New Fluctuation Theory Approaches for Calculation of Total, Partial Molar Properties, and Phase Equilibria of Mixtures

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ABSTRACT
This paper consists of the review of the contributions of the authors and their collaborators on the development of new fluctuation theory approaches for calculation of total, partial molar properties, and phase equilibria of mixtures. These contributions consist of three parts:

(i) Development of new mixing rules based on the fluctuation and conformal solution theories. The resulting mixing rules are shown to be applicable for calculation of properties of molecular fluids with varying size and interaction energy differences.

(ii) Development of a new fluctuation theory technique for derivation of analytic expressions for chemical potentials and activity coefficients of components of mixtures. This new technique is based upon the newly developed exact relations among the mixture direct correlation function integrals and the closures for unlike-interaction direct correlation function integrals. It is shown that vapor-liquid and liquid-liquid phase equilibria of mixtures can be predicted accurately by this technique. It is also demonstrated that this technique is capable of predicting phase splitting in liquid mixtures quite accurately.

(iii) Introduction of the concept of local particle numbers and compositions with respect to fluctuation integrals. This has also resulted in a rigorous definition of the radius of the sphere of influence of local compositions which can be utilized in order to specify this radius at different thermodynamic state conditions.

One major advantage of these new fluctuation theory approaches is the fact that it is now possible to produce analytic expressions for total and partial molar properties of mixtures at, both, infinite dilution and finite concentrations. Also because of their independence from the nature of intermolecular interaction potentials in solutions these approaches are applicable for mixtures consisting of complex molecules with or without intermolecular polar and association forces.

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INTRODUCTION

One of the interesting problems in statistical mechanics is the prediction of mixture properties from those of the pure components comprising the mixture. There exist a number of techniques to do this. The conformal solution theory (Brown 1957; Massih and Mansoori 1983) has offered a practical and rather accurate approach to this problem. In this theory it is assumed there exists a hypothetical pure fluid that has the same properties as those of the mixture at the same density and temperature. This hypothetical pure fluid is described by the same equation of state as the pure fluids which form the mixture. The parameters of the hypothetical pure fluid are related to the parameters of the components of the mixture, composition, and possibly temperature and density by what are usually called the mixing rules. Many mixing rules have been suggested in the literature. Some are based on empirical grounds, and others are derived by making certain assumptions about the mixture radial distribution functions (Mansoori and Ely 1985; Mansoori 1986; Mansoori and Leland 1972). The latter approach will be used here to derive mixing rules using the fluctuation theory of mixtures.

By joining the concepts of the conformal solution theory and the fluctuation theory of mixtures it is possible to derive mixing rules which can be then used for mixture property calculations (Hamad et al, 1987). Two sets of calculations using these mixing rules are performed and reported here: In the first set an equimolar mixture of hard-spheres is studied. The deviations of the Helmholtz free energy, the compressibility factor and the isothermal compressibility from the exact hard-sphere mixture properties are calculated as a function of reduced density at three different molecular size ratios. In the second set of calculations the mixing rules are used to derive the Henry's constant for a binary mixture of Lennard-Jones fluid. The Henry's constant is calculated for: (i) The same energies of interaction $\varepsilon_{ij}$, but at different size ratios; (ii) The same molecular sizes $\sigma_{ij}$, but at different energies of interaction. The calculations are compared with the results of the van der Waals mixing rules and the computer simulation data.

Definition of activity coefficients provides a convenient way of describing the non-idealities encountered in solution thermodynamics (Guggenheim 1952; Chao and Greenkorn 1975; Kreglewski 1984). The activity coefficient of component $i$, $\gamma_i$, in a mixture is defined by the following relation

$$\ln (x_i \gamma_i) = (\mu_i - \mu_{io})/kT$$  \hspace{1cm} (1)

where $\mu_i$ is the chemical potential of component $i$ in the mixture, $\mu_{io}$ is the standard state chemical potential of $i$, $k$ is the Boltzmann constant and $T$ is the absolute temperature. There exist very limited theoretical understanding through which one can derive expressions for activity coefficients using the principles of statistical mechanics (Haile and Mansoori 1983). As a result, most of the available analytic expressions for activity coefficients are empirical or semi-empirical which are based on classical thermodynamic correlations of excess properties.
Lattice theories of statistical mechanics were successful in providing us with analytic expressions for activity coefficients (Guggenheim 1952). There exist numerous group-contribution expressions for activity coefficients which are based on the lattice theories of statistical mechanics. Due to the high degree of combinatorial approximations which are used in the lattice theories, their resulting activity coefficient expressions have met with limited success.

Another statistical mechanical route for the development of analytic expressions of activity coefficients is the use of the Gibbs, or NPT, ensemble (Mansoori 1980). The Gibbs ensemble, joined with the conformal solution theory of statistical mechanics, have provided us with the formalism in systematically deriving analytic expressions of activity coefficients. The success of this technique is presently limited to simple molecular fluid mixture for which the intermolecular potential energy functions are available. In the case of polar mixtures and mixtures possessing hydrogen-bonding species the route through the Gibbs ensemble is subject to further investigation.

The third statistical mechanical route to activity coefficients is the fluctuation solution theory of statistical mechanics (Kirkwood and Buff 1951). By utilizing this theory, activity coefficients in solutions are obtained from the relations between the chemical potentials, \( \mu_i \), and the fluctuation integrals, \( G_{ij} \)'s. According to this theory the expression for the chemical potential of component \( i \), \( \mu_i \), in a binary mixture takes the following form:

\[
x_i \left[ \frac{\partial \mu_i}{\partial x_i} \right]_{P,T} = kT \left[ \frac{1 - x_1 x_2 \rho (G_{11} + G_{22} - 2G_{12})}{1 + x_1 x_2 \rho (G_{11} + G_{22} - 2G_{12})} \right]
\] (2)

where

\[
G_{ij} = \int_{0}^{\infty} [g_{ij}(r) - 1] 4\pi r^2 dr \tag{3}
\]

\( x_i \) is the mole fraction of component \( i \), \( P \) is the pressure, \( \rho \) is the density and \( g_{ij}(r) \) is the radial distribution function of the pair of molecules \( i \) and \( j \). Expression for \( \left[ \frac{\partial \mu_i}{\partial x_i} \right]_{P,T} \) are also written in terms of direct correlation integrals

\[
x_i \left[ \frac{\partial \mu_i}{\partial x_i} \right]_{P,T} = kT \frac{1 - x_1 \rho C_{11} - x_2 \rho C_{22} + x_1 x_2 \rho^2 (C_{11} C_{22} - C_{12}^2)}{1 - \sum x_i x_j \rho C_{ij}} \tag{4}
\]

where

\[
C_{ij} = \int_{0}^{\infty} c_{ij}(r) 4\pi r^2 dr \tag{5}
\]

and the direct correlation function, \( c_{ij}(r) \), is defined with respect to the radial
distribution function, \( g_{ij}(r) \), in an n-component mixture by

\[
c_{ij}(r_{12}) = \left[ g_{ij}(r_{12})^{-1} \right] - \sum_{k=1}^{n} x_k \rho \int_{\Omega} c_{ik}(r_{13}) [g_{jk}(r_{23})^{-1}] \, dr_3. \tag{6}
\]

Finally, the activity coefficient, \( \gamma_i \), of component i is obtained by integrating Eqs. (2) or (4) with respect to the mole fraction. Equation (1) then becomes

\[
\ln \gamma_i = \int (1-x_i) \rho (G_{11} + G_{22} - 2G_{12}) \left[ 1 + x_1 x_2 \rho (G_{11} + G_{22} - 2G_{12}) \right]^{-1} \, dx_i \tag{7}
\]

This equation, in principle, can be used to calculate the activity coefficients provided information about \( G_{ij} \) integrals are available. One major advantage of this formalism is the fact that there is no need for information about the intermolecular potential energy functions of species of the mixture as it is the case for other mixture theories. However, the lack of sufficient knowledge about \( G_{ij} \) (or \( C_{ij} \)) integrals and their relationships has limited the utility of this theory. For mixtures of species with model intermolecular potential energy functions it has been possible to calculate \( G_{ij} \) (or \( C_{ij} \)) integrals and as a result the activity coefficients from statistical mechanics. Eq. (7) has had also some utility for complex solutions (mixtures consisting of highly asymmetric, polar, and hydrogen-bonding species) only at infinite dilutions.

The fourth statistical mechanical route to activity coefficients is a new fluctuation theory introduced recently (Hamad and Mansoori 1989) that provides us with a strong tool for developing analytic expressions for activity coefficients of multicomponent mixtures using Eq. (7) and a number of newly discovered characteristics of direct correlation function integrals in mixtures. This theory is shown to be applicable to complex multicomponent mixtures at finite concentrations as well as solutions at infinite dilutions. It has also been applied for phase equilibrium (vapor-liquid and liquid-liquid equilibrium) of mixtures with success.

There has been a great deal of interest during the past few decades in the concept of local composition and macroscopic thermodynamic properties of mixtures (Wilson 1964; Renon and Prausnitz 1968; Prausnitz 1969; McDermott and Ashton 1977; Nakanishii, et al. 1979, 1982, 1983; Mollerup 1981; Kemeny and Rasmussen 1981; Whiting and Prausnitz 1982; Fischer 1983; Mathias and Copeman 1983; Hu et al. 1983; Lee et al. 1983; Gierycz and Nakanashii 1984; Hoheisel and Kohler 1984; see also Rubio et al's chapter in this book). These analyses have been based on lattice theories of fluids, distribution functions, computer simulation studies, and empirical interpretation of local composition. In a more recent report it is demonstrated that the fluctuation theory can be used to interpret the concept of local compositions from statistical mechanical point of view (Mansoori and Ely 1985). In this work it is also shown how common liquid theory approximations such as the

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composition concept in a theoretically rigorous manner are introduced using explicit relation for isothermal compressibility in terms of the local particle numbers. The isothermal compressibility of a mixture is given by (Kirkwood and Buff 1951)

$$\kappa_T = \frac{1}{|B|} \left\{ \rho^2 kT \sum x_i x_j |B|_{ij} \right\}$$

(8)

where $B$ is a $n \times n$ matrix with its elements $B_{ij} = \rho x_i [\delta_{ij} + x_j G_{ij}]$ and $|B|_{ij}$ is the cofactor of the element $B_{ij}$ in the determinant $|B|$, $\delta_{ij}$ is the Kronecker delta, and $G_{ij}$ is the fluctuation integral as defined by Eq. (3).

