIN')
      WRITE(NOUT2,20)SOFTD(3),KEPSI(3)
 20   FORMAT(3X,'SIGMA12: ',D11.4,' ANSTROMS,  EPSILON12: ',
     $D11.4,' KELVIN')
      WRITE(NOUT2,30)SOFTD(2),KEPSI(2)
 30   FORMAT(3X,'SIGMA22: ',D11.4,' ANGSTROMS,  EPSILON22: ',
     $D11.4,' KELVIN')
      WRITE(NOUT2,70)TEMP
 70   FORMAT(/3X,'            TEMPERATURE= ',D11.4,' KELVIN')
      WRITE(NOUT2,80)RO(1)/X1
 80   FORMAT(3X,'                DENSITY= ',D11.4,' (DENSITY*
     $SIGMA11**3)')
      WRITE(NOUT2,90)X1
 90   FORMAT(3X,'MOLE FRACTION SPECIES 1= ',D11.4)
      IF(ERROR.EQ.1) THEN
         WRITE(NOUT2,100)
100      FORMAT(3X,'MIXTURE RDF CALC. FAILED. BAD MATRIX.')
      END IF
      IF(ERROR.EQ.2) THEN
         WRITE(NOUT2,200)
200      FORMAT(3X,'MIXTURE RDF CALC. FAILED. RDF NOT CONVERGED.')
      END IF
      IF(ERROR.EQ.3) THEN
         WRITE(NOUT2,300)
300      FORMAT(3X,'MIXTURE RDF CALC. FAILED. ALPHA NOT CONVERGED.')
      END IF
      RETURN
      END
C ***********************************************************************
```

```
C        SUBROUTINE MUGOOF
C
C        PURPOSE-PRINTS A NASTY MESSAGE TEST PARTICLE CALCULATIONS
C                FAIL.
C
C        DATE 10/24/88
C
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS:-
C ******************************************************************
      SUBROUTINE MUGOOF(ERROR,DLIKE,DUNLKE)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 DLIKE,DUNLKE
      INTEGER ERROR
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
      WRITE(NOUT2,3)
  3   FORMAT(/1X,'CHEMICAL POTENTIAL CALC. FAILED FOR THE FOLLOWING
     $ASSUMED PARAMETERS:')
      WRITE(NOUT2,10)DLIKE,DUNLKE
 10   FORMAT(3X,'DAA/SIGMA11: ',D13.6,' DAB/SIGMA11: ',D13.6)
      IF(ERROR.EQ.4) THEN
         WRITE(NOUT2,400)
400   FORMAT(3X,'TEST PARTICLE RDF CALC. FAILED. RDF NOT CONVERGED.')
      END IF
      IF(ERROR.EQ.5) THEN
C NOTE, THIS ERROR SHOULD NO LONGER OCCUR SINCE THE NEWTON ITERATIONS
C HAVE BEEN REMOVED FROM SUBROUTINE DILUTE.
         WRITE(NOUT2,500)
500   FORMAT(3X,'TEST PARTICLE RDF CALC. FAILED. BAD MATRIX.')
      END IF
      IF(ERROR.EQ.6) THEN
         WRITE(NOUT2,600)
600   FORMAT(3X,'DERIVATIVE CALC. FAILED. MIXTURE RDF NOT CONVERGED.')
      END IF
      RETURN
      END
C ******************************************************************
C        SUBROUTINE PRINTR
C        PURPOSE-PRINTS RESULTS OF THE CALCULATIONS FOR THE BULK PHASE.
C        DATE 6/9/86
C        REVISED 1/15/88 TO PRINT (COMPRESS. EQN. - VIRIAL EQN.)
C                        COMPRESSIBILITIES DIVIDED BY KT AND ALPHA
C                        ITERATION COUNT.
C               10/24/88 REMOVED THE CHEMICAL POTENTIAL CALCULATION
C                        RESULTS.
C
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS:-
C ******************************************************************
      SUBROUTINE PRINTR(LOTS,DR,PAIR,DIRECT,TOTAL,BATH,
     $                  KEPSI,SOFTD,TEMP,RO,X1,G,ACOUNT,
     $                  ALPHA,PRESSU,ENERGY,CERROR,COMPC,AFFINS)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 G(2048,3)
      REAL*8 PAIR(2048,3),DIRECT(2048,3),TOTAL(2048,3),BATH(2048,3)
      REAL*8 AFFINS(2,2)
```

```
      REAL*8 KEPSI(3)
      REAL*8 SOFTD(3)
      REAL*8 RO(3)
      REAL*8 TEMP,X1
      REAL*8 DR
      REAL*8 PRESSU,ENERGY
      REAL*8 CERROR
      REAL*8 COMPC
      INTEGER N
      INTEGER L,M
      INTEGER ACOUNT
      LOGICAL LOTS
      COMMON/TYP/JT,N
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
      DATA CONV/0.6022045D0/
      WRITE(NOUT2,5)
 5    FORMAT(/1X,'INPUT PARAMETERS FOR LENNARD-JONES  POTENTIAL:')
      WRITE(NOUT2,10)SOFTD(1),KEPSI(1)
 10   FORMAT(3X,'SIGMA11: ',D11.4,' ANGSTROMS,  EPSILON11: ',
     $D11.4,' KELVIN')
      WRITE(NOUT2,20)SOFTD(3),KEPSI(3)
 20   FORMAT(3X,'SIGMA12: ',D11.4,' ANGSTROMS,  EPSILON12: ',
     $D11.4,' KELVIN')
      WRITE(NOUT2,30)SOFTD(2),KEPSI(2)
 30   FORMAT(3X,'SIGMA22: ',D11.4,' ANGSTROMS,  EPSILON22: ',
     $D11.4,' KELVIN')
      WRITE(NOUT2,65)ACOUNT
 65   FORMAT(/1X,'AFTER ',I3,' ITERATIONS ON THE HMSA PARAMETER: ')
      WRITE(NOUT2,70)TEMP
 70   FORMAT(/1X,'SOLUTION FOR TEMPERATURE= ',D11.4,' KELVIN')
      WRITE(NOUT2,80)RO(1)/X1
 80   FORMAT(1X,'                  DENSITY= ',D11.4,
     $' (DENSITY*SIGMA11**3)')
      WRITE(NOUT2,82)X1
 82   FORMAT(1X,' MOLE FRACTION SPECIES 1= ',D11.4)
      WRITE(NOUT2,83)ALPHA
 83   FORMAT(/1X,'HMSA PARAMETER: ',D11.4)
      WRITE(NOUT2,84)COMPC
C COMPC=(1/KT)*(THE PARTIAL DERIVATIVE OF THE PRESSURE W.R.T. THE
C DENSITY AT CONST TEMPERATURE AND COMPOSITION).
 84   FORMAT(1X,'COMPRESSIBILITY/KT: ',D13.6)
      WRITE(NOUT2,85)CERROR
 85   FORMAT(1X,'(COMPRESS-VIRIAL)COMPRESSIBILITY/KT: ',D13.6)
C WE'RE PRINTING OUT THE COMPRESSIBILITY FACTOR Z=P/(RHO*KT) HERE:
      WRITE(NOUT2,86)PRESSU/(RO(1)+RO(2))
 86   FORMAT(1X,'VIRIAL PRESSURE/(RHO*KT): ',D13.6)
C ENERGY=CONFIGURATIONAL (OR RESIDUAL) INTERNAL ENERGY *(1/KT).
      WRITE(NOUT2,88)ENERGY
 88   FORMAT(/1X,'CONFIGURATIONAL ENERGY/KT: ',D13.6)
C CONVERT AFFINITIES FROM CU.ANGSTROM/(SOFTD(1)**3) TO CU.ANGSTROMS
C BEFORE PRINTING. THE AFFINITIES ARE ACTUALLY THE KIRKWOOD FLUCTUATION
C INTEGRALS.  THE MAGNITUDE IN CU. ANGSTROMS DEPENDS ON THE SIZES (IN
C ANGSTROMS) OF THE MOLECULES IN THE FLUID.
      CUBE=SOFTD(1)*SOFTD(1)*SOFTD(1)
      AFFINS(1,1)=AFFINS(1,1)*CUBE
      AFFINS(1,2)=AFFINS(1,2)*CUBE
      AFFINS(2,1)=AFFINS(1,2)
      AFFINS(2,2)=AFFINS(2,2)*CUBE
```

```
      WRITE(NOUT2,92)
   92 FORMAT(/1X,'KIRKWOOD-BUFF FLUCTUATION INTEGRALS:')
      WRITE(NOUT2,93)AFFINS(1,1)
   93 FORMAT(3X,'G11= ',D13.6,' CU. ANGSTROMS')
      WRITE(NOUT2,94)AFFINS(1,2)
   94 FORMAT(3X,'G12= ',D13.6,' CU. ANGSTROMS')
      WRITE(NOUT2,95)AFFINS(2,2)
   95 FORMAT(3X,'G22= ',D13.6,' CU. ANGSTROMS')
      IF(LOTS) THEN
C USER WANTS THE LONG FORMAT PRINT OUT.
C PRINT OUT ALL CORRELATION FUNCTIONS (CURRENT FORMAT IS VERY
C SLOPPY).
         DO 150 J=1,3
            L=J
            M=J
            IF(J.EQ.3) THEN
               L=1
               M=2
            END IF
            WRITE(NOUT2,99)L,M
 99         FORMAT(/1X,'FOR L= ',I3,' M= ',I3)
            WRITE(NOUT2,105)
105         FORMAT(/1X,2X,'R/SIGMA11',8X,'G(L,M)',8X,'C(L,M)',
     $8X,'Y(L,M)')
            DO 120 I=60,404
               REALI=I
               RADIUS=DR*REALI
C              BRIDGE=DLOG(BATH(I,J))-((PAIR(I,J)-1.0D0)-DIRECT(I,J))
C              WRITE(NOUT2,110)RADIUS,PAIR(I,J),DIRECT(I,J),BRIDGE
               WRITE(NOUT2,110)RADIUS,PAIR(I,J),DIRECT(I,J),BATH(I,J)
C              SWT=SWITC2(RADIUS,ALPHA)
C              WRITE(NOUT2,110)RADIUS,G(I,J),DIRECT(I,J),SWT,BATH(I,J)
110            FORMAT(1X,D13.6,4X,D13.6,4X,D13.6,4X,D13.6)
C110            FORMAT(1X,D12.5,2X,D12.5,2X,D12.5,2X,D12.5,2X,D12.5)
120         CONTINUE
            DO 140 I=408,600,4
               REALI=I
               RADIUS=DR*REALI
C              BRIDGE=DLOG(BATH(I,J))-((PAIR(I,J)-1.0D0)-DIRECT(I,J))
C              WRITE(NOUT2,130)RADIUS,PAIR(I,J),DIRECT(I,J),BRIDGE
               WRITE(NOUT2,130)RADIUS,PAIR(I,J),DIRECT(I,J),BATH(I,J)
C              SWT=SWITC2(RADIUS,ALPHA)
C              WRITE(NOUT2,130)RADIUS,G(I,J),DIRECT(I,J),SWT,BATH(I,J)
130           FORMAT(1X,D13.6,4X,D13.6,4X,D13.6,4X,D13.6)
C130           FORMAT(1X,D12.5,2X,D12.5,2X,D12.5,2X,D12.5,2X,D12.5)
140         CONTINUE
150      CONTINUE
      ELSE
         WRITE(NOUT2,200)
200      FORMAT(/1X,2X,'R/SIGMA11',11X,'G11',14X,'G12',14X,'G22')
         DO 300 I=60,300,1
            REALI=I
            RADIUS=DR*REALI
            WRITE(NOUT2,250)RADIUS,PAIR(I,1),PAIR(I,3),PAIR(I,2)
250         FORMAT(1X,D13.6,4X,D13.6,4X,D13.6,4X,D13.6)
300      CONTINUE
         DO 400 I=304,416,4
            REALI=I
```

```
            RADIUS=DR*REALI
            WRITE(NOUT2,350)RADIUS,PAIR(I,1),PAIR(I,3),PAIR(I,2)
350         FORMAT(1X,D13.6,4X,D13.6,4X,D13.6,4X,D13.6)
400      CONTINUE
         DO 500 I=424,2048,8
            REALI=I
            RADIUS=DR*REALI
            WRITE(NOUT2,450)RADIUS,PAIR(I,1),PAIR(I,3),PAIR(I,2)
450         FORMAT(1X,D13.6,4X,D13.6,4X,D13.6,4X,D13.6)
500      CONTINUE
      END IF
      RETURN
      END
C ***********************************************************************
C        SUBROUTINE PRNTMU
C        PURPOSE-PRINTS RESULTS OF THE CHEMICAL POTENTIAL CALCULATIONS.
C        DATE 10/24/88
C
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS:-
C ***********************************************************************
      SUBROUTINE PRNTMU(IPOT,DR,DLIKE,DUNLKE,
     $            INT1,INT2,E1,E2,YU,YUIDL,YUHS,MW,DMUDRO)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 YU,YUIDL,YUHS
      REAL*8 INT1,INT2
      REAL*8 E1,E2
      REAL*8 MW
      REAL*8 DLIKE,DUNLKE
      REAL*8 DMUDRO
      INTEGER IPOT
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
      WRITE(NOUT2,5)
  5   FORMAT(/1X,'INPUT PARAMETERS CHEM. POTENTIAL CALCULATION:')
      WRITE(NOUT2,10)DLIKE,DUNLKE
 10   FORMAT(3X,'DAA/SIGMA11: ',D13.6,' DAB/SIGMA11: ',D13.6)
      IF(IPOT.EQ.0) THEN
         WRITE(NOUT2,50)YU
 50      FORMAT(/1X,'CHEMICAL POTENTIAL OF SPECIES 2/KT: ',D13.6)
      END IF
      IF(IPOT.EQ.1) THEN
         WRITE(NOUT2,100)YU
100      FORMAT(/1X,'CHEMICAL POTENTIAL OF SPECIES 1/KT: ',D13.6)
      END IF
C CORE= THE WORK OF INSERTING THE EFFECTIVE HARD SPHERE TEST PARTICLE
C DIVIDED BY KT.
      CORE=YUHS-YUIDL
      WRITE(NOUT2,200)CORE
200   FORMAT(1X,'          (CORE CONTRIBUTION/KT WAS: ',D13.6,')')
C BE= A CRUDE UPPER BOUND ON THE ABSOLUTE VALUE OF THE NEGLECTED BRIDGE
C FUNCTION INTEGRALS IN THE WORK OF SOFTENING FORMULA *(1/KT).
      BE=E1+E2
      WRITE(NOUT2,300)INT1,INT2,BE
C INT1=THE CONTRIBUTION TO THE WORK OF SOFTENING/KT DUE TO INTERACTIONS
C OF THE TEST PARTICLE WITH SPECIES 1 IN THE BATH.
C INT2=THE CONTRIBUTION TO THE WORK OF SOFTENING/KT DUE TO INTERACTIONS
C OF THE TEST PARTICLE WITH SPECIES 2 IN THE BATH.
```

```
300   FORMAT(1X,'(SOFT REPULSIVE CONTRIBUTION/KT WAS: ',D13.6,' + ',
     $D13.6,' +/- ',D13.6,')')
      YUATTR=YU-YUHS-INT1-INT2
      WRITE(NOUT2,400)YUATTR
400   FORMAT(1X,'    (ATTRACTIVE CONTRIBUTION/KT WAS: ',D13.6,')')
      WRITE(NOUT2,500)YUIDL
500   FORMAT(1X,'     (IDEAL GAS CONTRIBUTION/KT WAS: ',D13.6,')')
      WRITE(NOUT2,600)MW
600   FORMAT(1X,'              (BASED ON A MOL.WT. OF: ',D13.6,')')
C     WRITE(NOUT2,700)
C700   FORMAT(1X,'SPECIES DENSITY*(DERIVATIVE OF THE COMPONENT ')
C      WRITE(NOUT2,800)DMUDRO
C800   FORMAT(1X,'CHEM. POTENTIAL W.R.T. DENSITY): ',D13.6)
      RETURN
      END
C ***********************************************************************
C        FUNCTION CONFIG
C        PURPOSE-DETERMINES THE CONFIGURATIONAL INTERNAL ENERGY
C                DIVIDED BY KT.
C
C        DATE 8/24/87
C        REVISED 8/28/87 - ADDED TAIL CORRECTION.
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS: SUBROUTINE SIMP-INTEGRATES THE REQUIRED
C                            PRODUCTS OF ENERGIES,DENSITIES AND RDF'S.
C                            SUBROUTINE TAIL- COMPUTES THE TAIL
C                            CORRECTION TO THE CONFIGURATIONAL
C                            INTERNAL ENERGY DIVIDED BY KT.
C ***********************************************************************
      REAL FUNCTION CONFIG(DR,IPOT,RO,BUIJ,PAIR,TRED,EPSI,
     $SIGMA,TC)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 DR
      REAL*8 RO(3)
      REAL*8 EPSI(3),SIGMA(3)
      REAL*8 BUIJ(2048,3)
      REAL*8 PAIR(2048,3)
      REAL*8 FUNCT(2048,3)
      REAL*8 ENERGY
      REAL*8 TRED
      REAL*8 TC
      REAL*8 RHO
      INTEGER IPOT
      INTEGER ERROR
      INTEGER JT,N
      INTEGER IFUNC
      LOGICAL PNOW
      COMMON/TYP/JT,N
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
      PNOW=.FALSE.
C NEED TOTAL DENSITY:
      RHO=RO(1)+RO(2)
C PREPAIR INTEGRAND:
      DO 100 I=1,N
         FUNCT(I,1)=BUIJ(I,1)*PAIR(I,1)
         FUNCT(I,2)=BUIJ(I,2)*PAIR(I,2)
         FUNCT(I,3)=BUIJ(I,3)*PAIR(I,3)
```

```
  100 CONTINUE
C INTEGRATE...
      PNOW=.FALSE.
      CALL SIMP(DR,RO,FUNCT,ENERGY,PNOW)
      ENERGY=0.5D0*ENERGY/RHO
C COMPUTE TAIL CORRECTION.
C "IFUNC" IS A SELECTOR. IFUNC=0 MEANS DO TAIL CORRECTION TO THE
C INTERNAL ENERGY.
      IFUNC=0
      CALL TAIL(IFUNC,DR,IPOT,TRED,EPSI,SIGMA,RO,TC,ERROR)
      ENERGY=ENERGY+TC
      CONFIG=ENERGY
C RESULT IS ENERGY DIVIDED BY
C KT; IT IS DIMENSIONLESS.
      RETURN
      END
```

```
C ******************************************************************
C        SUBROUTINE DO3D
C        PURPOSE-CALCULATES THE DISTRIBUTION FUNCTIONS AT FOUR
C                DENSITIES FOR A GIVEN VALUE OF THE PARAMETER
C                "ALPHA".  THE (VIRIAL PRESSURE*(ASIGMA(1)**3))/KT
C                IS CALCULATED
C                AT EACH OF THESE DENSITIES AND THE RESULTS ARE
C                USED THE ESTIMATE THE COMPRESSIBILITY. THE
C                COMPRESSIBILITY IS ALSO CALCULATED FROM THE
C                COMPRESSIBILITY EQUATION.
C                SUBROUTINE DO3D ALSO RETURNS THE DISTRIBUTION
C                FUNCTIONS AND THE VIRIAL PRESSURE DIVIDED BY KT.
C                (C.F. ZERAH AND HANSEN, J. CHEM. PHYS.,
C                 VOL. 84, NO 4, P. 2336, FEBRUARY 1986)
C
C        DATE 8/14/87
C        REVISED 2/18/88- TO MAKE FOUR CALCULATIONS OF THE VIRIAL
C                         PRESSURE INSTEAD OF JUST THREE AND TO
C                         PASS COMPV AND COMPC BACK TO SUBROUTINE
C                         FINDA.
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS: SUBROUTINE MINS- EVALUATES MINIMUM
C                            PAIR POTENTIALS DIVIDED BY KT  AND THE
C                            SEPARATION DISTANCES AT THE MINIMA
C                            DIVIDED BY THE SMALL CORE DIAMETER.
C                            SUBROUTINE LABIK-CALCULATES THE
C                            DISTRIBUTION FUNCTIONS.
C                            SUBROUTINE VIRIAL-CALCULATES THE VIRIAL
C                            PRESSURE DIVIDED BY KT.
C                            FUNCTION DERIV-NUMERICALLY ESTIMATES THE
C                            THE DENSITY DERIVATIVE OF THE VIRIAL
C                            PRESSURE DIVIDED BY KT.
C                            FUNCTION COMPRS-CALCULATES THE DENSITY
C                            DERIVATIVE OF THE COMPRESSIBILTY PRESSURE
C                            DIVIDED BY KT.
C ******************************************************************
      SUBROUTINE DO3D(ALPHA,IPOT,SIGMA,EPSI,CORE,RO,TRED,G,BUIJ,UPRIME,
     $    F,PAIR,DIRECT,TOTAL,BATH,IE,BADMAT,DR,JP,NM,
     $     PRESSV,COMPV,COMPC)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 G(2048,3)
      REAL*8 PAIR(2048,3),DIRECT(2048,3),TOTAL(2048,3),BATH(2048,3)
      REAL*8 SIGMA(3),RO(3),EPSI(3)
      REAL*8 F(2048,3)
      REAL*8 UPRIME(2048,3)
      REAL*8 BUIJ(2048,3)
      REAL*8 ALPHA
      REAL*8 PV0,PV1,PV2,PRESSV
      REAL*8 TRED,DR
      REAL*8 DELTA
      REAL*8 RHO(3)
      REAL*8 CORE(3)
      REAL*8 SIJ(3),VIJ(3)
      REAL*8 ALFNEW
      INTEGER IPOT,IE,JP
      INTEGER JT,N,NM
      LOGICAL BADMAT
```

```
      COMMON/HMSA/ALFNEW,VIJ,SIJ
      COMMON/TYP/JT,N
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
      DATA DELTA/-0.0005D0/
C     DATA DELTA/-0.00025D0/
C ALPHA IS THE HMSA PARAMETER. IT IS PASSED THROUGH COMMON/HMSA/
C TO SUBROUTINE CFG, WHERE IS IS USED IN THE HMSA THEORY'S
C CLOSURE EQUATION. COMMON/HMSA/ IS ALSO USED TO PASS ALPHA TO
C SUBROUTINE CORFU, WHERE THE CORRELATION FUNCTIONS ARE CALCULATED.
C VIJ ARE (POTENTIAL MINIMA)/KT.
C SIJ=(SEPARATION OF I AND J AT THE POT. MINIMUM)/ASIGMA(1)
      CALL MINS(IPOT,SIGMA,EPSI,TRED,VIJ,SIJ)
      ALFNEW=ALPHA
C DELTA=STEP SIZE FOR THE NUMERICAL ESTIMATE OF THE DENSITY DERIVATIVE.
      RHO(1)=(1.0D0+(4.0D0*DELTA))*RO(1)
      RHO(2)=(1.0D0+(4.0D0*DELTA))*RO(2)
      RHO(3)=(1.0D0+(4.0D0*DELTA))*RO(3)
C COMPUTE DISTRIBUTION FUNCTIONS:
      CALL LABIK(IPOT,BUIJ,F,SIGMA,EPSI,RHO,TRED,G,PAIR,
     $           DIRECT,TOTAL,BATH,IE,BADMAT,DR,JP,NM)
      IF((IE.GT.0).AND.(.NOT.BADMAT)) THEN
C COMPUTE THE (VIRIAL PRESSURE*(ASIGMA(1)**3))KT:
      CALL VIRIAL(IPOT,DR,RHO,TRED,SIGMA,EPSI,CORE,BUIJ,UPRIME,PAIR,
     $PV0)
      RHO(1)=(1.0D0+(2.0D0*DELTA))*RO(1)
      RHO(2)=(1.0D0+(2.0D0*DELTA))*RO(2)
      RHO(3)=(1.0D0+(2.0D0*DELTA))*RO(3)
C JP=2 => USE HARD SPHERE INITIAL GUESS WHEN CALCULATING
C DISTRIBUTION FUNCTIONS.
C JP=1 => USE LAST RESULT AS INITIAL GUESS
C (THE PROGRAM BEGINS WITH JP=2 THEN SWITCHES TO JP=1 IF THE
C  FIRST CALL TO LABIK RETURNS SUCESSFULLY).
      JP=1
      CALL LABIK(IPOT,BUIJ,F,SIGMA,EPSI,RHO,TRED,G,PAIR,
     $           DIRECT,TOTAL,BATH,IE,BADMAT,DR,JP,NM)
      IF((IE.GT.0).AND.(.NOT.BADMAT)) THEN
      CALL VIRIAL(IPOT,DR,RHO,TRED,SIGMA,EPSI,CORE,BUIJ,UPRIME,PAIR,
     $PV1)
         RHO(1)=(1.0D0+DELTA)*RO(1)
         RHO(2)=(1.0D0+DELTA)*RO(2)
         RHO(3)=(1.0D0+DELTA)*RO(3)
C DO TWO MORE TIMES. GOTTA GET THAT NUMERICAL DERIVATIVE ACCURATE:
         CALL LABIK(IPOT,BUIJ,F,SIGMA,EPSI,RHO,TRED,G,PAIR,
     $              DIRECT,TOTAL,BATH,IE,BADMAT,DR,JP,NM)
         IF((IE.GT.0).AND.(.NOT.BADMAT)) THEN
      CALL VIRIAL(IPOT,DR,RHO,TRED,SIGMA,EPSI,CORE,BUIJ,UPRIME,PAIR,
     $PV2)
            CALL LABIK(IPOT,BUIJ,F,SIGMA,EPSI,RO,TRED,G,PAIR,
     $                 DIRECT,TOTAL,BATH,IE,BADMAT,DR,JP,NM)
            IF((IE.GT.0).AND.(.NOT.BADMAT)) THEN
      CALL VIRIAL(IPOT,DR,RO,TRED,SIGMA,EPSI,CORE,BUIJ,UPRIME,PAIR,
     $PRESSV)
C NUMERICALLY ESTIMATE THE DERIVATIVE OF THE (VIRIAL
C PRESSURE)/KT
C W.R.T. DENSITY.
               COMPV=DERIV(PV0,PV1,PV2,PRESSV,DELTA,RO)
C CALCULATE THE (COMPRESSIBILTY PRESSURE)/KT
C FROM THE COMPRESSIBILITY EQUATION.
```

```
              COMPC=COMPRS(IPOT,DR,RO,TRED,SIGMA,EPSI,DIRECT)
C             WRITE(NOUT2,100)PVO,PV1,PV2,PRESSV
C 100 FORMAT(/1X,'PVO=',D13.6,' PV1=',D13.6,' PV2=',D13.6,' PV=',D13.6)
C             WRITE(NOUT2,200)COMPV,COMPC
C 200 FORMAT(1X,'COMPV=',D13.6,' COMPC=',D13.6)
           END IF
         END IF
      END IF
      END IF
      RETURN
      END
C ******************************************************************
C        SUBROUTINE GUESSA
C        PURPOSE-PROVIDES TWO INITIAL GUESSES OF THE HMSA PARAMETER
C                "ALPHA" (C.F. ZERAH AND HANSEN, J. CHEM. PHYS.,
C                 VOL. 84, NO 4, P. 2336, FEBRUARY 1986)
C
C        DATE 8/14/87
C        REVISED 10/23/87- TO ATTEMPT TO PROVIDE INITIAL GUESSES
C                          WHICH WILL BE MORE LIKELY TO BRACKET
C                          THE SOLUTION WITHOUT LEADING TO
C                          EXCESSIVE ITERATIONS IN SUBROUTINE
C                          FINDA.
C                 2/18/88- ADDED AN EMPIRICAL CORRELATION FOR A
C                          PREDICTED ALPHA VALUE AS A FUNCTION OF
C                          DENSITY AND COMPOSITION.  ADDED LOGIC
C                          TO GIVE UPPER AND LOWER BOUNDS BASED ON
C                          THE PREDICTED VALUE.
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS:-
C ******************************************************************
      SUBROUTINE GUESSA(TEMP,RO,SOFTD,KEPSI,ALPHO,ALPH1)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 SOFTD(3),KEPSI(3)
      REAL*8 RO(3)
      REAL*8 TEMP
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C FOR ROUGH ESTIMATES FOR INTIAL GUESSES C.F. TABLE II IN ZERAH AND
C HANSEN.
      RHO=RO(1)+RO(2)
      S11=SOFTD(1)**3.0D0
      S22=SOFTD(2)**3.0D0
C COMPUTE AVERAGE SIGMA**3:
      S=((RO(1)*S11)+(RO(2)*S22))/RHO
C RHO=SOME APPROPRIATE REDUCED DENSITY.
      RHO=RHO*(S/S11)
C COMPUTE AVERAGE SIGMA:
      S=S**0.333333333D0
C DIMENSIONLESS ALPHA FROM CORRELATION OF PURE LENNARD-JONES AND
C STELL-WEIS RESULTS (VERY GOOD FOR PURES):
      AMEAN=(0.5736066D0/RHO)-0.648766D0
C PREDICTED ALPHA VALUE MUST BE REDUCED BY SOFTD(1)
      AMEAN=AMEAN*(SOFTD(1)/S)
C ESTIMATE UPPER AND LOWER BOUNDS ON ALPHA:
      ALPH1=1.333333D0*AMEAN
      ALPHO=0.666667D0*AMEAN
C YOU MAY FIND THAT ALPHO IS TOO SMALL WHEN WORKING NEAR THE CRITICAL
```

```
C POINT. IF SO, TURN ON THE NEXT LINE OF CODE.
C     ALPHO=AMEAN
      IF(AMEAN.LT.(0.6D0*SOFTD(1)/S)) THEN
         ALPHO=0.135D0
      END IF
      IF(ALPH1.LT.0.2D0) THEN
         ALPH1=0.2D0
      END IF
C ALPHO AND ALPH1 ARE ASSUMED TO CARRY A FACTOR OF SOFTD(1), AND
C SO ARE DIMENSIONLESS.
      RETURN
      END
C ******************************************************************
C        SUBROUTINE MAYER
C        PURPOSE-CALCULATES A VECTOR OF MAYER FACTORS FOR THE DESIRED
C                INTERMOLECULAR POTENTIAL.
C
C        REVISED 6/4/87
C
C        THIS ROUTINE CALLS: FUNCTION PSIIJ- TO CALCULATE THE PAIR
C                            POTENTIAL DIVIDED BY KT FOR A GIVEN
C                            SEPARATION DISTANCE.
C ******************************************************************
        SUBROUTINE MAYER(DR,SIGMA,EPSI,CORE,TRED,F,BUIJ,UPRIME,IPOT,N)
        IMPLICIT REAL*8(A-H,O-Z)
        REAL*8 F(2048,3),SIGMA(3),EPSI(3)
        REAL*8 CORE(3)
        REAL*8 BUIJ(2048,3)
        REAL*8 UPRIME(2048,3)
        REAL*8 BU,BUP
        INTEGER IP
        COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C       WRITE(NOUT1,10)IPOT,N,DR,TRED
C10     FORMAT(/1X,'IN MAYER',I3,' ',I3,' ',D11.4,' ',D11.4)
C       WRITE(NOUT1,*)SIGMA(1),SIGMA(2),SIGMA(3)
C       WRITE(NOUT1,*)EPSI(1),EPSI(2),EPSI(3)
C F => A VECTOR OF MAYER FACTORS.
C F(I,1) = MAYER FACTOR FOR SPECIES 1 - SPECIES 1 INTERACTIONS IN THE
C BATH.
C F(I,2) = MAYER FACTOR FOR SPECIES 2 - SPECIES 2 INTERACTIONS IN THE
C BATH.
C F(I,3) = MAYER FACTOR FOR SPECIES 1 - SPECIES 2 INTERACTIONS IN THE
C BATH.
C SIMILARLY FOR BUIJ AND UPRIME.
C BUIJ => A VECTOR OF PAIR POTENTIALS/KT
C UPRIME => A VECTOR OF DERIVATIVES OF PAIR POTENTIALS/KT - USED IN THE
C CALCULATION OF THE VIRIAL PRESSURE.
C W.R.T. REDUCED SEPARATION DISTANCE R/ASIGMA(1).
C "CORE" IS UNUSED FOR THE LENNARD-JONES POTENTIAL.
        IP=0
        RM=1.0D0
        DO 20 K=1,3
           DRR=DR*SIGMA(1)/SIGMA(K)
           T=TRED*EPSI(1)/EPSI(K)
           DO 30 I=1,N
              REALI=I
              RR=REALI*DRR
              BU=PSIIJ(IP,RR,RM,T,BUP)
```

