

Radial Distribution Functions and their Role in Modeling of Mixtures Behavior

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ABSTRACT

Radial distribution (Pair correlation) functions are the primary linkage between macroscopic thermodynamics properties and intermolecular interactions of fluids and fluid mixtures. Numerous theories of mixtures exist based on the definition of the radial distribution functions. Utilization of such theories require the knowledge about mixture radial distribution functions and their relations. Generally the exact radial distribution functions of real fluid mixtures are not available.

In this paper a number of approximations for the mixture radial distribution functions are presented. Application of these approximation can result in analytic mixture theories and mixing rules. A uniform statistical mechanical technique is presented through which one can derive equation of state mixing rules based on different RDF approximations. The relative merits of different sets of mixing rules derived by this technique and their applications for modeling of the behavior of mixtures are discussed.

INTRODUCTION AND BACKGROUND

Modern theories of fluids and fluid mixtures have benefited a great deal from the concept of radial distribution function (RDF). The RDF theories have been quite successful in describing the behavior of simple pure liquids [Hill, 1956; McDonald, 1973; McQuarrie, 1975; Haile and Mansoori, 1983]. However, the RDF theories of mixtures have lacked sufficient progress due to complexity of such theories and the increasing number of radial distribution functions in a multicomponent mixture [Matteoli and Mansoori, 1990]. Here we introduce a technique by which it is possible to use approximations for the mixture RDFs in order to develop analytic mixture theories. Recently, constraining relations between RDFs of multicomponent mixtures were derived using statistical mechanical theory of canonical ensembles [Hamad & Mansoori, 1989]. According to these constraints mixture RDFs are not all independent from one another, contrary to the common belief. In here we first introduce the

statistical mechanical basis of RDF and its approximations. Then we present the conformal solution theory of polar fluid mixtures and its relationship to the idea of mixing rules. Then the concept of the statistical mechanical mixing rules are presented and different sets of mixing rules are derived. Guidelines for the use of statistical mechanical mixing rules and combining rules in equations of state and their application are discussed.

In the canonical ensemble of statistical mechanics where the temperature, T , the volume, V , and the number of particles of each component in the system, N_i , are fixed, the partition function, Q , for a c -component system is:

$$Q(T, V, N) = \sum e^{-\epsilon_j/kT}, \quad (1)$$

where k is Boltzmann constant, ϵ_j is the energy of the particles at level j and $N=N_1, N_2, \dots, N_c$. The summation in eq.(1) is carried over all the molecules in all energy levels. The canonical partition function, Q , is related to the Helmholtz free energy, A , by

$$A = -kT \ln Q(T, V, N). \quad (2)$$

The relation between the microscopic and the macroscopic properties can be obtained for other ensembles as well. In the grand canonical ensemble, where the temperature, the volume and the chemical potential of each component in the system are fixed, the partition function, Ξ , is:

$$\Xi(T, V, \mu) = \sum_{N_1} \dots \sum_{N_c} Q(T, V, N) e^{\mu \cdot N/kT}, \quad (3)$$

where $N = \mu_1, \mu_2, \dots, \mu_c$ and the scalar product $\mu \cdot N$ is:

$$\mu \cdot N = \sum_{k=1}^c \mu_k N_k. \quad (4)$$

Equations (1 & 3) are completely general for equilibrium systems. However, it is very difficult to get the quantum mechanical energy levels for real systems. The small energy gap between consecutive energy levels for all molecules, except the lightest, such as H_2 and He , allows replacing the summation in eq.(1) by integration over the phase space, thus obtaining the semi-classical partition function. This partition function is:

$$Q(T, V, N) = Q_{int} \prod_{i=1}^c (N_i! \lambda_i^{3N_i})^{-1} \int_V \dots \int_V e^{-\Phi/kT} dr_1 \dots dr_N, \quad (5)$$

where N is the set of number of molecules, N_1, N_2, \dots, N_c , Q_{int} is partition function due to the internal motions of the molecules, Φ is the total potential energy of the system, k is Boltzmann constant, r_i is the position vector of