Different phenomenological and statistical mechanical approximations to local compositions are presented and compared and expressions for the partial molar volume and chemical potential of a mixture component in terms of local particle numbers are derived (Mansoori and Ely 1985). In the present state of the art review the part of the paper of Mansoori and Ely which is related to the fluctuation theory interpretation of the local composition concept will be discussed.

**FLUCTUATION THEORY OF MIXING RULES**

As it is shown in the first paper in this monograph the total thermodynamic properties of fluids are related to the radial distribution function by the energy, virial and compressibility equations of statistical mechanics. The statistical mechanical equation for the internal energy and virial equations require the assumption of a form for the intermolecular potential energy function. This is not the case with the compressibility equation, which is independent of this assumption. The statistical mechanical compressibility equation for pure fluids and mixtures are also reported in the first paper of this monograph.

To derive mixing rules (Mansoori and Ely 1985; Hamad, et al. 1987) from energy and virial equations we equate the internal energy and compressibility factor of the mixture to the same properties of the hypothetical pure fluid. Then, we scale the resulting equations using the respective size parameters to get the following set of two equations (Mansoori 1986):

$$\sigma_x^3 e_x \int_0^\infty \frac{g_{x}(r/\sigma_x)4\pi(r/\sigma_x)^2d(r/\sigma_x)}{e_{x}(r/\sigma_x)}$$

$$= \sum_{i=1}^{n} \sum_{j=1}^{n} \sigma_{ij}^3 e_{ij} x_i x_j \int_0^\infty \phi_{ij}(r/\sigma_{ij})g_{ij}(r/\sigma_{ij})4\pi(r/\sigma_{ij})^2d(r/\sigma_{ij})$$

(9)

and

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In the above two equations the subscript x refers to the hypothetical pure fluid, and 
\( \phi = u / \epsilon \) where \( u \) is the pair intermolecular potential and \( -\epsilon \) is the value of this 
potential at its minimum. At this stage let us assume conformality of the 
intermolecular potential energy functions of species of the mixture and the 
hypothetical pure fluid in the following form

\[
u_{ij} = (\epsilon_{ij} / \epsilon_{oo}) \, u_{oo} \, (\sigma_{ij} / \sigma_{oo})
\]

(11)

where the subscript oo indicates a pure reference fluid. In addition to assuming 
conformal potentials, we assume conformality of the radial distribution functions, 
g_{ii'}, of the species of the mixture and the hypothetical pure fluid. According to the 
latter assumption, the scaled radial distribution functions in the mixture and the 
hypothetical pure fluid are all identical (Mansoori 1986), i.e.

\[
g_{11}(r / \sigma_{11}) = g_{22}(r / \sigma_{22}) = \ldots = g_{ij}(r / \sigma_{ij}) = \ldots = g_{xx}(r / \sigma_{xx})
\]

(12)

The above two assumptions will make the integrals in the two sides of Eq.'s (9) and 
(10) equal, and hence, they will cancel from both sides of these equations. Finally 
Eq.'s (9) and (10) will reduce to the following single equation

\[
\sigma_x^3 \epsilon_x = \sum_{i=1}^{n} \sum_{j=1}^{n} \sigma_{ij}^3 \epsilon_{ij} x_i x_j
\]

(13)

In the above derivations it is assumed that the molecular interaction potential 
function has two parameters, \( \epsilon \) and \( \sigma \). Equation (13) gives one relation between 
the parameters of the hypothetical pure fluid (\( \sigma_x \) & \( \epsilon_x \)) and the parameters (\( \sigma_{ij} \) & \( \epsilon_{ij} \)) and compositions (\( x_i \)) in the mixture. To define \( \sigma_x \) and \( \epsilon_x \) uniquely we need another 
relation between (\( \sigma_x \) & \( \epsilon_x \)) and (\( \sigma_{ij} \), \( \epsilon_{ij} \) & \( x_i \)). This second expression can be obtained 
by using the conformal solution approximation for \( g_{ii} \) in the fluctuation integral \( G_{ij} \) 
which can be written in the following form

\[
G_{ij} = \sigma_{ij}^3 \int_{0}^{\infty} [g_{ij}(r^*) - 1] 4\pi r^2 dr^* = (\sigma_{ij}^3 / \sigma_x^3) G_x
\]

(14)

where \( r^* = r / \sigma_{ij} \). Let us also scale the hypothetical pure fluid isothermal 
compressibility equation in the following form
This leads to the relation:

\[ G_{ij} = \Delta_x (\sigma_{ij}/\sigma_x)^3 / \rho \]  \hspace{1cm} (16)

where

\[ \Delta_x = \rho kT / \kappa_{Tx} - 1. \]  \hspace{1cm} (17)

By replacing \( G_{ij} \) as defined by Eq. (16) in the expression for the mixture isothermal compressibility as given by Eq. (8) and derived in the first chapter of this monograph we will derive the following expression

\[ \rho kT \kappa_{Tx} = | \mathbf{B} | / \rho \sum_i x_i \sum_j x_j | \mathbf{B} |_{ij} \]  \hspace{1cm} (18)

where the elements of the determinant \( | \mathbf{B} | \) are given by

\[ B_{ij} = \rho x_i \left[ \delta_{ij} + x_j \Delta_x (\sigma_{ij}/\sigma_x)^3 \right] \]  \hspace{1cm} (19)

Equation (18), which is the second needed relation between \( (\sigma_x & \epsilon_x) \) and \( (\sigma_{ij}, \epsilon_{ij} & \sigma_i; i,j=1,2,...,n) \) is an implicit equation between \( \sigma_x \), which is also dependent on temperature and density, and \( \sigma_{ij} (i,j=1,2,...,n) \). Equations (13) and (18) form the necessary set of mixing rules to relate \( \sigma_x \) and \( \epsilon_x \) to the properties of the mixture. Note that Eq. (13) has the same form as the first (attractive) van der Waals mixing rule (Mansoori and Ely 1985; Mansoori 1986). However, the difference between the two mixing rules comes from Eq. (18) which is also density and temperature dependent.

It is important to realize that since the mixing rule reported as Eq. (18) is temperature and density dependent and it is derived from the compressibility equation it should only be used to calculate the mixture isothermal compressibility \( \kappa_{T} \). Any other thermodynamic property can then be calculated from the appropriate thermodynamic relation between that property and \( \kappa_{T} \). Note that such limitations will not exist for mixing rules which are independent of density and temperature.

As an example, let us write Eq's (13) and (18) for a two component mixture. In this case Eq.(13) will take the following form

\[ \sigma_x^3 \epsilon_x = x_1^2 \sigma_{11}^3 \epsilon_{11} + 2x_1x_2 \sigma_{12}^3 \epsilon_{12} + x_2^2 \sigma_{22}^3 \epsilon_{22} \]  \hspace{1cm} (20)

The determinant \( | \mathbf{B} | \) in Eq.(18) reduces to the following 2x2 determinant
Substituting Eq. (18) in Eq. (21) and solving for $\sigma_x^3$ we get

\[
\sigma_x^3 = (1/2) \left[ \sigma_{x,vdw}^3 - (\sigma_{11}^3 - 2\sigma_{12}^3 + \sigma_{22}^3) x_1 x_2 \Delta x + \left[ (\sigma_{x,vdw}^3 - (\sigma_{11}^3 - 2\sigma_{12}^3 + \sigma_{22}^3) x_1 x_2 \Delta x)^2 + 4(\sigma_{11}^3 - \sigma_{12}^3, \sigma_{12}^3) x_1 x_2 \Delta x \right]^{1/2} \right]
\]

where $\sigma_{x,vdw}^3$ is the second (repulsive) van der Waals mixing rule for molecular diameters in a binary mixture

\[
\sigma_{x,vdw}^3 = x_1^2 \sigma_{11}^3 + 2x_1 x_2 \sigma_{12}^3 + x_2^2 \sigma_{22}^3
\]

Equations (20) and (22) constitute the fluctuation theory mixing rules for binary mixtures while Eq.'s (20) and (23) constitute the van der Waals mixing rules for binary mixtures. These sets of mixing rules will be used later to calculate properties of hard-sphere mixtures and Lennard-Jones mixtures.

CHEMICAL POTENTIALS AND ACTIVITY COEFFICIENTS
A: THE CASE OF P, T, & x AS THE INDEPENDENT VARIABLES.

In deriving chemical potentials and activity coefficients from the fluctuation theory of mixtures when P, T, & x (pressure, temperature, and composition) are the independent variables, we consider a single-phase multi-component mixture consisting of n components. Chemical potential, $\mu_i$, of every species in this mixture is generally a function of n+1 independent variables, i.e.