```
              BUIJ(I,K)=BU
              UPRIME(I,K)=BUP*(SIGMA(1)/SIGMA(K))
C LENNARD-JONES PART
              IF((BU.GT.61.0D0).OR.((REALI*DR).LT.CORE(K))) THEN
                 F(I,K)=-1.0D0
              ELSE
                 F(I,K)=(DEXP(-BU))-1.0D0
              END IF
C             WRITE(NOUT2,18)I,K
C  18         FORMAT(1X,'I= ',I3,' K= ',I3)
C             WRITE(NOUT2,*)BUIJ(I,K),UPRIME(I,K),F(I,K)
30          CONTINUE
20       CONTINUE
C        STOP
         RETURN
         END
C ***********************************************************************
C         SUBROUTINE NEWALF
C         PURPOSE-FINDS THE ROOT OF A QUADRATIC IF COUNT>=1
C                 (IN SUBROUTINE FINDA).
C
C         DATE 2/19/88
C         CODED BY DAVID PFUND
C
C         THIS ROUTINE CALLS: -
C ***********************************************************************
      SUBROUTINE NEWALF(COUNT,B0,B1,B2,ALPHA)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 B0,B1,B2
      REAL*8 ALPHA
      REAL*8 DISCRM
      INTEGER COUNT
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C B0,B1,B2 ARE THE COEFFICIENTS OF A QUADRATIC FOR THE COMPRESSIBILITY
C ERROR (COMPV - COMPC) AS A FUNCTION OF ALPHA DERTERMINED BY
SUBROUTINE
C POLY.
C DON'T CALL THIS SUBROUTINE WHEN COUNT=0 IN FINDA.
         DISCRM=(B1*B1)-(4.0D0*(B0*B2))
         IF(DISCRM.LT.0.0D0) THEN
            ALPHA=-B0/B1
         ELSE
            ALPHA=((-B1)+(DSQRT(DISCRM)))/(2.0D0*B2)
C (THE OTHER ROOT OF THE QUADRATIC CAUSES DIVERGENCE)
         END IF
      RETURN
      END
C ***********************************************************************
C         SUBROUTINE POLY
C         PURPOSE-FITS THE DIFFERENCE OF THE COMPRESSIBILITIES FROM THE
C                 VIRIAL AND COMPRESSIBILITY EQUATIONS TO A QUADRATIC
C                 IN ALPHA.
C
C         DATE 2/19/88
C         CODED BY DAVID PFUND
C
C         THIS ROUTINE CALLS: -
C ***********************************************************************
```

```
      SUBROUTINE POLY(COUNT,A0,A1,A2,CV0,CV1,CV2,CC0,CC1,CC2,B0,B1,B2)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 CV0,CV1,CV2,CC0,CC1,CC2
      REAL*8 B0,B1,B2
      REAL*8 C0,C1,C2
      REAL*8 TERM0,TERM1,TERM2
      INTEGER COUNT
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C DIFFERENCES IN VIRIAL AND COMPRESSIBILITY COMPRESSIBILITIES AT EACH
C STEP:
      C0=CV0-CC0
      C1=CV1-CC1
      C2=CV2-CC2
C DON'T CALL THIS SUBROUTINE WHEN COUNT=0 IN SUBROUTINE FINDA.
C THIS IS THE LANGRANGIAN FORM OF THE POLYNOMIAL, REARRANGED SLIGHTLY.
         TERM0=C0/((A0-A1)*(A0-A2))
         TERM1=C1/((A1-A0)*(A1-A2))
         TERM2=C2/((A2-A0)*(A2-A1))
         B0=(A1*A2*TERM0)+(A0*A2*TERM1)+(A0*A1*TERM2)
         B1=((A1+A2)*TERM0)+((A0+A2)*TERM1)+((A0+A1)*TERM2)
         B1=-B1
         B2=(TERM0+TERM1+TERM2)
C B'S ARE THE COEFFICIENTS OF THE QUADRATIC REQUIRED BY SUBROUTINE
C NEWALF.
      RETURN
      END
C ***********************************************************************
C        FUNCTION DERIV
C        PURPOSE-NUMERICALLY ESTIMATES THE COMPRESSIBILITY FROM
C                PRESSURES OBTAINED FROM THE VIRIAL EQUATION.
C
C        DATE 8/17/87
C        REVISED 2/18/88 - CHANGED FROM A SECOND ORDER TO A FOURTH
C                          ORDER FORMULA.
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS: -
C ***********************************************************************
      REAL FUNCTION DERIV(PV0,PV1,PV2,PRESSV,DELTA,R0)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 DELTA
      REAL*8 PV0,PV1,PV2,PRESSV
      REAL*8 R0(3)
      REAL*8 RHO
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C THIS FUNCTION CURRENTLY USES A FOUR POINT FORWARD DIFFERENCE
C FORMULA WHICH HAS FOURTH ORDER ACCURACY.
C PV0 IS FOUR STEPS FORWARD.
C PV1 IS TWO STEPS FORWARD.
C PV2 IS ONE STEP FORWARD.
C PRESSV IS ON THE NODE OF INTEREST.
C (ACTUALLY, WHETHER THE STEPS ARE FORWARD OR BACKWARD DEPENDS
C  ON THE SIGN OF THE VARIABLE "DELTA" IN SUBROUTINE DO3D)
      RHO=R0(1)+R0(2)
      DERIV=(PV0-(12.0D0*PV1)+(32.0D0*PV2)-(21.0D0*PRESSV))/
     $(12.0D0*DELTA*RHO)
      RETURN
      END
```

```
C ******************************************************************
C        SUBROUTINE LABIK
C        PURPOSE-SOLVES THE OZ EQUATION FOR MIXTURES WITH THE HMSA
C                THEORY USING THE METHOD OF LABIK,MALIJEVSKY, AND
C                AND VONKA (MOLECULAR PHYSICS, VOL. 56, NO. 3,
C                PP.709-715 (1985) )
C
C        REVISED: 6/4/87 - ADDED COMMENTS, IMPROVED I/O, ETC.
C                 2/18/88- TIGHTEND TOLERANCES ON NEWTON AND
C                          DIRECT ITERATIONS TO BE DONE BY SUBROUTINE
C                          GALER (DONE TO IMPROVE THE REPRODUCABILITY
C                          OF THE VIRIAL PRESSURE AT LOW PRESSURES).
C
C        THIS PROGRAM CALLS:
C                            SUBROUTINE GALER-TO SOLVE THE OZ
C                            EQUATION.
C                            SUBROUTINE CORFU-CALCULATES THE PAIR,
C                            DIRECT, AND TOTAL CORRELATION FUNCTIONS
C                            FROM THE OZ SOLUTION.
C ******************************************************************
        SUBROUTINE LABIK(IPOT,BUIJ,F,SIGMA,EPSI,RO,TRED,G,PAIR,
     $                   DIRECT,TOTAL,BATH,IE,BADMAT,DR,JP,NM)
        IMPLICIT REAL*8(A-H,O-Z)
        REAL*8 G(2048,3)
        REAL*8 PAIR(2048,3),DIRECT(2048,3),TOTAL(2048,3),BATH(2048,3)
        REAL*8 F(2048,3)
        REAL*8 BUIJ(2048,3)
        REAL*8 SIGMA(3),RO(3),EPSI(3)
        LOGICAL BADMAT
        COMMON/TYP/JT,N
        COMMON/CONV/CONVDI,CONVNR
        COMMON/LUDOL/PI
        COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C NOTE:UP-DIMENSIONED THE ARRAYS FROM 256 TO 2048 (COMPARED TO
C LABIK'S ORIGINAL PROGRAM.
C THE INCREASED ARRAY SIZE ALLOWS A MAX NM OF 11.
C       WRITE(NOUT1,10)
C10     FORMAT(1X,'IN LABIK')
C       WRITE(NOUT1,*)IPOT,TRED
C       WRITE(NOUT1,*)EPSI(1),EPSI(2),EPSI(3)
        PI=3.1415926535897932D0
        BADMAT=.FALSE.
C
C               SET CONVERGENCE CRITERION FOR DIRECT ITERATION.
        CONVDI=0.000001
C
C               SET CONVERGENCE CRITERION FOR NEWTON-RAPHSON TRIALS.
        CONVNR=0.0001
C JT IS VESTIDUAL (SPELLING?). LEAVE IT ALONE.
        JT=1
C
C                    SOLVE THE OZ EQUATIONS FOR THE MIXTURE.
C THE "G" OBTAINED FROM THE LAST VALUE OF TEMP AND RO IS AUTOMATICALLY
C USED AS AN INITIAL GUESS FOR THE NEW CASE, AS LONG AS THE LJ PARMS
C DON'T CHANGE AND SUBROUTINE GALER DOESN'T FAIL.
C
        CALL GALER(G,BUIJ,F,NM,DR,RO,JP,IE,SIGMA,BADMAT)
        IF((IE.GT.0).AND.(.NOT.BADMAT)) THEN
```

```
C IF NOT ERRORS OCCURRED, CALCULATE THE PAIR,DIRECT,BATH, AND TOTAL
C CORRELATION FUNCTIONS.
      CALL CORFU(DR,BUIJ,F,G,PAIR,DIRECT,TOTAL,BATH)
      END IF
      RETURN
      END
C ******************************************************************
C       SUBROUTINE MINS
C       PURPOSE-CALCULATES THE MINIMUM VALUES OF ALL THREE PAIR
C               POTENTIALS DIVIDED BY KT. ALSO RETURNS THE
C               SEPARATION DISTANCES AT THE MINIMA DIVIDED
C               BY THE 1-1 LENNARD-JONES SIZE PARAMETER.
C
C       REVISED 8/21/87
C
C       THIS ROUTINE CALLS: FUNCTION PSIIJ- TO CALCULATE THE PAIR
C                           POTENTIAL DIVIDED BY KT AT THE POTENTIAL
C                           MININUM.
C ******************************************************************
      SUBROUTINE MINS(IPOT,RSOFTD,EPSI,TRED,VIJ,SIJ)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 RSOFTD(3),EPSI(3)
      REAL*8 TRED
      REAL*8 VIJ(3)
      REAL*8 SIJ(3)
      REAL*8 BUP
      INTEGER IPOT
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C SIJ(1) = THE REDUCED SEPARATION DISTANCE OF THE 1-1 POTENTIAL AT
C THE MINIMUM.
C VIJ(1) = VALUE OF THE 1-1 POTENTIAL AT THE MINIMUM.
      SIJ(1)=(2.0D0**(1.0D0/6.0D0))
      RM=1.0D0
      IP=0
      VIJ(1)=PSIIJ(IP,SIJ(1),RM,TRED,BUP)
      VIJ(3)=VIJ(1)*EPSI(3)/EPSI(1)
      VIJ(2)=VIJ(1)*EPSI(2)/EPSI(1)
      SIJ(3)=SIJ(1)*RSOFTD(3)
      SIJ(2)=SIJ(1)*RSOFTD(2)
      RETURN
      END
C ******************************************************************
C       FUNCTION PSIIJ
C       PURPOSE-CALCULATES THE PAIR POTENTIAL DIVIDED BY KT.
C               CURRENT VERSION DOES LENNARD-JONES.
C
C       DATE 1/8/87
C       CODED BY DAVID PFUND
C
C       THIS ROUTINE CALLS:-
C ******************************************************************
      REAL FUNCTION PSIIJ(IPOT,RSTAR,SSTAR,TEMP,BUP)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 RSTAR,TEMP,BUP
      REAL*8 SSTAR
      INTEGER IPOT
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
      DATA EOVERK/1.0D0/
```

```
C TEMP=SYSTEM TEMPERATURE. IF EOVERK=1.0, THE TEMP IS ASSUMED TO
C BE THE TEMPERATURE REDUCED BY EPSILON(I,J).
C BUP=THE DERIVATIVE OF (PAIR POTENTIAL/KT) W.R.T. REDUCED SEPARATION
C DISTANCE R/ASIGMA(J).
C IPOT=0 => USE LENNARD-JONES POTENTIAL.
C R=(ASIGMA IJ/SEPARATION DISTANCE)
C SSTAR= (LENNARD-JONES SIGMA I)/ASIGMA(I) -WHICH IS ONE FOR THE
LENNARD
C JONES POTENTIAL.
      R=1.0D0/RSTAR
C LENNARD-JONES POTENTIAL
      R=R*SSTAR
      PSI=(4.0D0*EOVERK)*((R**12.0D0)-(R**6.0D0))
      BUP=(24.0D0*EOVERK*R)*((R**6.0D0)-(2.0D0*(R**12.0D0)))
      BUP=BUP/TEMP
      PSIIJ=PSI/TEMP
      RETURN
      END
C ******************************************************************
C        SUBROUTINE VIRIAL
C        PURPOSE-DETERMINES THE VIRIAL PRESSURE TIMES
C                (ASIGMA(1)**3)/KT.
C
C        DATE 8/17/87
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS: SUBROUTINE SIMP-INTEGRATES THE REQUIRED
C                            PRODUCTS OF POTENTIAL GRADIENTS AND
C                            RADIAL DISTRIBUTION FUNCTIONS.
C                            SUBROUTINE TAIL-CALCULATES THE TAIL
C                            CORRECTION TO THE VIRIAL PRESSURE.
C ******************************************************************
      SUBROUTINE VIRIAL(IPOT,DR,RO,TRED,SIGMA,EPSI,CORE,BUIJ,UPRIME,
     $PAIR,PRESSU)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 DR
      REAL*8 RO(3)
      REAL*8 SIGMA(3)
      REAL*8 CORE(3)
      REAL*8 EPSI(3)
      REAL*8 BUIJ(2048,3)
      REAL*8 UPRIME(2048,3)
      REAL*8 PAIR(2048,3)
      REAL*8 FUNCT(2048,3)
      REAL*8 TRED
      REAL*8 PRESSU
      REAL*8 PHARD
      REAL*8 REALI
      REAL*8 RADIUS
      REAL*8 TC
      INTEGER IPOT
      INTEGER JT,N
      INTEGER ERROR
      INTEGER IFUNC
      LOGICAL PNOW
      COMMON/TYP/JT,N
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C PREPARE THE ARGUMENTS FOR SUBROUTINE SIMP.
```

```
C     WRITE(NOUT2,10)IPOT,DR,TRED
C  10 FORMAT(/1X,'IN VIRIAL, IPOT=',I3,' DR=',D11.4,' TRED=',D11.4)
C     WRITE(NOUT2,*)RO(1),RO(2),RO(3)
C     WRITE(NOUT2,*)SIGMA(1),SIGMA(2),SIGMA(3)
C     WRITE(NOUT2,*)VIJ(1),VIJ(2),VIJ(3)
C PAIR => PAIR CORRELATION FUNCTIONS.
C UPRIME => THE DERIVATIVE OF THE PAIR POTENTIAL W.R.T. REDUCED
C SEPARATION DISTANCE DIVIDED BY KT. ALL DISTANCES ARE REDUCED BY
C THE 1-1 LJ SIZE PARAMETER ("ASIGMA(1)").
C RO(1) = NUMBER DENSITY OF SPECIES 1* ASIGMA(1)**3.
C RO(2) = NUMBER DENSITY OF SPECIES 1* ASIGMA(1)**3.
C RO(3) = RO(1).
      DO 100 I=1,N
         REALI=I
         RADIUS=REALI*DR
         FUNCT(I,1)=UPRIME(I,1)*PAIR(I,1)*RADIUS
         FUNCT(I,2)=UPRIME(I,2)*PAIR(I,2)*RADIUS
         FUNCT(I,3)=UPRIME(I,3)*PAIR(I,3)*RADIUS
C        WRITE(NOUT2,20)RADIUS
C  20    FORMAT(/1X,D13.6)
C        WRITE(NOUT2,*)UPRIME(I,1),UPRIME(I,2),UPRIME(I,3)
C        WRITE(NOUT2,*)PAIR(I,1),PAIR(I,2),PAIR(I,3)
  100 CONTINUE
      PNOW=.FALSE.
C INTEGRATE...
      CALL SIMP(DR,RO,FUNCT,PRESSV,PNOW)
      PRESSV=-PRESSV/6.0D0
      PRESSV=PRESSV+RO(1)+RO(2)
C     WRITE(NOUT2,110)PRESSV
C 110 FORMAT(1X,'INTEGRAL+DENSITY= ',D13.6)
C CALCULATE THE TAIL CORRECTION TO THE VIRIAL PRESSURE.
      PHARD=COREPR(DR,SIGMA,CORE,RO,BUIJ,PAIR)
      PRESSV=PRESSV+PHARD
      IFUNC=1
      CALL TAIL(IFUNC,DR,IPOT,TRED,EPSI,SIGMA,RO,TC,ERROR)
C     WRITE(NOUT2,130)TC
C 130 FORMAT(1X,'TAIL CORRECTION= ',D13.6)
      PRESSV=PRESSV+TC
C     WRITE(NOUT2,200)PRESSV
C 200 FORMAT(1X,'TOTOL PRESS',D13.6)
C RESULT IS PRESSURE TIMES THE 1-1 LJ SIZE PARAMETER CUBED DIVIDED BY
C KT; IT IS DIMENSIONLESS.
      RETURN
      END
C ***********************************************************************
C        FUNCTION COMPRS
C        PURPOSE-DETERMINES THE COMPRESSIBILITY OVER KT FROM THE
C                COMPRESSIBILITY EQUATION.
C
C        DATE 8/17/87
C        REVISED 9/3/87- TO INCLUDE THE TAIL CORRECTION TO THE
C                        COMPRESSIBILITY.
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS: SUBROUTINE SIMP-INTEGRATES THE REQUIRED
C                            DIRECT CORRELATION FUNCTIONS.
C                            SUBROUTINE TAIL-ESTIMATES THE TAIL
C                            CORRECTION TO THE COMPRESSIBILITY.
```

```
C ******************************************************************
      REAL FUNCTION COMPRS(IPOT,DR,RO,TRED,SIGMA,EPSI,DIRECT)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 DR
      REAL*8 TRED
      REAL*8 RO(3)
      REAL*8 SIGMA(3),EPSI(3)
      REAL*8 DIRECT(2048,3)
      REAL*8 PRESSC
      INTEGER IPOT,IFUNC
      INTEGER ERROR
      LOGICAL PNOW
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
      PNOW=.FALSE.
C DIRECT => DIRECT CORELATION FUNCTIONS.
C RO(1) = NUMBER DENSITY OF SPECIES 1* ASIGMA(1)**3.
C RO(2) = NUMBER DENSITY OF SPECIES 1* ASIGMA(1)**3.
C RO(3) = RO(1).
C INTEGRATE...
      CALL SIMP(DR,RO,DIRECT,PRESSC,PNOW)
      PRESSC=-PRESSC/(RO(1)+RO(2))
C CALCULATE THE TAIL CORRECTION TO THE COMPRESSIBILITY.
      IFUNC=0
      CALL TAIL(IFUNC,DR,IPOT,TRED,EPSI,SIGMA,RO,TC,ERROR)
      PRESSC=PRESSC+(2.0D0*TC)
      PRESSC=PRESSC+1.0D0
      COMPRS=PRESSC
C RESULT IS COMPRESSIBILITY DIVIDED BY
C KT; IT IS DIMENSIONLESS.
      RETURN
      END
C ******************************************************************
C        SUBROUTINE CORFU
C        PURPOSE-CALCULATES THE PAIR,DIRECT,AND TOTAL
C                CORRELATION FUNCTIONS.
C                CURRENT VERSION ONLY DOES HMSA.
C
C       (C.F. ZERAH AND HANSEN, J.CHEM.PHYS. VOL.84, NO.4, P.2336,
C        FEBRUARY, 1986, FOR DETAILS ON THE HMSA CLOSURE)
C
C
C        DATE 1/8/87
C        REVISED FOR MIXTURES 6/9/87
C                FOR HMSA 8/20/87
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS: FUNCTION SWITCH-COMPUTES THE HMSA
C                            SWITCHING FUNCTION.
C ******************************************************************
      SUBROUTINE CORFU(DR,BUIJ,F,G,PAIR,DIRECT,TOTAL,BATH)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 BUIJ(2048,3)
      REAL*8 G(2048,3)
      REAL*8 F(2048,3)
      REAL*8 PAIR(2048,3),DIRECT(2048,3),TOTAL(2048,3),BATH(2048,3)
      REAL*8 DR,REALI
      REAL*8 UIJ(3),SIJ(3)
      REAL*8 BOLTZ
```

```
      COMMON/HMSA/ALFNEW,VIJ,SIJ
      COMMON/TYP/JT,N
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C G=R*(H(R)-C(R)); DETERMINED BY SUBROUTINE GALER.
C F=MAYER FUNCTION=EXP(-U(R)/KT)-1.
C     WRITE(NOUT1,*)N
      DO 200 I=1,N
         REALI=I
         RADIUS=REALI*DR
         DO 100,J=1,3
C IF JT=1 THEN HMSA.
C HMSA...
C SWT = HMSA SWITCHING FUNCTION. IT'S THE SAME FOR ALL THREE
C INTERACTIONS. ALFNEW = THE PARAMETER IN THE SWITCHING FUNCTION
C WHICH IS MANIPULATED BY SUBROUTINE FINDA TO ACHIEVE PRESSURE
C CONSISTENCY.
            SWT=SWITCH(RADIUS,ALFNEW)
            IF(RADIUS.GE.(1.0000001D0*SIJ(J))) THEN
               EXPO=SWT*((G(I,J)/RADIUS)-BUIJ(I,J))
               BOLTZ=BUIJ(I,J)
            ELSE
               EXPO=SWT*((G(I,J)/RADIUS)-VIJ(J))
               BOLTZ=VIJ(J)
            END IF
C           WRITE(NOUT2,*)RAD,G(I,J),BUIJ(I,J),SWT
            IF(EXPO.LT.-61.0D0) THEN
               EXPO=-61.0D0
            END IF
            IF(EXPO.GT.61.0D0) THEN
               EXPO=61.0D0
            END IF
            IF(BOLTZ.LT.-61.0D0) THEN
               BOLTZ=-61.0D0
            END IF
            BOLTZ=DEXP(BOLTZ)
            BATH(I,J)=0.0D0
            IF(DABS(SWT).GT.0.000000001D0) THEN
               BATH(I,J)=((DEXP(EXPO))-1.0D0)/SWT
            END IF
            BATH(I,J)=BATH(I,J)+1.0D0
            BATH(I,J)=BATH(I,J)*BOLTZ
            PAIR(I,J)=BATH(I,J)*(1.0D0+F(I,J))
            TOTAL(I,J)=PAIR(I,J)-1.0D0
            DIRECT(I,J)=TOTAL(I,J)-(G(I,J)/RADIUS)
100      CONTINUE
200   CONTINUE
      RETURN
      END
C ******************************************************************
C        SUBROUTINE SIMP
C        PURPOSE-INTEGRATES  A FUNCTION TIMES DENSITIES
C                OVER THE VOLUME OF THE SYSTEM. PROCEDURE SIMP USES
C                THE SIMPSON'S RULE.
C
C        DATE 6/16/87
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS: -
```

```
C ******************************************************************
      SUBROUTINE SIMP(DR,RO,FUNCT,INTGRL,PNOW)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 DR
      REAL*8 RO(3)
      REAL*8 FUNCT(2048,3)
      REAL*8 PLAST
      REAL*8 INTGRL
      REAL*8 SPUD
      INTEGER JT,N
      LOGICAL PNOW
      COMMON/TYP/JT,N
      COMMON/LUDOL/PI
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
      INTGRL=0.0D0
C NOTE: FOR THIS PARTICULAR APPLICATION THE INTEGRAND AT THE LEFT
C END POINT IS ZERO AND IS NOT EXPLICITLY INCLUDED IN THE SUMMATIONS
C BELOW.
C THIS SUBROUTINE IS NOT A GENERAL SIMPSON'S RULE SUBROUTINE.
      MAX=N-1
      DO 100 I=1,MAX,2
         REALI=I
         RADIUS=REALI*DR
C NOTE: RADIUS IS THE INTERMOLECULAR SEPARATION DISTANCE DIVIDED BY
C ASIGMA(1). SILLY VARIABLE SPUD IS USED FOR DIAGNOSTICS.
         SPUD=((RO(1)*RO(1)*FUNCT(I,1))+(RO(2)*RO(2)*FUNCT(I,2))
     $+(2.0D0*RO(1)*RO(2)*FUNCT(I,3)))*RADIUS*RADIUS
         INTGRL=INTGRL+(4.0D0*SPUD)
C DIAGNOSTIC PRINTINGS:
C        IF(PNOW.AND.(I.LE.255))THEN
C           WRITE(NOUT2,*)4.0D0*PI*SPUD
C        END IF
100   CONTINUE
      MAX=MAX-1
      DO 200 I=2,MAX,2
         REALI=I
         RADIUS=REALI*DR
         SPUD=((RO(1)*RO(1)*FUNCT(I,1))+(RO(2)*RO(2)*FUNCT(I,2))
     $+(2.0D0*RO(1)*RO(2)*FUNCT(I,3)))*RADIUS*RADIUS
        INTGRL=INTGRL+(2.0D0*SPUD)
C DIAGNOSTIC PRINTINGS:
C        IF(PNOW.AND.(I.LE.256))THEN
C           WRITE(NOUT2,*)RADIUS,4.0D0*PI*SPUD
C        END IF
200   CONTINUE
      MAX=N
      REALI=MAX
      RADIUS=REALI*DR
      PLAST=((RO(1)*RO(1)*FUNCT(MAX,1))+(RO(2)*RO(2)*FUNCT(MAX,2))
     $+(2.0D0*RO(1)*RO(2)*FUNCT(MAX,3)))*RADIUS*RADIUS
      INTGRL=INTGRL+PLAST
      INTGRL=INTGRL*(4.0D0*PI)
      INTGRL=INTGRL*DR/3.0D0
      RETURN
      END
```

```
C ******************************************************************
C        SUBROUTINE CFG
C        PURPOSE-CALCULATES EITHER C(R) IN TERMS OF G(R) OR THE
C                DERIVATIVE OF C(R) UNDER G(R). THIS PROCEDURE AND
C                SUBROUTINE CORFU
C                IS CHANGED FOR ANOTHER THEORY. THE PROGRAM IS
C                CURRENTLY SET UP TO USE ONLY THE HMSA CLOSURE.
C       (C.F. LABIK, MALIJEVSKY AND VONKA, MOL. PHYS. VOL.56, NO.3,
C        P.709, (1985), FOR DETAILS OF THE NUMERICAL PROCEDURE)
C
C       (C.F. ZERAH AND HANSEN, J.CHEM.PHYS. VOL.84, NO.4, P.2336,
C        FEBRUARY, 1986, FOR DETAILS ON THE HMSA CLOSURE)
C
C        REVISED 6/4/87
C                8/18/87-CHANGED TO HMSA CLOSURE
C
C        THIS ROUTINE CALLS: FUNCTION SWITCH-COMPUTES THE HMSA
C                            SWITCHING FUNCTION FOR A GIVEN SEPARATION
C                            DISTANCE AND ALPHA PARAMETER.
C ******************************************************************
        SUBROUTINE CFG(G,BUIJ,F,C,DR,K,RO)
        IMPLICIT REAL*8(A-H,O-Z)
        REAL*8 G(2048,3),F(2048,3),C(2048,3),RO(3)
        REAL*8 BUIJ(2048,3)
        REAL*8 REALI,RAD
        REAL*8 SWT,BOLTZ
        REAL*8 EXPO
        REAL*8 ALFNEW
        REAL*8 VIJ(3),SIJ(3)
        COMMON/HMSA/ALFNEW,VIJ,SIJ
        COMMON/TYP/JT,N
        COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C
C INPUT PARAMETERS-
C       G:    G(R)=R*(H(R)-C(R))
C       F:    MAYER FUNCTION
C       N:    NUMBER OF GRID POINTS
C       DR:   STEP SIZE IN R, AS A FRACTION OF 1-1 LJ SIZE PARM.
C       K:
C             K.EQ.0  ...  R*DIRECT CORRELATION FUNC. IS CALCULATED.
C             K.NE.0 ... 1ST DERIVATIVE OF C(R) IS CALCULATED.
C  ALFNEW:    THE HMSA MIXING PARAMETER. PASSED THROUGH COMMON/HMSA/
C             FROM SUBROUTINE DO3D. LAZY. IT IS ASSUMED TO CARRY A
C             OF ASIGMA(1) (I.E. THE SMALL DIAMETER) WHICH MAKES IT
C             DIMENSIONLESS.
C     VIJ:    THE MINIMUM VALUE OF THE IJ-TH PAIR POTENTIAL DIVIDED
C             BY KT.
C     SIJ:    THE SEPARATION DISTANCE (DIVIDED BY THE 1-1 SIZE PARM)
C             AT THE POTENTIAL MINIMUM.
C OUTPUT PARAMETERS-
C       C:
C             K.EQ.0  ...  R*DIRECT CORRELATION FUNC.
C             K.NE.0 ... 1ST DERIVATIVE OF C(R) W.R.T. G.
C       WRITE(NOUT1,10)
C10     FORMAT(1X,'IN CFG')
C       WRITE(NOUT1,*)RO(1),RO(2),RO(3)
C       WRITE(NOUT1,*)SIJ(1),SIJ(2),SIJ(3)
C       WRITE(NOUT1,*)VIJ(1),VIJ(2),VIJ(3)
```