molecule i , \prod denotes the product over i and λ_i is the thermal wavelength of component i , $\lambda_i = h / (2\pi m_i kT)$, h is Planck's constant, m_i is the mass of molecule i , Φ is the total potential energy of the system and r_i is the position vector of molecule i . All the integrals in eq.(5) are carried over the system volume. The partition function can be evaluated, at least in principle, by carrying out the integrations in eq.(6) for a substance with known potential function. However, this task is very difficult because of the very large number of molecules involved in real systems. A more convenient formulation is based on the concept of distribution functions. The probability, $P(N)$, of finding molecule 1 in volume element dr_1 at r_1 , molecule 2 in volume element dr_2 at r_2 , . . . , and molecule N in volume element dr_N at r_N is given by [Hill, 1956]

$$P(N) dr_1 \dots dr_N = e^{-\Phi/kT} dr_1 \dots dr_N / Z(T, V, N), \quad (6)$$

where $Z_c(T, V, N)$ is the configurational integral,

$$Z_c(T, V, N) = \int \dots \int e^{-\Phi/kT} dr_1 \dots dr_N. \quad (7)$$

Usually we are interested in the relative position of two molecules, irrespective of the location of the other molecules in the system. This can be obtained by integrating eq.(6) over the positions of all molecules except those which we are interested in. This leads to the definition of the distribution function, $\rho^{(2)}_{ij}(r_1, r_2)$, which gives the probability of finding a molecule of type i in dr_1 at r_1 and molecule of type j in dr_2 at r_2 ,

$$\rho^{(2)}_{ij}(r_1, r_2) = N_i(N_j - \delta_{ij}) \int \dots \int e^{-\Phi/kT} dr_3 \dots dr_N / Z_c(T, V, N), \quad (8)$$

where δ_{ij} is the Kronecker delta. Note that $\rho^{(2)}_{ij}(r_1, r_2)$ depends on temperature, density and composition in addition to r_1 and r_2 . For molecules which interact with radially symmetric potential functions $\rho^{(2)}_{ij}(r_1, r_2)$, in the fluid state, depends only on the distance between the centers of masses $r_{12} = |r_1 - r_2|$. In the limit of ideal gas ($\Phi/kT \rightarrow 0$) the distribution function $\rho^{(2)}_{ij}(r_1, r_2)$ approaches the value $N_i(N_j - \delta_{ij})/V^2$. This suggests defining the pair radial distribution function, $g_{ij}(r)$, by

$$g_{ij}(r) = \rho^{(2)}_{ij}(r) V^2 / (N_i N_j), \quad (9)$$

which approaches $1 - \delta_{ij}/N_j$ in the above limit. Combining eqs.(8 and 9) gives

$$g_{ij}(r) = V^2 (1 - \delta_{ij}/N_j) \int \dots \int e^{-\Phi/kT} dr_3 \dots dr_N / Z_c(T, V, N). \quad (10)$$

A similar definition for the distribution function in the grand canonical

ensemble exists [Hill, 1956; McQuarrie, 1975]

$$g_{ij}(r) = V^2 / (N_i N_j) \sum_{N_1 \geq 1} \sum_{N_2 \geq 1} \dots \sum_{N_c} \pi(N!_k) e^{\mu \cdot N / kT} \int \dots \int e^{-\Phi / kT} dr_3 \dots dr_N / \Xi(T, V, \mu). \quad (11)$$

The pair radial distribution function in the grand canonical ensemble approaches unity in the limit of ideal gas. Next the relationships between the distribution functions and the thermodynamic properties of fluids are considered.