$\mu_i = \mu_i (T, P, x_1, x_2, \ldots, x_{n-1})$

Using this expression one can write the following expressions between the mixed second derivatives of the chemical potential (Hamad and Mansoori 1989):

\[
\partial[\partial\mu_i / \partial x_j] / \partial \rho = \partial[\partial\mu_i / \partial \rho] / \partial x_j = [\partial \nu_i / \partial x_j]_{\rho,T} \quad i, j = 1, \ldots, n \tag{24}
\]

\[
\partial[\partial\mu_i / \partial x_j] / \partial x_k = \partial[\partial\mu_i / \partial x_k] / \partial x_j \quad i, j, k = 1, \ldots, n \quad \text{and} \quad j \neq k \tag{25}
\]

In the above equations, $\partial \mu_i / \partial x_j$ and partial molar volume, $\nu_i$, are related to the direct correlation function integrals by (Pearson and Rushbrooke 1957; O'Connell 1981)

\[
N_i (\partial \mu_i / \partial N_j)_{T,P,N_{kej}} = kT \left[ \delta_{ij} \sum_{k=1}^{n} x_k (C_{ik} + C_{jk}) + \rho \sum_{k=1}^{n} \sum_{\ell=1}^{n} \sum_{x_k x_\ell} (C_{ik} C_{j\ell} - C_{ij} C_{k\ell}) \right]
\]

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and

$$
\overline{\nu_i} = (p^{-1})(1-p) \sum_{j=1}^{n} x_j C_{ij} / (1-p) \sum_{j=1}^{n} \sum_{k=1}^{n} x_j x_k C_{jk}).
$$

(27)

By replacing Eqs (26) and (27) in Eqs (24) and (25) we will derive a number of expressions between \( C_{ij} \)'s of the mixture.

In an \( n \)-component mixture there exist \( n(n+1)/2 \) direct correlation function integrals which are considered as unknowns in Eqs (24) and (25). Note that there are \( n(n-1) \) relations of the type of Eq. (24) and \( n(n-1)(n-2)/2 \) relations of the type of Eq. (25). Of all these equations only \( n(n+1)/2-1 \) of them are independent. Since there are \( n(n+1)/2 \) unknowns then one additional relation will be needed to determine all the unknowns regardless of the number of components involved. The resulting equations for direct correlation function integrals consist of a set of non-linear partial differential equations. General analytic solution of this set of equations for multi-component mixtures does not seem feasible at the present time. Numerical solution of these equations is involved and lengthy and may require the use of multi-variable finite difference techniques. In what follows we report the analytic solution of these equations for mixtures at low to moderate pressures.

A1: Analytic Solutions for Low to Moderate Pressures: For liquids at low to moderate pressures it may be assumed that the activity coefficient is not dependent on pressure. In mathematical form using Eq. (1) this means

$$
[\partial \ln \gamma_i / \partial P]_{x_i, T} = \left[ \partial (\mu_i - \mu_{i0}) / \partial P \right]_{x_i, T} / kT = 0
$$

As a result of this approximation Eq. (24) reduces to \([\partial \overline{\nu_i} / \partial x_i]_{P,T}=0\), or \(\overline{\nu_i}=v_i\), where \(v_i\) is the molar volume of pure component \(i\). Then Eq. (27) can be written in the following form:

$$
\rho \sum_{j=1}^{n} x_j C_{ij} = 1-v_i \left(1-p \sum_{j=1}^{n} \sum_{l=1}^{n} x_j x_l C_{ij} \right) \quad i=1, \ldots, n
$$

(28)

where \(v_i\) is the molar volume of pure component \(i\). By considering that

$$
\rho \left(1-\sum_{j=1}^{n} x_j x_l C_{ij} \right) = (kT \kappa_T)^{-1}
$$

(29)

Eq. (28) then becomes
where the mixture isothermal compressibility is now given by

\[ \kappa_T = -\sum x_i \left( \frac{\partial v_i}{\partial p} \right) / \sum x_i v_i \]  

(31)

The set of relations in Eq. (25) do not simplify upon making the assumption of low pressure. To overcome this difficulty and to provide the one additional relation needed, the following closure relation is assumed to be valid for all the cross direct correlation function integrals \( \langle C_{ij} \rangle \) (Hamad 1988; Hamad, et al. 1989):

\[ C_{ij} = \alpha_{ji} C_{ii} + \alpha_{ij} C_{jj} \quad i, j = 1, \ldots, n \text{ and } i \neq j \]  

(32)

where \( \alpha_{ji} \) and \( \alpha_{ij} \) are binary interaction parameters \( \alpha_{ji} \neq \alpha_{ij} \). In an earlier publication (Hamad, et al. 1989) it is shown that this form of the closure expression is quite satisfactory in representing the cross direct correlation function integrals of varieties of non-polar, polar, and hydrogen-bonding binary mixtures. Substituting Eq. (32) in Eq. (30) gives the following set of linear equations:

\[
\begin{align*}
\sum x_j \rho C_{11} + x_2 \alpha_{12} \rho C_{22} + \ldots + x_n \alpha_{1n} \rho C_{nn} &= 1 - v_1 / (kT \kappa_T) \\
x_1 \alpha_{21} \rho C_{11} + \sum x_j \alpha_{2j} \rho C_{22} + \ldots + x_n \alpha_{2n} \rho C_{nn} &= 1 - v_2 / (kT \kappa_T) \\
\vdots & \vdots \\
x_1 \alpha_{n1} \rho C_{11} + x_2 \alpha_{n2} \rho C_{22} + \ldots + \sum x_j \alpha_{nj} \rho C_{nn} &= 1 - v_n / (kT \kappa_T)
\end{align*}
\]  

(33)

where summations run from \( j = 1 \rightarrow n \), and \( \alpha_{ii} = 1 \). The above relations represent a set of \( n \) linear equations in the unknowns \( \rho C_{ii} \). To solve for \( \rho C_{ii} \) it is more convenient to use matrix notations:

\[
\underline{\Delta} \cdot C = b
\]  

(34)

where \( \underline{\Delta} \) is a matrix with elements \( A_{ii} = \sum x_j \alpha_{ji} \), \( A_{ij} = x_i \alpha_{ij} \) and \( b \) and \( C \) are vectors with elements \( b_i = 1 - v_i / kT \kappa_T \) and \( C_i = \rho C_{ii} \), respectively. The solution of Eq. (34), is:

\[
\rho C_{kk} = \sum_{i=1}^{n} \left| \underline{\Delta} \right|_{ik} b_i / \left| \underline{\Delta} \right|
\]  

(35)

where \( \left| \underline{\Delta} \right|_{ik} \) is the cofactor of the element \( A_{ik} \) in the determinant \( \left| \underline{\Delta} \right| \).

By using the direct correlation function integrals calculated above one can derive the expression for the activity coefficients of a species in a multi-component mixture.
As an example of application of this theory, it will be used for derivation of activity coefficients and vapor-liquid and liquid-liquid equilibria calculation of binary mixtures.

B: THE CASE OF \( T \) & \( \rho_i \) (\( i=1,2,...,n \)) AS THE INDEPENDENT VARIABLES

In deriving chemical potentials and activity coefficients from the fluctuation theory of mixtures when \( T \) & \( \rho_i \) (\( i=1,2,...,n \)) (temperature and component densities) are the independent variables we consider a system which is described by the following set of independent variables \{\( T, \rho_1, \rho_2, \ldots, \rho_n \}\), where \( T \) is the absolute temperature, \( \rho_i = \frac{N_i}{V} \), \( N_i \) is the number of molecules \( i \) in the system, \( V \) is the system volume, and \( n \) is the number of components in the mixture. In the grand canonical ensemble the following expression for \( \frac{\partial \mu_i}{\partial \rho_j} \) is derived (Pearson and Rushbrooke 1957; O'Connell 1971):

\[
\left[ \frac{\partial \mu_i}{\partial \rho_j} \right]_{T, \rho_{k \neq j}} = kT \left\{ \delta_{ij}/\rho_1 - C_{ij} \right\}
\]

(37)

where \( \rho_{k \neq j} \) stands for the set \( (\rho_1, \rho_2, \ldots, \rho_n) \) excluding \( \rho_j \). This equation is actually equivalent to Eq. (4) except for the change of variables from \{\( P, T, \& x_i \) (\( i=1,2,...,n-1 \))\} to \{\( T, \rho_1, \rho_2, \ldots, \rho_n \)\). Exact relations can be derived among the direct correlation integrals, \( C_{ij} \) by equating the mixed second derivatives of the chemical potentials. For a binary mixture with \( T, \rho_1, \rho_2 \) as the independent variables one has:

\[
\left( \frac{\partial C_{12}}{\partial \rho_1} \right)_{T, \rho_2} = \left( \frac{\partial C_{11}}{\partial \rho_2} \right)_{T, \rho_1}
\]

(38)

and

\[
\left( \frac{\partial C_{12}}{\partial \rho_2} \right)_{T, \rho_1} = \left( \frac{\partial C_{22}}{\partial \rho_1} \right)_{T, \rho_2}
\]

(39)

The above two equations are exact, but one needs a closure relation among \( C_{11}, C_{22}, \) and \( C_{12} \) to solve for the three integrals. Variety of closure expressions for \( C_{12} \) may be considered. In what follows we use simple geometric mean and weighted arithmetic mean closures in order to solve analytically the above set of equations for chemical potentials.