```
        IF (K.GT.0) GO TO 120
C          WRITE(NOUT2,102)
C 102      FORMAT(/1X,'IN CFG..DOING C CALC')
           DO 115 J=1,3
              DO 110 I=1,N
C COMPUTE R*(DIRECT CORRELATION FUNCTION):
                 REALI=I
                 RAD=REALI*DR
                 SWT=SWITCH(RAD,ALFNEW)
C                WRITE(NOUT2,*)RAD,G(I,J),BUIJ(I,J),SWT
                 IF(RAD.GE.(1.0000001D0*SIJ(J))) THEN
                    EXPO=SWT*((G(I,J)/RAD)-BUIJ(I,J))
C                   WRITE(NOUT2,666)RAD
C 666               FORMAT(1X,'IN BLOCK 1',D13.6)
C                   WRITE(NOUT2,*)I,J,BUIJ(I,J)
                 ELSE
                    EXPO=SWT*((G(I,J)/RAD)-VIJ(J))
C                   WRITE(NOUT2,777)RAD
C 777               FORMAT(1X,'IN BLOCK 2',D13.6)
C                   WRITE(NOUT2,*)I,J,VIJ(J)
                 END IF
                 IF(EXPO.GT.61.0D0) THEN
                    EXPO=61.0D0
                 END IF
                 IF(EXPO.LT.-61.0D0) THEN
                    EXPO=-61.0D0
                 END IF
C                WRITE(NOUT2,*)EXPO
                 C(I,J)=0.0D0
                 IF(DABS(SWT).GT.0.0000000001D0) THEN
                    C(I,J)=((DEXP(EXPO))-1.0D0)/SWT
                 END IF
                 IF(RAD.GE.(1.0000001D0*SIJ(J))) THEN
                    BOLTZ=1.0D0
                 ELSE
                    BOLTZ=-(BUIJ(I,J)-VIJ(J))
                    IF(BOLTZ.LT.-61.0D0) THEN
                       BOLTZ=-61.0D0
                    END IF
                    BOLTZ=DEXP(BOLTZ)
                 END IF
                 C(I,J)=C(I,J)+1.0D0
                 C(I,J)=C(I,J)*BOLTZ
                 C(I,J)=C(I,J)-1.0D0
                 C(I,J)=RAD*C(I,J)
                 C(I,J)=C(I,J)-G(I,J)
C                WRITE(NOUT2,*)C(I,J)
110           CONTINUE
115        CONTINUE
C          STOP
           RETURN
120     CONTINUE
C          WRITE(NOUT2,122)
C 122      FORMAT(/1X,'IN CFG..DOING DERIV CALC')
           DO 140 J=1,3
              DO 130 I=1,N
C COMPUTE DERIVATIVE OF R*(DIRECT CORRELATION FUNCTION):
C C.F. LABIK'S EQUATION (10).
```

```
                REALI=I
                RAD=REALI*DR
                SWT=SWITCH(RAD,ALFNEW)
C               WRITE(NOUT2,*)RAD,G(I,J),BUIJ(I,J),SWT
                IF(RAD.GE.(1.0000001D0*SIJ(J))) THEN
                   EXPO=SWT*((G(I,J)/RAD)-BUIJ(I,J))
                ELSE
                   EXPO=SWT*((G(I,J)/RAD)-UIJ(J))
                END IF
                IF(EXPO.LT.-61.0D0) THEN
                   EXPO=-61.0D0
                END IF
                IF(EXPO.GT.61.0D0) THEN
                   EXPO=61.0D0
                END IF
C               WRITE(NOUT2,*)EXPO
                IF(RAD.GE.(1.0000001D0*SIJ(J))) THEN
                   BOLTZ=1.0D0
                ELSE
                   BOLTZ=-(BUIJ(I,J)-UIJ(J))
                   IF(BOLTZ.LT.-61.0D0) THEN
                      BOLTZ=-61.0D0
                   END IF
                   BOLTZ=DEXP(BOLTZ)
                END IF
                C(I,J)=DEXP(EXPO)
                C(I,J)=C(I,J)*BOLTZ
                C(I,J)=C(I,J)-1.0D0
C               WRITE(NOUT2,*)C(I,J)
130           CONTINUE
140        CONTINUE
           RETURN
        END
C ******************************************************************
C        SUBROUTINE FFS3D
C        PURPOSE-FAST FOURIER TRANSFORM IN ONE DIMENSION.
C        SIMULTANEOUSLY TRANSFORMS ALL THREE COLUMNS OF THE INPUT
C        ARRAY AT ONCE.
C        (SEE LABIK,MALIJEVSKY, AND VONKA,
C        MOLECULAR PHYSICS, VOL. 56, NO. 3,
C                PP.709-715 (1985) )
C
C        REVISED 6/4/87
C        REWRITTEN COMPLETELY 2/18/88 - NOW ONLY PREPARES ARGUMENTS
C                                       FOR DF2INT.
C
C        THIS ROUTINE CALLS: IMSL ROUTINE DF2INT- CALCULATES THE
C                            SINE TRANSFORMS AND THE INVERSIONS.
C                            THIS IS A ROUTINE USED FOR MULTIPLE
C                            TRANSFORMS WHICH REQUIRES THE ARRAY
C                            WFFTR BE INTIALIZED ( BY ROUTINE
C                            "DFSINI" -CALLED IN SUBROUTINE GALER ).
C ******************************************************************
        SUBROUTINE FFS3D(KAM,X,Y,N,NM,DR,WFFTR)
        IMPLICIT REAL*8(A-H,O-Z)
        REAL*8 X(2048,3),Y(2048,3)
        REAL*8 WFFTR(5133)
        REAL*8 XX(2047)
```

```
      REAL*8 YY(2048)
      REAL*8 DR
      REAL*8 COEFF
      INTEGER KAM
      COMMON/LUDOL/PI
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C
C  YY MUST HAVE DIMENSION N
C  XX MUST HAVE DIMENSION N-1
C  N=NM*NM,
C  DIRECT TRANS. KAM>0
C  INVERS TRANS. KAM<0
C  !!!!!!!! X(N,1) MUST BE ZERO !!!!!!!!
C     WRITE(NOUT1,5)
C5    FORMAT(1X,' IN FFS3D ')
      IF(KAM.LT.0) THEN
C INVERTING...
          REALN=N
          COEFF=1.0D0/(4.0D0*PI*DR*REALN)
C         DT=PI/(REALN*DR)
      ELSE
C TRANSFORMING...
          COEFF=2.0D0*PI*DR
C         RM=DR*N
C         DT=DR
      END IF
      NMIN1=N-1
      DO 100 I=1,3
        DO 50 J=1,NMIN1
            XX(J)=X(J,I)
  50    CONTINUE
C THE SUMMATION IN THE TRANSFORM RUNS FROM 1 TO N-1. THE ARGUMENTS
C OF THE SINE FUNCTIONS ARE (PI*I*J/N). THE SERIES RETURNED BY
C DF2INT HAS AN EXTRA FACTOR OF 2.0 ATTACHED TO IT. THUS, IN ORDER
C TO REPRODUCE THE EQUATION GIVEN IN LABIK'S PAPER AN ADDITIONAL
C FACTOR OF COEFF=2.0D0*PI*DR MUST BE INCLUDED WHEN TRANSFORMING.
         CALL DF2INT(NMIN1,XX,YY,WFFTR)
C        CALL OFFS3D(KAM,X,Y,N,NM,DT)
        DO 75 J=1,NMIN1
            Y(J,I)=COEFF*YY(J)
   75   CONTINUE
        Y(N,I)=0.0D0
  100 CONTINUE
      RETURN
      END
C ******************************************************************
C       SUBROUTINE GAUSEL
C       PURPOSE-SOLVES LINEAR EQUATIONS WITH GAUSS' METHOD.
C
C       REVISED 6/4/87
C
C       THIS ROUTINE CALLS:-
C ******************************************************************
      SUBROUTINE GAUSEL(N,R,RES,BADMAT)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 R(N+1,N+1),RES(N)
      REAL*8 S,YY
      LOGICAL BADMAT
```

```
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C     WRITE(NOUT1,10)
C10   FORMAT(1X,' IN GAUSEL')
      BADMAT=.FALSE.
      DO 450 I=1,N-1
         S=0.D0
         DO 430 K=1,N
            YY=DABS(R(K,I))
            IF (YY.LE.S) GO TO 425
               IS=K
               S=YY
425         CONTINUE
430      CONTINUE
      IF (S.EQ.0.D0) GO TO 999
         DO 435 K=I,N+1
            S=R(I,K)
            R(I,K)=R(IS,K)
            R(IS,K)=S
435      CONTINUE
         DO 445 K=I+1,N
            S=R(K,I)/R(I,I)
            DO 438 J=I,N+1
               R(K,J)=R(K,J)-S*R(I,J)
438         CONTINUE
445      CONTINUE
450   CONTINUE
      IF (R(N,N).EQ.0.D0) GO TO 999
         RES(N)=R(N,N+1)/R(N,N)
         DO 460 K=1,N-1
            KK=N-K
            S=0.D0
            DO 455 J=KK+1,N
               S=S+R(KK,J)*RES(J)
455         CONTINUE
            RES(KK)=(R(KK,N+1)-S)/R(KK,KK)
460      CONTINUE
      RETURN
999   CONTINUE
C ZERO PIVOT DETECTED...OUCH.
      BADMAT=.TRUE.
      END
C ***********************************************************************
C        SUBROUTINE GFC
C        PURPOSE- CALCULATES THE TRANSFORM OF GAMMA FROM THE TRANSFORM
C                 OF THE DIRECT CORRELATION FUNCTION.
C
C        REVISED 6/4/87
C
C        THIS ROUTINE CALLS:-
C ***********************************************************************
      SUBROUTINE GFC(C,G,ROT,T)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 C(3),G(3)
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C     WRITE(NOUT1,10)
C10   FORMAT(1X,' IN GFC ')
      C11=C(1)
      C22=C(2)
```

```
      C12=C(3)
      C12C21=C12*C12*ROT
      C11C22=C11*C22
      CT=C12C21-C11C22
      DET=(T-C11)*(T-C22)-C12C21
C THESE ARE THE OZ EQUATIONS IN TRANSFORM SPACE.
      G(1)=(T*(C11*C11+C12C21)+C11*CT)/DET
      G(2)=(T*(C22*C22+C12C21)+C22*CT)/DET
      G(3)=(T*(C11+C22)+CT)*C12/DET
      RETURN
      END
C ******************************************************************
C        SUBROUTINE HSANAL
C        PURPOSE- PROVIDES INITIAL GUESSES OF THE DIRECT CORRELATION
C                 FUNCTION TO SUBROUTINE GALER. IT USES THE ANALYTICAL
C                 SOLUTION FOR HARD SPHERE SYSTEMS GIVEN BY LEBOWITZ
C
C        REVISED 6/4/87
C                10/23/87-INCREASED THE RANGE OF THE DO LOOP FROM
C                         256 TO 2048 TO INSURE THAT ALL VALUES OF
C                         "C" ARE INITIALIZED ON NON-IBM MACHINES.
C
C        THIS ROUTINE CALLS:-
C ******************************************************************
      SUBROUTINE HSANAL(C,RO,SIGMA,DR)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 C(2048,3),RO(3),SIGMA(3)
      COMMON/LUDOL/PI
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C     WRITE(NOUT1,10)
C10   FORMAT(1X,' IN HSANAL ')
      RHO1=RO(1)
      RHO2=RO(2)
      D1=SIGMA(1)
      D2=SIGMA(2)
      RHO=RHO1+RHO2
      Y1=PI/6.*RHO1*D1**3
      Y2=PI/6.*RHO2*D2**3
      DD=D1-D2
      Y=Y1+Y2
      P1=1./(1-Y)
      P2=P1*P1
      P3=1+Y/2.
      G11=P2*(P3+1.5*Y2/D2*DD)
      G22=P2*(P3-1.5*Y1/D1*DD)
      G12=(D2*G11+D1*G22)/(D1+D2)
      P3=P2*P1
      T1=1+Y1+(1+Y2)*D1/D2
      T2=T1*(1+3*Y1*P1)+Y1
      T3=(1-D1/D2)**2
      T4=(1.+Y)*Y+1
      A1=P3*(T4+(Y+2)**2*P1*Y1*(1+RHO2/RHO1)-3*T3*Y2*T2)
      T1=1+Y2+(1+Y1)*D2/D1
      T2=T1*(1+3*Y2*P1)+Y2
      T3=(D2/D1-1)**2
      D13=D1**3
      D23=D2**3
      D12=(D1+D2)/2.
```

```
      A2=P3*(T4+(Y+2)**2*P1*Y2*(1+RHO1/RHO2)-3*T3*Y1*T2)
      B1=-6.*(Y1/D1*G11*G11+Y2/(D23)*G12*G12*D12*D12)
      B2=-6.*(Y2/D2*G22*G22+Y1/(D13)*G12*G12*D12*D12)
      B=-6.*(Y1/D1/D1*G11+Y2/D2/D2*G22)*G12*D12
      CC=0.5*(A1*Y1/D13+A2*Y2/D23)
      DLAM=(D2-D1)/2.
      DO 100 I=1,2048
         C(I,1)=0.
         C(I,2)=0.
         C(I,3)=0.
         R=I*DR
         R3=R**3
         IF (R.LT.D1) THEN
            C(I,1)=-A1-B1*R-CC*R3
         END IF
         IF (R.EQ.D1) THEN
            C(I,1)=(-A1-B1*R-CC*R3)*0.5
         END IF
         IF (R.LT.D2) THEN
            C(I,2)=-A2-B2*R-CC*R3
         END IF
         IF (R.EQ.D2) THEN
            C(I,2)=(-A2-B2*R-CC*R3)*0.5
         END IF
         X=R-DLAM
         IF (R.LT.DLAM) THEN
            C(I,3)=-A1
         ELSE
            IF (R.LT.D12.AND.R.GE.DLAM) THEN
               C(I,3)=-A1-(B*X*X+(4*DLAM+X)*X**3*CC)/R
            ELSE
               IF (R.EQ.D12) THEN
                  C(I,3)=(-A1-(B*X*X+(4*DLAM+X)*X**3*CC)/R)*0.5
               END IF
            END IF
         END IF
100   CONTINUE
      RETURN
      END
C ******************************************************************
C        SUBROUTINE JACOB
C        PURPOSE-?
C
C        DATE 6/4/87
C
C        THIS ROUTINE CALLS:-
C ******************************************************************
      SUBROUTINE JACOB(C,G,F,T,ROT)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 C(3),G(3),F(3,3)
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C     WRITE(NOUT1,10)
C10   FORMAT(1X,' IN JACOB ')
      C1=C(1)
      C2=C(2)
      C12=C(3)
      G1=G(1)
      G2=G(2)
```

```
      G12=G(3)
      C12C21=ROT*C12*C12
      DET=(T-C1)*(T-C2)-C12C21
      F(1,1)=(T-C2)*(G1+C1+C1)+C12C21
      F(1,2)=G1*(T-C1)-C1*C1
      F(1,3)=2*ROT*C12*(T+G1+C1)
      F(2,2)=(T-C1)*(G2+C2+C2)+C12C21
      F(2,1)=G2*(T-C2)-C2*C2
      F(2,3)=2*ROT*C12*(T+G2+C2)
      F(3,1)=(G12+C12)*(T-C2)
      F(3,2)=(G12+C12)*(T-C1)
      F(3,3)=ROT*C12*(G12+G12+3*C12)-C1*C2+T*(C1+C2)
      DO 110 I=1,3
         DO 100 J=1,3
            F(I,J)=F(I,J)/DET
100      CONTINUE
110   CONTINUE
      RETURN
      END
C ***********************************************************************
C        FUNCTION SWITCH
C        PURPOSE-COMPUTES THE FUNCTION WHICH GIVES A SMOOTH TRANSITION
C                BETWEEN HNC AND SMSA THEORIES IN THE HMSA CLOSURE.
C                THIS FUNCTION USED BY SUBROUTINE CFG IN THE
C                COMPUTATION OF THE CORRELATION FUNCTIONS FOR THE
C                BATH MOLECULES.
C        (C.F. ZERAH AND HANSEN, J.CHEM.PHYS. VOL.84, NO.4, P.2336,
C         FEBRUARY, 1986)
C
C        DATE 8/18/87
C
C        THIS ROUTINE CALLS:-
C ***********************************************************************
      REAL FUNCTION SWITCH(RADIUS,ALPHA)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 RADIUS,ALPHA
      REAL*8 EXPO,SAVE
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C RADIUS=SEPARATION DISTANCE/(1-1 LJ SIZE PARM).
C ALPHA=HMSA PARAMETER*(1-1 LJ SIZE PARM)
C SO, BOTH INPUTS ARE DIMENSIONLESS.
C BOTH HAD BETTER BE ALWAYS POSITIVE.
      EXPO=ALPHA*RADIUS
C     SO=0.0D0
      IF(EXPO.GT.61.0D0) THEN
         SAVE=1.0D0
      ELSE
         IF(EXPO.LT.0.00000001D0) THEN
            SAVE=0.00000001D0
C           SAVE=SO
         ELSE
            SAVE=1.0D0-(DEXP(-EXPO))
C           SAVE=1.0D0-((1.0D0-SO)*DEXP(-EXPO))
         END IF
      END IF
      SWITCH=SAVE
C     SWITCH=0.000001D0
C     SWITCH=1.0D0
```

```
      RETURN
      END
C ***********************************************************************
C        FUNCTION SWITCH2
C        PURPOSE-COMPUTES THE FUNCTION WHICH GIVES A SMOOTH TRANSITION
C                BETWEEN HNC AND SMSA THEORIES IN THE HMSA CLOSURE.
C                THIS FUNCTION USED BY SUBROUTINE CFG2 IN THE
C                COMPUTATION OF THE CORRELATION FUNCTIONS FOR THE
C                TEST PARTICLE.
C        (C.F. ZERAH AND HANSEN, J.CHEM.PHYS. VOL.84, NO.4, P.2336,
C         FEBRUARY, 1986)
C
C        DATE 8/18/87
C
C        THIS ROUTINE CALLS:-
C ***********************************************************************
      REAL FUNCTION SWITC2(RADIUS,ALPHA)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 RADIUS,ALPHA
      REAL*8 EXPO,SAVE
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C RADIUS=SEPARATION DISTANCE/(1-1 LJ SIZE PARM).
C ALPHA=HMSA PARAMETER*(1-1 LJ SIZE PARM)
C SO, BOTH INPUTS ARE DIMENSIONLESS.
C BOTH HAD BETTER BE ALWAYS POSITIVE.
      EXPO=ALPHA*RADIUS
C     SO=0.0D0
      IF(EXPO.GT.61.0D0) THEN
         SAVE=1.0D0
      ELSE
         IF(EXPO.LT.0.00000001D0) THEN
            SAVE=0.00000001D0
C           SAVE=SO
         ELSE
            SAVE=1.0D0-(DEXP(-EXPO))
C           SAVE=1.0D0-((1.0D0-SO)*DEXP(-EXPO))
         END IF
      END IF
      SWITC2=SAVE
C     SWITC2=0.000001D0
C     SWITC2=1.0D0
      RETURN
      END
C ***********************************************************************
C        SUBROUTINE TAIL
C        PURPOSE-SETS UP PARAMETERS NEEDED BY SUBROUTINE INTEGR.
C                COMPUTES THE TAIL CORRECTION TO THE CONFIGURATIONAL
C                INTERNAL ENERGY DIVIDED BY KT IF IFUNC=0. COMPUTES
C                TAIL CORRECTION TO THE VIRIAL PRESSURE IF IFUNC=1.
C
C        DATE: 7/14/87.
C
C        THIS PROGRAM CALLS: SUBROUTINE INTEGR-INTEGRATES THE PRODUCT
C                            OF THE  POTENTIAL OVER VOLUME
C                            FROM A LOWER LIMIT (WHERE THE R.D.F IS
C                            APPROXIMATELY 1.0) UP TO A VERY LARGE
C                            UPPER LIMIT.
C ***********************************************************************
```

```
      SUBROUTINE TAIL(IFUNC,DR,IPOT,TRED,EPSI,SIGMA,
     $RO,INTGRL,ERROR)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 SIGMA(3),RO(3),EPSI(3)
      REAL*8 INTGRL,LOWER,UPPER,TRED
      REAL*8 PRMS(30)
      REAL*8 RBIG
      INTEGER IFUNC
      INTEGER ERROR
      INTEGER IPOT
      COMMON/TYP/JT,N
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
      PRMS(1)=TRED
      PRMS(2)=EPSI(1)
      PRMS(3)=EPSI(2)
      PRMS(4)=EPSI(3)
      PRMS(5)=SIGMA(1)
      PRMS(6)=SIGMA(2)
      PRMS(7)=SIGMA(3)
C RESERVE 8,9,10 FOR STELL-WEIS OR KIHARA.
C     PRMS(8)=SOFTD(1)
C     PRMS(9)=SOFTD(2)
C     PRMS(10)=SOFTD(3)
      PRMS(11)=RO(1)
      PRMS(12)=RO(2)
      PRMS(13)=RO(3)
      RBIG=N
C UPPER LIMIT IS 51.2*ASIGMA(1) WHEN N=2048 AND DR=0.00625.
      UPPER=4.0D0*RBIG*DR
      LOWER=RBIG*DR
      CALL INTEGR(IFUNC,IPOT,PRMS,LOWER,UPPER,INTGRL,ERROR)
      RETURN
      END
C ***********************************************************************
C       SUBROUTINE TEST
C       PURPOSE-TESTS DIFFERENCES OF G(T) IN NEWTON ITERATION.
C
C       REVISED 6/4/87
C
C       THIS ROUTINE CALLS:-
C ***********************************************************************
      SUBROUTINE TEST(DG,DIF,NA,IK,N,DR)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 DG(NA,3),DIF(NA,3)
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C
C INPUT PARAMETERS-
C     DG:    VALUES OF DIFFERENC GT(T)
C    DIF:    THEIR MODIFICATION FROM ITERATION STEP.
C     NA:    NUMBER OF EQUATIONS IN NEWTON ITERATION.
C OUTPUT PARAMETERS-
C     NEW VALUES OF DIFFERENCE GT(T)
C            USUALLY DG(T)=DG(T) +DIF(T)
C     IK:
C          IK.EQ.0  ...  NEWTON ITERATION MAY CONTINUE.
C          IK.NE.0 ... FORCES SUBROUTINE GALER TO PERFORM DIRECT
C                      ITERATION (PROBABLY DUE TO TOO HIGH VALUES
C                      OF DG(T) ).
```

```
C       WRITE(NOUT1,10)
C10     FORMAT(1X,' IN TEST')
        IK=0
        DO 20 J=1,3
           DO 10 K=1,NA
              DG(K,J)=DG(K,J)+DIF(K,J)
10         CONTINUE
20      CONTINUE
        IF (JT.EQ.1) RETURN
        END
C ***********************************************************************
C        FUNCTION FUNCO
C        PURPOSE-CALCULATES THE INTEGRAND FOR THE TAIL CORRECTION
C                TO THE INTERNAL ENERGY. ALSO USED TO CALCULATE
C                THE TAIL CORRECTION TO THE COMPRESSIBILITY FROM
C                THE COMPRESSIBILITY EQUATION.
C
C        DATE 6/29/87
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS: SUBROUTINE PSIIJ-CALCULATES THE PAIR
C                            POTENTIALS DIVIDED BY KT FOR A GIVEN
C                            SEPARATION DISTANCE.
C ***********************************************************************
      REAL FUNCTION FUNCO(PRMS,IPOT,ARG,ERROR)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 ARG
      REAL*8 T,RR,PI
      REAL*8 BU1,BU2,BU12
      REAL*8 BUP
      REAL*8 SAVE,RHO
      REAL*8 PRMS(30)
      INTEGER IPOT
      INTEGER IP
      INTEGER ERROR
      COMMON/LUDOL/PI
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C DO 1-1 INTERACTION
      T=PRMS(1)
      RR=ARG
      RM=1.0D0
      IP=0
      BU1=PSIIJ(IP,RR,RM,T,BUP)
C DO 1-2 INTERACTION
      T=PRMS(1)/PRMS(4)
      RR=ARG*PRMS(5)/PRMS(7)
      BU12=PSIIJ(IP,RR,RM,T,BUP)
C DO 2-2 INTERACTION
      T=PRMS(1)/PRMS(3)
      RR=ARG*PRMS(5)/PRMS(6)
      BU2=PSIIJ(IP,RR,RM,T,BUP)
      SAVE=(PRMS(11)*PRMS(11)*BU1)+(PRMS(12)*PRMS(12)*BU2)
      SAVE=SAVE+(2.0D0*PRMS(11)*PRMS(12)*BU12)
      RHO=PRMS(11)+PRMS(12)
      SAVE=SAVE/RHO
      FUNCO=2.0D0*PI*ARG*ARG*SAVE
      RETURN
      END
```

```
C ******************************************************************
C        FUNCTION FUNC1
C        PURPOSE-CALCULATES THE INTEGRAND FOR THE TAIL CORRECTION
C                TO THE VIRIAL PRESSURE.
C
C        DATE 9/3/87
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS: SUBROUTINE PSIIJ-CALCULATES THE PAIR
C                            POTENTIALS DIVIDED BY KT FOR A GIVEN
C                            SEPARATION DISTANCE.
C ******************************************************************
      REAL FUNCTION FUNC1(PRMS,IPOT,ARG,ERROR)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 ARG
      REAL*8 T,RR,PI
      REAL*8 BU1,BU2,BU12
      REAL*8 BUP11,BUP12,BUP22
      REAL*8 SAVE
      REAL*8 PRMS(30)
      INTEGER IPOT
      INTEGER IP
      INTEGER ERROR
      COMMON/LUDOL/PI
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C DO 1-1 INTERACTION
      RM=1.0D0
      IP=0
      T=PRMS(1)
      RR=ARG
      BU1=PSIIJ(IP,RR,RM,T,BUP11)
C DO 1-2 INTERACTION
      T=PRMS(1)/PRMS(4)
      RR=ARG*PRMS(5)/PRMS(7)
      BU12=PSIIJ(IP,RR,RM,T,BUP12)
      BUP12=BUP12*(PRMS(5)/PRMS(7))
C DO 2-2 INTERACTION
      T=PRMS(1)/PRMS(3)
      RR=ARG*PRMS(5)/PRMS(6)
      BU2=PSIIJ(IP,RR,RM,T,BUP22)
      BUP22=BUP22*(PRMS(5)/PRMS(6))
      SAVE=(PRMS(11)*PRMS(11)*BUP11)+(PRMS(12)*PRMS(12)*BUP22)
      SAVE=SAVE+(2.0D0*PRMS(11)*PRMS(12)*BUP12)
      FUNC1=-2.0D0*PI*ARG*ARG*ARG*SAVE/3.0D0
      RETURN
      END
C ******************************************************************
C        FUNCTION FUNC2
C        PURPOSE-CALCULATES THE INTEGRAND FOR THE TAIL CORRECTION TO
C                THE CHEMICAL POTENTIAL.
C
C        DATE 6/29/87
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS: SUBROUTINE PSIIJ-CALCULATES THE PERTURBING
C                            POTENTIALS DIVIDED BY KT FOR A GIVEN
C                            SEPARATION DISTANCE.
C ******************************************************************
```

```
      REAL FUNCTION FUNC2(PRMS,IPOT,ARG,ERROR)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 ARG
      REAL*8 T,RR,SSTAR,PI
      REAL*8 BU1,BU2
      REAL*8 BUP
      REAL*8 PRMS(30)
      INTEGER IPOT
      INTEGER ERROR
      COMMON/LUDOL/PI
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
      SSTAR=1.0D0
      IP=0
C DO 1-2 INTERACTION
      T=PRMS(1)/PRMS(4)
      RR=ARG*PRMS(5)/PRMS(7)
      BU1=PSIIJ(IP,RR,SSTAR,T,BUP)
C DO LIKE-LIKE INTERACTION
      IF(IPOT.EQ.0) THEN
C SPECIES 2 IS SOLUTE
         T=PRMS(1)/PRMS(3)
         RR=ARG*PRMS(5)/PRMS(6)
      ELSE
C SPECIES 1 IS SOLUTE
         T=PRMS(1)
         RR=ARG
C        SSTAR=PRMS(8)/PRMS(5)
      END IF
      BU2=PSIIJ(IP,RR,SSTAR,T,BUP)
      IF(IPOT.EQ.0) THEN
         SAVE=4.0D0*PI*ARG*ARG*((PRMS(11)*BU1)+(PRMS(12)*BU2))
      ELSE
         SAVE=4.0D0*PI*ARG*ARG*((PRMS(12)*BU1)+(PRMS(11)*BU2))
      END IF
      FUNC2=SAVE
      RETURN
      END
C ******************************************************************
C        SUBROUTINE GAUSS
C        PURPOSE-PERFORMS THE GAUSS-LEGENDRE INTEGRATION FOR A
C        GIVEN NUMBER OF PANELS. SUBROUTINE "GAUSS" CURRENTLY USES
C        A THIRD ORDER LEGENDRE POLYNOMIAL.
C
C        DATE 2/17/86
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS: FUNCTION SUBINT-ESTIMATES THE INTEGRAL
C                            FOR A SINGLE PANEL."GAUSS" THEN ADDS UP
C                            THE VALUES FOR ALL PANELS.
C ******************************************************************
      SUBROUTINE GAUSS(IFUNC,SIZE,PRMS,IPOT,LOWER,UPPER,NUMPAN,
     $LAMBDA,WEIGHT,INTGRL,ERROR)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 INTGRL,LOWER,UPPER
      INTEGER ERROR,SIZE,NUMPAN
      INTEGER IPOT,IFUNC
      REAL*8 PRMS(30)
      REAL*8 LAMBDA(SIZE),WEIGHT(SIZE)
```

```
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
      ERROR=0
      INTGRL=0.0D0
      RNUM=NUMPAN
C CALCULATE THE WIDTH OF EACH INTEGRATION PANEL.
      DELTAX=(UPPER-LOWER)/RNUM
C A=LOWER LIMIT OF THE CURRENT PANEL. B=UPPER LIMIT OF THE CURRENT
C PANEL.
      A=LOWER
      B=A+DELTAX
C I IS THE PANEL COUNTER.
      I=1
 1000 CONTINUE
C        WRITE(NOUT2,1100)A,B
C1100    FORMAT(/1X,'IN GAUSS. A=',D11.4,' B=',D11.4)
C ESTIMATE THE AREA UNDER THE CURVE OVER THE CURRENT PANEL USING
C FUNCTION "SUBINT". ADD THE RESULT TO THE VALUE OF THE INTEGRAL.
         INTGRL=INTGRL+SUBINT(IFUNC,SIZE,PRMS,IPOT,A,B,LAMBDA,
     $WEIGHT,ERROR)
C     WRITE(NOUT2,1150)INTGRL,ERROR
C1150 FORMAT(/1X,'INTGRL= ',D11.4,' ERROR= ',I3)
C THE LOWER LIMIT OF THE NEXT PANEL=THE UPPER LIMIT OF THE CURRENT
C ONE.
         A=B
C GET THE UPPER LIMIT OF THE NEXT PANEL.
         B=B+DELTAX
         I=I+1
C REPEAT ADDING ON AREAS UNTIL ALL PANELS HAVE BEEN ADDED ON.
      IF((I.LE.NUMPAN).AND.(ERROR.EQ.0))GO TO 1000
C     WRITE(NOUT2,1200)INTGRL
C1200 FORMAT(/1X,'LEAVING GAUSS. INTGRL= ',D11.4)
      RETURN
      END
C ******************************************************************
C        SUBROUTINE INDVRS
C        PURPOSE-DETERMINES AN ORDER NUMBER OF UNEQUALLY SPACED
C        WITHIN THE INTEGRATION PANEL FOR WHICH THE INTEGRAND WILL
C        BE EVALUATED.
C
C        DATE 2/18/86
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS: FUNCTION MAP-SOMEHOW MAPS THE DESIRED
C                            PANEL ONTO SOME KIND OF STANDARD GAUSS-
C                            LEGENDRE INTERVAL.I FORGOT HOW IT WORKS.
C ******************************************************************
      SUBROUTINE INDVRS(SIZE,ORDER,LOWER,UPPER,LAMBDA,XARRAY)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 LOWER,MAP
      INTEGER ORDER,SIZE
      REAL*8 LAMBDA(SIZE)
      REAL*8 XARRAY(ORDER)
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
      XARRAY(1)=MAP(LOWER,UPPER,LAMBDA(1))
C REMEMBER, ORDER MUST BE IN 2..10
      IF((ORDER.EQ.3).OR.((ORDER.EQ.5).OR.((ORDER.EQ.7).OR.(ORDER.EQ.9)
     $))) THEN
         I=2
```