The relation between $g(r)$ and the internal energy, u , is derived from the definition of the internal energy in terms of the canonical ensemble partition function:

$$u = u_{ig} + kT^2 [\partial \ln Z_c(T, V, N) / \partial T]_{N, V}, \quad (12)$$

where u_{ig} is the ideal gas internal energy. Substituting for $Z_c(T, V, N)$ from eq.(12) with the assumption of pairwise additivity,

$$\Phi = \sum_{i=1}^N \sum_{j < i}^N \phi(r_{ij}). \quad (13)$$

The relation between the internal energy and the radial distribution function for pure fluids is obtained:

$$u = u_{ig} + (1/2) N \rho \int_0^{\infty} \phi(r) g(r) 4\pi r^2 dr, \quad (14)$$

where ρ is the molecular number density, N/V . Equation (14) can also be derived from the grand canonical ensemble distribution function. For mixtures of c components eq.(14) takes the form [Hill, 1956]

$$u = u_{ig} + (1/2) N \rho \sum_{i=1}^c \sum_{j=1}^c x_i x_j \int_0^{\infty} \phi_{ij}(r) g_{ij}(r) 4\pi r^2 dr, \quad (15)$$

where x_i is the mole fraction of component i and ϕ_{ij} is the pair intermolecular potential energy function for molecules of type i and j .

For pure fluids the pressure is given in terms of $g(r)$ by [Hill, 1956]

$$p = kT\rho - \rho^2 / 6 \int_0^{\infty} r \phi'(r) g(r) 4\pi r^2 dr. \quad (16)$$

For mixtures, eq.(15) takes the form [Hill, 1956]

$$p = kT\rho - \rho^2 / 6 \sum_{i=1}^c \sum_{j=1}^c x_i x_j \int_0^{\infty} r \phi'_{ij}(r) g_{ij}(r) 4\pi r^2 dr, \quad (17)$$

where ϕ' is the derivative of the potential function with respect to the distance r . The assumption of pairwise additivity of the potential energy function is also

needed in deriving the pressure eqs.(16 and 17).

A relation between the isothermal compressibility, $\kappa_T = \rho^{-1}(\partial\rho/\partial p)_T$, and $g(r)$ can be derived without assuming pairwise additivity of the potential function. This relation is obtained from the grand canonical ensemble radial distribution function [Hill, 1956]

$$\rho kT\kappa_T = 1 + \rho \int_0^{\infty} [g(r) - 1] 4\pi r^2 dr. \quad (18)$$

The corresponding relation for mixtures was derived by Kirkwood and Buff (1951)

$$\rho kT\kappa_T = \frac{|B|}{\rho \sum_i \sum_j x_i x_j |B|_{ij}}, \quad (19)$$

where $|B|_{ij}$ symbolizes the cofactor of the element B_{ij} in the $c \times c$ matrix B and $|B|$ is the determinant of B . The elements, B_{ij} , of the matrix are:

$$B_{ij} = \rho x_i [\delta_{ij} + \rho x_j G_{ij}], \quad (20)$$

where G_{ij} is the radial distribution function integral defined by

$$G_{ij} = \int_0^{\infty} [g_{ij}(r) - 1] 4\pi r^2 dr. \quad (21)$$

Theories of Radial Distribution Function (RDF): Historically the first theory that allows calculating the distribution functions was suggested by Kirkwood. This theory is called the superposition approximation [Kirkwood, 1935]:

$$\rho^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_3) \rho^{(2)}(\mathbf{r}_2, \mathbf{r}_3). \quad (22)$$

The motivation for making this approximation is the existence of exact equations (within the pairwise additivity assumption) for n -molecule distribution functions in terms of $(n+1)$ -molecule functions which were first derived by Yvon (1935). For $n=2$ the equation is [Hill, 1956; Boublik et al. 1980]:

$$kT\partial \ln \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) / \partial \mathbf{r}_1 = -\partial \phi(\mathbf{r}_1, \mathbf{r}_2) / \partial \mathbf{r}_1 - \int \partial \phi(\mathbf{r}_1, \mathbf{r}_3) / \partial \mathbf{r}_1 \rho^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) / \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_3 \quad (23)$$

Combining eqs.(22) and (23) yields the Yvon-Born-Green integro-differential equation [Yvon, 1935; Born and Green, 1946]. A similar equation was derived based on the notion of the coupling parameter [Kirkwood and Monroe, 1941; Kirkwood and Boggs, 1942]. Unfortunately, both equations are nonlinear and difficult to solve, even numerically. Salpeter (1958) derived a second exact relation between the two-body and three-body distribution functions. However,

this relation is found to be of limited practical use because of its infinite number of terms which are related to irreducible clusters [Salpeter, 1958].