B1: Geometric Mean Closure: In this case we derive analytic solution for chemical

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potentials using the simple geometric mean closure, $C_{12} = (C_{11}C_{22})^{1/2}$. By substituting this expression for $C_{12}$ in Eqs. (38) and (39) and using Eq. (37), we can derive the following expression for, $\mu_{1r}$, the residual chemical potential of component 1 in a binary mixture

$$
\left(\partial \mu_{1r}/\partial \rho_2\right)^2 \left(\partial^2 \mu_{1r}/\partial \rho_1^2\right) - 2\left(\partial \mu_{1r}/\partial \rho_1\right)\left(\partial \mu_{1r}/\partial \rho_2\right)\left(\partial^2 \mu_{1r}/\partial \rho_1 \partial \rho_2\right)
$$

$$
+ \left(\partial \mu_{1r}/\partial \rho_1\right)^2 \left(\partial^2 \mu_{1r}/\partial \rho_2^2\right) = 0
$$

This nonlinear partial differential equation can be solved analytically utilizing its symmetry with respect to $\rho_1$ & $\rho_2$ variables. First, we write this differential equation in the following form

$$
\left(\partial \mu_{1r}/\partial \rho_1\right) \left(\partial R/\partial \rho_2\right) - \left(\partial \mu_{1r}/\partial \rho_2\right) \left(\partial R/\partial \rho_1\right) = 0
$$

where $R = (\partial \mu_{1r}/\partial \rho_2)/(\partial \mu_{1r}/\partial \rho_1)$. Integration of Eq. (41) results in

$$
R = (\partial \mu_{1r}/\partial \rho_2)/(\partial \mu_{1r}/\partial \rho_1) = h(\mu_{1r})
$$

or

$$
(\partial \mu_{1r}/\partial \rho_2) = h(\mu_{1r}) \left(\partial \mu_{1r}/\partial \rho_1\right)
$$

where $h$ is an unknown function to be determined from the pure component properties. Now, integrating Eq. (42) will produce

$$
\mu_{1r} = F[\rho_2 \ h(\mu_{1r}) + \rho_1]
$$

where $F$ is also an unknown function which can be determined from the following condition

$$
\mu_{1r}(\rho_2=0) = \mu_{1r,p} = kT f_1(p)
$$

In this equation subscript $(p)$ indicates a pure component property. From equation (44) we can conclude $F(t) = kT f_1(t)$ and as a result Eq. (43) will become

$$
\mu_{1r}/kT = f_1[\rho_2 \ h(\mu_{1r}) + \rho_1]
$$

In order to determine the functional form of $h$ one needs first to find the chemical potential of component 2. Using the following thermodynamic relation

$$
\partial \mu_{1r}/\partial \rho_2 = \partial \mu_{2r}/\partial \rho_1
$$

one gets

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where $H$ is defined by

$$H(\mu_{Ir}) = \int h(\mu_{Ir}) d\mu_{Ir}.$$  

Integrating Eq. (47) with respect to $\rho_1$ gives

$$\mu_2 = H(\mu_{Ir}) + K(\rho_1)$$  \hspace{1cm} (48)

The function $K(\rho_1)$ can be shown to be zero considering assumption of

$C_{12} = (C_{11} C_{22})^{1/2}$

and the fact that $\mu_{Ir}$ and $\mu_{2r}$ vanish at zero total density. As a result Eq. (48) becomes

$$\mu_{2r} = H(\mu_{Ir})$$  \hspace{1cm} (49)

At $\rho_1 = 0$ the chemical potential of component 2 in pure state, $\mu_{2r}(\rho_1 = 0) = \mu_{2r,p} = kT f_2(\rho)$, is now used to determine the function $H(\rho_{Ir})$. From Eqs. (47), (48) and (49) one can show

$$h = \frac{dH}{dt} = f_1^{-1}(t) f_2^{-1}(t)$$  \hspace{1cm} (50)

where $f_1^{-1}$ is the inverse function so that $f(f^{-1}(t)) = t$. Using the thermodynamic relation

$$\rho \left( \frac{\partial \mu_{Ir,p}}{\partial \rho} \right) = (\frac{\partial P_{Ir,p}}{\partial \rho}),$$

the following relation is finally obtained

$$p_{2r} [f_2^{-1}(t)] = P_{Ir} [f_1^{-1}(H)]$$  \hspace{1cm} (52)

where $P_{Ir}[\rho]$ is the residual pressure of pure component $i$. Joining Equations (45) and (52) will give us the chemical potential according to the simple geometric mean closure, $C_{12} = (C_{11} C_{22})^{1/2}$.

B2: The Arithmetic Mean Closure: In this case the weighted arithmetic mean closure, $C_{12} = \alpha_{21} C_{11} + \alpha_{12} C_{22}$, can be used to derive analytic expressions for the chemical potentials of components in a mixture. When this closure is combined with Eqs. (37) and (38), and (39) the following linear partial differential equation for $\mu_{Ir}$ is obtained:
The solution of this differential equation depends on the quantity \((1-4\alpha_{21}\alpha_{12})\). When \((1-4\alpha_{21}\alpha_{12})\) is positive the differential equation is hyperbolic and the solution is obtained in terms of a power series expansion. When \((1-4\alpha_{21}\alpha_{12})\) is zero, Eq. (22) is parabolic with the following solution

\[
\mu_{1r} = F(2\alpha_{21}\rho_1 + \rho_2) + \rho_2 H(2\alpha_{21}\rho_1 + \rho_2)
\]  

(54)

where \(F\) and \(H\) are undetermined functions. The choice of \(\alpha_{12} = \frac{1}{4}\alpha_{21}\) in \(C_{12} = \alpha_{21}C_{11} + \alpha_{12}C_{22}\) has then the advantage of producing a closed-form solution.

As in the case of geometric mean closure, the pure component chemical potentials are used to determine the unknown functions \(F\) and \(H\). The chemical potential of component 1 in a binary mixture then takes the following form

\[
\mu_{1r} = a_{1r,p}(\rho_1 + 2\alpha_{21}\rho_2) + kT \left[ x_1Z_{1r,p}(\rho_1 + 2\alpha_{21}\rho_2) + x_2Z_{2r,p}(\alpha_1/2\alpha_{21} + \rho_2) \right]/(x_1 + 2\alpha_{21}x_2)
\]  

(55)

where \(a_{1r,p}\) and \(Z_{1r,p}\) are the residual molar Helmholtz free energy and residual compressibility factor of pure component \(i\), respectively. The mixture compressibility factor then takes the form:

\[
Z = x_1Z_{1,p}(\rho_1 + 2\alpha_{21}\rho_2) + x_2Z_{2,p}(\rho_1 / 2\alpha_{21} + \rho_2)
\]  

(56)

The above expression reduces to the ideal mixture case when \(\alpha_{21} = 1/2\), which is equivalent to assuming the validity of the simple (unweighted) arithmetic mean closure for \(C_{12}\). It is interesting to note that according to Equation (56) all the mixture virial coefficients, obtained by expanding this equations in powers of density have the correct dependences on composition (quadratic for \(B\), cubic for \(C\), and so on).

FLUCTUATION THEORY ASPECT OF LOCAL COMPOSITIONS

According to statistical mechanics, the local structure or environment experienced by a molecule in a mixture is reflected in the \(n\)-body correlation functions which are essentially the probabilities of observing a certain configuration of \(n\) molecules. Of particular interest is the radial distribution function \(g_i(r,\rho_k,T,\sigma_{kl},\varepsilon_{kl})\) which is proportional to the probability of observing a molecule of type \(i\) at a distance \(r\) from a central molecule of type \(j\) in the mixture. If one assumes spherically symmetric molecules, the radial distribution function depends upon the temperature \(T\) as well as the set of component number-densities \([\rho_k]\) and potential energy size \([\sigma_{kl}]\) and energy \([\varepsilon_{kl}]\) parameters for all pairs in the mixture.
Given these functions it is possible to calculate local particle numbers, i.e., the number of molecules of type \( i \) contained within a sphere of radius \( R_{ij} \) centered around a molecule of type \( j \) via the relation (Nakanishi 1982, 1983)

\[
n_{ij}(R_{ij}) = \frac{[(N_i \delta_{ij})/V]}{\int_{0}^{R_{ij}} g_{ij}(r, [\rho_k], T, [\sigma_{kl}], [e_{kl}])4\pi r^2 dr}
\]

where \( g_{ij} \) is the radial distribution function for the \( ij \) pair, \( V \) is the system volume and \( N_i \) is the total number of molecules of type \( i \) in the mixture and \( \delta_{ij} \) is the Kronecker delta function. Normally \( N_i \) is large compared with the \( \delta_{ij} \) in Eq. (57) so that \( N_i - \delta_{ij} \sim N_i \).

As mentioned above, Eq. (57) is strictly only valid for mixtures of molecules whose intermolecular potentials are spherically symmetric. Extension of these definitions to angle-dependent radial distribution functions is straightforward. According to some previous investigations (Lebowitz and Percus 1983; Massih and Mansoori 1983) one can effectively represent the properties of polar molecules through angle averaging techniques which provide an effective spherical potential. Consequently, the local composition about a central \( j \) molecule is defined in terms of Eq. (57), viz.

\[
x_{ij}(R_{ij}) = \frac{n_{ij}(R_{ij})}{\sum_{k=1}^{n} n_{kj}(R_{ij})}
\]

where \( n \) is the number of components in the mixture.

Exact relationships between the \( x_{ij} \) and \( x_{ij} \) as well as relationships between the \( [x_{ij}] \) and the bulk mole fractions \( [x_i] \) are not well known due to the fact that the composition dependence of the radial distribution functions in mixtures is not well understood. It is possible, however, to derive several relations between the local and bulk mole fractions and local particle numbers.

Generally \( R_{ij} \) is a function of \( r \) and \( T \) and does not have to have the same value for each binary pair. If, however, \( R_{ij} = R_{ji} \) or if \( R_{ij} \) is a universal constant, then since \( g_{ij} = g_{ji} \), we find

\[
n_{ij}(R_{ij})/n_j(R_{ij}) = x_i/x_j
\]

\[
n_{ij}(R_{ij})/n_{jj}(R_{ij}) = x_{ij}/x_j
\]

and combining (59) and (60) we find

\[
n_{ii}(R_{ij})/n_{jj}(R_{ij}) = (x_{ii}/x_{jj}) (x_{ij}/x_{ji}) (x_j/x_i)
\]

Finally, differentiating Eq. (57) and rearranging terms one obtains
Equation (62) can be used to express the concept of local compositions with respect to fluctuation integrals (Mansoori and Ely 1985). Isothermal compressibility \( \kappa_T = (1/T)(\partial P/\partial T)_T \), of a multicomponent mixture with respect to the mixture radial distribution functions is expressed by Eq. (8). To express the isothermal compressibility, Eq. (8), with respect to the local particle numbers we write Eq. (3) in the following form (Mansoori and Ely 1985)

\[
G_{ij} = \frac{1}{(\rho x_i)} \left[ n_{ij}(R_{ij}) - \langle n_i(R_{ij}) \rangle - \int_{R_{ij}}^{\infty} (g_{ij} - 1) dR \right] + \int_0^{R_{ij}} (g_{ij} - 1) dR
\]

where \( \langle n_i(R_{ij}) \rangle = 4\pi R_{ij}^3 / 3 \) is the average number of molecules of type \( i \) in a spherical volume of radius \( R_{ij} \). \( R_{ij} \), the radius of the sphere of influence of local compositions, is chosen such that the integral remaining in Eq. (63) vanishes (Mansoori and Ely 1985). The details of this choice are given in the concluding section. We find, therefore, that

\[
G_{ij} = 1/(\rho x_i) \Delta n_{ij}(R_{ij})
\]

where \( \Delta n_{ij}(R_{ij}) = n_{ij}(R_{ij}) - \langle n_{ij}(R_{ij}) \rangle \). Note that for a pure fluid using Eq. (64) in Eq. (8) results in

\[
\rho k T \kappa_T = 1 + \rho G = 1 + \Delta n_x(R)
\]

where the subscript \( x \) denotes a pure fluid. Substituting Eq. (64) into \( B_{ij} = \rho x_i (\delta_{ij} + x_j G_{ij}) \) one finds

\[
B_{ij} = \rho x_i (\delta_{ij} + (x_j / x_i) \Delta n_{ij}(R_{ij}))
\]

Equations (8) and (65) together express the isothermal compressibility of a mixture with respect to the local particular numbers.