```
         J=2
      ELSE
         XARRAY(2)=MAP(LOWER,UPPER,-LAMBDA(1))
         I=3
         J=2
      END IF
      IF(I.LE.ORDER) THEN
 1000    CONTINUE
            XARRAY(I)=MAP(UPPER,LOWER,LAMBDA(J))
            XARRAY(I+1)=MAP(UPPER,LOWER,-LAMBDA(J))
            J=J+1
            I=I+2
         IF(I.LE.ORDER) GO TO 1000
      END IF
      RETURN
      END
C ***********************************************************************
C        SUBROUTINE INTEGR
C        PURPOSE-INTEGRATES ....
C
C        SUBROUTINE INTEGR USES THE GAUSS-LEGENDRE METHOD FOR NUMERICAL
C        INTEGRATION. CURRENTLY USES A THIRD ORDER LEGENDRE POLYNOMIAL.
C        "INTEGR" PROGRESSIVELY DOUBLES THE NUMBER OF INTEGRATION
PANELS
C        USED UNTIL A CONVERGED RESULT IS OBTAINED.
C
C        DATE 2/17/86
C        REVISED 2/20/88 - COMMENTED-OUT AUTOMATIC CONVERGENCE TO
C                          SPEC'ED TOLERANCE AND SET THE NUMBER OF
C                          PANELS TO BE USED TO 64; THESE ARE ENOUGH
C                          PANELS FOR SIX FIGURE ACCURACY OF THE TAIL
C                          CORRECTION INTEGRALS.
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS: SUBROUTINE RTSWTS-LOADS THE ROOTS AND
C                            WEIGHTS OF THE LEGENDRE POLYNOMIAL INTO
C                            ARRAYS.
C                            SUBROUTINE GAUSS-PERFORMS THE GAUSS-
C                            LEGENDRE INTEGRATION FOR A GIVEN
C                            NUMBER OF PANELS.
C ***********************************************************************
      SUBROUTINE INTEGR(IFUNC,IPOT,PRMS,LOWER,UPPER,INTGRL,ERROR)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 INTGRL,LOWER,INTN1,INTN2
      REAL*8 PRMS(30)
      REAL*8 LAMBDA(2),WEIGHT(2)
      INTEGER ERROR,SIZE,SIGFIG
      INTEGER IPOT,IFUNC
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
      DATA MAXPAN,SIZE,SIGFIG/256,2,6/
C MAXPAN=MAXIMUM NUMBER OF PANELS ALLOWED FOR INTEGRATION.
C LOWER=LOWER INTEGRATION LIMIT.
C UPPER=UPPER INTEGRATION LIMIT.THESE ARE THE LIMITS OF THE INTEGRATION
C PATH PARAMETER AS DESCRIBED ABOVE.
C SIGFIG=NUMBER OF SIGNIFICANT FIGURES IN THE CONVERGED RESULT.
C SIZE=AH...
C LAMBDA WILL CONTAIN THE ROOTS OF THE LEGRENDRE POLYNOMIAL, WEIGHT
WILL
```

```
C CONTAIN THE WEIGHTS.NOTE: IN ALL ROUTINES BUT THIS ONE LAMBDA AND
C WEIGHT ARE DIMENSIONED BY "SIZE". CURRENTLY SIZE=2. ALWAYS SET THE
C CONSTANT DIMENSION IN THIS ROUTINE TO SIZE.
C INTN1 WILL CONTAIN AN ESTIMATE OF THE INTEGRAL.
C INTN2 WILL CONTAIN AN ESTIMATE OF THE INTEGRAL OBTAINED BY USING
C TWICE THE NUMBER OF PANELS USED TO GET INTN1.
      INTGRL=0.0D0
C ESTIMATE THE RELATIVE TOLERANCE NEEDED TO GIVE THE REQUIRED NUMBER
C OF SIGNIFICANT FIGURES.
      TOL=(10.0D0)**(-SIGFIG)
      NUMPAN=64
C PUT THE ROOTS AND WEIGHTS INTO ARRAYS LAMBDA AND WEIGHT,RESPECTIVELY.
      CALL RTSWTS(SIZE,LAMBDA,WEIGHT)
C     WRITE(NOUT2,100)LAMBDA(1),LAMBDA(2)
C 100 FORMAT(/1X,'IN INTEGR. LAMBDA1=',D11.4,' LAMBDA2=',D11.4)
C     WRITE(NOUT2,200)WEIGHT(1),WEIGHT(2)
C 200 FORMAT(/1X,'WEIGHT1=',D11.4,' WEIGHT2=',D11.4)
C OBTAIN AN ESTIMATE OF THE INTEGRAL USING ONLY ONE PANEL. RESULT
C IS INTN1.
C     CALL GAUSS(IFUNC,SIZE,PRMS,IPOT,LOWER,UPPER,NUMPAN,LAMBDA,
C    $WEIGHT,INTN1,ERROR)
C1000 CONTINUE
C        IF(ERROR.EQ.0) THEN
C DOUBLE THE NUMBER OF INTEGRATION PANELS AND GET A NEW ESTIMATE=INTN2.
C           NUMPAN=NUMPAN+NUMPAN
      CALL GAUSS(IFUNC,SIZE,PRMS,IPOT,LOWER,UPPER,NUMPAN,LAMBDA,
     $WEIGHT,INTN2,ERROR)
C           IF(ERROR.EQ.0) THEN
C CALCULATE THE RELATIVE CHANGE IN THE INTEGRAL THAT RESULTED FROM
C DOUBLING THE NUMBER OF PANELS.
C              IF(DABS(INTN2).GE.(10.0D0**(-14.0D0))) THEN
C                 EPSILN=DABS((INTN2-INTN1)/INTN2)
C              ELSE
C                 INTGRL=0.0D0
C                 EPSILN=0.0D0
C              END IF
C     WRITE(NOUT2,1100)INTN1,INTN2,EPSILN
C1100 FORMAT(/1X,'INTN1=',D11.4,'INTN2=',D11.4,'EPSILN=',D11.4)
C              INTN1=INTN2
C           END IF
C        END IF
C IF THE RELATIVE CHANGE IF GREATER THAN THE DESIRED TOLERANCE,REPEAT.
C     IF((EPSILN.GT.TOL).AND.((ERROR.EQ.0).AND.(NUMPAN.LE.MAXPAN)))
C    $GO TO 1000
C     WRITE(NOUT2,*)NUMPAN
C     IF (NUMPAN.GT.MAXPAN) THEN
C HAVE USED THE MAXIMUM NUMBER OF PANELS AND INTEGRAL HAS NOT
C CONVERGED. SET ERROR FLAG BEFORE QUITTING.
C        ERROR=4
C     END IF
      IF(ERROR.EQ.0) THEN
         INTGRL=INTN2
      END IF
      RETURN
      END
C ***********************************************************************
C        SUBROUTINE RTSWTS
C        PURPOSE-LOADS THE ROOTS AND WEIGHTS FOR THE LEGENDRE
```

```
C        POLYNOMIAL IN TO ARRAYS LAMBDA AND WEIGHT, RESPECTIVELY.
C
C        SUBROUTINE RTSWTS CURRENTLY CONTAINS ROOTS AND WEIGHTS FOR A
C        THIRD ORDER LEGENDRE POLYNOMIAL.
C
C        DATE 2/17/86
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS: -
C ***********************************************************************
      SUBROUTINE RTSWTS(SIZE,LAMBDA,WEIGHT)
      IMPLICIT REAL*8(A-H,O-Z)
      INTEGER SIZE
      REAL*8 LAMBDA(SIZE),WEIGHT(SIZE)
      REAL*8 LAM1,LAM2
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
      DATA LAM1,LAM2,WGHT1,WGHT2/0.0D0,0.774596669241483D0,
     $0.888888888888889D0,0.555555555555556D0/
      LAMBDA(1)=LAM1
      LAMBDA(2)=LAM2
      WEIGHT(1)=WGHT1
      WEIGHT(2)=WGHT2
C     WRITE(NOUT2,100)LAM1,LAM2
C 100 FORMAT(/1X,'IN RTSWTS. LAM1=',D11.4,' LAM2=',D11.4)
C     WRITE(NOUT2,200)LAMBDA(1),LAMBDA(2)
C 200 FORMAT(/1X,'LAMBDA(1)=',D11.4,' LAMBDA(2)=',D11.4)
      RETURN
      END
```

```
C ******************************************************************
C        FUNCTION SUBINT
C        PURPOSE-ESTIMATES THE INTEGRAL FOR A SINGLE PANEL. SUBINT
C        CURRENTLY USES A THIRD ORDER LEGENDRE POLYNOMIAL.
C
C        DATE 2/17/86
C        REVISED 9/3/87- ADDED A SWITCH ("IFUNC") AND DUPLICATED
C                        CODE FOR USE WITH THREE DIFFERENT INTEGRANDS.
C
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS: SUBROUTINE INDVRS-DETERMINES AN ORDER
C                            NUMBER OF UNEQUALLY SPACED POINTS WITHIN
C                            THE INTERVAL (LOWER,UPPER) FOR WHICH THE
C                            THE INTEGRAND WILL BE EVALUATED.
C                            FUNCTION FUNC0-CALCULATES THE FUNCTION
C                            TO BE INTEGRATED."SUBINT" EVALUATES
C                            THE INTEGRAND AT THE POINTS GIVEN BY
C                            "INDVRS" FOR INTERNAL ENERGY CALC.
C                            FUNCTION FUNC1-CALCULATES THE FUNCTION
C                            TO BE INTEGRATED."SUBINT" EVALUATES
C                            THE INTEGRAND AT THE POINTS GIVEN BY
C                            "INDVRS" FOR VIRIAL PRESSURE CALC.
C                            FUNCTION FUNC2-CALCULATES THE FUNCTION
C                            TO BE INTEGRATED."SUBINT" EVALUATES
C                            THE INTEGRAND AT THE POINTS GIVEN BY
C                            "INDVRS" FOR CHEM. POTENTIAL CALC.
C ******************************************************************
      REAL FUNCTION SUBINT(IFUNC,SIZE,PRMS,IPOT,LOWER,UPPER,
     $LAMBDA,WEIGHT,ERROR)
      IMPLICIT REAL*8(A-H,O-Z)
      INTEGER ERROR,ERR1,ERR2,ORDER,SIZE
      REAL*8 LOWER
      REAL*8 PRMS(30)
      REAL*8 LAMBDA(SIZE),WEIGHT(SIZE)
      REAL*8 XARRAY(3)
      INTEGER IPOT,IFUNC
      COMMON/DEVICE/NIN,NOUT
      DATA ORDER/3/
C ORDER=ORDER OF LEGENDRE POLYNOMIAL USED. NOTE:XARRAY=ARRAY(1..ORDER)
      ERROR=0
      ERR1=0
      ERR2=0
      SUM=0.0D0
      CALL INDVRS(SIZE,ORDER,LOWER,UPPER,LAMBDA,XARRAY)
C     WRITE(NOUT2,100)XARRAY(1),XARRAY(2)
C 100 FORMAT(/1X,'IN SUBINT. XARRAY1=',D11.4,' XARRAY2=',D11.4)
C     WRITE(NOUT2,200)XARRAY(3)
C 200 FORMAT(/1X,'XARRAY3=',D11.4)
C ORDER HAD BETTER BE IN 2..10 OR THING WILL NOT WORK RIGHT.
      IF(IFUNC.EQ.0) THEN
C ENERGY CALC (PRETTY SHABBY).
      IF((ORDER.EQ.3).OR.((ORDER.EQ.5).OR.((ORDER.EQ.7).OR.(ORDER.EQ.9)
     $))) THEN
         SUM=SUM+(WEIGHT(1)*FUNC0(PRMS,IPOT,XARRAY(1),ERR1))
      ELSE
         SUM=SUM+(WEIGHT(1)*FUNC0(PRMS,IPOT,XARRAY(1),
     $ERR1))+(WEIGHT(1)*FUNC0(PRMS,IPOT,XARRAY(2),ERR2))
```

```
      END IF
      I=2
      J=2
C     WRITE(NOUT2,300)ERR1,ERR2
C 300 FORMAT(/1X,'IN SUBINT. ERR1= ',I3,' ERR2= ',I3)
      IF((I.LE.SIZE).AND.((ERR1.EQ.0).AND.(ERR2.EQ.0)))THEN
 1000    CONTINUE
      IF((ORDER.EQ.3).OR.((ORDER.EQ.5).OR.((ORDER.EQ.7).OR.(ORDER.EQ.9)
     $))) THEN
         SUM=SUM+(WEIGHT(I)*FUNC0(PRMS,IPOT,XARRAY(J),
     $ERR1))+(WEIGHT(I)*FUNC0(PRMS,IPOT,XARRAY(J+1),ERR2))
         I=I+1
         J=J+1
      ELSE
         J=J+1
         SUM=SUM+(WEIGHT(I)*FUNC0(PRMS,IPOT,XARRAY(J),
     $ERR1))+(WEIGHT(I)*FUNC0(PRMS,IPOT,XARRAY(J+1),ERR2))
         I=I+1
      END IF
         IF((I.LE.SIZE).AND.((ERR1.EQ.0).AND.(ERR2.EQ.0)))GO TO 1000
      END IF
      IF((ERR1.EQ.0).AND.(ERR2.EQ.0)) THEN
         SUBINT=SUM*((UPPER-LOWER)/2.0D0)
      ELSE
         SUBINT=0.000000001D0
         IF(ERR1.NE.0)THEN
            ERROR=ERR1
         ELSE
            ERROR=ERR2
         END IF
      END IF
      END IF
C
      IF(IFUNC.EQ.1) THEN
C PRESSURE CALC.
      IF((ORDER.EQ.3).OR.((ORDER.EQ.5).OR.((ORDER.EQ.7).OR.(ORDER.EQ.9)
     $))) THEN
         SUM=SUM+(WEIGHT(1)*FUNC1(PRMS,IPOT,XARRAY(1),ERR1))
      ELSE
         SUM=SUM+(WEIGHT(1)*FUNC1(PRMS,IPOT,XARRAY(1),
     $ERR1))+(WEIGHT(1)*FUNC1(PRMS,IPOT,XARRAY(2),ERR2))
      END IF
      I=2
      J=2
C     WRITE(NOUT2,300)ERR1,ERR2
C 300 FORMAT(/1X,'IN SUBINT. ERR1= ',I3,' ERR2= ',I3)
      IF((I.LE.SIZE).AND.((ERR1.EQ.0).AND.(ERR2.EQ.0)))THEN
 2000    CONTINUE
      IF((ORDER.EQ.3).OR.((ORDER.EQ.5).OR.((ORDER.EQ.7).OR.(ORDER.EQ.9)
     $))) THEN
         SUM=SUM+(WEIGHT(I)*FUNC1(PRMS,IPOT,XARRAY(J),
     $ERR1))+(WEIGHT(I)*FUNC1(PRMS,IPOT,XARRAY(J+1),ERR2))
         I=I+1
         J=J+1
      ELSE
         J=J+1
         SUM=SUM+(WEIGHT(I)*FUNC1(PRMS,IPOT,XARRAY(J),
     $ERR1))+(WEIGHT(I)*FUNC1(PRMS,IPOT,XARRAY(J+1),ERR2))
```

```
         I=I+1
      END IF
         IF((I.LE.SIZE).AND.((ERR1.EQ.0).AND.(ERR2.EQ.0)))GO TO 2000
      END IF
      IF((ERR1.EQ.0).AND.(ERR2.EQ.0)) THEN
         SUBINT=SUM*((UPPER-LOWER)/2.0D0)
      ELSE
         SUBINT=0.000000001D0
         IF(ERR1.NE.0)THEN
            ERROR=ERR1
         ELSE
            ERROR=ERR2
         END IF
      END IF
      END IF
C
      IF(IFUNC.EQ.2) THEN
C CHEMICAL POTENTIAL CALC.
      IF((ORDER.EQ.3).OR.((ORDER.EQ.5).OR.((ORDER.EQ.7).OR.(ORDER.EQ.9)
     $))) THEN
         SUM=SUM+(WEIGHT(1)*FUNC2(PRMS,IPOT,XARRAY(1),ERR1))
      ELSE
         SUM=SUM+(WEIGHT(1)*FUNC2(PRMS,IPOT,XARRAY(1),
     $ERR1))+(WEIGHT(1)*FUNC2(PRMS,IPOT,XARRAY(2),ERR2))
      END IF
      I=2
      J=2
C     WRITE(NOUT2,300)ERR1,ERR2
C 300 FORMAT(/1X,'IN SUBINT. ERR1= ',I3,' ERR2= ',I3)
      IF((I.LE.SIZE).AND.((ERR1.EQ.0).AND.(ERR2.EQ.0)))THEN
 3000    CONTINUE
      IF((ORDER.EQ.3).OR.((ORDER.EQ.5).OR.((ORDER.EQ.7).OR.(ORDER.EQ.9)
     $))) THEN
         SUM=SUM+(WEIGHT(I)*FUNC2(PRMS,IPOT,XARRAY(J),
     $ERR1))+(WEIGHT(I)*FUNC2(PRMS,IPOT,XARRAY(J+1),ERR2))
         I=I+1
         J=J+1
      ELSE
         J=J+1
         SUM=SUM+(WEIGHT(I)*FUNC2(PRMS,IPOT,XARRAY(J),
     $ERR1))+(WEIGHT(I)*FUNC2(PRMS,IPOT,XARRAY(J+1),ERR2))
         I=I+1
      END IF
         IF((I.LE.SIZE).AND.((ERR1.EQ.0).AND.(ERR2.EQ.0)))GO TO 3000
      END IF
      IF((ERR1.EQ.0).AND.(ERR2.EQ.0)) THEN
         SUBINT=SUM*((UPPER-LOWER)/2.0D0)
      ELSE
         SUBINT=0.000000001D0
         IF(ERR1.NE.0)THEN
            ERROR=ERR1
         ELSE
            ERROR=ERR2
         END IF
      END IF
      END IF
C
C     WRITE(NOUT2,2000)SUM,SUBINT
```

```
C2000 FORMAT(/1X,'LEAVING SUBINT.SUM=',D11.4,' SUBINT=',D11.4)
      RETURN
      END
C ******************************************************************
C        FUNCTION COREPR
C        PURPOSE-CALCULATES THE CONTRIBUTION TO THE VIRIAL PRESSURE
C                DUE TO HARD CORE REPULSIVE FORCES.
C                (USED WITH STELL-WEIS POTENTIAL. NOT USED WITH
C                 LENNARD-JONES POTENTIAL).
C
C        DATE 9/1/87
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS: FUNCTION CONRDF-NUMERICALLY ESTIMATES
C                            THE CONTACT VALUES OF THE PAIR CORRELATION
C                            FUNCTIONS.
C ******************************************************************
      REAL FUNCTION COREPR(DR,SIGMA,CORE,RO,BUIJ,PAIR)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 DR
      REAL*8 SIGMA(3),RO(3)
      REAL*8 BUIJ(2048,3)
      REAL*8 PAIR(2048,3)
      REAL*8 CORE(3)
      REAL*8 XCON
      REAL*8 G11CON,G12CON,G22CON
      REAL*8 SAVE,CUBE
      INTEGER NCON
      COMMON/LUDOL/PI
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C ESTIMATE CONTACT VALUES OF THE PAIR CORRELELATION FUNCTIONS.
C DO 1-1 FIRST.
C GET THE LOCATION AT CONTACT (WHICH IS REDUCED BY SOFTD(1)):
      XCON=CORE(1)/DR
C TRUNCATE:
      NCON=XCON
      XN=NCON
      XN=XN+1.0D0
      IF(DABS(XCON-XN).LT.0.001D0) THEN
         NCON=NCON+1
      END IF
C EXTRAPOLATE FROM MESH POINTS TO THE RIGHT OF THE CONTACT DISTANCE
C TO ESTIMATE THE CORRELATION FUNCTION AT CONTACT.
      G11CON=CONRDF(NCON,XCON,PAIR(NCON+1,1),PAIR(NCON+2,1),
     $PAIR(NCON+3,1))
C     WRITE(NOUT2,*)G11CON
      IF(G11CON.LT.0.00001) THEN
         G11CON=0.0D0
      END IF
C
C DO 1-2:
      XCON=CORE(3)/DR
      NCON=XCON
      XN=XN+1.0D0
      IF(DABS(XCON-XN).LT.0.001D0) THEN
         NCON=NCON+1
      END IF
      G12CON=CONRDF(NCON,XCON,PAIR(NCON+1,3),PAIR(NCON+2,3),
```

```
     $PAIR(NCON+3,3))
      IF(G12CON.LT.0.00001) THEN
         G12CON=0.0D0
      END IF
C DO 2-2:
      XCON=CORE(2)/DR
      NCON=XCON
      XN=NCON
      XN=XN+1.0D0
      IF(DABS(XCON-XN).LT.0.001D0) THEN
         NCON=NCON+1
      END IF
      G22CON=CONRDF(NCON,XCON,PAIR(NCON+1,2),PAIR(NCON+2,2),
     $PAIR(NCON+3,2))
      IF(G22CON.LT.0.00001) THEN
         G22CON=0.0D0
      END IF
C ADD UP SEPARATE CONTRIBUTIONS TO THE PRESSURE FROM EACH PAIR
C INTERACTION.
      SAVE=RO(1)*RO(1)*G11CON
      CUBE=(SIGMA(3))**3.0D0
      SAVE=SAVE+(2.0D0*RO(1)*RO(2)*CUBE*G12CON)
      CUBE=(SIGMA(2))**3.0D0
      SAVE=SAVE+(RO(2)*RO(2)*CUBE*G22CON)
      SAVE=(2.0D0*PI/3.0D0)*SAVE
C     WRITE(NOUT2,*)G11CON,G12CON,G22CON
      COREPR=SAVE
C RESULT IS PRESSURE TIMES THE SMALL DIAMETER CUBED DIVIDED BY
C KT; IT IS DIMENSIONLESS.
      RETURN
      END
C ******************************************************************
C        SUBROUTINE GALER
C        PURPOSE-SOLUTION OF THE MIXTURE OZ EQUATION FOR SPHERICALLY
C                SYMMETRIC SYSTEMS.
C
C        REVISED 6/4/87
C                10/23/87 -TO DAMPEN OUT NEWTON AND FIXED POINT
C                          ITERATIONS WHEN THE UPDATED RESULTS
C                          ARE TOO LARGE.
C                2/18/88  -REVISED FOURIER TRANSFORM SUBROUTINES.
C                          INCREASED THE MAX NEWTON AND DIRECT
C                          ITERATIONS ALLOWED TO LET TIGHER SPECS
C                          BE MET.
C        ORIGINAL VERSION FOR PURE SYSTEMS WRITTEN BY S.LABIK
C        AND A. MALIJEVSKY, INSTITUTE OF CHEMICAL TECHNOLOGY
C        PRAGUE, CZECHOSLOVAKIA
C        (VERSION 1, FEBRUARY 1985)
C
C        THIS ROUTINE CALLS: SUBROUTINE FFS3D- FOURIER TRANSFORM
C                            SUBROUTINE HSANAL-CALCULATES THE ANALYTIC
C                            SOLUTION FOR THE HARD-SPHERE DISTRIBUTION
C                            FUNCTIONS FOR USE AS AN INITIAL GUESS, IF
C                            DESIRED BY THE USER.
C                            SUBROUTINE GFC- CALCULATES THE TRANSFORM
C                            OF G FROM THE TRANSFORM OF C USING THE
C                            OZ EQUATIONS.
C                            SUBROUTINE CFG- CALCULATES C FROM G USING
```

```
C                                THE CLOSURE EQUATION.
C                                SUBROUTINE JACOB
C                                SUBROUTINE GAUSEL
C                                SUBROUTINE TEST
C                                IMSL ROUTINE DSFINI- PREPARE WORKARRAY FOR
C                                THE IMSL SINE FFT PROCEDURE.
C ***********************************************************************
      SUBROUTINE GALER(G,BUIJ,F,NM,DR,RO,JP,IE,SIGMA,BADMAT)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 GN(2048,3),GT(2048,3),GNT(2048,3),DC(2048,3),CT(2048,3)
      REAL*8  C(2048,3)
      REAL*8 P(65,3),DGT(32,3),DIF(32,3)
      REAL*8 CSN(2048)
      REAL*8 W(97,97),G(2048,3),F(2048,3)
      REAL*8 BUIJ(2048,3)
      REAL*8 HT(2048,3)
      REAL*8 DIFF(96)
      REAL*8 CS(32,3),FJ(3,3)
      REAL*8 CCT(3),GGNT(3),CTI(3),GNTI(3),DGTC(3),RO(3),SIGMA(3)
      REAL*8 WFFTR(5133)
      REAL*8 DR
      REAL*8 SIG(3)
      REAL*8 RM,DT,TM,P1,P2
      INTEGER KAM
      LOGICAL BADMAT
      COMMON /CONV/CONVDI,CONVNR
      COMMON/LUDOL/PI
      COMMON/HTHING/HT
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
      DATA OUCH,WAIT,WAIT2/1.25D0,0.25D0,0.25D0/
      DATA CUTI,CUTR/0.01D0,0.01D0/
C INPUT PARAMETERS-
C       G:    G(R)=R*(H(R)-C(R))
C       F:    MAYER FUNCTION=EXP(-U(R)/T*) - 1
C      NM:    NUMBER OF DEFINING NUMBER OF GRID POINTS (?)
C              N=2**NM
C WITH CURRENT ARRAY DIMENSIONS, MAX NM=11.
C      RO:    REDUCED DENSITY=N*(ASIGMA(1)**3)/V
C      DR:    REDUCED STEP SIZE
C      JP:
C            JP.EQ.0  ...  LOW DENSITY LIMIT - G(R) = 0.
C            JP.EQ.1 ... INPUT G(R) IS USED.
C            JP.EQ.2 ... HARD SPHERE G(R) IS USED.
C OUTPUT PARAMETERS-
C       G:    G(R)=R*(H(R)-C(R))
C      IE:    NUMBER OF ITERATION STEPS
C             IE<0 MEANS GALER FAILED, NO SOLN. FOUND.
C      HT:    THE FOURIER TRANSFORMS OF THE TOTAL
C             CORRELATION FUNCTIONS, H. THESE ARE PASSED
C             THROUGH COMMON/HTHING/ TO SUBROUTINE
C             DILUTE (THEY'RE USED THERE IN THE OZ
C             EQUATIONS FOR A TEST PARTICLE).
C
C (NOTE: THE STRUCTURE OF SUBROUTINE GALER IS TERMINAL- SORRY)
C       WRITE(NOUT1,1)
C1      FORMAT(1X,' IN GALER ')
        ROT=RO(2)/RO(1)
        N=2**NM
```

```
      N2=2*N
      RM=DR*N
      DT=PI/RM
      TM=PI/DR
      P1=PI/N
      DO 5 I=1,N
         P2=I*P1
         CSN(I)=DCOS(P2)
5     CONTINUE
C INITIAL WORKARRAY FOR IMSL SINE FFT ROUTINE:
      NN=N-1
      CALL DFSINI(NN,WFFTR)
C WFFTR MUST HAVE DIMENSION INT(2.5*NN+15).
C
C              DEFINITION OF INITIAL VALUES OF G(R) AND GT(T)
C
      IF (JP.EQ.0)  THEN
         DO 20 J=1,3
            DO 10 I=1,N
               G(I,J)=0.0D0
               GT(I,J)=0.0D0
10          CONTINUE
20       CONTINUE
      ELSE
         IF (JP.EQ.1) THEN
            DO 25 J=1,3
               DO 24 I=1,N
                  DC(I,J)=G(I,J)*RO(J)
24             CONTINUE
25          CONTINUE
            KAM=1
            DC(N,1)=0.0D0
            DC(N,2)=0.0D0
            DC(N,3)=0.0D0
            CALL FFS3D(KAM,DC,GT,N,NM,DR,WFFTR)
         ELSE
C     USE HARD-SPHERE AS INITIAL GUESS
C           PRINT*, 'INITIAL GUESS BY HARD-SPHERE POTENTIAL'
            SIG(1)=0.9D0*SIGMA(1)
            SIG(2)=0.9D0*SIGMA(2)
            SIG(3)=SIGMA(3)
            CALL HSANAL(C,RO,SIG,DR)
            DO 27 J=1,3
               DO 26 I=1,N
                  RR=I*DR
                  DC(I,J)=C(I,J)*RO(J)*RR
26             CONTINUE
27          CONTINUE
            KAM=1
            DC(N,1)=0.0D0
            DC(N,2)=0.0D0
            DC(N,3)=0.0D0
            CALL FFS3D(KAM,DC,CT,N,NM,DR,WFFTR)
            DO 140 J=1,N
               T=J*DT
               DO 141 IB=1,3
                  CCT(IB)=CT(J,IB)
141            CONTINUE
```

```
                CALL GFC(CCT,GGNT,ROT,T)
                DO 142 IB=1,3
                   GT(J,IB)=GGNT(IB)
142             CONTINUE
                IF (J.GT.64) GO TO 139
C                  PRINT*, (GT(J,IB),IB=1,3)
                   DO 143 IB=1,3
                      IF (GT(J,IB).LT.0.) GT(J,IB)=0.
143                CONTINUE
139             CONTINUE
140          CONTINUE
             KAM=-1
             CALL FFS3D(KAM,GT,G,N,NM,DR,WFFTR)
             DO 127 J=1,3
                DO 126 I=1,N
                   G(I,J)=G(I,J)/RO(J)
126             CONTINUE
127          CONTINUE
          END IF
       END IF
       IF (JP.EQ.4) RETURN
       IE=0
       IR=0
       CONOLD=10000.
C
C              START OF DIRECT ITERATION
1000   CONTINUE
          IE=IE+1
          CONCUX=10000.
       IF (IE.GT.160) GO TO 3000
C
C                 CALCULATION OF C(R) FROM G(R)
C
          KONST=0
          CALL CFG(G,BUIJ,F,C,DR,KONST,RO)
          DO 85 J=1,3
             DO 80 I=1,N
                C(I,J)=C(I,J)*RO(J)
80           CONTINUE
85        CONTINUE
C
C         CALCULATION OF CT(T), THE FOURIER TRANSFORM OF C(R)
C
          KAM=1
          C(N,1)=0.0D0
          C(N,2)=0.0D0
          C(N,3)=0.0D0
          CALL FFS3D(KAM,C,CT,N,NM,DR,WFFTR)
C
C                   CALCULATION OF NEW GT(T)
C
          DO 40 J=1,N
             T=J*DT
             DO 41 IB=1,3
                CCT(IB)=CT(J,IB)
41           CONTINUE
             CALL GFC(CCT,GGNT,ROT,T)
             DO 42 IB=1,3
```