The method of topological reduction was utilized to derive integral equations for the distribution functions. In this approach a relation between the total and the direct correlation functions is assumed, in addition to the relation which defines the direct correlation function. The Percus-Yevick [Percus and Yevick, 1958] and the hypernetted chain [van Leeuwen et al., 1959] integral equations are derived using this method. They are, respectively, based on the assumptions $c(r)=g(r)[1-e^{-\phi/kT}]$ and $c(r)=g(r)-\ln[g(r)]-1-\phi/kT$. The distribution functions $c(r)$ and $g(r)$ can be solved for by combining either (25) or (26) with the definition of $c(r)$. The extension of the above equations to mixtures is straightforward.

Except for the simplest models of pair interactions, such as the hard sphere model, mixture calculations using the integral equations approach are extremely complicated and do not always produce analytic results [Boublik et al., 1980]. This and the fact that for real fluids the potential energy functions are not well known makes the above approach unsuitable for getting real fluid mixture properties for practical purposes. For the time being it seems that the best approach is to start from known pure fluid properties (in the form of equations of state, for example) and develop mixture models that utilize these properties in predicting mixture behavior. Some of the models which have been successful in this field are the perturbation and variational theory and the conformal solution theory.

The perturbation theory [McQuarrie and Katz, 1966; Barker et al. 1968; Weeks et al., 1971] divides the potential function into a reference part and a perturbation part. The reference part represents a potential model for which the thermodynamic properties are known, such as the hard sphere model. The variational theory [Mansoori, 1972a] provides inequalities which give least upper bound and highest lower bound to the Helmholtz free energy. In both theories a reference system, for which thermodynamic properties and radial distribution functions are known, is needed. Mixture calculations based on these theories, although simpler than the integral equations approach, are still lengthy and usually no closed form expressions can be obtained.

The conformal solution theory [Brown, 1957a, b, c; Hoheisel and Lucas, 1984] presents another alternative for calculating mixture properties by allowing us to produce mixing rules as discussed below.

CONFORMAL SOLUTION THEORY (CST) OF MIXTURES

Conformal solutions refer to substances whose intermolecular potential energy function, ϕ_{ij} , are related to each other and to those of a reference fluid, usually designated by subscript (oo), according to [Brown, 1957; Massih and Mansoori, 1983, Shukla et al., 1986]

$$\phi_{ij} = f_{ij}\phi_{oo}(r/h_{ij}^{1/3}) \quad (24)$$

For substances whose intermolecular potential energy function can be represented by an equation of the form

$$\phi_{ij} = E_{ij}[(L_{ij}/r)^n - (L_{ij}/r)^m] \quad (28)$$

and for which exponents m and n are the same as for the reference substance, conformal parameters f_{ij} and h_{ij} will be defined by the following relations with respect to the intermolecular potential energy parameters E_{ij} and L_{ij} :

$$f_{ij} = E_{ij}/E_{00}, \quad h_{ij} = (L_{ij}/L_{00})^3 \quad (29)$$

Thus the configurational Helmholtz free energy of a pure substance of type (i) are related to those of the reference substance denoted by subscript (o) according to the following relation:

$$F_1(V, T) = f_{ij}F_0(V/h_{ij}, T/f_{ij}) - NkT \ln h_{ij} \quad (27)$$

All the other thermodynamic properties of substance (i) can also be expressed in terms of the properties of a reference pure substance (o) through the conformal parameters f_{ij} and h_{ij} . The conformal solution treatment of fluids composed of polar molecules is more complicated than for non-polar fluids due to electrostatic interactions which cause the departure of the intermolecular potential from spherical symmetry. In order to extent utility of the conformal solution theory to polar fluids the following expressions for conformal parameters f_{ij} & h_{ij} were proposed [Massih and Mansoori, 1983]