Other thermodynamic properties of interest to fluid phase equilibria calculations, which can also be expressed rigorously with respect to the local particle numbers, are the partial molar volumes and chemical potentials of the mixture components. According to the fluctuation theory (see Chapter One) the partial molar volume of component \( i \) of a \( n \)-component mixture is given by the following equation
\[ \bar{\nu}_i = \frac{(1/\rho) \sum x_i B_{ij}}{\sum \sum x_k y_{ik} B_{jk}} \]  

(66)

where \( B \) is a \( n \times n \) matrix with its elements \( B_{ij} = \rho x_i [\delta_{ij} + \rho G_{ij}] \) and \( \Delta \) is the cofactor of the element \( B_{ik} \) in the determinant \( I_B \), \( \delta_{ij} \) is the Kronecker delta, and \( G_{ij} \) is the fluctuation integral as defined by Eq. (3). Likewise, the chemical potential of a component of the mixture can be expressed through the fluctuation theory of solutions as discussed in Chapter One in the following form

\[ \left( \frac{\partial \mu_i}{\partial N_j} \right)_{T,P,N_{kej}} = \left[ \frac{(kT)/\rho x_j}{\Delta} \right] \left( \frac{\Delta}{\Delta} \right) \]  

(67)

In this equation \( \Delta \) symbolizes the determinant of the \( n \times n \) matrix \( \Delta \) elements \( \Delta_{ij} \) given by

\[ \Delta_{ij} = (\delta_{ij}/\rho x_i) + (1/\rho x_i) + G_{ij} + G_{1i} + G_{1j} \]  

(68)

and \( \Delta \) is the cofactor of term \( \Delta_{ij} \). In terms of the local particle numbers we can write

\[ \Delta_{ij} = \left( 1/\rho x_i \right) \left\{ \delta_{ij} + \Delta n_{ij} R_{ij} + \left( x_i/x_l \right) \left[ 1 + \Delta n_{1i} R_{1i} - \Delta n_{1i} R_{1j} \right] \right\} \]  

(69)

By replacing different local composition approximations in Eq. (69) one may solve Eqs. (66) and (69) simultaneously for the chemical potential of components in the mixture.

CALCULATIONS AND RESULTS

A: TEST OF MIXING RULES FOR HARD-SPHERE MIXTURES.

For a hard-sphere fluid mixture, Equation (9), which is a result of the energy equation, will vanish. On the other hand, Equation (10), which is a result of the virial equation, will reduce to the van der Waals (repulsive) mixing rule for \( \sigma \) as given by Eq. (23). Thus, we have two mixing rules for \( \sigma \); one is derived from the virial equation and the other is derived from the compressibility equation. For comparison both of these mixing rules will be used to calculate mixture properties. In such calculations one needs also a pure fluid equation of state which can be joined with the mixing rules. For a pure fluid of hard-spheres the Carnahan-Starling equation of state is used here (Carnahan and Starling 1969)

\[ p/kT = \left( 1 + y + y^2 - y^3 \right) / (1 - y)^3 \]  

(70)

where \( y = \pi \rho c_3^3 / 6 \). The quantities \( (\partial p/\partial \rho)_T \) and hence \( \Delta \) appearing in Eq. (22) can be derived from the above equation as the following:

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\[
(\frac{\partial p}{\partial \rho})_T = kT(1+4y+4y^2-4y^3+y^4)/(1-y)^4
\]  

(71)
\[
\Delta_x = (-8y+2y^2)/(1+4y+4y^2-4y^3+y^4)
\]  

(72)

For a binary mixture, \( \sigma_x \) at a given \( \rho, T \) and \( x_i \) can be calculated by solving Eqs (22) and (72) simultaneously. The isothermal compressibility, \( \kappa_T \), of the mixture can be calculated directly from Eq. (71) after obtaining \( \sigma_x \). However, the compressibility factor \( Z \), and the Helmholtz free energy \( A \), of the mixture have to be calculated from the following thermodynamic relations, respectively

\[
Z = \frac{p}{kT} = 1 + \frac{1}{kT} \int_0^\rho \left[ \frac{\partial p}{\partial \rho} \right]_{\sigma=\sigma_x} - kT \, d\rho
\]  

(73)
\[
A - A^0 = \int (p-kT) d\rho / \rho^2
\]  

(74)

where \( A^0 \) is the ideal gas Helmholtz free energy. Equations (73) and (74) can be integrated numerically to obtain \( A \) and \( Z \), respectively. The percentage deviations of \( A, Z \) and \( \kappa_T \), as calculated using the above equations, from those predicted by the exact hard-sphere mixture equation of state, are plotted versus the mixture reduced density in Figures 1-3 for equimolar binary hard-sphere mixtures.

Figure 1. The percentage deviation of the isothermal compressibility of three hard-sphere mixtures from the hard-sphere equation of state (Mansoori et al., 1971) as predicted by: the van der Waals mixing rule for hard spheres, Eqs (13) & (23), (vdw); the fluctuation mixing rule for hard spheres, Eqs. (13) & (20, 22); and Eqs. (13) & (76) (ave). The curves represent: --- \( \sigma_{22}/\sigma_{11}=2 \), ---- \( \sigma_{22}/\sigma_{11}=4 \), --- \( \sigma_{22}/\sigma_{11}=6 \).
Figure 2. The percentage deviation of the compressibility factor of three hard-sphere mixtures from the hard-sphere equation of state (Mansoori, et al. 1971) as predicted by the van der Waals mixing rule for hard spheres and the fluctuation mixing rule for hard spheres. See Figure 1 for notations.

Figure 3. The percentage deviation of the Helmholtz free energy of three hard-sphere mixtures from the hard-sphere equation of state (Mansoori, et al. 1971) as predicted by the van der Waals mixing rule for hard spheres and the fluctuation mixing rule for hard spheres. See Figure 1 for notations.
The equimolar mixture reduced density, \( \xi \), reported in Figures 1-3 is defined as (Mansoori et al. 1971)

\[
\xi = \pi \rho (\sigma_{11}^3 + \sigma_{22}^3)/12
\]  

(75)

Calculations reported in Figures 1-3 were performed for three different size ratios of \( \sigma_{22}/\sigma_{11} = 2, 4, 6 \) (Hamad et al. 1987). According to these figures, as the size ratio increases the deviations from the exact mixture results increase. This reflects the approximate nature of the mixing rules. For comparison, similar calculations were repeated using the van der Waals mixing rule as given by Eq. (23). These results are also reported in Figures 1-3. Deviations based on the van der Waals mixing rule are always in the opposite direction of the deviations based on the mixing rule resulting from the fluctuation theory. The reason for the opposite deviations resulting from the two mixing rules lies in the fact that at the same density the van der Waals mixing rule predicts a lower value for \( \sigma_x \) than the fluctuation mixing rule. The exact value of \( \sigma_x \) lies somewhere in between the two calculations. The thermodynamic stability condition \( [\partial p/\partial \rho]_T > 0 \) implies that pressure is a monotonic increasing function of the reduced density \( \rho \xi^3 \). Therefore, one may conclude that at higher value of \( \sigma_x \) the pressure will be higher. Similar arguments can be made for the Helmholtz free energy and the isothermal compressibility.

From mathematical point of view it can be also concluded that the value of \( \sigma_x \) calculated from Eq.(22) is larger than the calculation by the van der Waals mixing rule, Eq.(23): According to Eq.(15) since \( \int [g-1] \rho^2 d\rho \leq 0 \) then \( \Delta_x \leq 0 \). Also since \( (\sigma_{11}^3 - 2\sigma_{12}^3 + \sigma_{22}^3) \geq 0 \) this implies that \( \sigma_x^3 \) [Eq.(22)] \( \geq \sigma_{vdw}^3 \) when \( (\sigma_{11}^3 - \sigma_{22}^3 - \sigma_{12}^6) < 0 \) or, since \( \Delta_x \leq 0 \), \( \sigma_x^3 \) [Eq.(22)] \( \geq \sigma_{vdw}^3 \). The latter inequality also holds when \( \Delta_x > 0 \), but small compared to \( (\sigma_{11}^3 - 2\sigma_{12}^3 + \sigma_{22}^3) \), and since it can be shown that \( (\sigma_{11}^3 - 2\sigma_{12}^3 + \sigma_{22}^3) - (\sigma_{11}^3 \sigma_{22}^3 - \sigma_{12}^6) \geq 0 \), then we conclude that \( \sigma_x^3 \) [Eq.(22)] \( \geq \sigma_{vdw} \). These observations suggest that if one uses an average of the two mixing rules then the result will be better than either of the two. For simplicity the arithmetic average of the two mixing rules will be used which is:

\[
\sigma_x^3 = (3/4) \sigma_x^3 (\text{vdw}) - (1/4) \left[ (\sigma_{11}^3 - 2\sigma_{12}^3 + \sigma_{22}^3) x_1 x_2 \Delta_x + \left[ (\sigma_x^3 (\text{vdw}) - (\sigma_{11}^3 - 2\sigma_{12}^3 + \sigma_{22}^3) x_1 x_2 \Delta_x \right]^{1/2} \right]
\]  

(76)

The Helmholtz free energy, the compressibility factor, and the isothermal compressibility can be calculated using the procedure discussed above. The results for the average mixing rule are shown in Figures 1-3. It is clear that Eq.(76) gives a better prediction than either Eq.(22) or the van der Waals mixing rule as reported by Eq. (23).