```
                GNT(J,IB)=GGNT(IB)
C SAVE THE TRANSFORMS OF THE TOTAL CORRELATION FUNCTIONS.
                HT(J,IB)=(GGNT(IB)+CCT(IB))/T
                HT(J,IB)=HT(J,IB)/RO(IB)
42            CONTINUE
40         CONTINUE
C
C            NUMBER OF EQUATIONS (NA) IN NEWTON ITERATION.
C
           NA=32
C
C     CALCULATION OF DERIVATIVE OF C(R) UNDER G(R) AND ITS TRANSFORM.
C
           KONST=1
           CALL CFG(G,BUIJ,F,DC,DR,KONST,RO)
           DO 55 M=0,2*NA
              DO 56 IB=1,3
                 P1=0
                 L=N
                 P2=-1
                 DO 57 J=1,N
                    L=L+M
                    IF(L.LE.N) GO TO 50
                       L=L-N
                       P2=-P2
50                  CONTINUE
                    P1=P1+P2*DC(J,IB)*CSN(L)
                    P(M+1,IB)=P1/N
57               CONTINUE
56            CONTINUE
55         CONTINUE
           DO 96 J=1,NA
              DO 95 IB=1,3
                 DGT(J,IB)=0
95            CONTINUE
96         CONTINUE
C
C                 START OF NEWTON ITERATION
C
2000       CONTINUE
              IR=IR+1
        IF (IR.GT.160) GO TO 3000
              DO 200 M=1,NA
                 T=M*DT
                 DO 110 IB=1,3
                    CTI(IB)=CT(M,IB)
                    DO 109 J=1,NA
                       IP=J+M+1
                       IM=IABS(M-J)+1
                       CS(J,IB)=P(IM,IB)-P(IP,IB)
                       CTI(IB)=CTI(IB)+DGT(J,IB)*CS(J,IB)
109                 CONTINUE
110              CONTINUE
                 CALL GFC (CTI,GNTI,ROT,T)
                 CALL JACOB (CTI,GNTI,FJ,T,ROT)
                 DO 111 IB=1,3
                    DGTC(IB)=GT(M,IB)+DGT(M,IB)-GNTI(IB)
                    W(32*(IB-1)+M,3*NA+1)=DGTC(IB)
```

```
111             CONTINUE
                DO 130 IA=1,3
                   DO 125 IB=1,3
                      DO 120 J=1,NA
                         W(32*(IA-1)+M,32*(IB-1)+J)=FJ(IA,IB)*CS(J,IB)
120                   CONTINUE
125                CONTINUE
130             CONTINUE
200          CONTINUE
             DO 201 I=1,3*NA
                W(I,I)=W(I,I)-1
201          CONTINUE
             NSIZE=3*NA
             CALL GAUSEL(NSIZE,W,DIFF,BADMAT)
             IF(BADMAT) GO TO 3000
             DO 202 I=1,NA*3
                IP=(I-1)/NA+1
                IQ=I-NA*(IP-1)
                DIF(IQ,IP)=DIFF(I)
202          CONTINUE
             P3=0.
             P4=0.
             DO 210 IB=1,3
                DO 205 J=1,NA
                   P3=P3+(DIF(J,IB)+GT(J,IB)+DGT(J,IB))**2
                   P4=P4+DIF(J,IB)**2
205             CONTINUE
210          CONTINUE
             P2=SQRT(P4/P3)
             CALL TEST(DGT,DIF,NA,IK,N,DR)
             IF (MOD(IR,5).NE .1) GO TO 399
                DO 389 M=1,NA
                   DO 388 IB=1,3
                      CTI(IB)=GT(M,IB)+DGT(M,IB)
388                CONTINUE
C                  PRINT*, M,(CTI(IB),IB=1,3)
389             CONTINUE
399          CONTINUE
C
C          TEST TO END NEWTON ITERATION.
C
             IF (P2.GT.CONVNR.AND.IK.EQ.0.AND.P2.LT.CONCVX) THEN
                CONCVX=P2
          GO TO 2000
             END IF
          DO 310 M=1,NA
             DO 390 J=1,3
C DAMPEN OUT NEWTON CYCLES. "IF" STATEMENTS AND TUNING PARAMETERS ARE
C USED IN AN ATTEMPT TO ALLOW LARGE CHANGES IN THE "GT" UNDER SOME
C CONDITIONS AND TO CRUSH SUCH CHANGES UNDER OTHER CONDITIONS.
                IF(DABS(GT(M,J)).GT.CUTR) THEN
                   IF(DABS(DGT(M,J)).GE.DABS(OUCH*GT(M,J))) THEN
                      DGT(M,J)=WAIT*DGT(M,J)*DABS(GT(M,J)/DGT(M,J))
                   END IF
                END IF
                GT(M,J)=GT(M,J)+DGT(M,J)
390          CONTINUE
310       CONTINUE
```

```
          DO 335 I=1,3
             DO 330 J=NA+1,N
                GT(J,I)=GNT(J,I)
330          CONTINUE
335       CONTINUE
C
C          CALCULATION OF NEW APPROX. FOR DIRECT ITERATION.
C
          KAM=-1
          CALL FFS3D(KAM,GT,GN,N,NM,DR,WFFTR)
C          DO 119 I=30,40
C              WRITE(NOUT2,*)GT(I,1),GT(I,2),GT(I,3)
C              WRITE(NOUT2,*)GN(I,1),GN(I,2),GN(I,3)
C119       CONTINUE
          P3=0
          DO 195 J=1,3
             DO 190 I=1,N
                GN(I,J)=GN(I,J)/RO(J)
                P1=G(I,J)-GN(I,J)
                P3=P3+(P1/I)**2
C DAMPEN OUT DIRECT ITERATIONS.
                IF(DABS(G(I,J)).GT.CUTI) THEN
C                   WRITE(NOUT2,119)
C119        FORMAT(1X,'DIRECT''S EXCEEDED CUTOFF')
C                WRITE(NOUT2,*)I,J,G(I,J)
                   IF(DABS(P1).LT.DABS(OUCH*G(I,J))) THEN
                      G(I,J)=GN(I,J)
                   ELSE
                      G(I,J)=((1.0D0-WAIT2)*G(I,J))+(WAIT2*GN(I,J))
                      G(I,J)=(0.9D0*G(I,J))+(0.1D0*GN(I,J))
                   END IF
                ELSE
                   G(I,J)=GN(I,J)
                END IF
190          CONTINUE
195       CONTINUE
          P3=SQRT(P3)
C
C                TEST TO END ITERATIONS.
C
          IF (P3.LT.CONVDI) THEN
C         WRITE(NOUT2,*)IE,IR
       RETURN
          ELSE
             IF (P3.LT.CONOLD) THEN
                ICO=0
                CONOLD=P3
        GO TO 1000
             ELSE
                IF (ICO.EQ.0) THEN
                   ICO=ICO+1
        GO TO 1000
                END IF
             END IF
          END IF
C         WRITE(NOUT2,*)IE,IR
C       RETURN
        GO TO 1000
```

```
3000    CONTINUE
C IF IT'S HERE,
C SUBROUTINE GALER HAS FAILED...SORRY.
        IE=-IE
        WRITE(NOUT2,*)IE,IR
        RETURN
        END
C ******************************************************************
C        FUNCTION MAP
C        PURPOSE-MAPS THE DESIRED PANEL INTERVAL ONTO SOME KIND OF
C        STANDARD GAUSS-LEGENDRE INTERVAL. I'M NOT QUITE SURE
C        HOW THIS THING WORKS ANYMORE.
C
C        DATE 2/18/86
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS: -
C ******************************************************************
      REAL FUNCTION MAP(LOWER,UPPER,ALPHA)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 LOWER
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
      MAP=(0.5D0)*((LOWER+UPPER)+((UPPER-LOWER)*ALPHA))
      RETURN
      END
C ******************************************************************
C        FUNCTION CONRDF
C        PURPOSE-NUMERICALLY ESTIMATES THE CONTACT VALUES OF THE PAIR
C                CORRELATION FUNCTIONS FOR SYSTEMS WITH AN INFINITE
C                REPULSION AT CONTACT. CURRENT VERSION EXTRAPOLATES
C                TO CONTACT WITH A QUADRATIC LAGRANGIAN POLYNOMIAL.
C                (USED WHEN THE TEST PARTICLE IS A HARD SPHERE)
C
C        DATE 9/1/87
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS: -
C ******************************************************************
      REAL FUNCTION CONRDF(NCON,XCON,G1,G2,G3)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 XCON,G1,G2,G3
      REAL*8 XN1,XN2,XN3
      REAL*8 SAVE
      INTEGER NCON
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C XCON=VALUE OF SEPARATION AT CONTACT IN REDUCED UNITS R/ASIGMA(1).
C NCON=TRUNC(XCON)
C G1=VALUE OF THE CORRELATION FUNCTION AT THE MESH POINT IMMEDIATELY
C TO THE RIGHT OF THE CONTACT DISTANCE=PAIR(NCON+1,J).
C G2=PAIR(NCON+2,J), I.E. TWO MESH POINTS FROM CONTACT.
C G3=PAIR(NCON+3,J), I.E. THREE MESH POINTS FROM CONTACT.
      XN1=NCON
      IF(XN1.LT.(XCON-0.0001D0)) THEN
C DO NOT EXTRAPOLATE TOO FAR TO THE LEFT OF THE BEST COMPUTED VALUE.
         SAVE=G1
      ELSE
         XN1=XN1+1.0D0
         XN2=XN1+1.0D0
```

```
      XN3=XN1+2.0D0
      SAVE=((XCON-XN3)*G1)+((XCON-XN1)*G3)
      SAVE=SAVE*((XCON-XN2)*0.5D0)
      SAVE=SAVE-((XCON-XN1)*(XCON-XN3)*G2)
    END IF
    CONRDF=SAVE
    RETURN
    END
C ******************************************************************
C       SUBROUTINE INSIDE
C       PURPOSE-SETS UP PARAMETERS NEEDED BY SUBROUTINE SIMP.
C
C       DATE: 6/29/87.
C       REVISED 9/20/87 -TO USE THE TEST PARTICLE RDF FROM THE
C                        HMSA INTEGRAL EQUATION THEORY.
C               6/4/88- TO USE WCA POTENTIAL DIVISION.
C
C
C       THIS PROGRAM CALLS: SUBROUTINE NEWGIJ-CALCULATES THE
C                           ESTIMATED PAIR CORRELATION FUNCTION
C                           FOR THE TEST PARTICLE.
C                           SUBROUTINE SIMP-INTEGRATES THE PRODUCT
C                           OF THE PERTURBING POTENTIAL TIMES THE
C                           ESTIMATED PAIR CORRELATION FUNCTION.
C                           FUNCTION CONRDF-COMPUTES THE CONTACT
C                           VALUES OF THE CAVITY RDF.
C ******************************************************************
      SUBROUTINE INSIDE(ALPHA,NBIG,NM,DR,IPOT,RSOFTD,EPSI,RO,TRED,
    $LAMBDA,TUIJ,AWCO,PSI,GAMMA,DIRECT,INTGRL,ERROR,SIGMA,
    $GCAA,GCAB,RDFNEW,BATHNW,DIRNEW,JP)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 RSOFTD(3),EPSI(3)
      REAL*8 SIGMA(3)
      REAL*8 DR,TRED,LAMBDA
      REAL*8 PSI(NBIG,3),GAMMA(NBIG,3)
      REAL*8 TUIJ(NBIG,3),AWCO(NBIG,3)
      REAL*8 DIRECT(NBIG,3)
      REAL*8 RDFNEW(2048,3)
      REAL*8 BATHNW(2048,3)
      REAL*8 DIRNEW(2048,3)
      REAL*8 FUNCT(2048,3)
      REAL*8 RO(3)
      REAL*8 ALPHA
      REAL*8 INTGRL
      REAL*8 GCAA,GCAB
      INTEGER ERROR
      INTEGER IPOT
      LOGICAL PNOW
      COMMON/LUDOL/PI
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C "PSI"=> THE PERTURBING POTENTIAL DIVIDED BY KT.
C "LAMBDA"=> THE COUPLING PARAMETER.
C RO(I)=(DENSITY)*(ITH MOLE FRAC.)*((LJ DIA. OF COMPONENT 1)**3)
C ESTIMATE THE PAIR CORRELATION FUNCTION FROM THE HARD SPHERE
C CORRELATION FUNCTION.
C "PNOW" => PRINT DIAGNOSTIC NOW.
C GCAA=LIKE-LIKE CONTACT VALUE OF THE CAVITY RDF. GCAB= CONTACT
C VALUE OF THE UNLIKE CAVITY RDF. THESE ARE COMPUTED ONLY WHEN
```

```
C LAMBDA=0.
        CALL NEWGIJ(NBIG,NM,DR,IPOT,RSOFTD,EPSI,RO,TRED,LAMBDA,TUIJ,
     $AWCO,PSI,GAMMA,DIRECT,RDFNEW,BATHNW,DIRNEW,ERROR,
     $SIGMA,WAY,TOTAL,JP)
        GCAA=0.0D0
        GCAB=0.0D0
C IF LAMBDA=-1 THE TEST PARTICLE IS A HARD SPHERE. GET THE CONTACT
VALUES
C OF THE CAVITY RDF:
C SOMETIME IN THE FUTURE, NEED TO MOVE THIS CONTACT RDF STUFF INTO
C IT'S OWN SUBROUTINE AND REMOVE THE DETERMINATION OF CONTACT
C RDF'S FROM SUBROUTINE INSIDE.
        IF(LAMBDA.LE.-0.000001D0) THEN
           IF(IPOT.EQ.0) THEN
C WANT GCAA=2-2 CONTACT VALUE. GET THE LOCATION AT CONTACT
C             XCON=(SIGMA(2)/DR)+1.0D0
              XCON=(SIGMA(2)/DR)
              NCON=XCON
              XN=NCON
              XN=XN+1.0D0
              IF(DABS(XCON-XN).LT.0.001D0) THEN
                 NCON=NCON+1
              END IF
              GCAA=CONRDF(NCON,XCON,RDFNEW(NCON+1,2),
     $              RDFNEW(NCON+2,2),RDFNEW(NCON+3,2))
           ELSE
C WANT GCAA=1-1 CONTACT VALUE.
C             XCON=(SIGMA(1)/DR)+1.0D0
              XCON=(SIGMA(1)/DR)
              NCON=XCON
              XN=NCON
              XN=XN+1.0D0
              IF(DABS(XCON-XN).LT.0.001D0) THEN
                 NCON=NCON+1
              END IF
              GCAA=CONRDF(NCON,XCON,RDFNEW(NCON+1,1),
     $              RDFNEW(NCON+2,1),RDFNEW(NCON+3,1))
           END IF
C GCAB=1-2 CONTACT VALUE ALWAYS.
C             XCON=(SIGMA(3)/DR)+1.0D0
              XCON=(SIGMA(3)/DR)
              NCON=XCON
              XN=NCON
              XN=XN+1.0D0
              IF(DABS(XCON-XN).LT.0.001D0) THEN
                 NCON=NCON+1
              END IF
              GCAB=CONRDF(NCON,XCON,RDFNEW(NCON+1,3),
     $              RDFNEW(NCON+2,3),RDFNEW(NCON+3,3))
           WRITE(NOUT2,*)GCAA,GCAB
        END IF
        INTGRL=0.0D0
        IF(LAMBDA.GE.-0.0000001D0) THEN
C COMPUTE THE INTEGRAND FOR SUBROUTINE SIMP:
           IF(IPOT.EQ.0) THEN
C WANT CHEMICAL POTENTIAL OF SPECIES 2
              DO 5 I=1,NBIG
                 REALI=I
```

```
                 RAD=REALI*DR
                 FUNCT(I,1)=RDFNEW(I,3)*PSI(I,3)/RO(1)
                 FUNCT(I,2)=RDFNEW(I,2)*PSI(I,2)/RO(2)
                 FUNCT(I,3)=0.0D0
                 TERM=RDFNEW(I,3)*PSI(I,3)*RO(1)
                 TERM=TERM+(RDFNEW(I,2)*PSI(I,2)*RO(2))
                 TERM=TERM*4.0D0*PI*RAD*RAD
C                IF((I.GE.140).AND.(I.LE.210)) THEN
C                   WRITE(NOUT2,*)I,RDFNEW(I,3),PSI(I,3)
C                   WRITE(NOUT2,*)RDFNEW(I,2),PSI(I,2)
C                   WRITE(NOUT2,*)FUNCT(I,1),FUNCT(I,2)
C                END IF
    5         CONTINUE
           ELSE
C WANT CHEMICAL POTENTIAL OF SPECIES 1
              DO 7 I=1,NBIG
                 REALI=I
                 RAD=REALI*DR
                 FUNCT(I,2)=RDFNEW(I,3)*PSI(I,3)/RO(2)
                 FUNCT(I,1)=RDFNEW(I,1)*PSI(I,1)/RO(1)
                 FUNCT(I,3)=0.0D0
                 TERM=RDFNEW(I,3)*PSI(I,3)*RO(2)
                 TERM=TERM+(RDFNEW(I,1)*PSI(I,1)*RO(1))
                 TERM=TERM*4.0D0*PI*RAD*RAD
    7         CONTINUE
           END IF
C INTEGRATE THE PRODUCT OF THE CORRELATION FUNCTION AND THE
C PERTURBING POTENTIAL.
C "PNOW" => PRINT DIAGNOSTIC NOW.
           PNOW=.FALSE.
C          IF((LAMBDA.GT.0.499D0).AND.(LAMBDA.LT.0.501D0)) THEN
C             PNOW=.TRUE.
C          END IF
           CALL SIMP(DR,RO,FUNCT,INTGRL,PNOW)
        END IF
C       IF((LAMBDA.GT.0.499D0).AND.(LAMBDA.LT.0.501D0)) THEN
C          WRITE(NOUT2,10)LAMBDA,INTGRL
C  10      FORMAT(/1X,'LAMBDA= ',D13.6,' INSIDE= ',D13.6)
C       END IF
C      WRITE(NOUT2,32)
C32    FORMAT(/1X,'LEAVING INSIDE')
C      DO 40 I=35,50
C         WRITE(NOUT2,35)PSI(I,1),PSI(I,2),PSI(I,3)
C35       FORMAT(1X,'PSI:',D13.6,1X,D13.6,1X,D13.6)
C         WRITE(NOUT2,37)RDFNEW(I,1),RDFNEW(I,2),RDFNEW(I,3)
C37       FORMAT(1X,'RDFNEW:',D13.6,1X,D13.6,1X,D13.6)
C40    CONTINUE
        RETURN
        END
C ******************************************************************
C        SUBROUTINE NEWGIJ
C        PURPOSE-ESTIMATES THE PAIR CORRELATION FUNCTIONS FOR THE
C        TEST PARTICLE FROM AN INTEGRAL EQUATION CALCULATION.
C
C        DATE: 9/20/87.
C              6/4/88- TO USE THE WCA DIVISION OF THE PAIR
C                      POTENTIAL.
C              3/13/89- TO ELIMINATE THE ASSUMPTION THAT WHEN THE
```

```
C                       TEST PARTICLE IS A HARD SPHERE THAT THE
C                       1-1 INTERACTION DIAMETER IS THE SMALLEST.
C
C        THIS PROGRAM CALLS: SUBROUTINE MAYER2-CALCULATES THE MAYER
C                            FACTORS FOR INTERACTIONS WITH THE TEST
C                            PARTICLE.
C                            SUBROUTINE DILUTE-SOLVES THE OZ EQUATIONS
C                            FOR A TEST PARTICLE AT INFINITE DILUTION
C                            IN A BATH OF THE ACTUAL MIXTURE.
C                            SUBROUTINE CORFU2-COMPUTES THE
DISTRIBUTION
C                            FUNCTIONS FOR THE TEST PARTICLE FROM THE
C                            OZ SOLUTION.
C                            SUBROUTINE FLIP-SWAPS COMPONENTS 1 AND
C                            2 IN ALL ARRAYS. USED WHEN CALCULATING
C                            THE CHEMICAL POTENTIAL OF COMPONENT 1
C                            BEFORE CALLING SUBROUTINE DILUTE.
C ***********************************************************************
      SUBROUTINE NEWGIJ(NBIG,NM,DR,IPOT,RSOFTD,EPSI,RO,TRED,LAMBDA,
     $TUIJ,AWCO,PSI,GAMMA,DIRECT,RDFNEW,BATHNW,DIRNEW,ERROR,
     $SIGMA,JP)
        IMPLICIT REAL*8(A-H,O-Z)
        REAL*8 RSOFTD(3),EPSI(3)
        REAL*8 SIGMA(3)
        REAL*8 VIJ(3),SIJ(3)
        REAL*8 VIJT(3),SIJT(3)
        REAL*8 RO(3)
        REAL*8 PSI(NBIG,3),GAMMA(NBIG,3)
        REAL*8 TUIJ(NBIG,3),AWCO(NBIG,3)
        REAL*8 AFFINS(2,2)
        REAL*8 DIRECT(NBIG,3),RDFNEW(NBIG,3)
        REAL*8 DIRNEW(2048,3),TOTNEW(2048,3),BATHNW(2048,3)
        REAL*8 G(2048,3)
        REAL*8 BUIJ(2048,3)
        REAL*8 F(2048,3)
        REAL*8 RC(2048,3)
        REAL*8 TRED,LAMBDA
        REAL*8 ALFNEW
        INTEGER NBIG
        INTEGER ERROR
        LOGICAL BADMAT
        LOGICAL LOTS
        COMMON/HMSA/ALFNEW,VIJ,SIJ
        COMMON/HMSAT/ALPHAT,VIJT,SIJT
        COMMON/TYP/JT,N
        COMMON/CONV/CONVDI,CONVNR
        COMMON/LUDOL/PI
        COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C NOTE: THE PAIR POTENTIAL HAS ALREADY BEEN DIVIDED BY KT.
        BADMAT=.FALSE.
C       CONVDI=0.000001D0
C       CONVNR=0.0001D0
        N=NBIG
        JT=1
C       JP=1
        DO 100 I=1,NBIG
C USE GAMMA FOR THE MIXTURE AS AN INITIAL GUESS FOR THE TEST PARTICLE.
C MAKE A COPY.
```

```
          G(I,1)=GAMMA(I,1)
          G(I,2)=GAMMA(I,2)
          G(I,3)=GAMMA(I,3)
          REALI=I
          RADIUS=REALI*DR
          RC(I,1)=RADIUS*DIRECT(I,1)
          RC(I,2)=RADIUS*DIRECT(I,2)
          RC(I,3)=RADIUS*DIRECT(I,3)
C COMPUTE THE INTERACTION PAIR POTENTIALS FOR THE TEST PARTICLE WITH
C THE REST OF THE MIXTURE.
           IF(LAMBDA.LT.-0.000001D0) THEN
C            JP=2
             IF(IPOT.EQ.0) THEN
C A COMPONENT OF SPECIES 2 IS BEING CHARGED
                BUIJ(I,1)=TUIJ(I,1)
                BUIJ(I,2)=100.0D0
                BUIJ(I,3)=100.0D0
             ELSE
C A COMPONENT OF SPECIES 1 IS BEING CHARGED
                BUIJ(I,2)=TUIJ(I,2)
                BUIJ(I,1)=100.0D0
                BUIJ(I,3)=100.0D0
             END IF
             IF(RADIUS.GE.(0.999999D0*SIGMA(1))) THEN
                IF(IPOT.EQ.1) THEN
                   BUIJ(I,1)=0.0D0
                END IF
             END IF
             IF(RADIUS.GE.(0.999999D0*SIGMA(3))) THEN
                BUIJ(I,3)=0.0D0
             END IF
             IF(RADIUS.GE.(0.999999D0*SIGMA(2))) THEN
                IF(IPOT.EQ.0) THEN
                   BUIJ(I,2)=0.0D0
                END IF
             END IF
          ELSE
             IF(IPOT.EQ.0) THEN
C A COMPONENT OF SPECIES 2 IS BEING CHARGED
                BUIJ(I,1)=TUIJ(I,1)
                BUIJ(I,2)=AWCO(I,2)+(LAMBDA*PSI(I,2))
             ELSE
C A COMPONENT OF SPECIES 1 IS BEING CHARGED
                BUIJ(I,2)=TUIJ(I,2)
                BUIJ(I,1)=AWCO(I,1)+(LAMBDA*PSI(I,1))
             END IF
             BUIJ(I,3)=AWCO(I,3)+(LAMBDA*PSI(I,3))
          END IF
  100   CONTINUE
C    HMSA PARAMETER :
        ALPHAT=ALFNEW
C COMPUTE OTHER PARAMETERS FOR TEST PARTICLE INTERACTIONS NEEDED IN
C THE HMSA CLOSURE EQUATION.
C   SIZE:
        SIJT(1)=SIJ(1)
        SIJT(2)=SIJ(2)
        SIJT(3)=SIJ(3)
C   ENERGY
```

```
      IF(IPOT.EQ.0) THEN
         VIJT(1)=VIJ(1)
         VIJT(2)=LAMBDA*VIJ(2)
         IF(LAMBDA.LE.-0.00001D0) THEN
            VIJT(2)=0.0D0
            SIJT(2)=SIGMA(2)
         END IF
      ELSE
         VIJT(2)=VIJ(2)
         VIJT(1)=LAMBDA*VIJ(1)
         IF(LAMBDA.LE.-0.00001D0) THEN
            VIJT(1)=0.0D0
            SIJT(1)=SIGMA(1)
         END IF
      END IF
      VIJT(3)=LAMBDA*VIJ(3)
      IF(LAMBDA.LE.-0.00001D0) THEN
         VIJT(3)=0.0D0
         SIJT(3)=SIGMA(3)
      END IF
C     WRITE(NOUT2,*)SIJT(1),SIJT(2),SIJT(3)
C     WRITE(NOUT2,*)VIJT(1),VIJT(2),VIJT(3)
C CALCULATE MAYER FACTORS FOR THE TEST PARTICLE INTERACTIONS.
      CALL MAYER2(DR,LAMBDA,SIGMA,RSOFTD,EPSI,TRED,F,BUIJ,
     $IPOT,NBIG)
C SOLVE THE OZ EQUATIONS FOR AN INFINITELY DILUTE PARTICLE OF SPECIES
C "2" (THE TEST PARTICLE) IN A MIXTURE OF SPECIES 1 AND 2, WHERE THE
C TEST PARTICLE INTERACTIONS WITH SPECIES 1 AND 2 VIA THE MAYER FACTORS
C DEFINED ABOVE.
      IF(IPOT.EQ.1) THEN
C OH VERY LAZY..
         CALL FLIP(NBIG,G,BUIJ,F,PSI,AWCO,RO,RSOFTD,SIGMA,RC)
      END IF
      CALL DILUTE(G,BUIJ,F,PSI,LAMBDA,NM,DR,RO,JP,IE,RSOFTD,
     $            SIGMA,RC,BADMAT,AWCO)
      IF(IPOT.EQ.1) THEN
         CALL FLIP(NBIG,G,BUIJ,F,PSI,AWCO,RO,RSOFTD,SIGMA,RC)
      END IF
      IF(IE.LT.0) THEN
C "G" FUNCTION NOT FOUND-TOO MANY TRIALS TAKEN.
         ERROR=4
      END IF
      IF(BADMAT) THEN
C "G" FUNCTION NOT FOUND-BAD MATRIX FOUND IN THE CALCULATION.
         ERROR=5
      END IF
      IF(ERROR.EQ.0) THEN
C SUBROUTINE DILUTE WORKED OK, CAN NOW CALCULATE THE DISTRIBUTION
C FUNCTIONS FOR THE TEST PARTICLE.
      CALL CORFU2(NBIG,DR,RSOFTD,BUIJ,F,PSI,LAMBDA,G,RDFNEW,
     $DIRNEW,TOTNEW,BATHNW,IPOT,AWCO)
C        LOTS=.FALSE.
C        IF((DABS(LAMBDA-1.0D0)).LT.0.25D0) THEN
C           LOTS=.TRUE.
C        END IF
C         X1=0.5D0
C         ICOUNT=0.0D0
C         PRESSU=0.0D0
```

```
C           ENERGY=0.0D0
C           CERROR=0.0D0
C           COMPC=0.0D0
C           YU=0.0D0
C           YUIDL=0.0D0
C           YUHS=0.0D0
C           MW=0.0D0
C           ID=0
C          IF(LAMBDA.LT.0.0D0) THEN
C          IF(LAMBDA.LT.0.24D0) THEN
C             CALL PRINTR(LOTS,DR,RDFNEW,F,TOTNEW,BUIJ,
C             CALL PRINTR(LOTS,DR,RDFNEW,PSI,TOTNEW,BATHNW,
C             CALL PRINTR(LOTS,DR,RDFNEW,DIRNEW,TOTNEW,BATHNW,
C     $                   EPSI,SIGMA,TRED,RO,X1,G,ICOUNT,
C     $                   ALFNEW,PRESSU,ENERGY,CERROR,COMPC,AFFINS)
C          END IF
        END IF
        RETURN
        END
```

```
C ******************************************************************
C        SUBROUTINE PERT
C        PURPOSE-CALCULATES ARRAYS OF WCA ATTRACTIVE AND REPULSIVE
C                POTENTIALS FOR INTERACTIONS WITH THE TEST PARTICLE.
C
C        DATE 6/30/87
C        REVISED 9/8/87- TO CALCULATE THE DERIVATIVE OF THE PAIR
C                        POTENTIAL.
C                6/2/88- TO USE THE WCA DIVISION OF THE
C                        POTENTIAL.
C               10/22/88-CHANGED ARGUMENT LIST OF REDUC TO FIT NEW
C                        VERSION.
C               11/03/88-REMOVED DERIVATIVE CALCULATION. UNNECESSARY.
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS: SUBROUTINE REDUC- TO CONVERT THE
C                            LENNARD-JONES PARAMETERS TO REDUCED
C                            UNITS.
C                            SUBROUTINE MINS- TO CALCULATE THE
C                            POTENTIAL MINIMUMS AND FIND THE
C                            CORRESPONDING SEPARATION DISTANCES.
C                            FUNCTION PSIIJ- TO CALCULATE THE
C                            POTENTIAL FOR A GIVEN SEPARATION
C                            DISTANCE.
C ******************************************************************
      SUBROUTINE PERT(NBIG,IPOT,DR,TEMP,CORF1,CORF2,ASIGMA,KEPSI,
     $SOFTD,TUIJ,AWCO,PSI)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 ASIGMA(3),KEPSI(3)
      REAL*8 EPSI(3)
      REAL*8 SIJ(3),UIJ(3)
      REAL*8 SOFTD(3)
      REAL*8 RSOFTD(3)
      REAL*8 PSI(NBIG,3)
      REAL*8 TUIJ(NBIG,3)
      REAL*8 AWCO(NBIG,3)
      REAL*8 TEMP
      REAL*8 TRED
      REAL*8 BUP
      INTEGER IPOT
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
      RM=1.0D0
      IP=0
      ASIGMA(1)=CORF1*SOFTD(1)
      ASIGMA(2)=CORF2*SOFTD(2)
      ASIGMA(3)=0.5D0*(ASIGMA(1)+ASIGMA(2))
      CALL REDUC(KEPSI,SOFTD,EPSI,RSOFTD)
      TRED=TEMP/KEPSI(1)
      CALL MINS(IPOT,RSOFTD,EPSI,TRED,UIJ,SIJ)
      DO 20 K=1,3
         DRR=DR*SOFTD(1)/SOFTD(K)
         T=TEMP/KEPSI(K)
         DO 30 I=1,NBIG
            REALI=I
            RR=REALI*DRR
            RAD=REALI*DR
C "PSI" IS THE WCA ATTRACTIVE PART OF THE
C POTENTIAL DIVIDED BY KT. "AWCO" IS THE WCA REPULSIVE
```