$$f_{ij} = E_{ij}(T, r)/E_{00}(T, r); \quad h_{ij} = (L_{ij}(T, r)/L_{00}(r, r)) \quad (28)$$

with $E_{ij}(T, r) = K\epsilon_{ij}A_{ij}(T, r)[H_{ij}(T, r)]^{n/m}$, $L_{ij}(T, r) = \sigma_{ij}[H_{ij}(T, r)]^{-1/m}$,

$$H_{ij}(T, r) = [C_{ij}(T, r)/A_{ij}(T, r)]^{m/(n-m)}, \quad A_{ij}(T, r) = 1 + 7\mu_i^4\mu_j^4/[1800(kT)^3r^{12-m}\sigma_{ij}^nK\epsilon_{ij}],$$

$$\text{and } C_{ij}(T, r) = 1 + \mu_i^2\mu_j^2/[12kTr^{6-m}\sigma_{ij}^mK\epsilon_{ij}] + (7/20)Q_i^2Q_j^2/[kTr^{10-m}\sigma_{ij}^6K\epsilon_{ij}] \\ + (\mu_i^2Q_j^2 + \mu_j^2Q_i^2)/[8kTr^{8-m}\sigma_{ij}^mK\epsilon_{ij}] + (\alpha_i\mu_j^2 + \alpha_j\mu_i^2)/[4r^{6-m}\sigma_{ij}^mK\epsilon_{ij}].$$

and where μ_i , Q_i , and α_i are the dipole moment, quadrupole moment, and polarizability of molecule i , respectively, and $K = [n/(n-m)](n/m)^{m/(n-m)}$ with m and n being integers ($n > m > 3$).

There exist two categories of CST for mixtures: One-fluid and multi-fluid theories. The basic concept of the one-fluid CST of mixtures is the same as for pure fluids where there is one reference fluid to deal with, except that f_{ij} and

h_{ij} in eq.(27) should be replaced with f_{xx} and h_{xx} ,

$$F_x(V, T) = f_{xx}F_0(V/h_{xx}, T/f_{xx}) - NkT \ln h_{xx}$$

where f_{xx} and h_{xx} are the mixture conformal parameters which are generally functions of f_{ij} , h_{ij} , compositions, density and temperature.

$$f_{xx} = f_{xx}(f_{ij}, h_{ij}; x_i, \rho, T); \quad h_{xx} = h_{xx}(f_{ij}, h_{ij}, x_i, \rho, T) \quad (29)$$

Eqs.(29) are called the one-fluid conformal solution mixing rules. Functional forms of these mixing rules will be different for different theories of mixtures as it will be demonstrated later in this report.

In the case of the multi-fluid CST of mixtures it is assumed there exists a c -component ideal solution which represents the real mixture. Helmholtz free energy of this mixture is shown by the following equation

$$F_x(V, T) = \sum_i f_{ix} F_0(V/h_{ix}, T/f_{ix}) - NkT \sum_i \ln h_{ix} \quad (30)$$

Then, f_{ix} and h_{ix} are conformal parameters of components of this ideal solution as shown by,

$$f_{ix} = f_{ix}(f_{ij}, h_{ij}, x_i); \quad h_{ix} = h_{ix}(f_{ij}, h_{ij}, x_i) \quad (31)$$

where eqs.(31) are the multi-fluid conformal solution mixing rules.

In the formulation of a mixture theory we also need to know the combining rules for unlike-interaction potential parameters which are usually expressed by the following expressions

$$f_{ij} = (1 - \kappa_{ij})(f_{ii} f_{jj})^{1/2}; \quad h_{ij} = (1 - \lambda_{ij})[(h_{ii}^{1/3} + h_{jj}^{1/3})/2]^3 \quad (32)$$

where κ_{ij} and λ_{ij} are adjustable parameters. The remaining requirement in the application of the CST for mixtures is development of analytic expressions for mixing rules given by eqs.(29) or (31).