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The Henry's constant can be calculated from the fluctuation mixing rules, Eqs (13) and (22), and the van der Waals mixing rules, Eqs (13) and (23), for a mixture of Lennard-Jones (LJ) fluids. For the pure LJ fluid the equation of state proposed by Nicolas et al. (1979) will be used. To derive the Henry's constant we use the following relation

$$\ln(\frac{H_i}{p k T}) = \frac{\mu_{ir}}{k T}$$  \hspace{1cm} (77)

where \( H_i \) is the Henry's constant for component \( i \) and \( \mu_{ir} \) is the residual chemical potential of component \( i \) in the mixture at infinite dilution. The chemical potential can be calculated from the relation

$$\frac{\mu_{ir}}{k T} = \int_0^\rho \left[ \frac{\partial \rho}{\partial N_i} (N/k T) - \rho \right] dp / \rho^2$$  \hspace{1cm} (78)

To use Eqs (13) and (22) one has to write Eq.(78) in terms of the derivative \( \frac{\partial \rho}{\partial \rho} \), i.e.

$$\frac{\mu_{ir}}{k T} = \int_0^\rho \left( \frac{\partial \rho}{\partial N_i} (N/k T) - \rho \right) dp / \rho^2$$  \hspace{1cm} \text{(79)}

$$\frac{\mu_{ir}}{k T} = \int_0^\rho \left( \frac{\partial \rho}{\partial N_i} (N/k T) - \rho \right) dp / \rho^2$$  \hspace{1cm} \text{(80)}

To derive the expression for the Henry's constant from Eq. (80) one needs \( \partial \sigma_x^3 \partial N_i \) and \( \partial e_x \partial N_i \). For binary mixtures, in the limit of \( x_1 \to 0 \), \( \partial \sigma_x^3 \partial N_1 \) and \( \partial e_x \partial N_1 \) will be in the following forms

$$N[\partial \sigma_x^3 / \partial N_1]_{x_1=0} = 2 \sigma_{12}^3 - 2 \sigma_{12} \Delta_{22} \sigma_{22}^3 - C \sigma_{22}^3 \hspace{1cm} \text{(81)}$$

$$N[\partial e_x / \partial N_1]_{x_1=0} = 2 \varepsilon_{12} (\sigma_{12} / \sigma_{22})^3 - 2 \varepsilon_{22} (\sigma_{22} / \sigma_{22})^3 N \sigma_x^3 / \partial N_1 \hspace{1cm} \text{(82)}$$

In addition to the above conditions one has:

Limit of \( e_x \) (as \( x_1 \to 0 \)) = \( \varepsilon_{22} \) and limit of \( \sigma_x \) (as \( x_1 \to 0 \)) = \( \sigma_{22} \).

Using the above relations in Eq. (80) and after a lengthy, but straight forward, manipulation one obtains:
\[ \mu_{1r,r}/kT = \mu_{2r}/kT + 2h(f-1)u_{2r}/kT + 2(h-1)(Z_{2r}-1)/kT - F(T,\rho) \]  

(83)

where \( \mu_{2r}, u_{2r}, \) and \( Z_{2r} \) are the residual chemical potential, the residual internal energy, and the compressibility factor of pure component 2 at the same temperature and density of the mixture, and

\[ f = \varepsilon_{12}/\varepsilon_{22} \]  

(84)

\[ h = (\sigma_{12}/\sigma_{22})^3 \]  

(85)

\[ F(T,\rho) = \int \left[ \rho \frac{\partial^2 P}{\partial \rho^2} + \rho \frac{\partial T}{\partial \rho} \right] d\rho - \rho \]  

(86)

For the van der Waals mixing rules, the expression for the residual chemical potential is given by

\[ \mu_{1r,r}/kT = \mu_{2r}/kT + 2h(f-1)u_{2r}/kT + 2(h-1)(Z_{2r}-1) \]  

(87)

Note that the difference between this expression and Eq. (83) is the last term of Eq. (83), the quadratic term in \( h-1 \), which is missing from Eq. (87). In Figures 4 and 5, Eqs. (83) and (87) are compared to the simulation data for different values of \( f \) and \( h \) when \( \rho \sigma_{22}^3 = 0.7 \) and \( kT/\varepsilon_{22} = 1.2 \). At these conditions Eqs. (83) and (87) become:

\[ \mu_{1r,r}/kT = -1.986 - 7.946h(f-1) - 0.485(h-1) + 12.03(h-1)^2 \]  

(88)

\[ \mu_{1r,r}/kT = -1.986 - 7.946h(f-1) - 0.485(h-1) \]  

(89)

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(88)

\[ \mu_{1r,r}/kT = -1.986 - 7.946h(f-1) - 0.485(h-1) \]  

(89)

Figure 4 shows the simulation data and Eqs. (88) and (89) for \( h = 1 \), i.e. for mixture of molecules with the same sizes, but different energies of interaction. In this case fluctuation mixing rules, Eqs. (13&22), and the van der Waals mixing rules, Eqs. (13&23), predict the same results for \( \mu_{1r,r}^{\infty} \), which turns out to be a straight line. The agreement is generally good except for the small region near \( f = 0 \).

Figure 5 shows the results for \( f = 1 \) i.e. the energies of interaction are the same for the two fluids but the molecules have different sizes. In this case the agreement is only good in the region near \( h = 1 \). While the van der Waals mixing rules predict a linear behavior, fluctuation mixing rules predict the correct qualitative behavior of the simulation data. The curved shape is due to the quadratic, \( (h-1)^2 \), term in Eq. (83) which is missing from the van der Waals expression, Eq. (87). This term can be thought of as a correction to the van der Waals expression. However, this correction is too large, and is making the prediction to go to the opposite side of the simulation data. It is worth mentioning that this simulation data (where the size ratio is
different) is not very accurate as pointed out by Shing, et al. (1988), but it should give an idea about the qualitative behavior of $\mu_{ir}^{-\infty}$.

Figure 4. Variation of $\mu_{ir}^{-\infty}/kT$ with $f=\varepsilon_{12}/\varepsilon_{22}$. The points represent the simulation data (Shing 1982, Shing et al. 1988) and the curves represent the following: — van der Waals mixing rules, Eqs. (13 & 23), and — the average mixing rules, Eqs. (13 & 76).

Figure 5. Variation of $\mu_{ir}^{-\infty}/kT$ with $h=(\sigma_{12}/\sigma_{22})^3$. The points represent the simulation data (Shing 1982, Shing et al. 1988) and the curves represent the following: — van der Waals, Eqs. (13 & 23); the fluctuation mixing rules ——- Eqs (13 & 22); ———— the average mixing rules, Eqs. (13 & 76); ——— Eq. (97) with $\sigma_x$ calculated from Eq. (23); ———— Eq. (97) with $\sigma_x$ calculated from Eq. (22).

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As observed in the case of hard-sphere mixture the deviations of the two mixing rules are on opposite sides from the exact values. The average mixing rule, Eq. (76), gives the following expression for $\mu_{tr}$:

$$\mu_{tr} = \frac{\mu_1}{kT} = \frac{\mu_2}{kT} + 2h(f-1.25)\frac{u_2}{kT} + 2(1.25h-1)(Z_2-1) + (h-1)^2[Z_2-1-u_2/kT-F(T,p)] \quad (90)$$

This expression gives a better prediction of the actual value when $h$ is far from unity which corresponds to the ideal mixture. The reason for this can be seen from the derivative of $\sigma$ with respect to $N_1$ for the arithmetic-average mixing rule. This derivative is given by

$$N[\partial \sigma^3_{x_1}/\partial N_1]_{x_1=0} = \frac{5}{2}\sigma_{12}^3 - 2\sigma_{22}^3 + (1/2)(A/\sigma_{22}^3-C)\Delta_{22} \quad (91)$$

This expression predicts a non-zero value of the derivative at equal sizes ($\sigma_{11}=\sigma_{22}$). This is the cause of the incorrect behavior near $h=1$. However, since the ideal mixture behavior is known ($\mu_{1r}/kT=\mu_{2r}/kT$), one can subtract the additional terms which show up in Eq. (90) when we put $h=f=1$ (the extra terms are $(1/2)[Z-1-u_2/kT]$). The resulting expression is then:

$$\mu_{tr} = \frac{\mu_1}{kT} = \frac{\mu_2}{kT} + 2[h(f-1.25)+0.25]u_2/kT + 2.5(h-1)(Z_2-1) + (h-1)^2[Z_2-1-u_2/kT-F(T,p)] \quad (92)$$

This equation is plotted in Figures 4 and 5. It is clear that this equation is better than Eq. (82), but still there is a need for improvement at small and large values of $h$.