```
C PART/KT. "TUIJ" IS THE TOTAL PAIR POTENTIAL FOR
C INTERACTIONS WITH THE TEST PARTICLE/KT.
            PSI(I,K)=VIJ(K)
            BU=PSIIJ(IP,RR,RM,T,BUP)
            TUIJ(I,K)=BU
            AWCO(I,K)=BU-VIJ(K)
            IF(RAD.GT.(0.9999999D0*SIJ(K))) THEN
C OUTSIDE OF THE POTENTIAL MIN THE WCA ATTRACTIVE PART
C EQUALS THE TOTAL PAIR POTENTIAL AND THE REPULSIVE PART
C IS ZERO.
               PSI(I,K)=BU
               AWCO(I,K)=0.0D0
            END IF
30        CONTINUE
20     CONTINUE
C       WRITE(NOUT2,*)ASIGMA(1),ASIGMA(2),ASIGMA(3)
C       WRITE(NOUT2,32)
C32     FORMAT(/1X,'LEAVING PERT')
C       DO 40 I=35,50
C          WRITE(NOUT2,35)PSI(I,1),PSI(I,2),PSI(I,3)
C35        FORMAT(1X,'PSI:',D13.6,1X,D13.6,1X,D13.6)
C          WRITE(NOUT2,37)AWCO(I,1),AWCO(I,2),AWCO(I,3)
C37        FORMAT(1X,'AWCO:',D13.6,1X,D13.6,1X,D13.6)
C40     CONTINUE
      RETURN
      END
C ***********************************************************************
C        FUNCTION YUIDL
C        PURPOSE-CALCULATES THE IDEAL GAS CONTRIBUTION TO THE
C                SOLUTE CHEMICAL POTENTIAL DIVIDED BY KT.
C
C        DATE 6/16/87
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS:-
C ***********************************************************************
      REAL FUNCTION YUIDL(IPOT,MW,TEMP,RO,SOFTD)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 RO(3)
      REAL*8 SOFTD(3)
      REAL*8 TEMP,RHO2
      REAL*8 MW,MESS,DEBROG
      COMMON/LUDOL/PI
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
      DATA MESS/4.37547995D1/
C MESS=PLANCK'S CONST.*ANGSTROMS PER CM./SQRT(BOLTZ. CONST/AVG.NUMBER)
C TEMPERATURE, KELVIN.
C DEBROGLE THERMAL WAVELENGTH IN ANGSTROMS.
      DEBROG=2.0D0*PI*MW*TEMP
      DEBROG=MESS/(DSQRT(DEBROG))
C SOLUTE DENSITY, NUMBER PER CUBIC ANGSTROM:
      IF(IPOT.EQ.0) THEN
         RHO2=RO(2)/(SOFTD(1)*SOFTD(1)*SOFTD(1))
      ELSE
         RHO2=RO(1)/(SOFTD(1)*SOFTD(1)*SOFTD(1))
      END IF
C IDEAL GAS CONTRIBUTION TO THE SOLUTE CHEMICAL POTENTIAL, IN ERGS:
      SAVE=DLOG(RHO2*DEBROG*DEBROG*DEBROG)
```

```
C     WRITE(NOUT2,*)DEBROG,RHO2,SAVE
C     WRITE(NOUT2,*)SAVE
      YUIDL=SAVE
      RETURN
      END
C ******************************************************************
C        FUNCTION XI3
C        PURPOSE- CALCULATES A WEIRD FUNCTION OF DENSITY THAT APPEARS
C                 IN SCALED PARTICLE THEORY. FUNCTION XI3 ALSO APPEARS
C                 IN THE ANALYTICAL SOLUTION OF PY FOR HARD SPHERES
C                 GIVEN BY LEBOWITZ. XI3 IS ACTUALLY A SORT OF PACKING
C                 FRACTION FOR THE MIXTURE.
C        (C.F. LEBOWITZ, HELFAND, AND PRAESTGAARD, J.CHEM. PHYS.,
C         VOL. 43, NO. 3, P. 774, AUGUST 1965)
C
C        DATE 6/17/87
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS:-
C ******************************************************************
      REAL FUNCTION XI3(RO,ASIGMA)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 ASIGMA(3)
      REAL*8 RO(3)
      REAL*8 SAVE
      COMMON/LUDOL/PI
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C L-H-P'S EQUATION 2.8 WITH L=3.
      SAVE=ASIGMA(2)/ASIGMA(1)
      XI3=(RO(1)+(RO(2)*SAVE*SAVE*SAVE))*PI/6.0D0
      RETURN
      END
C ******************************************************************
C        SUBROUTINE CORFU2
C        PURPOSE-CALCULATES THE PAIR,DIRECT,AND TOTAL
C                CORRELATION FUNCTIONS FOR THE TEST PARTICLE.
C                CURRENT VERSION ONLY DOES HMSA.
C
C        DATE 9/21/87
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS: FUNCTION SWITC2-COMPUTES THE HMSA
C                            SWITCHING FUNCTION.
C ******************************************************************
      SUBROUTINE CORFU2(NBIG,DR,RSOFTD,BUIJ,F,PSI,ETA,G,
     $PAIR,DIRECT,TOTAL,BATH,IPOT,AWCO)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 BUIJ(NBIG,3)
      REAL*8 PSI(NBIG,3)
      REAL*8 G(NBIG,3)
      REAL*8 F(NBIG,3)
      REAL*8 AWCO(NBIG,3)
      REAL*8 PAIR(NBIG,3),DIRECT(NBIG,3),TOTAL(NBIG,3),BATH(NBIG,3)
      REAL*8 RSOFTD(3)
      REAL*8 ETA
      REAL*8 DR,REALI
      REAL*8 VIJT(3),SIJT(3)
      REAL*8 VIJ(3),SIJ(3)
```

```
      REAL*8 BOLTZ
      INTEGER IPOT
      LOGICAL HIT
      COMMON/HMSA/ALFNEW,VIJ,SIJ
      COMMON/HMSAT/ALPHAT,VIJT,SIJT
      COMMON/TYP/JT,N
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C G=R*(H(R)-C(R))
C F=MAYER FUNCTION=EXP(-U(R)/KT)-1 FOR INTERACTIONS WITH
C THE TEST PARTICLE.
C     WRITE(NOUT2,*)N
C SUBROUTINE CORFU2 IS A SLIGHTLY MODIFIED SUBROUTINE CORFU.
      DO 200 I=1,N
         REALI=I
         RADIUS=REALI*DR
         DO 100,J=1,3
            ALPHA=ALPHAT
            HIT=.FALSE.
            IF((IPOT.EQ.0).AND.(J.EQ.1)) THEN
               ALPHA=ALFNEW
               HIT=.TRUE.
            END IF
            IF((IPOT.EQ.1).AND.(J.EQ.2)) THEN
               ALPHA=ALFNEW
               HIT=.TRUE.
            END IF
            BATH(I,J)=0.0D0
              SWT=SWITC2(RADIUS,ALPHA)
              EXPO=SWT*(G(I,J)/RADIUS)
              IF((ETA.GE.0.0D0).OR.HIT) THEN
                 IF(RADIUS.GE.(1.0000001D0*SIJT(J))) THEN
                    BOLTZ=BUIJ(I,J)
                    EXPO=EXPO-(SWT*BUIJ(I,J))
                 ELSE
                    BOLTZ=BUIJ(I,J)-AWCO(I,J)
                    EXPO=EXPO-(SWT*VIJT(J))
                 END IF
              ELSE
                 BOLTZ=0.0D0
              END IF
C             WRITE(NOUT2,*)RAD,G(I,J),BUIJ(I,J),SWT
              IF(EXPO.LT.-61.0D0) THEN
                 EXPO=-61.0D0
              END IF
              IF(EXPO.GT.61.0D0) THEN
                 EXPO=61.0D0
              END IF
              IF(BOLTZ.LT.-61.0D0) THEN
                 BOLTZ=-61.0D0
              END IF
              BOLTZ=DEXP(BOLTZ)
              IF(DABS(SWT).GT.0.0000000001D0) THEN
                 BATH(I,J)=((DEXP(EXPO))-1.0D0)/SWT
              END IF
              BATH(I,J)=BATH(I,J)+1.0D0
              BATH(I,J)=BATH(I,J)*BOLTZ
            PAIR(I,J)=BATH(I,J)*(1.0D0+F(I,J))
            TOTAL(I,J)=PAIR(I,J)-1.0D0
```

```
            DIRECT(I,J)=TOTAL(I,J)-(G(I,J)/RADIUS)
100       CONTINUE
C        IF((I.GE.30).AND.(I.LE.50)) THEN
C            WRITE(NOUT2,*)PAIR(I,1),PAIR(I,2),PAIR(I,3)
C        END IF
200    CONTINUE
       RETURN
       END
C ******************************************************************
C         SUBROUTINE FLIP
C         PURPOSE-WHEN IPOT.EQ. 1 (USER WANTS CHEMICAL POTENTIAL OF
C                 COMPONENT 1) SWAPS ELEMENTS 1 AND 2 IN EVERY ARRAY
C                 USED BY SUBROUTINE DILUTE). A QUICK AND DIRTY SOLN.
C                 TO A VERY CONFUSING PROBLEM.
C
C         DATE 2/29/88
C         CODED BY DAVID PFUND
C
C         THIS ROUTINE CALLS:-
C ******************************************************************
       SUBROUTINE FLIP(NBIG,G,BUIJ,F,PSI,TOTAL,RO,RSOFTD,SIGMA,
      $RC)
       IMPLICIT REAL*8(A-H,O-Z)
       REAL*8 BUIJ(NBIG,3)
       REAL*8 PSI(NBIG,3)
       REAL*8 G(NBIG,3)
       REAL*8 F(NBIG,3)
       REAL*8 RC(NBIG,3)
       REAL*8 TOTAL(NBIG,3)
       REAL*8 HT(2048,3)
       REAL*8 RO(3)
       REAL*8 RSOFTD(3)
       REAL*8 SIGMA(3)
       REAL*8 VIJT(3),SIJT(3)
       COMMON/HMSAT/ALPHAT,VIJT,SIJT
       COMMON/HTHING/HT
       COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C IF IPOT.EQ.1 NEED TO FLIP COMMON BLOCK/HMSAT/ (SINCE I WAS FOOLISH
C ENOUGH TO USE COMMON) BEFORE CALLING SUBROUTINE DILUTE (WHICH IS
C NOT SYMMETRICAL W.R.T. COMPONENTS 1 AND 2).
       SAVE=VIJT(2)
       VIJT(2)=VIJT(1)
       VIJT(1)=SAVE
       SAVE=SIJT(2)
       SIJT(2)=SIJT(1)
       SIJT(1)=SAVE
C FLIP THE LITTLE ARRAYS
       RO(3)=RO(2)
       SAVE=RO(2)
       RO(2)=RO(1)
       RO(1)=SAVE
       SAVE=RSOFTD(2)
       RSOFTD(2)=RSOFTD(1)
       RSOFTD(1)=SAVE
       SAVE=SIGMA(2)
       SIGMA(2)=SIGMA(1)
       SIGMA(1)=SAVE
C FLIP THE BIG ONES.
```

```
      DO 100 I=1,NBIG
         SAVE=G(I,2)
         G(I,2)=G(I,1)
         G(I,1)=SAVE
C
         SAVE=BUIJ(I,2)
         BUIJ(I,2)=BUIJ(I,1)
         BUIJ(I,1)=SAVE
C
         SAVE=F(I,2)
         F(I,2)=F(I,1)
         F(I,1)=SAVE
C
         SAVE=RC(I,2)
         RC(I,2)=RC(I,1)
         RC(I,1)=SAVE
C
         SAVE=TOTAL(I,2)
         TOTAL(I,2)=TOTAL(I,1)
         TOTAL(I,1)=SAVE
C
         SAVE=PSI(I,2)
         PSI(I,2)=PSI(I,1)
         PSI(I,1)=SAVE
C
         SAVE=HT(I,2)
         HT(I,2)=HT(I,1)
         HT(I,1)=SAVE
  100 CONTINUE
      RETURN
      END
C ******************************************************************
C        SUBROUTINE MAYER2
C        PURPOSE-CALCULATES A VECTOR OF MAYER FACTORS FOR INTERACTIONS
C                OF THE TEST PARTICLE WITH THE MIXTURE.
C
C        DATE 9/21/87
C
C        THIS ROUTINE CALLS: -
C ******************************************************************
        SUBROUTINE MAYER2(DR,LAMBDA,SIGMA,RSOFTD,EPSI,TRED,F,BUIJ,
     $IPOT,N)
         IMPLICIT REAL*8(A-H,O-Z)
         REAL*8 F(N,3),RSOFTD(3),EPSI(3)
         REAL*8 SIGMA(3)
         REAL*8 BUIJ(N,3)
         REAL*8 DR,TRED
         REAL*8 LAMBDA
         INTEGER IPOT,N
         COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C        WRITE(NOUT2,10)IPOT,N,DR,TRED
C10      FORMAT(/1X,'IN MAYER',I3,' ',I3,' ',D11.4,' ',D11.4)
C        WRITE(NOUT2,*)SIGMA(1),SIGMA(2),SIGMA(3)
C        WRITE(NOUT2,*)EPSI(1),EPSI(2),EPSI(3)
C F => A VECTOR OF MAYER FACTORS FOR TEST PARTICLE
C INTERACTIONS.
         DO 20 K=1,3
            T=TRED*EPSI(1)/EPSI(K)
```

```
          DRR=DR*RSOFTD(1)/RSOFTD(K)
C IPOT=0 : WANT CHEMICAL POTENTIAL OF SPECIES 2.
C THE TEST PARTICLE BECOMES A MOLECULE OF SPECIES 2
C WHEN FULLY CHARGED.
C IPOT=1 : WANT CHEMICAL POTENTIAL OF SPECIES 1.
C THE TEST PARTICLE BECOMES A MOLECULE OF SPECIES 1
C WHEN FULLY CHARGED.
          DO 30 I=1,N
             IF((IPOT.EQ.0).AND.(K.EQ.1)) THEN
C LJ MAYER:
                IF(BUIJ(I,K).GT.61.0D0) THEN
                   F(I,K)=-1.0D0
                ELSE
                   F(I,K)=(DEXP(-BUIJ(I,K)))-1.0D0
                END IF
             ELSE
                IF((IPOT.EQ.1).AND.(K.EQ.2)) THEN
C LJ MAYER:
                   IF(BUIJ(I,K).GT.61.0D0) THEN
                      F(I,K)=-1.0D0
                   ELSE
                      F(I,K)=(DEXP(-BUIJ(I,K)))-1.0D0
                   END IF
                ELSE
                   IF(LAMBDA.LT.0.0D0) THEN
C CAVITY MAYER (TEST PARTICLE IS HARD SPHERE):
                      IF(BUIJ(I,K).GT.61.0D0) THEN
C INSIDE CAVITY:
                         F(I,K)=-1.0D0
                      ELSE
C OUTSIDE CAVITY:
                         F(I,K)=0.0D0
C FIX-UP CONTACT VALUES. WANT MAYER FACTORS FOR
C INTERACTIONS OF A HARD SPHERE TEST PARTICLE WITH THE
C BATH MOLECULES TO BE -0.5 AT THE CONTACT DISTANCE.
                         REALI=I
                         RR=REALI*DR
                         IF((DABS(RR-SIGMA(K))).LT.0.001D0) THEN
                            F(I,K)=-0.5D0
                            BUIJ(I,K)=0.6931471D0
                         END IF
                      END IF
                   ELSE
C TEST PARTICLE (NOT A CAVITY) MAYER:
                      IF(BUIJ(I,K).GT.61.0D0) THEN
                         F(I,K)=-1.0D0
                      ELSE
                         F(I,K)=(DEXP(-BUIJ(I,K)))-1.0D0
                      END IF
                   END IF
                END IF
             END IF
C            WRITE(NOUT2,18)I,K
C  18        FORMAT(1X,'I= ',I3,' K= ',I3)
C            WRITE(NOUT2,*)BUIJ(I,K),UPRIME(I,K),F(I,K)
30         CONTINUE
20      CONTINUE
        RETURN
```

```
      END
C ******************************************************************
C       SUBROUTINE CFG2
C       PURPOSE-CALCULATES C(R) IN TERMS OF G(R).
C               THIS PROCEDURE AND SUBROUTINE CORFU IS CHANGED
C               FOR ANOTHER THEORY. THE PROGRAM IS CURRENTLY SET UP
C               TO USE ONLY THE HMSA CLOSURE.
C      (C.F. LABIK, MALIJEVSKY AND VONKA, MOL. PHYS. VOL.56, NO.3,
C       P.709, (1985), FOR DETAILS OF THE NUMERICAL PROCEDURE)
C
C      (C.F. ZERAH AND HANSEN, J.CHEM.PHYS. VOL.84, NO.4, P.2336,
C       FEBRUARY, 1986, FOR DETAILS ON THE HMSA CLOSURE)
C
C       REVISED 6/4/87
C               8/18/87-CHANGED TO HMSA CLOSURE
C               9/22/87-CREATED FROM A COPY OF SUBROUTINE CFG.
C                       COMMON/HMSA/ WAS REPLACED WITH
C                       WITH COMMON/HMSAT/ (CONTAINS PARAMETERS
C                       FOR THE TEST PARTICLE INTERACTIONS).
C
C       THIS ROUTINE CALLS: FUNCTION SWITC2-COMPUTES THE HMSA
C                           SWITCHING FUNCTION FOR A GIVEN SEPARATION
C                           DISTANCE AND ALPHA PARAMETER.
C ******************************************************************
      SUBROUTINE CFG2(G,BUIJ,F,PSI,ETA,C,DR,K,RO,AWCO)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 G(2048,3),F(2048,3),C(2048,3),RO(3)
      REAL*8 BUIJ(2048,3)
      REAL*8 PSI(2048,3)
      REAL*8 AWCO(2048,3)
      REAL*8 REALI,RAD
      REAL*8 SWT,BOLTZ
      REAL*8 EXPO
      REAL*8 ETA
      REAL*8 ALPHAT
      REAL*8 VIJT(3),SIJT(3)
      REAL*8 VIJ(3),SIJ(3)
      COMMON/HMSA/ALFNEW,VIJ,SIJ
      COMMON/HMSAT/ALPHAT,VIJT,SIJT
      COMMON/TYP/JT,N
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C
C INPUT PARAMETERS-
C       G:    G(R)=R*(H(R)-C(R)) FOR INTERACTIONS WITH
C             THE TEST PARTICLE.
C       F:    TEST PARTICLE MAYER FUNCTIONS.
C       N:    NUMBER OF GRID POINTS
C       DR:   STEP SIZE IN R
C       K:    NO LONGER USED.
C   ALPHAT:   THE HMSA MIXING PARAMETER. PASSED THROUGH COMMON/HMSAT/
C     VIJT:   THE MINIMUM VALUE OF THE IJ-TH PAIR POTENTIAL DIVIDED
C             BY KT.
C     SIJT:   THE SEPARATION DISTANCE (DIVIDED BY THE 1-1 LJ SIZE
C             PARAMETER) AT THE POTENTIAL MINIMUM.
C OUTPUT PARAMETERS-
C       C:    R*DIRECT CORRELATION FUNC.
C
C       WRITE(NOUT2,10)
```

```
C10     FORMAT(1X,'IN CFG2')
C       WRITE(NOUT2,*)RO(1),RO(2),RO(3)
C       WRITE(NOUT2,*)SIJT(1),SIJT(2),SIJT(3)
C       WRITE(NOUT2,*)VIJT(1),VIJT(2),VIJT(3)
C       WRITE(NOUT2,*)ALPHAT,ALFNEW
C       STOP
C          WRITE(NOUT2,102)
C 102      FORMAT(/1X,'IN CFG2..DOING C CALC')
           DO 115 J=1,3
              DO 110 I=1,N
C COMPUTE TOTAL CORRELATION FUNCTION:
                 REALI=I
                 RAD=REALI*DR
                 C(I,J)=0.0D0
                 ALPHA=ALPHAT
                 IF(J.EQ.1) THEN
                    ALPHA=ALFNEW
                 END IF
                    SWT=SWITC2(RAD,ALPHA)
                    EXPO=SWT*(G(I,J)/RAD)
                    IF((ETA.GE.0.0D0).OR.(J.EQ.1)) THEN
                    IF(RAD.GE.(1.0000001D0*SIJT(J))) THEN
                       EXPO=EXPO-(SWT*BUIJ(I,J))
C                      IF((I.GE.150).AND.(.LE.290)) THEN
C                         WRITE(NOUT2,666)I,J,RAD
C 666                     FORMAT(1X,'IN BLOCK 1',I4,1X,I4,1X,D13.6)
C                         WRITE(NOUT2,*)BUIJ(I,J),F(I,J)
C                      END IF
                    ELSE
                       EXPO=EXPO-(SWT*VIJT(J))
C                      IF((I.GE.150).AND.(I.LE.290)) THEN
C                         WRITE(NOUT2,777)I,J,RAD
C 777                     FORMAT(1X,'IN BLOCK 2',I4,1X,I4,1X,D13.6)
C                         WRITE(NOUT2,*)BUIJ(I,J),F(I,J)
C                      END IF
                    END IF
                    END IF
                    IF(EXPO.GT.61.0D0) THEN
                       EXPO=61.0D0
                    END IF
                    IF(EXPO.LT.-61.0D0) THEN
                       EXPO=-61.0D0
                    END IF
C                   WRITE(NOUT2,*)EXPO
                    IF(DABS(SWT).GT.0.0000000001D0) THEN
                       C(I,J)=((DEXP(EXPO))-1.0D0)/SWT
                    END IF
                    IF(RAD.GE.(1.0000001D0*SIJT(J))) THEN
                       BOLTZ=1.0D0
                    ELSE
                       BOLTZ=-AWCO(I,J)
                       IF(BOLTZ.LT.-61.0D0) THEN
                          BOLTZ=-61.0D0
                       END IF
                       BOLTZ=DEXP(BOLTZ)
                    END IF
                    IF((ETA.LT.0.0D0).AND.(J.NE.1)) THEN
                       BOLTZ=F(I,J)+1.0D0
```

```
                  END IF
                  C(I,J)=C(I,J)+1.0D0
                  C(I,J)=(C(I,J)*BOLTZ)
               C(I,J)=C(I,J)-1.0D0
               C(I,J)=RAD*C(I,J)
               C(I,J)=C(I,J)-G(I,J)
110          CONTINUE
115       CONTINUE
C         STOP
          RETURN
       END
C ***********************************************************************
C        SUBROUTINE INTGRD
C        PURPOSE-SETS UP PARAMETERS NEEDED BY SUBROUTINE TRAP.
C
C        DATE: 4/28/88.
C
C        THIS ROUTINE CALLS: SUBROUTINE TRAP-ESTIMATES THE DIFFERENCE
C                            BETWEEN THE WORK OF INSERTING A WCA
C                            REPLUSIVE PARTICLE AND THE WORK OF
C                            INSERTING A HARD SPHERE.
C ***********************************************************************
       SUBROUTINE INTGRD(NBIG,IPOT,DR,RO,PAIR,PAIR2,BATH,BATH2,
     $                   DIRECT,DIR2,INT1,INT2,E1,E2,SIGMA)
       IMPLICIT REAL*8(A-H,O-Z)
       REAL*8 PAIR(NBIG,3)
       REAL*8 PAIR2(NBIG,3)
       REAL*8 BATH(NBIG,3)
       REAL*8 BATH2(NBIG,3)
       REAL*8 DIRECT(NBIG,3)
       REAL*8 DIR2(NBIG,3)
       REAL*8 FUNCT(2048)
       REAL*8 FUN2(2048)
       REAL*8 RO(3)
       REAL*8 SIGMA(3)
       REAL*8 DR
       REAL*8 INT1,INT2
       REAL*8 E1,E2
       REAL*8 DELG,DELC
       INTEGER NBIG,IPOT
       COMMON/LUDOL/PI
       COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C RO(I)=(DENSITY)*(ITH MOLE FRAC.)*((LJ SIZE OF COMPONENT 1)**3)
C RO(3)=RO(1)
C COMPUTE THE INTEGRAND FOR SUBROUTINE SIMP:
       IF(IPOT.EQ.0) THEN
C WANT CHEMICAL POTENTIAL OF SPECIES 2. TEST PARTICLE BECOMES
C SPECIES 2.
          DO 5 I=1,NBIG
             REALI=I
             RAD=REALI*DR
C SUFFIX "2" INDICATES CORRELATION FUNCTIONS ABOUT THE WCA REPULSIVE
C TEST PARTICLE.
C NO SUFFIX INDICATES CORRELATION FUNCTIONS ABOUT THE EFFECTIVE HARD
C SPHERE.
             DELG=PAIR2(I,3)-PAIR(I,3)
             DELC=DIR2(I,3)-DIRECT(I,3)
             FUNCT(I)=0.5D0*DELG*(DELG-DELC)
```

```
            FUNCT(I)=FUNCT(I)+DELG
            FUN2(I)=DLOG(BATH2(I,3)/BATH(I,3))
            FUNCT(I)=FUNCT(I)-(PAIR2(I,3)*FUN2(I))
            FUN2(I)=FUN2(I)-DELG+DELC
            FUN2(I)=DABS(FUN2(I))
            FUN2(I)=FUN2(I)*DABS(DELG)
            FUNCT(I)=4.0D0*PI*RAD*RAD*RO(1)*FUNCT(I)
            FUN2(I)=4.0D0*PI*RAD*RAD*RO(1)*FUN2(I)
C           WRITE(NOUT2,*)RAD,FUNCT(I)
    5     CONTINUE
C INTEGRATE THE PRODUCT OF THE CORRELATION FUNCTION AND THE
C PERTURBING POTENTIAL. GET THE CONTRIBUTION OF SPECIES 1 IN
C THE BATH TO THE WORK OF SOFTENING ("INT1)".
          DIA=SIGMA(3)
          CALL TRAP(NBIG,DR,FUNCT,DIA,INT1)
C ESTIMATE AN UPPER BOUND OF THE ERROR IN ABS(INT1) DUE TO
C NEGLECTING THE DIFFERENCE IN BRIDGE FUNCTIONS FOR HS AND
C WCA REPULSIVE TEST PARTICLES ("E1").
          CALL TRAP(NBIG,DR,FUN2,DIA,E1)
C         STOP
          DO 10 I=1,NBIG
            REALI=I
            RAD=REALI*DR
            DELG=PAIR2(I,2)-PAIR(I,2)
            DELC=DIR2(I,2)-DIRECT(I,2)
            FUNCT(I)=0.5D0*DELG*(DELG-DELC)
            FUNCT(I)=FUNCT(I)+DELG
            FUN2(I)=DLOG(BATH2(I,2)/BATH(I,2))
            FUNCT(I)=FUNCT(I)-(PAIR2(I,2)*FUN2(I))
            FUN2(I)=FUN2(I)-DELG+DELC
            FUN2(I)=DABS(FUN2(I))
            FUN2(I)=FUN2(I)*DABS(DELG)
            FUNCT(I)=4.0D0*PI*RAD*RAD*RO(2)*FUNCT(I)
            FUN2(I)=4.0D0*PI*RAD*RAD*RO(2)*FUN2(I)
   10     CONTINUE
          DIA=SIGMA(2)
C GET THE CONTRIBUTION OF SPECIES 2 IN THE BATH TO THE
C WORK OF SOFTENING ("INT2").
          CALL TRAP(NBIG,DR,FUNCT,DIA,INT2)
          CALL TRAP(NBIG,DR,FUN2,DIA,E2)
       ELSE
C WANT CHEMICAL POTENTIAL OF SPECIES 1. THE TEST
C PARTICLE BECOMES A MOLECULE OF SPECIES 1 WHEN
C FULLY CHARGED.
          DO 20 I=1,NBIG
            REALI=I
            RAD=REALI*DR
            DELG=PAIR2(I,1)-PAIR(I,1)
            DELC=DIR2(I,1)-DIRECT(I,1)
            FUNCT(I)=0.5D0*DELG*(DELG-DELC)
            FUNCT(I)=FUNCT(I)+DELG
            FUN2(I)=DLOG(BATH2(I,1)/BATH(I,1))
            FUNCT(I)=FUNCT(I)-(PAIR2(I,1)*FUN2(I))
            FUN2(I)=FUN2(I)-DELG+DELC
            FUN2(I)=DABS(FUN2(I))
            FUN2(I)=FUN2(I)*DABS(DELG)
            FUNCT(I)=4.0D0*PI*RAD*RAD*RO(1)*FUNCT(I)
            FUN2(I)=4.0D0*PI*RAD*RAD*RO(1)*FUN2(I)
```