ONE-FLUID CST APPROXIMATIONS OF RDF

To develop one-fluid mixing rules we introduce a pseudo-pure fluid which can represent the configurational properties of a mixture provided that the pseudo-pure fluid and the mixture molecular interactions obey eq.(24). By replacing eq.(24) in eqs.(12, 13, 16, and 17) and then equating configurational internal energy, pressure, and isothermal compressibility of the pseudo-pure fluid and the mixture we will obtain the following equations

$$f_{xx}h_{xx} \int \phi_{oo}(y)g_{oo}(y)y^2 dy = \sum_i \sum_j x_i x_j f_{ij} h_{ij} \int \phi_{oo}(y)g_{ij}(y)y^2 dy \quad (33)$$

$$f_{xx}h_{xx} \int y \phi'_{oo}(y)g_{oo}(y)y^2 dy = \sum_i \sum_j x_i x_j f_{ij} h_{ij} \int y \phi'_{oo}(y)g_{ij}(y)y^2 dy \quad (34)$$

$$\{1 - 4\pi\rho h_{xx} \int [g_{oo}(y) - 1]y^2 dy\} - 1 = \sum_i \sum_j x_i x_j |B|_{ij} / |B| \quad (35)$$

where $y = r/d$ and r/d_{ij} is the dimensionless-intermolecular distance or the integration variable. With the use of appropriate relations between g_{oo} and g_{ij} solution of eqs.(33-35) could produce the necessary expressions (mixing rules) relating f_{xx} and h_{xx} of the pseudo-pure fluid to f_{ij} and h_{ij} of components of the mixture. In what follows different approximations will be used for relating g_{ij} to g_{oo} in order to derive different sets of mixing rules.

It should be pointed out that for the case of the hard-sphere fluid eq.(33) vanishes, eq.(35) remains the same, while eq.(34) reduces to

$$h_{xx} g_{oo}^{hs}(1) = \sum_i \sum_j x_i x_j h_{ij} g_{ij}^{hs}(1) \quad (36)$$

where $g_{oo}^{hs}(1)$ and $g_{ij}^{hs}(1)$ are the hard-sphere RDFs at contact.

Random Mixing Approximation (RMA): According to this approximation (Mansoori, 1986)

$$g_{oo}(r) = g_{11}(r) = g_{22}(r) = \dots = g_{ij}(r) = \dots \quad (37)$$

With this approximation replaced in eqs.(33-35), eq.(35) will vanish and eq.(33 and 34) will produce the following mixing rules, respectively

$$\phi_{xx}(r) = \sum_i \sum_j x_i x_j \phi_{ij}(r) \quad \text{and} \quad \phi'_{xx}(r) = \sum_i \sum_j x_i x_j \phi'_{ij}(r) \quad (38)$$

In the case of the Lennard-Jones (12-6) intermolecular potential function (38) will reduce to the mixing rules reported in Table I [Scott, 1956] from eqs.(12 and 13).

Conformal Solution Approximation (CSA): According to this approximation [Leland et al., 1968],

$$g_{11}(y) = g_{22}(y) = \dots = g_{ij}(y) = \dots \quad (39)$$

When we use this approximation in eqs.(33 and 34) they both produce

$$f_{xx}h_{xx} = \sum_i \sum_j x_i x_j f_{ij} h_{ij} \quad (40)$$

Now, by replacing eq.(39) in (35) an additional mixing rule will be produced,

$$|B^*|/\rho RT_{k_{T_{xx}}} = \sum_i \sum_j x_i x_j |B^*|_{ij}. \quad (41)$$

where $|B^*|_{ij} = x_i [\delta_{ij} + x_j (h_{ij}/h_{xx}) (\rho RT_{k_{T_{xx}}} - 1)]$. Eq.(40) is actually the second van der Waals mixing rule which is well known, but eq.(41) is a new mixing rule for h_{xx} which is composition-, temperature-, and density-dependent due to appearance of $k_{T_{xx}}$ in this equation. eq.(41) can be solved for h_{xx} . For example, for a binary mixture eq.(41) gives

$$h_{xx} = \{ \sum_i \sum_j x_i x_j h_{ij} + x_1 x_2 (h_{11} h_{22} - h_{12}^2) (\rho RT_{k_{T_{xx}}} - 1) \} / \{ 1 + x_1 x_2 (h_{11} + h_{22} - 2h_{12}) (\rho RT_{k_{T_{xx}}} - 1) \} \quad (42)$$