Henry's constant can also be calculated directly (without going through mixing rules) from the fluctuation theory. The derivative of the chemical potential of component one, in a binary mixture, with respect to composition is given by:

$$\frac{1}{kT}(\partial \mu_{1r}/\partial x_1)_{T,p} = 1/x_1 \left\{ x_2\rho (G_{11}+G_{22}-2G_{12}) \right\} / \left\{ 1 + x_1x_2\rho (G_{11}+G_{22}-2G_{12}) \right\} \quad (93)$$

For a component of an ideal gas mixture

$$\frac{1}{kT}(\partial \mu_{1r}^0/\partial x_1)_{T,p} = 1/x_1 \quad (94)$$

From Eqs (93) and (94) one obtains the relation for the residual chemical potential

$$\frac{\partial \mu_{1r}/\partial x_1}{T,p} = -kT \left[ x_2\rho \left( G_{11} + G_{22} - 2G_{12} \right) \right] / \left[ 1 + x_1x_2\rho \left( G_{11} + G_{22} - 2G_{12} \right) \right] \quad (95)$$

Integrating Eq. (95) at constant $T$ and $p$ from $x_1=0$ to $x_1=1$ one obtains:

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\[ \mu_{1r}^\infty = \mu_{1r}^{\text{pure}} + kT \int_{0}^{1} \frac{x_2 \rho (G_{11} + G_{22} - 2G_{12})}{1 + x_1 x_2 \rho (G_{11} + G_{22} - 2G_{12})} \, dx_1 \]  

(96)

The conformal solution approximation for the radial distribution function, Eq. (12), can be used to integrate the above equation. Substituting Eq. (16) in Eq. (96) one gets

\[ \mu_{1r}^\infty = \mu_{1r}^{\text{pure}} + \left( \sigma_{11}^3 - 2\sigma_{12}^3 + \sigma_{22}^3 \right) kT \int_{0}^{1} x_2 \Delta_x / \left( \sigma_x^3 + (\sigma_{11}^3 - 2\sigma_{12}^3 + \sigma_{22}^3) x_1 x_2 \Delta_x \right) \, dx_1 \]  

(97)

In the case of equal molecular sizes, \( \sigma_{11}^3 - 2\sigma_{12}^3 + \sigma_{22}^3 = 0 \), and the integral in Eq. (97) drops. On the other hand, if the molecular sizes are different, the integral has to be evaluated numerically by using an appropriate equation of state to calculate \( \Delta_x \). The term \( \sigma_x^3 \) can be calculated from either Eq. (22) or Eq. (23), which gives almost the same result as shown in Figure 5. The curves were terminated at \( h = 0.409 \) which corresponds to the saturation condition at \( T^* = 1.2 \). Beyond this point the Nicolas et. al. LJ equation of state predicts a vapor phase.

Equation (97) predicts the correct qualitative dependence of \( \mu_{1r}^\infty \) on \( f \) as seen in figure 4. On the other hand, it predicts almost a linear dependence of \( \mu_{1r}^\infty \) on \( h \) which is not like the simulation data as reported in Figure 5. In all cases studied the prediction around \( h = f = 1 \) is accurate, which is expected because of the ideal behavior of the mixtures at these values of \( f \) and \( h \).

C: PHASE EQUILIBRIUM IN BINARY COMPLEX MIXTURES

For binary liquid mixtures at low to moderate pressures the following expressions for the direct correlation function integrals were derived

\[ \rho C_{11} = \frac{W(1 - \alpha_{12} v_2 / v_1)x_2^2 + Wx_1(\alpha_{12} x_1 + x_2)v_1 / v_2 + (1 - \alpha_{12}) x_2 + \alpha_{12} x_1}{\alpha_{12} x_1^2 + x_1 x_2 + \alpha_{21} x_2^2} \]  

(98)

\[ \rho C_{22} = \frac{W(1 - \alpha_{21} v_1 / v_2)x_1^2 + Wx_2(\alpha_{21} x_2 + x_1)v_2 / v_1 + (1 - \alpha_{21}) x_1 + \alpha_{21} x_2}{\alpha_{12} x_1^2 + x_1 x_2 + \alpha_{21} x_2^2} \]  

(99)

\[ \rho C_{12} = \frac{W(\alpha_{12} x_1^2 + \alpha_{21} x_1 x_2 v_1 / v_2 + \alpha_{12} x_1 x_2 v_2 / v_1 + \alpha_{21} x_2^2) + \alpha_{12} x_1 + \alpha_{21} x_2}{\alpha_{12} x_1^2 + x_1 x_2 + \alpha_{21} x_2^2} \]  

(100)

In these expressions \( \alpha_{21} \) and \( \alpha_{12} \) are the binary parameters, and

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where $\kappa_{T_i}$ is the isothermal compressibility of the pure component $i$.

Given the direct correlation function integrals, activity coefficients can be obtained by substituting the $C_{ij}$'s in Eq. (36), which for binary mixtures can also be written as

$$\ln \gamma_1 = -\int_{0}^{x_2} (\rho C_{12} - W - 1) dx_2 / x_1$$

(102)

Substituting for $\rho C_{12}$ from Eq. (100) and performing the integration, analytical expression for activity coefficient results

$$\ln \gamma_1 = -L_1 \tau \ln[x_1 + (L_2 / L_1) x_2] + (1/2)(L_1 \tau - 1) \ln[a / \alpha_{12} x_2^2 + (\alpha_{12} - 2) x_2 + 1]
+ (1/2)[(2\alpha_{12} L_2 / L_1) \tau + 1 - 2 \tau_{12}] / q \ln[(1 + x_2 / r^+)/(1 + x_2 / r^-)]$$

(103)

where $L_1 = kT \kappa_{T_1} / v_2$, $L_2 = kT \kappa_{T_2} / v_1$, $\alpha = \alpha_{21} + \alpha_{12} - 1$, $q = (1 - 4\alpha_{21}\alpha_{12})^{1/2}$,
$$r^\pm = (1/2)(1 - 2\alpha_{12} \pm q) / a$$

and

$$\tau = (\alpha_{21} v_1 / v_2 + \alpha_{12} v_2 / v_1 - 1) / (\alpha_{21} L_1^2 + \alpha_{12} L_2^2 - L_1 L_2).$$

(104)

The expression for $\ln \gamma_2$ is obtained by inter-changing subscripts 1 and 2 in Eq. (103) and in the expression for $r^\pm$. The quantities $a$, $q$ and $\tau$ remain unchanged under this operation. To test the activity coefficient expressions, vapor-liquid and liquid-liquid equilibria calculations of a number of binary systems are here carried out.

D: APPLICATIONS FOR VAPOR-LIQUID PHASE EQUILIBRIA CALCULATIONS

To test the possibility of vapor-liquid equilibrium (VLE) prediction by the new activity coefficient expressions a number of complex systems are chosen at low pressures. The vapor phase is assumed to be an ideal gas and the vapor pressure of the pure components, $p_i^\circ$ is represented by the Antoine equation. Two kinds of pure liquid property data are needed in the activity coefficient equation: They are the specific volume and isothermal compressibility data. The VLE data are fitted to the activity coefficient expressions by minimizing the following objective function

$$S = \Sigma(p - p_{\exp})^2 / S_p + \Sigma(y - y_{\exp})^2 / S_y$$

(105)

where $S_p$ and $S_y$ are the sum of squares resulting from minimizing $\Sigma(p - p_{\exp})^2$ and $\Sigma(y - y_{\exp})^2$ individually. The results of calculations are shown in Table 1.


Table 1. Parameters of the present activity coefficient model and comparisons with Wilson correlation (Hamad and Mansoori 1989).

<table>
<thead>
<tr>
<th>System</th>
<th>T/°C</th>
<th>$\alpha_{21}$</th>
<th>$\alpha_{12}$</th>
<th>$S_p$</th>
<th>$S_y$</th>
<th>$S_p$</th>
<th>$S_y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol+Water</td>
<td>60.</td>
<td>0.3869</td>
<td>0.3562</td>
<td>2.0</td>
<td>0.10</td>
<td>1.0</td>
<td>0.07</td>
</tr>
<tr>
<td>Ethanol+Water</td>
<td>40.</td>
<td>0.2900</td>
<td>0.3561</td>
<td>1.4</td>
<td>0.09</td>
<td>1.1</td>
<td>0.06</td>
</tr>
<tr>
<td>Ethanol+Water</td>
<td>55.</td>
<td>0.2920</td>
<td>0.3799</td>
<td>0.7</td>
<td>0.14</td>
<td>0.4</td>
<td>0.13</td>
</tr>
<tr>
<td>Ethanol+Water</td>
<td>70.</td>
<td>0.2942</td>
<td>0.4048</td>
<td>1.6</td>
<td>0.11</td>
<td>0.6</td>
<td>0.13</td>
</tr>
<tr>
<td>1-Propanol+Water</td>
<td>30.</td>
<td>0.2392</td>
<td>0.2722</td>
<td>0.07</td>
<td>0.46</td>
<td>0.09</td>
<td>0.64</td>
</tr>
<tr>
<td>Ethyl Acetate+Ethanol</td>
<td>40.</td>
<td>0.5105</td>
<td>0.2989</td>
<td>.03</td>
<td>0.04</td>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>Ethanol+Benzene</td>
<td>25.</td>
<td>0.1028</td>
<td>0.6393</td>
<td>.009</td>
<td>0.008</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td>Ethanol+Benzene</td>
<td>40.</td>
<td>0.09741</td>
<td>0.6458</td>
<td>0.2</td>
<td>0.07</td>
<td>0.1</td>
<td>0.05</td>
</tr>
<tr>
<td>Ethanol+Benzene</td>
<td>55.</td>
<td>0.09688</td>
<td>0.6498</td>
<td>0.9</td>
<td>0.13</td>
<td>0.5</td>
<td>0.13</td>
</tr>
<tr>
<td>Acetone+Chloroform</td>
<td>25.</td>
<td>0.2907</td>
<td>0.6404</td>
<td>0.04</td>
<td>0.24</td>
<td>0.04</td>
<td>0.24</td>
</tr>
</tbody>
</table>

In this table, $S_p = 10^{-2} \Sigma (p-p_{exp})^2$, and $S_y = 10^2 \Sigma (y-y_{exp})^2$.

Experimental data taken from VLE Data Collection (Dechema).

In this table comparisons are also made with the results of Wilson (1964) correlation which is selected because it gave the best over all fit to the large number of mixtures studied in VLE calculations. Table 1 also includes parameters $\alpha_{21}$ and $\alpha_{12}$, and optimized values of $S_p$ and $S_y$. Figures 6-8 show the vapor-liquid equilibrium composition $(x-y)$ diagrams for the systems methanol+water, 1-propanol+water and ethanol+benzene.