```
   20       CONTINUE
            DIA=SIGMA(1)
            CALL TRAP(NBIG,DR,FUNCT,DIA,INT1)
            CALL TRAP(NBIG,DR,FUN2,DIA,E1)
            DO 30 I=1,NBIG
               REALI=I
               RAD=REALI*DR
               DELG=PAIR2(I,3)-PAIR(I,3)
               DELC=DIR2(I,3)-DIRECT(I,3)
               FUNCT(I)=0.5D0*DELG*(DELG-DELC)
               FUNCT(I)=FUNCT(I)+DELG
               FUNCT(I)=DLOG(BATH2(I,3)/BATH(I,3))
               FUNCT(I)=FUNCT(I)-(PAIR2(I,3)*FUN2(I))
               FUN2(I)=FUN2(I)-DELG+DELC
               FUN2(I)=DABS(FUN2(I))
               FUN2(I)=FUN2(I)*DABS(DELG)
               FUNCT(I)=4.0D0*PI*RAD*RAD*RO(2)*FUNCT(I)
               FUN2(I)=4.0D0*PI*RAD*RAD*RO(2)*FUN2(I)
   30       CONTINUE
            DIA=SIGMA(3)
            CALL TRAP(NBIG,DR,FUNCT,DIA,INT2)
            CALL TRAP(NBIG,DR,FUN2,DIA,E2)
         END IF
C        WRITE(NOUT2,32)
C32      FORMAT(/1X,'LEAVING INTGRD')
C        DO 40 I=35,50
C           WRITE(NOUT2,35)PSI(I,1),PSI(I,2),PSI(I,3)
C35         FORMAT(1X,'PSI:',D13.6,1X,D13.6,1X,D13.6)
C           WRITE(NOUT2,37)RDFNEW(I,1),RDFNEW(I,2),RDFNEW(I,3)
C37         FORMAT(1X,'RDFNEW:',D13.6,1X,D13.6,1X,D13.6)
C40      CONTINUE
          RETURN
          END
C ***********************************************************************
C         SUBROUTINE MUDRVR
C         PURPOSE-CALCULATES THE CHEMICAL POTENTIAL OF THE DESIRED
C                 SPECIES.  ALSO DETERMINES (DERIVATIVE OF THAT
C                 CHEMICAL POTENTIAL W.R.T. TOTAL DENSITY AT CONSTANT
C                 TEMPERATURE AND COMPOSITION)*DENSITY OF THAT SPECIES.
C                 THE DERIVATIVE IS FOR USE IN CHECKING TO SEE IF THE
C                 GIBBS-DUHEM CONSISTANCY TEST FOR THE CHEMICAL
C                 POTENTIAL IS SATISFIED. THE DERIVATIVE IS ESTIMATED
C                 USING A THREE POINT FINITE DIFFERENCE FORMULA AFTER
C                 CALCULATING THE CONTRIBUTIONS TO THE CHEMICAL
POTENTIAL
C                 AT THREE DIFFERENT DENSITIES. THE THERMO. CONSISTANCY
C                 PARAMETERS FOR THE BATH AND TEST PARTICLE DISTRIBUTION
C                 FUNCTIONS ARE TAKEN TO BE CONSTANT WHEN DOING THIS.
C
C         DATE 10/27/88
C         REVISED 1/10/89- TO USE A THREE POINT FORMULA INSTEAD OF A
C                          FOUR POINT FORMULA.
C         CODED BY DAVID PFUND
C
C         THIS ROUTINE CALLS: SUBROUTINE SMOOTH-INTERPOLATES THE
C                             DISTRIBUTION FUNCTIONS OBTAINED BY "FINDA"
C                             TO FIT THE STEP SIZE (IN GENERAL
DIFFERENT)
```

```
C                                 USED BY THIS SUBROUTINE. RESULT IS USED
C                                 ONLY AS AN INITIAL GUESS TO "LABIK" BELOW.
C                                 SUBROUTINE MAYER-CALCULATES A VECTOR OF
C                                 MAYER FACTORS FOR THE DESIRED INTERACTION
C                                 POTENTIAL WHICH IS USED IN THE
DISTRIBUTION
C                                 FUNC. CALCS. FOR THE BATH MOLECULES.
C                                 SUBROUTINE LABIK-CALCULATES THE
C                                 DISTRIBUTION FUNCTIONS FOR THE BATH AT THE
C                                 THREE DIFFERENT DENSITIES.
C                                 SUBROUTINE VIRIAL-COMPUTES THE VIRIAL
C                                 PRESSURE AT THE DIFFERENT DENSITY STEPS.
C                                 SUBROUTINE PERT-CALCULATES THE PERTURBING
C                                 POTENTIAL DIVIDED BY KT (WHICH IS THE
C                                 W.C.A. ATTRACTIVE PART). ALSO CALCULATES
C                                 THE W.C.A. REPLUSIVE PART OF THE
C                                 POTENTIAL.
C                                 SUBROUTINE CEMPOT-COMPUTES THE CHEMICAL
C                                 POTENTIAL OF THE SPECIES OF INTEREST.
C                                 SUBROUTINE RHODMU-COMPUTES THE DENSITY
C                                 DERIVATIVE OF THAT CHEMICAL POTENTIAL
TIMES
C                                 THE DENSITY OF THAT SPECIES.
C ***********************************************************************
      SUBROUTINE MUDRVR(N,NM,DROLD,DR,IPOT,KEPSI,SOFTD,EPSI,RSOFTD,
     $TEMP,TRED,RO,X1,JP,ALPHA,PRESSV,COMPC,DLIKE,DUNLKE,MW,
     $GOLD,ASIGMA,YU,YUSTR,YUHS,INT1,INT2,E1,E2,DMUDRO,ERROR)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 GOLD(N,3)
      REAL*8 G(2048,3),PAIR(2048,3),DIRECT(2048,3),TOTAL(2048,3)
      REAL*8 BATH(2048,3)
      REAL*8 BUIJ(2048,3),F(2048,3)
      REAL*8 TUIJ(2048,3),AWCO(2048,3),PSI(2048,3)
      REAL*8 UPRIME(2048,3)
      REAL*8 SIGMA(3),EPSI(3)
      REAL*8 ASIGMA(3),KEPSI(3)
      REAL*8 RSOFTD(3),SOFTD(3)
      REAL*8 RO(3),RHO(3)
      REAL*8 CORE(3)
      REAL*8 INT1,INT2
      REAL*8 E1,E2
      REAL*8 DR,DROLD
      REAL*8 DMUDRO
      REAL*8 DELTA
      REAL*8 TEMP,TRED
      REAL*8 PV3,PV2,PRESSV
      REAL*8 COMPC
      REAL*8 DLIKE,DUNLKE
      REAL*8 CORF1,CORF2
      REAL*8 ALPHA
      REAL*8 YU,YUSTR,YUHS
      REAL*8 SOFT3,SOFT2,SOFTO
      REAL*8 GAAC3,GAAC2,GAAC
      REAL*8 GABC3,GABC2,GABC
      REAL*8 MW
      INTEGER ERROR
      INTEGER COUNT
      INTEGER N,NM,IE,JP,IPOT
```

```
      LOGICAL BADMAT
      LOGICAL LOTS
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C     DATA DELTA/-0.0005D0/
C     DATA DELTA/-0.001D0/
      DATA DELTA/-0.00025D0/
C DROLD= STEP SIZE AUTOMATICALLY SELECTED BY SUBROUTINE FINDA.
C DR=STEP SIZE INPUT BY THE USER SO THAT IT DIVIDES BOTH THE
C SPECIES 1/TEST PARTICLE AND SPECIES 2/TEST PARTICLE EFFECTIVE
C DIAMETERS (ALSO INPUT).
C MAKE DISTRIBUTION FUNCTIONS CONFORM TO THE NEW MESH BY
C INTERPOLATING.
      CALL SMOOTH(N,DROLD,DR,GOLD,G)
C DELTA=STEP SIZE FOR THE NUMERICAL ESTIMATE OF THE DENSITY DERIVATIVE.
C STEP THE DENSITY BACK:
C     RHO(1)=(1.0D0+(2.0D0*DELTA))*RO(1)
C     RHO(2)=(1.0D0+(2.0D0*DELTA))*RO(2)
C     RHO(3)=(1.0D0+(2.0D0*DELTA))*RO(3)
C COMPUTE BATH DISTRIBUTION FUNCTIONS:
      CORE(1)=0.0D0
      CORE(2)=0.0D0
      CORE(3)=0.0D0
      CALL MAYER(DR,RSOFTD,EPSI,CORE,TRED,F,BUIJ,UPRIME,IPOT,N)
C     CALL LABIK(IPOT,BUIJ,F,RSOFTD,EPSI,RHO,TRED,G,PAIR,
C    $           DIRECT,TOTAL,BATH,IE,BADMAT,DR,JP,NM)
C     IF((IE.GT.0).AND.(.NOT.BADMAT)) THEN
C COMPUTE THE VIRIAL PRESSURE AT DENSITY + 2*DELTA.
C        CALL VIRIAL(IPOT,DR,RHO,TRED,RSOFTD,EPSI,CORE,BUIJ,UPRIME,
C    $               PAIR,PV3)
C        WRITE(NOUT2,*)PV3
C COMPUTE THE CHEMICAL POTENTIAL, SOFT (ATTRACTIVE AND SOFT REPLUSIVE)
C CONTRIBUTIONS, AND THE CONTACT VALUES OF THE PAIR CORRELATION
C FUNCTIONS WITH THE CAVITY.
         IF(IPOT.EQ.1) THEN
            CORF1=DLIKE
            CORF2=(SOFTD(1)/SOFTD(2))*((2.0D0*DUNLKE)-CORF1)
         ELSE
            CORF2=DLIKE*(SOFTD(1)/SOFTD(2))
            CORF1=(2.0D0*DUNLKE)-DLIKE
         END IF
         CALL PERT(N,IPOT,DR,TEMP,CORF1,CORF2,ASIGMA,KEPSI,SOFTD,TUIJ,
     $             AWCO,PSI)
C        CALL CEMPOT(N,NM,DR,IPOT,KEPSI,SOFTD,EPSI,RSOFTD,TEMP,TRED,
C    $               RHO,X1,ALPHA,PV3,CORF1,CORF2,MW,
C    $               TUIJ,AWCO,PSI,
C    $               G,PAIR,DIRECT,TOTAL,BATH,ASIGMA,YU,
C    $              YUSTR,YUHS,INT1,INT2,E1,E2,GAAC3,GABC3,ERROR)
C        STOP
C        SOFT3=(YU-YUHS)/(RHO(1)+RHO(2))
C        SOFT3=(YU-YUSTR)/(RHO(1)+RHO(2))
C        IF(ERROR.EQ.0) THEN
C           RHO(1)=(1.0D0+(DELTA))*RO(1)
C           RHO(2)=(1.0D0+(DELTA))*RO(2)
C           RHO(3)=(1.0D0+(DELTA))*RO(3)
C COMPUTE DISTRIBUTION FUNCTIONS:
C           CALL LABIK(IPOT,BUIJ,F,RSOFTD,EPSI,RHO,TRED,G,PAIR,
C    $                 DIRECT,TOTAL,BATH,IE,BADMAT,DR,JP,NM)
C           IF((IE.GT.0).AND.(.NOT.BADMAT)) THEN
```

```
C         CALL VIRIAL(IPOT,DR,RHO,TRED,RSOFTD,EPSI,CORE,BUIJ,UPRIME,
C     $                 PAIR,PV2)
C         WRITE(NOUT2,*)PV2
C               CALL CEMPOT(N,NM,DR,IPOT,KEPSI,SOFTD,EPSI,RSOFTD,TEMP,
C     $                 TRED,RHO,X1,ALPHA,PV2,CORF1,CORF2,MW,
C     $                 TUIJ,AWCO,PSI,
C     $                 G,PAIR,DIRECT,TOTAL,BATH,ASIGMA,YU,
C     $              YUSTR,YUHS,INT1,INT2,E1,E2,GAAC2,GABC2,ERROR)
C               SOFT2=(YU-YUHS)/(RHO(1)+RHO(2))
C         SOFT2=(YU-YUSTR)/(RHO(1)+RHO(2))
C                     IF(ERROR.EQ.0) THEN
                         JP=1
                  CALL LABIK(IPOT,BUIJ,F,RSOFTD,EPSI,RO,TRED,G,PAIR,
     $                      DIRECT,TOTAL,BATH,IE,BADMAT,DR,JP,NM)
                         IF((IE.GT.0).AND.(.NOT.BADMAT)) THEN
C                           LOTS=.FALSE.
C                           X1=RO(1)/(RO(1)+RO(2))
C                           COUNT=0
C                           ENERGY=0.0D0
C                           CERROR=0.0D0
C                           COMPC=0.0D0
C                           CALL PRINTR(LOTS,DR,PAIR,DIRECT,TOTAL,BATH,
C     $                                 EPSI,RSOFTD,TRED,RO,X1,G,COUNT,
C     $                                 ALPHA,PRESSU,ENERGY,CERROR,COMPC)
C                           STOP
C         WRITE(NOUT2,*)PRESSU
               CALL CEMPOT(N,NM,DR,IPOT,KEPSI,SOFTD,EPSI,RSOFTD,
     $               TEMP,TRED,RO,X1,ALPHA,PRESSU,CORF1,CORF2,
     $               MW,TUIJ,AWCO,PSI,
     $               G,PAIR,DIRECT,TOTAL,BATH,ASIGMA,YU,
     $               YUSTR,YUHS,INT1,INT2,E1,E2,GAAC,GABC,ERROR)
C                           SOFTO=(YU-YUHS)/(RO(1)+RO(2))
C         SOFTO=(YU-YUSTR)/(RO(1)+RO(2))
C                            IF(ERROR.EQ.0) THEN
C                               CALL RHODMU(IPOT,DELTA,X1,COMPC,RO,
CC      $                             ASIGMA,SOFTD,GAAC3,GAAC2,
C      $                            GAAC,GABC3,GABC2,GABC,SOFT3,
C      $                         SOFT2,SOFTO,YU,YUHS,YUSTR,DMUDRO)
C                            END IF
                         END IF
C                     END IF
C            END IF
C         END IF
C      END IF
       IF((IE.LE.0).OR.BADMAT) THEN
          ERROR=6
       END IF
       RETURN
       END
C ***********************************************************************
C         FUNCTION DERIV2
C         PURPOSE-NUMERICALLY DIFFERENTIATES THE CHEMICAL POTENTIAL
C                 OF A SPECIES/KT W.R.T. THE TOTAL DENSITY.
C
C         DATE 1/10/89
C         CODED BY DAVID PFUND
C
C         THIS ROUTINE CALLS: -
```

```
C ******************************************************************
      REAL FUNCTION DERIV2(PV0,PV1,PRESSV,DELTA,R0)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 DELTA
      REAL*8 PV0,PV1,PRESSV
      REAL*8 R0(3)
      REAL*8 RHO
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C THIS FUNCTION CURRENTLY USES A THREE POINT BACKWARD DIFFERENCE
C FORMULA WHICH HAS THIRD ORDER ACCURACY.
C PV0 IS TWO STEPS BACKWARD.
C PV1 IS ONE STEP BACKWARD.
C PRESSV IS ON THE NODE OF INTEREST.
      RHO=R0(1)+R0(2)
      DERIV2=((-PV0)+(4.0D0*PV1)-(3.0D0*PRESSV))/
     $(2.0D0*DELTA*RHO)
      RETURN
      END
```

```
C ******************************************************************
C        SUBROUTINE DILUTE
C        PURPOSE-SOLUTION OF THE TEST PARTICLE OZ EQUATIONS FOR A
C                MOLECULE (INFINITELY DILUTE) OF SPECIES "2" IN A
C                MIXTURE OF SPECIES "1" AND "2".
C
C        REVISED 9/21/87 -DEVELOPED FROM A COPY OF SUBROUTINE
C                         GALER FOR USE WITH THE OZ EQUATIONS
C                         FOR A TEST PARTICLE.
C        ORIGINAL VERSION FOR PURE SYSTEMS WRITTEN BY S.LABIK
C        AND A. MALIJEVSKY, INSTITUTE OF CHEMICAL TECHNOLOGY
C        PRAGUE, CZECHOSLOVAKIA
C        (VERSION 1, FEBRUARY 1985, C.F. LABIK, MALIJEVSKY, AND
C         VONKA, MOL. PHYS., VOL.56 (3), P.709, (1985).)
C
C        THIS ROUTINE CALLS: SUBROUTINE FFS3D- FOURIER TRANSFORM AND
C                            INVERSE FOURIER TRANSFORM.
C                            SUBROUTINE GFC2- INPUT THE TRANSFORM OF
C                            THE R*(DIRECT CORRELATION FUNCTION)-OUTPUT
C                            THE TRANSFORM OF THE "GAMMA" FUNCTION
C                            OBTAINED FROM DIRECT SUBSTITION OF "C"
C                            INTO THE TRANFORMED OZ EQUATIONS FOR
C                            INTERACTIONS WITH A TEST PARTICLE.
C                            SUBROUTINE CFG2- INPUT "GAMMA". OUTPUT
C                            "C". THESE OUTPUTS ARE
C                            OBTAINED FROM SUBSTITUTION INTO THE
C                            CLOSURE EQUATION.
C ******************************************************************
      SUBROUTINE DILUTE(G,BUIJ,F,PSI,ETA,NM,DR,RO,JP,
     $IE,RSOFTD,SIGMA,RC,BADMAT,AWCO)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 GN(2048,3),GT(2048,3),GNT(2048,3),DC(2048,3),CT(2048,3)
      REAL*8 C(2048,3)
      REAL*8 CSN(2048)
      REAL*8 G(2048,3),F(2048,3)
      REAL*8 BUIJ(2048,3)
      REAL*8 PSI(2048,3)
      REAL*8 RC(2048,3)
      REAL*8 HT(2048,3)
      REAL*8 AWCO(2048,3)
      REAL*8 CCT(3),GGNT(3),RO(3)
      REAL*8 TTT(3)
      REAL*8 RSOFTD(3),SIGMA(3)
      REAL*8 WFFTR(5133)
      REAL*8 ETA
      INTEGER SELECT
      LOGICAL BADMAT
      COMMON/CONV/CONVDI,CONVNR
      COMMON/LUDOL/PI
      COMMON/HTHING/HT
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
      DATA OUCH,WAIT/0.99D0,1.0D0/
C INPUT PARAMETERS-
C       G:    GAMMA FUNCTIONS=G(R)=R*(H(R)-C(R))
C       F:    MAYER FUNCTIONS=EXP(-U(R)/T*) - 1 FOR
C             INTERACTIONS WITH THE TEST PARTICLE.
C      RC:    THE R*(DIRECT CORRELATION FUNCTIONS) OF THE SPECIES IN
C             THE MIXTURE. THESE ARE CONSTANTS.
```

```
C       NM:     NUMBER OF DEFINING NUMBER OF GRID POINTS
C               N=2**NM
C       HT:     TRANSFORMS OF TOTAL CORRELATION FUNCTIONS
C               IN THE BATH.  PASSED FROM SUBROUTINE GALER.
C      ETA:     IF ETA>=0 ITS THE COUPLING PARAMETER FOR THE WCA
C               ATTRACTIVE PART. IF ETA<0 IT INDICATES THAT THE
C               TEST PARTICLE IS A HARD SPHERE.
C WITH CURRENT ARRAY DIMENSIONS, MAX NM=11.
C       RO:     REDUCED DENSITY=N*(1-1 LJ SIZE PARM**3)/V
C       DR:     REDUCED STEP SIZE
C       JP:
C             JP.EQ.0  ...  LOW DENSITY LIMIT - G(R) = 0.
C             JP.EQ.1 ... INPUT G(R) IS USED.
C             JP.EQ.2 ... HARD SPHERE G(R) IS USED.
C OUTPUT PARAMETERS-
C        G:     G(R)=R*(H(R)-C(R))
C               G(I,1) IS UNCHANGED BY THE SUBROUTINE.
C               G(I,2) DENOTES LIKE-LIKE INTERACTIONS WITH THE
C                      TEST PARTICLE.
C               G(I,3) DENOTES UNLIKE-LIKE INTERACTIONS WITH THE
C                      TEST PARTICLE.
C       IE:     NUMBER OF ITERATION STEPS
C               IE<0 MEANS SOLUTION NOT FOUND
C
C (NOTE: THE STRUCTURE OF SUBROUTINE GALER IS TERMINAL- SORRY)
C       WRITE(NOUT2,1)
C1      FORMAT(1X,' IN DILUTE')
        ROT=RO(2)/RO(1)
        N=2**NM
        N2=2*N
        RM=DR*N
        DT=PI/RM
        TM=PI/DR
        P1=PI/N
        DO 5 I=1,N
C INITIALIZE AN ARRAY OF COSINE FUNCTIONS FOR USE LATER.
           P2=I*P1
C START BY ASSUMING "C" FUNCTIONS FOR THE TEST PARTICLE ARE
APPROXIMATED
C BY THE BATH VALUES.
           C(I,1)=RC(I,1)
           C(I,2)=RC(I,2)
           C(I,3)=RC(I,3)
5       CONTINUE
        NN=N-1
        CALL DFSINI(NN,WFFTR)
C
C               DEFINITION OF INITIAL VALUES OF G(R) AND GT(T)
C
              DO 25 J=1,3
                 DO 24 I=1,N
                    DC(I,J)=G(I,J)*RO(J)
24               CONTINUE
25            CONTINUE
C             STOP
              SELECT=1
C FIND THE TRANSFORM OF THE DENSITY MULTIPLIED GAMMA FUNCTIONS FOR
C THE TEST PARTICLE INTERACTIONS.
```

```
            CALL FFS3D(SELECT,DC,GT,N,NM,DR,WFFTR)
        IF(JP.EQ.2) THEN
C JP=2 => HARD SPHERE INTIAL GUESS.
            CALL HSANAL(C,RO,SIGMA,DR)
            DO 26 I=1,N
               RR=DR*I
               C(I,1)=RC(I,1)
               DC(I,1)=C(I,1)*RO(1)*RR
               DC(I,2)=C(I,2)*RO(2)*RR
               DC(I,3)=C(I,3)*RO(3)*RR
   26       CONTINUE
            SELECT=1
C FIND THE TRANSFORM OF THE DENSITY MULTIPLIED GAMMA FUNCTIONS FOR
C THE TEST PARTICLE INTERACTIONS.
            CALL FFS3D(SELECT,DC,CT,N,NM,DR,WFFTR)
            DO 140 J=1,N
               T=J*DT
               DO 141 IB=1,3
                  CCT(IB)=CT(J,IB)
                  TTT(IB)=HT(J,IB)
  141          CONTINUE
               CALL GFC2(TTT,CCT,GGNT,RO,ROT,T)
C (NOTE: 1-1 DIDN'T CHANGE- IT'S JUST ALONG FOR THE RIDE)
               GT(J,2)=GGNT(2)
               GT(J,3)=GGNT(3)
  140       CONTINUE
            SELECT=-1
            CALL FFS3D(SELECT,GT,G,N,NM,DR,WFFTR)
            DO 126 I=1,N
               G(I,1)=G(I,1)/RO(1)
               G(I,2)=G(I,2)/RO(2)
               G(I,3)=G(I,3)/RO(3)
  126       CONTINUE
        END IF
        IE=0.
        IR=0.
        CONOLD=10000.
C
C              START OF DIRECT ITERATION
1000    CONTINUE
           IE=IE+1
           CONCUX=10000.
        IF (IE.GT.300) GO TO 3000
C
C                  CALCULATION OF C(R) FROM G(R)
C
           SELECT=0
C FROM DIRECT SUBSTITUTION OF "GAMMA" INTO THE CLOSURE
C EQUATIONS GET NEW "C"'S (FOR THE TEST PARTICLE).
       CALL CFG2(G,BUIJ,F,PSI,ETA,C,DR,SELECT,RO,AWCO)
           DO 85 J=1,3
              DO 80 I=1,N
                 C(I,J)=C(I,J)*RO(J)
80            CONTINUE
85         CONTINUE
C
C          CALCULATION OF CT(T), THE FOURIER TRANSFORM OF C(R)
C
```

```
          SELECT=1
          CALL FFS3D(SELECT,C,CT,N,NM,DR,WFFTR)
C
C                    CALCULATION OF NEW GT(T)
C
          DO 40 J=1,N
             T=J*DT
             DO 41 IB=1,3
                CCT(IB)=CT(J,IB)
                TTT(IB)=HT(J,IB)
41           CONTINUE
C FROM DIRECT SUBSTITUTION OF THE TRANSFORM OF "C" INTO THE OZ
C EQUATIONS GET NEW "GAMMA"'S (FOR THE TEST PARTICLE; IN TRANSFORM
C SPACE).
             CALL GFC2(TTT,CCT,GGNT,RO,ROT,T)
             GNT(J,1)=GT(J,1)
C (NOTE: 1-1 DIDN'T CHANGE- IT'S JUST ALONG FOR THE RIDE)
             GNT(J,2)=GGNT(2)
             GNT(J,3)=GGNT(3)
40        CONTINUE
          NA=32
2000      CONTINUE
          DO 310 M=1,NA
             GT(M,1)=GNT(M,1)
             GT(M,2)=GNT(M,2)
             GT(M,3)=GNT(M,3)
310       CONTINUE
          DO 335 I=1,3
             DO 330 J=NA+1,N
                GT(J,I)=GNT(J,I)
330          CONTINUE
335       CONTINUE
C
C          CALCULATION OF NEW APPROX. FOR DIRECT ITERATION.
C
          SELECT=-1
          CALL FFS3D(SELECT,GT,GN,N,NM,DR,WFFTR)
          P3=0
          DO 195 J=1,3
             DO 190 I=1,N
                GN(I,J)=GN(I,J)/RO(J)
                P1=G(I,J)-GN(I,J)
                P3=P3+(P1/I)**2
                G(I,J)=((1.0D0-WAIT)*G(I,J))+(WAIT*GN(I,J))
C                WRITE(NOUT2,188)
C188             FORMAT(1X,'OUCH')
190          CONTINUE
195       CONTINUE
          P3=SQRT(P3)
C
C                TEST TO END ITERATIONS.
C
          IF (P3.LT.CONVDI) THEN
C            WRITE(NOUT2,*)IE
       RETURN
          ELSE
             IF (P3.LT.CONOLD) THEN
                ICO=0
```

```
                CONOLD=P3
        GO TO 1000
              ELSE
                IF (ICO.EQ.0) THEN
                   ICO=ICO+1
        GO TO 1000
                END IF
              END IF
           END IF
C             WRITE(NOUT2,*)IE
C       RETURN
        GO TO 1000
3000    CONTINUE
C IF IT'S HERE,
C SUBROUTINE DILUTE HAS FAILED...SORRY.
        IE=-IE
C       WRITE(NOUT2,*)IE,IR
        RETURN
        END
C ******************************************************************
C        SUBROUTINE GFC2
C        PURPOSE-IMPLIMENTS A REARRANGED, TRANSFORMED OZ EQUATION
C                FOR INTERACTIONS OF BATH MOLECULES WITH A
C                TEST PARTICLE.
C
C        REVISED 6/4/87
C                9/22/87-COPIED FROM SUBROUTINE GFC AND CHANGED TO
C                        TRANFORMED OZ EQUATIONS FOR A TEST PARTICLE
C                        IN A MIXTURE.
C
C        THIS ROUTINE CALLS:-
C ******************************************************************
        SUBROUTINE GFC2(TTT,C,G,RO,ROT,T)
        IMPLICIT REAL*8(A-H,O-Z)
        REAL*8 C(3),G(3)
        REAL*8 TTT(3)
        REAL*8 RO(3)
        COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C       WRITE(NOUT2,10)
C10     FORMAT(1X,' IN GFC2')
C C: TRANSFORM OF (ITH DENSITY*(BIG C FOR  I-TEST PARTICLE))
C G: TRANSFORM OF (ITH DENSITY*(BIG GAMMA FOR  I-TEST PARTICLE))
C THE ORDER OF CONVOLUTION USED IS:
C TOTAL CORRELATIONS FOR BATH*DIRECT CORRELATIONS FOR TEST PARTICLE.
C TOTAL CORRELATION FUNCTIONS FOR INTERACTIONS IN THE BATH:
        H11=TTT(1)*RO(1)
        H22=TTT(2)*RO(2)
        H12=TTT(3)*RO(3)
        DET=((1.0D0+H11)*(1.0D0+H22))-(H12*H12*ROT)
C DIRECT CORRELATION FUNCTIONS FOR INTERACTIONS WITH
C THE TEST PARTICLE:
        C2C=C(2)
        C1C=C(3)
        TRH1C=C1C+(H11*C1C)+(H12*C2C)
        TRH2C=C2C+(H12*C1C*ROT)+(H22*C2C)
C
        G(1)=0.0D0
C SPECIES 2-TEST PARTICLE INTERACTIONS:
```

```
      G(2)=TRH2C*(H22+(H11*H22)-(H12*H12*ROT))
      G(2)=G(2)+(TRH1C*H12*ROT)
      G(2)=G(2)/DET
C SPECIES 1-TEST PARTICLE INTERACTIONS:
      G(3)=TRH1C*(H11+(H11*H22)-(H12*H12*ROT))
      G(3)=G(3)+(TRH2C*H12)
      G(3)=G(3)/DET
      RETURN
      END
C ******************************************************************
C       SUBROUTINE CEMPOT
C       PURPOSE-CALCULATES THE CHEMICAL POTENTIAL OF THE SOLUTE.
C       THE SOLUTE CHEMICAL POTENTIAL IS CALULATED USING THE METHOD
C       OF COUPLING. CHEMICAL POTENTIALS ARE DIMENSIONLESS,
C       HAVING BEEN DIVIDED BY KT.
C
C       DATE 6/15/87
C       REVISED
C               9/20/87- TO USE DISTRIBUTION FUNCTIONS FROM AN
C                        INTEGRAL EQUATION CALCULATION (HMSA).
C               6/4/88 - TO USE A WCA DIVISION OF THE PAIR
C                        POTENTIAL.
C              10/22/88- TO ALLOW MULTIPLE CALCULATIONS OF TEST
C                        PARTICLE DISTRIBUTION FUNCTIONS PER CALC.
C                        OF BATH MOLECULE DISTRIBUTION FUNCTIONS.
C               3/14/89- TO CALL NEW PARTICLE SCALING SUBROUTINE
C                        "CEMREP" TO CALC. THE REPULSIVE
C                        CONTRIBUTION TO THE CHEMICAL POTENTIAL.
C       CODED BY DAVID PFUND
C
C       THIS ROUTINE CALLS: SUBROUTINE PERT- CALCULATES THE PERTURBING
C                           POTENTIAL DIVIDED BY KT  AND ITS
C                           DERIVATIVE.
C                           SUBROUTINE INSIDE- CALCULATES THE INTEGRAL
C                           OVER VOLUME OF THE PRODUCT OF THE
C                           PERTURBING POTENTIALS AND THE ESTIMATED
C                           PAIR CORRELATION FUNCTIONS FOR THE TEST
C                           PARTICLE.
C                           SUBROUTINE TAIL-CALCULATES THE TAIL
C                           CORRECTION TO THE CHEMICAL POTENTIAL OF
C                           THE DILUTE SOLUTE.
C                           FUNCTION YUIDL-CALCULATES THE IDEAL GAS
C                           CONTRIBUTION TO THE SOLUTE CHEMICAL
C                           POTENTIAL.
C                           SUBROUTINE CEMREP- CALCULATES THE WORK
C                           CHANGE IN INFLATING AN INSERTED HARD
C                           SPHERE FROM A RADIUS OF ZERO TO A
C                           A RADIUS OF THE EFFECTIVE DIAMETER/2.
C                           FUNCTION YUCORE- CALCULATES THE HARD CORE
C                           CONTRIBUTION TO THE SOLUTE CHEMICAL
C                           POTENTIAL.
C                           FUNCTION INTGRD - COMPUTES THE FREE ENERGY
C                           CHANGE FOR SOFTENING THE INSERTED HARD
C                           SPHERE INTO A WCA PARTICLE.
C ******************************************************************
      SUBROUTINE CEMPOT(NBIG,NM,DR,IPOT,KEPSI,SOFTD,EPSI,
     $                  RSOFTD,TEMP,TRED,RO,X1,ALPHA,
     $                  PRESSU,CORF1,CORF2,MW,
```