By using the hard-sphere potential [by replacing eq.(39) in (36)] we will derive,

$$h_{xx} = \sum_i \sum_j x_i x_j h_{ij} \quad (43)$$

This mixing rule is the first van der Waals mixing rule which, in conjunction with eq.(40) is usually used for calculation of mixture thermodynamic properties (Leland et al., 1968).

Hard-Sphere Expansion (HSE) Approximation: It is demonstrated that the RDF of a pure fluid (x) can be expanded around the hard-sphere (hs) RDF in the form (Hill, 1956)

$$g_{xx}(y) = g^{hs}(y) + (f_{xx}/T_o^*) g_1(y) + (f_{xx}/T_o^*)^2 g_2(y) + \dots \quad (44)$$

Let us also assume we could make a similar expansion for RDFs in a mixture around the hard-sphere mixture RDFs

$$g_{ij}(y) = g_{ij}^{hs}(y) + (f_{ij}/T_o^*) g_1(y) + (f_{ij}/T_o^*)^2 g_2(y) + \dots \quad (45)$$

The justification behind this expansion is given elsewhere [Hill, 1956]. By replacing eqs.(44 and 45) in either of eqs.(33 or 34) and equating the coefficients of the second and third order inverse temperature terms of the resulting expression we will derive the expressions reported in Table I. These mixing rules are to be used for calculation of excess properties of a mixture over the hard-sphere mixture [Mansoori and Leland, 1972; Lan and Mansoori, 1977] at the same thermodynamic conditions. By using the HSE approximation in eq.(35) we could not produce any additional mixing rule.

Density Expansion (DEX) Approximation: It has been demonstrated that the RDF of a pure fluid can be expanded around the dilute gas RDF, $\exp[-\phi(r)/kT]$, in the form [Hill, 1956]

$$g_{xx}(y) = [1 + \rho_{xx}^* F_{xx}^{(1)}(y, T_{xx}^*) + (\rho_{xx}^*)^2 F_{xx}^{(2)}(y, T_{xx}^*) + \dots] \exp[-\phi_{xx}(r)/kT] \quad (46)$$

Let us also assume we could make a similar expansion of mixture RDFs around

the dilute gas mixture RDFs [Mansoori and Ely, 1985a],

$$g_{ij}(y) = [1 + \rho^*_{ij} F^{(1)}_{ij}(y, T^*_{ij}) + (\rho^*_{ij})^2 F^{(2)}_{ij}(y, T^*_{ij}) + \dots] \exp[-\phi_{ij}(r)/kT] \quad (47)$$

By replacing eqs.(46 and 47) in eq.(33) and after a number of algebraic manipulations we get

$$f_{xx} h_{xx} = \sum_i \sum_j x_i x_j f_{ij} h_{ij} \{1 - (f_{ij}/f_{xx} - 1)[u - u_{ig}]/kT + T(C_v - C_{v,ig})/(u - u_{ig})\} \quad (48)$$

This mixing rule can be used, joined with another mixing rule, for calculation of mixture properties. This approximations may be also used in the virial and compressibility equations which would produce other, but more complex, mixing rules.

In Table I the mixing rules for conformal parameters f & h derived by different one-fluid CST approximations of RDF are reported.