According to Table 1 and Figures 6-8 it can be concluded that the present theory can predict the vapor-liquid equilibria of the systems studied as good as the Wilson (1964) equation.

E: APPLICATIONS FOR LIQUID-LIQUID PHASE EQUILIBRIA CALCULATIONS

Phase splitting in liquid mixtures occurs when two phases have a lower total Gibbs free energy than one phase at constant temperature and pressure. A necessary condition for stability of a two-component homogeneous mixture is (Van Ness and Abbott 1982):

$$\frac{d\mu_i}{dx_i} > 0 \quad i=1,2$$  \hspace{1cm} (106)

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Figure 6. The vapor-liquid equilibrium composition (x-y) diagram for methanol (1) + water (2) at 60°C. The squares are the experimental data, the solid curve is the present theory and the dashed curve is Wilson correlation.

Figure 7. The vapor-liquid equilibrium composition (x-y) diagram for 1-propanol (1) + water (2) at 30°C. The squares are the experimental data, the solid curve is the present theory and the dashed curve is Wilson correlation.
In terms of the activity coefficients, Eq. (106) becomes:

\[
\frac{d(\ln \gamma_i)}{d\xi} + \frac{1}{\xi_i} > 0
\]  

Substituting for \(\ln \gamma_i\) in this equation from Eq. (103) gives

\[
(\alpha_{12}x_1 + \alpha_{21}x_2)(1-x_1-L_2x_2) + x_1x_2(\frac{\alpha_{21}v_1}{v_2} + \frac{\alpha_{12}v_2}{v_1} - 1) > 0
\]  

provided parameters \(\alpha_{21}\) and \(\alpha_{12}\) are positive. For liquid-liquid equilibria (LLE) the left-hand side of inequality (108) should be negative. Considering the magnitudes of the different quantities one concludes that the present activity coefficient model is capable of predicting LLE. The Wilson (1964) correlation, on the other hand, is known to be unable to predict LLE, because it always satisfies inequality (107).

The present activity coefficient theory is tested versus experimental LLE data. For the variation of the isothermal compressibilities with temperature, which is needed in this calculation, a three-parameter equation is used (Brostow and Maynadier 1972).
Temperature and pure component volume dependence of parameters $\alpha_{21}$ and $\alpha_{12}$ for a number of organic binary systems exhibiting LLE are represented by the following expressions (Hamad and Mansoori 1989):

$$\alpha_{21} = \frac{v_2}{v_1} \exp(\alpha_{021}/RT)$$

(109)

$$\alpha_{12} = \alpha_{012} \frac{v_1}{v_2},$$

(110)

in which $\alpha_{021}$ and $\alpha_{012}$ are constants (independent of temperature and composition). The experimental LLE data is fitted to the activity coefficient equation with Eqs. (109) and (110) for $\alpha_{21}$ and $\alpha_{12}$ by minimizing the difference between the activities in the two liquid phases:

$$S = \sum\left[1-x_1^{(1)} \gamma_1^{(1)} /[x_1^{(2)} \gamma_1^{(2)}]\right]^2 + \sum\left[1-x_2^{(1)} \gamma_2^{(1)} /[x_2^{(2)} \gamma_2^{(2)}]\right]^2$$

(111)

where superscripts (1) and (2) are for phases 1 and 2, respectively.

Table 2 shows values of parameters $\alpha_{021}$ and $\alpha_{012}$ and optimum S for a number of binary systems.

The variation of the compositions of two LLE systems (methanol+heptane and formic acid+benzene) with temperature is shown in Figures 9 and 10.

<table>
<thead>
<tr>
<th>System</th>
<th>$\alpha_{021}$</th>
<th>$\alpha_{012}$</th>
<th>SX$10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol+Heptane</td>
<td>-1070.9</td>
<td>1.0243</td>
<td>0.12</td>
</tr>
<tr>
<td>Methanol+Cyclohexane</td>
<td>-980.29</td>
<td>1.0191</td>
<td>0.21</td>
</tr>
<tr>
<td>Formic Acid+Benzene</td>
<td>-748.15</td>
<td>0.97983</td>
<td>1.7</td>
</tr>
<tr>
<td>Phenol+Octane</td>
<td>-1077.0</td>
<td>1.0031</td>
<td>7.3</td>
</tr>
<tr>
<td>Methanol+Carbondisulfide</td>
<td>-797.20</td>
<td>1.0186</td>
<td>0.45</td>
</tr>
<tr>
<td>Nitrobenzene+Hexane</td>
<td>-975.97</td>
<td>1.0027</td>
<td>2.0</td>
</tr>
<tr>
<td>1,3-Dihydroxybenzene+</td>
<td>-937.02</td>
<td>1.0032</td>
<td>5.5</td>
</tr>
<tr>
<td>Benzene</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In this table: $S = \sum\left[1-x_1^{(1)} \gamma_1^{(1)} /[x_1^{(2)} \gamma_1^{(2)}]\right]^2 + \sum\left[1-x_2^{(1)} \gamma_2^{(1)} /[x_2^{(2)} \gamma_2^{(2)}]\right]^2$. $\alpha_{021}$ dim.: 1/mol.
Figure 9. The composition versus temperature (x-T) diagram for liquid-liquid equilibrium of methanol (1) + heptane (2). The squares are the experimental data and the solid curve is the present theory.

Figure 10. The composition versus temperature (x-T) diagram for liquid-liquid equilibrium of formic acid (1) + benzene (2). The squares are the experimental data and the solid curve is the present theory.

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According to these figures the agreement with the data is satisfactory. The largest deviation of theory from experimental data occurs near the upper critical solution temperature.

Overall, the present technique is capable of formulating analytic expressions for activity coefficients in mixtures. For this purpose it is necessary to define closure expressions for the cross direct correlation function integrals. Application of the activity coefficient expressions resulting from this technique for vapor-liquid and liquid-liquid equilibria calculations has been as successful as the other activity coefficient expressions available.

**F: THE RADIUS OF THE SPHERE OF INFLUENCE OF LOCAL COMPOSITIONS**

In the basic definition of the local particle numbers, Eq. (57), $R_{ij}$, the radius of the sphere of influence of local compositions must be defined. In the formulation which is provided above, no numerical value of this radius was specified for the sake of generality of the results. In the calculation of partial molar properties one has to take into account the numerical value of this radius. To assign a value of the radius of the sphere of influence of local compositions, one must consider the basic approximation which was made in deriving Eq. (64) from Eq. (63). According to this approximation the radius of the sphere of effectiveness of local composition can be defined by the following equation

$$
\int_{0}^{\infty} (g_{ij}(r) - 1) 4\pi r^2 dr = 0
$$

where $g_{ij}(r)$ is the pair correlation function.

![Diagram](image.png)

Figure 11. Schematic diagram of the radial dependence of the isothermal compressibility integrand $r^2[g(r)-1]$ in a dense fluid. The approximate radius of influence of local composition (R) is shown as the point where the oscillations of $g(r)$ about unity cancel each other.

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This expression indicates that $R_{ij}$ should be defined such that the dashed areas in Figure 11 above and below the horizontal axis are equal to each other.

Knowing that $g_{ij}$ is generally a function of temperature, density, and composition it becomes clear that $R_{ij}$ will also have to be a function of temperature, density, and composition. Since $g_{ij}$ varies significantly with density it can be expected that $R_{ij}$ will be a strong function of density decreasing as the density increases.

It is certainly possible that Eq. (112) can have more than one solution and one must, therefore, impose some secondary constraint to obtain the correct value. For dense soft-spheres it is shown that [Hanley and Evans (1981)] the statistical mechanical energy and virial equations reproduce the "experimental" values when the upper limit of integration is changed from infinity to roughly 2.5 molecular diameters. In particular, Figure 6 of Hanley and Evans (1981) shows that properties such as the internal energy and pressure are completely determined by interactions of relatively short range. It would seem safe, therefore, to choose the solution to Eq. (112) which is in the vicinity of 2-3 molecular diameters. Nonetheless, it is clear that in order to have a more quantitative knowledge about $R_{ij}$ one has to use accurate radial distribution function data, preferably, using computer simulation values. A second problem is that the intermolecular potential is usually truncated at 2.5 molecular diameters in simulation studies. Thus, it is difficult to obtain accurate $g_{ij}$ information which one can use to study Eq. (112). Recently, molecular dynamics computer simulation data for radial distribution functions of binary Lennard-Jones mixtures with a size ratio of two and energy ratios of 0.5 to 3.0 have been published (Huber and Ely 1989). This data may be used for the study of the radius of influence of local compositions.

It has become possible to introduce the concept of local particle numbers and compositions with respect to fluctuation integrals. Incorporation of the local composition concept in the fluctuation theory has produced a direct method for calculating partial molar properties from different molecular theories of solutions. The method does not require the use of mixing rules or any other approximation about the nature of the mixture under consideration. Finally, this study has also resulted in a rigorous equation, Eq. (112), for the definition of the radius of influence of local compositions which can be utilized in order to specify this radius at different thermodynamic state conditions.

CONCLUSIONS
The techniques presented here have allowed us to perform calculations of total, partial molar, and phase equilibria of mixtures using the concept of fluctuation theory. There are several points to be noted about the advantages of these techniques versus the existing state-of-the-art of thermodynamic calculations of mixtures and fluctuation theory: (i) The present techniques allow us to perform thermodynamic calculations for the whole range of mixture compositions and not
just at the infinite dilution and high concentration limits as it had been the case for most of the other fluctuation theory techniques. (ii) The present techniques are applicable for mixtures consisting of species with large differences in molecular size, shape, and energetics. They are specifically useful for polar and associating molecular fluids for which, generally, no accurate intermolecular potential energy functions are available, (iii) With the application of the weighted arithmetic mean closure for the cross direct correlation function integrals it has become possible to derive analytic expressions for activity coefficients in complex mixtures. the resulting activity coefficient expressions allow us to perform vapor-liquid and liquid-liquid equilibria computations of mixtures. Accuracy of these calculations are as good as the best available phase equilibria computational techniques for mixtures.

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