```
     $                    TUIJ,AWCO,PSI,
     $                    G,PAIR,DIRECT,TOTAL,BATH,ASIGMA,
     $                    YU,YUSTR,YUHS,INT1,INT2,E1,E2,SGCAA,SGCAB,
     $                    ERROR)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 RO(3)
      REAL*8 ASIGMA(3),KEPSI(3)
      REAL*8 SIGMA(3),EPSI(3)
      REAL*8 SOFTD(3)
      REAL*8 RSOFTD(3)
      REAL*8 PSI(2048,3),UPRIME(2048,3)
      REAL*8 TUIJ(2048,3),AWCO(2048,3)
      REAL*8 G(2048,3),PAIR(2048,3),DIRECT(2048,3)
      REAL*8 TOTAL(2048,3),BATH(2048,3)
      REAL*8 PAIRO(2048,3),BATHO(2048,3)
      REAL*8 PAIRTP(2048,3)
      REAL*8 BATHTP(2048,3)
      REAL*8 DIRTP(2048,3),DIRO(2048,3)
      REAL*8 TEMP,TRED
      REAL*8 ALPHA
      REAL*8 CORF1,CORF2
      REAL*8 YU,YUHS,YUSTR
      REAL*8 RNUM,DELTA,LAMBDA,INTGRL,PANEL,ROMBRG,ROFF
      REAL*8 MW
      REAL*8 TPARTS
      REAL*8 PRESSU
      REAL*8 X1
      REAL*8 GCAA,GCAB
      REAL*8 INT1,INT2
      REAL*8 E1,E2
      REAL*8 DR
      INTEGER NBIG,NM
      INTEGER IPOT,JP
      INTEGER NUMPAN,ICOUNT,ERROR
      INTEGER SWAP,OFF
      INTEGER IFUNC
      COMMON/LUDOL/PI
      COMMON/CONV/CONVDI,CONVNR
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
      DATA NUMPAN/4/
C     WRITE(NOUT2,*)NBIG,NM,DR,IPOT
C     WRITE(NOUT2,*)KEPSI(1),KEPSI(2),KEPSI(3)
C     WRITE(NOUT2,*)SOFTD(1),SOFTD(2),SOFTD(3)
C     WRITE(NOUT2,*)EPSI(1),EPSI(2),EPSI(3)
C     WRITE(NOUT2,*)RSOFTD(1),RSOFTD(2),RSOFTD(3)
C     WRITE(NOUT2,*)TEMP,TRED
C     WRITE(NOUT2,*)RO(1),RO(2),RO(3)
C     WRITE(NOUT2,*)X1,JP,ALPHA,PRESSU,CORF1,CORF2,MW
C     WRITE(NOUT2,*)ASIGMA(1),ASIGMA(2),ASIGMA(3)
      YU=0.0D0
      YUHS=0.0D0
      YUSTR=0.0D0
C NUMPAN- NUMBER OF INTEGRATION PANELS FOR THE INTEGRATION OVER THE
C COUPLING PARAMETER FOR THE WCA ATTRACTIVE PART.
C NBIG- NUMBER OF MESH POINTS USED TO CALCULATE THE RADIAL DISTRIBUTION
C FUNCTIONS.
      RNUM=NUMPAN
C STEP THE COUPLING PARAMETER BACKWARDS BEGINING WITH A FULLY CHARGED
```

```
C TEST PARTICLE (IDENTICAL TO A BATH MOLECULE).
      DELTA=-1.0D0/RNUM
      INTGRL=0.0D0
      PANEL=0.0D0
C UNITS: TEMP, KEPSI- KELVIN.
C        ASIGMA (HARD DIA.), SOFTD (SOFT DIA.)- ANGSTROMS
C        PSI (WCA ATTRACTIVE POTENTIAL/KT)- DIMENSIONLESS.
C DR ( (STEP SIZE FOR INNER INTEGRAL)/'11' SOFT DIA.)- DIMENSIONLESS
C
C CALCULATE REDUCED EFFECTIVE HS SIZES FROM ABSOLUTE VALUES.
      SIGMA(1)=ASIGMA(1)/SOFTD(1)
      SIGMA(2)=ASIGMA(2)/SOFTD(1)
      SIGMA(3)=ASIGMA(3)/SOFTD(1)
C INITIAL VALUE OF THE COUPLING PARAMETER IS ONE
      LAMBDA=1.0D0
C FOR A COUPLING PARAMETER OF ZERO THE POTENTIAL TO BE USED IS
C WCA REPLUSIVE PART. "LAMBD1"=>THE COUPLING PARAMETER.\
      JP=1
      CONVDI=0.000001D0
      CONVNR=0.0001D0
      RSTAR=RO(1)+RO(2)
      CALL
INSIDE(ALPHA,NBIG,NM,DR,IPOT,RSOFTD,EPSI,RO,TRED,LAMBDA,TUIJ,
     $AWCO,PSI,G,DIRECT,INTGRL,ERROR,SIGMA,GCAA,GCAB,PAIRTP,
     $BATHTP,DIRTP,JP)
C       WRITE(NOUT2,*)LAMBDA,INTGRL
      IF(ERROR.EQ.0) THEN
            ICOUNT=1
            LAMBDA=LAMBDA+DELTA
C THIS SUBROUTINE ALSO TAKES ONE ROMBERG STEP FOR EXTRA ACCURACY.
C GET READY:
            ROMBRG=INTGRL
            SWAP=-1
 100        CONTINUE
C FIND THE INSIDE INTEGRAL(OVER VOLUME) FOR COUPLING PARAMETERS
C BETWEEN ZERO AND ONE.
      CALL
INSIDE(ALPHA,NBIG,NM,DR,IPOT,RSOFTD,EPSI,RO,TRED,LAMBDA,TUIJ,
     $AWCO,PSI,G,DIRECT,PANEL,ERROR,SIGMA,GCAA,GCAB,PAIRTP,
     $BATHTP,DIRTP,JP)
C               WRITE(NOUT2,*)LAMBDA,PANEL
               IF(ERROR.EQ.0) THEN
C INTEGRATION OVER COUPLING PARAMETER IS DONE WITH THE TRAPAZOIDAL
C RULE.
                  INTGRL=INTGRL+(2.0D0*PANEL)
                  LAMBDA=LAMBDA+DELTA
                  ICOUNT=ICOUNT+1
C SAVE UP EVERY OTHER PANEL FOR THE ROMBERG EXTRAPOLATION:
                  OFF=SWAP+1
                  ROFF=OFF
                  ROMBRG=ROMBRG+(ROFF*PANEL)
C       WRITE(NOUT2,*)LAMBDA,INTGRL,ROMBRG
                  SWAP=-1*SWAP
               END IF
C BE CAREFULL, THING DOESN'T WORK IF NUMPAN=1 (OR 2 WITH ROMBERG).
         IF((ICOUNT.LE.(NUMPAN-1)).AND.(ERROR.EQ.0))
     $GO TO 100
            IF(ERROR.EQ.0) THEN
```

```
C CALCULATE THE INSIDE INTEGRAL FOR THE FULLY DECOUPLED TEST PARTICLE
C WHICH IS WCA REPULSIVE
C (THE FULLY COUPLED TEST PARTICLE WAS LENNARD-JONES).
      CALL
INSIDE(ALPHA,NBIG,NM,DR,IPOT,RSOFTD,EPSI,RO,TRED,LAMBDA,TUIJ,
     $AWCO,PSI,G,DIRECT,PANEL,ERROR,SIGMA,GCAA,GCAB,PAIRTP,
     $BATHTP,DIRTP,JP)
C                WRITE(NOUT2,*)LAMBDA,PANEL
                IF(ERROR.EQ.0) THEN
                   INTGRL=INTGRL+PANEL
                   ROMBRG=ROMBRG+PANEL
C      WRITE(NOUT2,*)LAMBDA,INTGRL,ROMBRG
                   INTGRL=(INTGRL*DABS(DELTA))/2.0D0
                   ROMBRG=(ROMBRG*DABS(DELTA))
C      WRITE(NOUT2,*)LAMBDA,INTGRL,ROMBRG
C MAKE THE ROMBERG EXTRAPOLATION TO THE LIMIT- GET FOURTH
C ORDER ACCURACY!:
                   INTGRL=INTGRL+((INTGRL-ROMBRG)/3.0D0)
C      WRITE(NOUT2,*)LAMBDA,INTGRL
C NOTE: I'M ASSUMING THAT YU HAS BEEN DIVIDED BY KT ALREADY, THAT
C IS THAT "PSI" INCLUDED A FACTOR OF 1/KT.
C
C CALCULATE THE TAIL CORRECTION TO THE COUPLING INTEGRAL. INTEGRATE
C OVER THE RANGE WHERE THE TEST PARTICE  R.D.F. IS APPROXIMATELY 1.0.
         IFUNC=2
C ABSOLUTE RATHER THAN REDUCED TEMPERATURE IS USED IN THIS CALL TO
C SUBROUTINE TAIL. ALSO ALL PARMS HAVE UNITS IN THIS CALL.
         CALL TAIL(IFUNC,DR,IPOT,TEMP,KEPSI,SOFTD,
     $RO,TPARTS,ERROR)
                   YU=INTGRL+TPARTS
C CALCULATE THE IDEAL GAS CONTRIBUTION TO THE CHEMICAL POTENTIAL
C DIVIDED BY KT.
                   YUSTR=YUIDL(IPOT,MW,TEMP,RO,SOFTD)
C                  WRITE(NOUT2,*)YUSTR
C CALCULATE THE HARD CORE CONTRIBUTION TO THE SOLUTE CHEMICAL POTENTIAL
C DIVIDED BY KT.
      CONVDI=0.00001D0
      CONVNR=0.00001D0
      CALL CEMREP(ALPHA,NBIG,NM,DR,IPOT,RSOFTD,EPSI,
     $SOFTD,ASIGMA,RO,TRED,TUIJ,AWCO,PSI,G,DIRECT,TOTAL,CORF1,CORF2,
     $PAIRO,BATHO,DIRO,SGCAA,SGCAB,PANEL,ERROR)
                   IF(ERROR.EQ.0) THEN
                      YUHS=YUCOR(IPOT,PANEL,YUSTR,RO,ASIGMA,SOFTD)
C YU= THE CHEMICAL POTENTIAL OF THE SOLUTE DIVIDED BY KT.
                      YU=YU+YUHS
C COMPUTE THE FREE ENERGY DIFFERENCE BETWEEN THE PROCESS OF INSERTING
C A HARD SPHERE AND THE PROCESS OF INSERTING A WCA (SOFTLY) REPLUSIVE
C PARTICLE (=INT1+INT2). INT1 IS THE CONTRIBUTION TO THE WORK OF
C SOFTENING/KT DUE TO INTERACTIONS BETWEEN SPECIES 1 IN THE BATH AND
C THE TEST PARTICLE. INT2 IS THE CONTRIBUTION DUE TO SPECIES 2 - TEST
C PARTICLE INTERACTIONS.
C PAIRTP: PAIR CORRELATION FUNCTIONS ABOUT THE WCA REPULSIVE TEST
C PARTICLE.
C PAIRO: PAIR CORRELATION FUNCTIONS ABOUT THE EFFECTIVE HARD SPHERE.
                      CALL INTGRD(NBIG,IPOT,DR,RO,PAIRTP,PAIRO,BATHTP,
     $                            BATHO,DIRTP,DIRO,INT1,INT2,E1,E2,
     $                            SIGMA)
C                     WRITE(NOUT2,190)CORF1,CORF2
```

```
C 190                 FORMAT(/1X,'FOR CORF1= ',D13.6,' CORF2= ',D13.6)
C                     WRITE(NOUT2,192)YU,INT1,INT2
C 192          FORMAT(3X,'MUO= ',D13.6,' INT1= ',D13.6,' INT2= ',D13.6)
C                     WRITE(NOUT2,194)YU+INT1+INT2
C 194                 FORMAT(3X,'TOTAL= ',D13.6)
                      YU=YU+INT1+INT2
                   END IF
             END IF
        END IF
        END IF
C       WRITE(NOUT2,200)ERROR
C 200 FORMAT(/1X,'CEMPOT MISSION ACCOMPLISHED. ERROR= ',I3)
        RETURN
        END
C ******************************************************************
C          SUBROUTINE CEMREP
C          PURPOSE-CALCULATES THE WORK OF INFLATING AN INSERTED HARD
C          SPHERE FROM A RADIUS OF ZERO TO A RADIUS EQUAL TO THE
C          EFFECTIVE DIAMETER/2.
C
C          DATE 3/14/89
C          CODED BY DAVID PFUND
C
C          THIS ROUTINE CALLS: SUBROUTINE INSIDE- CALCULATES THE INTEGRAL
C                              OVER VOLUME OF THE PRODUCT OF THE
C                              PERTURBING POTENTIALS AND THE ESTIMATED
C                              PAIR CORRELATION FUNCTIONS FOR THE TEST
C                              PARTICLE.
C                              FUNCTION XI3- TO COMPUTE THE
C                              PACKING FRACTION WHICH
C                              APPEARS IN THE SPT.
C ******************************************************************
        SUBROUTINE CEMREP(ALPHA,NBIG,NM,DR,IPOT,RSOFTD,EPSI,
       $SOFTD,ASIGMA,RO,TRED,TUIJ,AWCO,PSI,G,DIRECT,TOTAL,CORF1,CORF2,
       $PAIRO,BATHO,DIRO,SGCAA,SGCAB,INTGRL,ERROR)
        IMPLICIT REAL*8(A-H,O-Z)
        REAL*8 RO(3)
        REAL*8 RHO(3)
        REAL*8 ASIGMA(3)
        REAL*8 SIGMA(3),EPSI(3)
        REAL*8 SOFTD(3)
        REAL*8 SIG(3)
        REAL*8 RSOFTD(3)
        REAL*8 PSI(2048,3)
        REAL*8 TUIJ(2048,3),AWCO(2048,3)
        REAL*8 G(2048,3),PAIR(2048,3),DIRECT(2048,3)
        REAL*8 TOTAL(2048,3),BATH(2048,3)
        REAL*8 PAIRO(2048,3),BATHO(2048,3)
        REAL*8 PAIRTP(2048,3)
        REAL*8 BATHTP(2048,3)
        REAL*8 DIRTP(2048,3),DIRO(2048,3)
        REAL*8 TRED
        REAL*8 ALPHA
        REAL*8 CORF1,CORF2
        REAL*8 INTGRL,ICRUDE
        REAL*8 GCAA,GCAB
        REAL*8 DR
        REAL*8 LAMBDA
```

```
      INTEGER NBIG,NM
      INTEGER IPOT,JP
      INTEGER NUMPAN,ICOUNT,ERROR
      INTEGER SWAP,OFF
      INTEGER COUNT
      COMMON/LUDOL/PI
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
      DATA NSTEP/2/
C     WRITE(NOUT2,*)NBIG,NM,DR,IPOT
C     WRITE(NOUT2,*)SOFTD(1),SOFTD(2),SOFTD(3)
C     WRITE(NOUT2,*)EPSI(1),EPSI(2),EPSI(3)
C     WRITE(NOUT2,*)RSOFTD(1),RSOFTD(2),RSOFTD(3)
C     WRITE(NOUT2,*)TRED
C     WRITE(NOUT2,*)RO(1),RO(2),RO(3)
C     WRITE(NOUT2,*)JP,ALPHA,CORF1,CORF2
C     WRITE(NOUT2,*)ASIGMA(1),ASIGMA(2),ASIGMA(3)
      INTGRL=0.0D0
      SIGMA(1)=ASIGMA(1)/SOFTD(1)
      SIGMA(2)=ASIGMA(2)/SOFTD(1)
      SIGMA(3)=ASIGMA(3)/SOFTD(1)
      JP=2
C DAA = DISTANCE OF CLOSEST APPROACH OF CENTERS BETWEEN THE TEST
C       PARTICLE AND LIKE MOLECULES IN THE BATH.
C DAB = UNLIKE DISTANCE OF CLOSEST APPROACH.
      IF(IPOT.EQ.0) THEN
C SPECIES 2 IS TEST PARTICLE.
         RAF=SIGMA(2)/2.0D0
         DAA=SIGMA(2)
         RHOA=RO(2)
         RHOB=RO(1)
      ELSE
C SPECIES 1 IS TEST PARTICLE.
         RAF=SIGMA(1)/2.0D0
         DAA=SIGMA(1)
         RHOA=RO(1)
         RHOB=RO(2)
      END IF
      DAB=SIGMA(3)
C INSERTED HARD SPHERE IS FULL SIZED:
      LAMBDA=-1.0D0
      CALL
INSIDE(ALPHA,NBIG,NM,DR,IPOT,RSOFTD,EPSI,RO,TRED,LAMBDA,TUIJ,
     $AWCO,PSI,G,DIRECT,PANEL,ERROR,SIGMA,SGCAA,SGCAB,PAIRO,
     $BATHO,DIRO,JP)
      WRITE(NOUT2,*)SIGMA(1),SIGMA(2),SIGMA(3)
C     WRITE(NOUT2,*)SGCAA,SGCAB
      IF(ERROR.EQ.0) THEN
         F1=4.0D0*PI*((DAA*DAA*RHOA*SGCAA)+(DAB*DAB*RHOB*SGCAB))
C        WRITE(NOUT2,*)F1
         FINT=F1
         R1=DAA-RAF
C START PARTICLE SCALING. REDUCE DISTANCES OF CLOSEST APPROACH BY
C NSTEP*DR. USE OF NSTEP=2 GIVES THE NUMERICAL INTEGRAL TO AT WORST
C FOUR DECIMAL PLACES OF ACCURACY.
         IF(IPOT.EQ.0) THEN
            SIG(1)=SIGMA(1)
            SIG(2)=SIGMA(2)-(DR*NSTEP)
            DAA=SIG(2)
```

```
         ELSE
            SIG(2)=SIGMA(2)
            SIG(1)=SIGMA(1)-(DR*NSTEP)
            DAA=SIG(1)
         END IF
         SIG(3)=SIGMA(3)-(DR*NSTEP)
         DAB=SIG(3)
         COUNT=0
  100    CONTINUE
         IF(DAA.LE.(1.4D0*RAF)) THEN
            JP=2
         END IF
      CALL
INSIDE(ALPHA,NBIG,NM,DR,IPOT,RSOFTD,EPSI,RO,TRED,LAMBDA,TUIJ,
     $AWCO,PSI,G,DIRECT,PANEL,ERROR,SIG,GCAA,GCAB,PAIRTP,
     $BATHTP,DIRTP,JP)
            WRITE(NOUT2,*)SIG(1),SIG(2),SIG(3)
C           WRITE(NOUT2,*)GCAA,GCAB
            IF(ERROR.EQ.0) THEN
               F0=4.0D0*PI*((DAA*DAA*RHOA*GCAA)+(DAB*DAB*RHOB*GCAB))
C              WRITE(NOUT2,*)F0
               R0=DAA-RAF
               INTGRL=INTGRL+((F1+F0)*(R1-R0)/2.0D0)
               COUNT=COUNT+1
               F2=F1
               R2=R1
               F1=F0
               R1=R0
C KEEP REDUCING THE DIAMETERS UNTIL THE TEST PARTICLE IS A HARD
C POINT (OCCURS WHEN THE LIKE DISTANCE OF CLOSEST APPROACH = RAF).
               IF(IPOT.EQ.0) THEN
                  SIG(1)=SIGMA(1)
                  SIG(2)=SIG(2)-(DR*NSTEP)
                  DAA=SIG(2)
               ELSE
                  SIG(2)=SIGMA(2)
                  SIG(1)=SIG(1)-(DR*NSTEP)
                  DAA=SIG(1)
               END IF
               SIG(3)=SIG(3)-(DR*NSTEP)
               DAB=SIG(3)
            END IF
         IF((DAA.GT.(1.0000001D0*RAF)).AND.(ERROR.EQ.0)) GO TO 100
         IF(ERROR.EQ.0) THEN
C COMPUTE FINAL FUNCTION VALUE FROM THE SPT FORMULA FOR SPHERE SIZE
C OF ZERO.
            IF(IPOT.EQ.0) THEN
               SIG(1)=SIGMA(1)
C NOTE: IF THE TEST PARTICLE DIAMETERS DON'T FALL ON THE MESH POINTS
THE
C THING WON'T WORK (CONTACT MAYER FACTORS AND RDF'S WILL BE BAD).
C CAREFULL !!!
               SIG(2)=SIGMA(2)/2.0D0
               DAA=SIG(2)
               SIG(3)=SIGMA(1)/2.0D0
            ELSE
               SIG(2)=SIGMA(2)
               SIG(1)=SIGMA(1)/2.0D0
```

```
            DAA=SIG(1)
            SIG(3)=SIGMA(2)/2.0D0
         END IF
         DAB=SIG(3)
      CALL
INSIDE(ALPHA,NBIG,NM,DR,IPOT,RSOFTD,EPSI,RO,TRED,LAMBDA,TUIJ,
     $AWCO,PSI,G,DIRECT,PANEL,ERROR,SIG,GCAA,GCAB,PAIRTP,
     $BATHTP,DIRTP,JP)
      WRITE(NOUT2,*)SIG(1),SIG(2),SIG(3)
C     WRITE(NOUT2,*)GCAA,GCAB
         IF(ERROR.EQ.0) THEN
            FO=4.0D0*PI*((DAA*DAA*RHOA*GCAA)+(DAB*DAB*RHOB*GCAB))
            ICRUDE=(FINT+F1)*(RAF-R1)/2.0D0
            XCOUNT=COUNT
C           WRITE(NOUT2,*)COUNT
            XCOUNT=XCOUNT*XCOUNT
C           WRITE(NOUT2,*)ICRUDE,INTGRL
            DELI=INTGRL-ICRUDE
            INTGRL=INTGRL+(DELI/((XCOUNT)-1.0D0))
C           WRITE(NOUT2,*)INTGRL
            PIECE=((F1+FO)*(R1/2.0D0))
C           WRITE(NOUT2,*)PIECE
            FIX=(F2/R2)-(F1/R1)-(FO/R2)+(FO/R1)
            FIX=FIX/(R2-R1)
            PIECE=PIECE-(FIX*R1*R1*R1/3.0D0)
C           WRITE(NOUT2,*)PIECE
            INTGRL=INTGRL+PIECE
         END IF
      END IF
      END IF
C     WRITE(NOUT2,200)ERROR
C 200 FORMAT(/1X,'CEMREP MISSION ACCOMPLISHED. ERROR= ',I3)
      RETURN
      END
C ******************************************************************
C        FUNCTION YUCOR
C        PURPOSE- CALCULATES THE HARD SPHERE CONTRIBUTION TO THE
C                 SOLUTE CHEMICAL POTENTIAL. THE PROCEDURE USES THE
C                 EXPRESSIONS FROM SCALED PARTICLE THEORY.
C
C        DATE 6/17/87
C        REVISED 3/14/88 TO USE THE CONTACT VALUES OF THE CAVITY
C                        RDF'S OBTAINED FROM THE SOLUTION OF INTEGRAL
C                        EQUATIONS FOR THE TEST PARTICLE TO IMPROVE
C                        THE ESTIMATE OF THE WORK OF CAVITY FORMATION.
C                3/14/89 TO DUMP SPT EXCEPT FOR WORK OF INSERTING A
C                        POINT PARTICLE.
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS: FUNCTION X13- CALCULATES THE PACKING
C                            FRACTION.
C ******************************************************************
      REAL FUNCTION YUCOR(IPOT,PANEL,YUSTR,RO,ASIGMA,SOFTD)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 ASIGMA(3)
      REAL*8 SOFTD(3)
      REAL*8 PRESSU
      REAL*8 YUSTR
```

```
      REAL*8 RO(3)
      REAL*8 RHO(3)
      REAL*8 Y3
      REAL*8 WORK
      REAL*8 HARD3,SOFT3
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
C     WRITE(NOUT2,*)YUSTR
      SOFT3=SOFTD(1)*SOFTD(1)*SOFTD(1)
      HARD3=ASIGMA(1)*ASIGMA(1)*ASIGMA(1)
      RHO(1)=RO(1)*HARD3/SOFT3
      RHO(2)=RO(2)*HARD3/SOFT3
      RHO(3)=RO(3)*HARD3/SOFT3
      Y3=X13(RHO,ASIGMA)
C WORK TO FORM A CAVITY OF DIAMETER EQUAL TO THE SOLUTE DIAMETER,
C PLUS THE LIBERATION ENERGY EQUALS HARD SPHERE SOLUTE CHEMICAL
C POTENTIAL.
C     WRITE(NOUT2,*)YUSTR,PRES,WORK
      WORK=PANEL-DLOG(1.0D0-Y3)
      WRITE(NOUT2,*)Y3,PANEL,WORK
      YUCOR=YUSTR+WORK
      RETURN
      END
C ***********************************************************************
C        SUBROUTINE TRAP
C        PURPOSE-ESTIMATES THE DIFFERENCE BETWEEN THE WCA REFERENCE
C                CONTRIBUTION TO THE CHEMICAL POTENTIAL AND THE
C                WORK OF INSERTING A HARD SPHERE.  THE PROCEDURE
C                INTEGRATES FROM ZERO TO THE MESH POINT LEFT OF THE
C                DIAMETER, THEN FROM THE MESH PT. TO THE RIGHT OF
C                THE DIAMETER TO INFINITY. IN THE GAP SURROUNDING
C                THE DISCONTINUITY POLYNOMIALS ARE EXTRAPOLATED TO
C                CONTACT ON EACH SIDE, INTEGRATED, THEN ADDED TO
C                THE RESULT.  THE FUNCTIONS BEING INTEGRATED ARE
C                SIMILAR TO THOSE OF LADO.
C
C        DATE 6/7/87
C        REVISED 6/29/89 ADDED A SECOND ORDER EXTRAPOLATION TO CONTACT.
C                        CORRECTED AN ERROR IN THE COMPUTATION OF "K".
C        CODED BY DAVID PFUND
C
C        THIS ROUTINE CALLS: -
C ***********************************************************************
      SUBROUTINE TRAP(NBIG,DR,FUNCT,DIA,INTGRL)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 DR,DIA
      REAL*8 FUNCT(NBIG)
      REAL*8 INTGRL
      REAL*8 XK,ROFF,ROMBRG,SAV1,SAV2
      REAL*8 RK,RK1,REST,THING
      INTEGER I,NBIG
      INTEGER K,SWAP,OFF
      COMMON/DEVICE/NIN,NOUT1,NOUT2,INOPT
      INTGRL=0.0D0
      XK=(DIA+0.000000001D0)/DR
      K=XK
C      WRITE(NOUT2,*)K
C WILL BE USING TRAPAZOIDAL RULE PLUS ROMBERG EXTRAPOLATION.
C INTEGRATE LEFT OF CONTACT POINT.
```

```
C IF THE DIAMETER LIES PRECISELY ON A MESH POINT THE GIVEN
C VALUE OF FUNCT(K) IS ASSUMED TO BE THAT FROM THE RIGHT
C BRANCH OF THE FUNCTION.
      SAV1=FUNCT(1)
      ROMBRG=FUNCT(1)
      SWAP=-1
      DO 100 I=2,K-2
         SAV1=SAV1+(2.0D0*FUNCT(I))
         OFF=SWAP+1
         ROFF=OFF
         ROMBRG=ROMBRG+(ROFF*FUNCT(I))
         SWAP=-1*SWAP
  100 CONTINUE
      SAV1=SAV1+FUNCT(K-1)
      ROMBRG=ROMBRG+FUNCT(K-1)
      SAV1=SAV1*DR/2.0D0
      ROMBRG=ROMBRG*DR
C      WRITE(NOUT2,*)SAV1,ROMBRG
      SAV1=SAV1+((SAV1-ROMBRG)/3.0D0)
C      WRITE(NOUT2,*)SAV1
C
C INTEGRATE RIGHT OF CONTACT POINT.
      SAV2=FUNCT(K+1)
      ROMBRG=FUNCT(K+1)
      SWAP=-1
      DO 200 I=K+2,NBIG-1
         SAV2=SAV2+(2.0D0*FUNCT(I))
         OFF=SWAP+1
         ROFF=OFF
         ROMBRG=ROMBRG+(ROFF*FUNCT(I))
         SWAP=-1*SWAP
  200 CONTINUE
      SAV2=SAV2+FUNCT(NBIG)
      ROMBRG=ROMBRG+FUNCT(NBIG)
      SAV2=SAV2*DR/2.0D0
      ROMBRG=ROMBRG*DR
C      WRITE(NOUT2,*)SAV2,ROMBRG
      SAV2=SAV2+((SAV2-ROMBRG)/3.0D0)
C      WRITE(NOUT2,*)SAV2
C ESTIMATE INTEGRAL FROM ONE MESH POINT LEFT OF
C CONTACT TO ONE MESH POINT RIGHT OF CONTACT.
      XK=K
      RK=(XK-1.0D0)*DR
      RK1=(XK+1.0D0)*DR
C     WRITE(NOUT2,*)XK,RK,RK1
      REST=(FUNCT(K-1)*(DIA-RK))-(FUNCT(K+1)*(DIA-RK1))
      THING=(DIA*DIA)-(2.0D0*DIA*RK)+(RK*RK)
      REST=REST+(((FUNCT(K-1)-FUNCT(K-2))/(2.0D0*DR))*THING)
      THING=(DIA*DIA)-(2.0D0*DIA*RK1)+(RK1*RK1)
      REST=REST-(((FUNCT(K+2)-FUNCT(K+1))/(2.0D0*DR))*THING)
C ADD ON QUADRATIC TERMS:
      THING=(DIA-RK)*(DIA-RK)*(DIA-RK)/(DR*DR*DR)
      REST2=(FUNCT(K-1)-(2.0D0*FUNCT(K-2))+FUNCT(K-3))*(THING*DR/6.0D0)
      REST=REST+REST2
      THING=(DIA-RK1)*(DIA-RK1)*(DIA-RK1)/(DR*DR*DR)
      REST2=(FUNCT(K+1)-(2.0D0*FUNCT(K+2))+FUNCT(K+3))*(THING*DR/6.0D0)
      REST=REST-REST2
C      WRITE(NOUT2,*)REST
```

INTERNAL DISTRIBUTION

1. J. M. Begovich
2. J. T. Bell
3. C. H. Brown
4. C. H. Byers
5. H. D. Cochran
6. E. D. Collins
7. A. G. Croff
8. R. K. Genung
9. J. R. Hightower
10. E. K. Johnson
11. T. H. Row
12. C. D. Scott
13. M. G. Stewart
14. Central Research Library

15–16. Laboratory Records

17. Laboratory Records, RC
18. ORNL Y-12 Technical Library
    Document Reference Section
19. ORNL Patent Section

EXTERNAL DISTRIBUTION

20. Office of Assistant Manager for Energy Research and Development, DOE-ORO, Oak Ridge, TN 37831
21. R. L. Gordon, Office of Basic Energy Sciences, DOE, Room G-339/GTN, Washington, D.C. 20454
22. F. Dee Stevenson, Office of Basic Energy Sciences, DOE, Room G-341/GTN, Washington, D.C. 20454
23. L. L. Lee, Department of Chemical Engineering and Materials Science, University of Oklahoma, Norman, OK 73019

24–28. D. M. Pfund, 1751 Chester, Lansing, MI 48913

29–38. Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831