TABLE I

One-Fluid Conformal Solution Mixing Rules According to Different RDF Theories

BMA

$$f_{xx} h_{xx} = [\sum_i \sum_j x_i x_j f_{ij} h_{ij}^2]^{3/2} / [\sum_i \sum_j x_i x_j f_{ij} h_{ij}^4]^{1/2}$$

$$h_{xx} = [\sum_i \sum_j x_i x_j f_{ij} h_{ij}^4 / \sum_i \sum_j x_i x_j f_{ij} h_{ij}^2]^{1/2}$$

vdW

$$f_{xx} h_{xx} = \sum_i \sum_j x_i x_j f_{ij} h_{ij}$$

$$h_{xx} = \sum_i \sum_j x_i x_j h_{ij}$$

HSE

$$f_{xx} h_{xx} = \sum_i \sum_j x_i x_j f_{ij} h_{ij}$$

$$h_{xx} = [\sum_i \sum_j x_i x_j f_{ij} h_{ij}]^2 / \sum_i \sum_j x_i x_j f_{ij}^2 h_{ij}$$

DEX

$$f_{xx} h_{xx} = \sum_i \sum_j x_i x_j f_{ij} h_{ij} \{1 - (f_{ij}/f_{xx} - 1)[u - u_{ig}]/kT + T(C_v - C_{v,ig})/(u - u_{ig})\}$$

$$h_{xx} = \sum_i \sum_j x_i x_j h_{ij}$$

CSA

$$f_{xx} h_{xx} = \sum_i \sum_j x_i x_j f_{ij} h_{ij}$$

$$1 + \Delta_{xx} = |B^*| / \sum_i \sum_j x_i x_j |B^*|_{ij}; \quad B^*_{ij} = x_i (\delta_{ij} + x_j \Delta_{xx} h_{ij} / h_{xx})$$

$$\Delta_{xx} = \rho RT \kappa_{Tx}; \quad \kappa_T = -(1/V)(\partial V / \partial P)_T$$

MULTI-FLUID CST APPROXIMATIONS OF RDF

In this case eqs.(33-35) will be replaced by the following set of equations

$$f_{ix}h_{ix}\int\phi_{oo}(y)g_{oo}(y)y^2dy=\sum_jx_jf_{ij}h_{ij}\int\phi_{oo}(y)g_{ij}(y)y^2dy \quad (49)$$

$$f_{ix}h_{ix}\int y\phi'_{oo}(y)g_{oo}(y)y^2dy=\sum_jx_jf_{ij}h_{ij}\int y\phi'_{oo}(y)g_{ij}(y)y^2dy \quad (50)$$

$$\{1-4\pi\rho h_{ix}\int[g_{oo}(y)-1]y^2dy\}-1=\sum_jx_j|B|_{ij}/|B| \quad (51)$$

Expressions for B_{ij} and G_{ij} will be the same as in eq.(17). In the case of the hard-sphere fluid eq.(50) will vanish, eq.(51) will remain the same and eq.(49) will reduce to

$$h_{ix}g_{oo}^{hs}(1)=\sum_jx_jh_{ij}g_{ij}^{hs}(1). \quad (52)$$

Average Potential Model (APM): According to this approximation (Mansoori, 1986),

$$g_{ij}(r) = [g_{ii}(r) + g_{jj}(r)]/2; \quad g_{ii}(r) \approx g_{jj}(r) \quad (53)$$

When this approximation is replaced in eqs.(34-36), eq.(36) will vanish and eq.(34) and (35) will produce the following mixing rules [Scott, 1956]

$$\phi_{ix}(r) = \sum_jx_j\phi_{ij}(r) \quad \text{and} \quad \phi'_{ix}(r) = \sum_jx_j\phi'_{ij}(r) \quad (54)$$

In the case of the Lennard-Jones (12-6) intermolecular potential function (Scott, 1956) these equations reduce to the expressions reported in Table II.

Multi-fluid CSA Approximation: According to this approximation

$$g_{ij}(y) = [g_{ii}(y) + g_{jj}(y)]/2; \quad g_{ii}(r) \approx g_{jj}(y); \quad (55)$$

When we use this approximation in eqs.(34 and 35) they both produce the same mixing rule,

$$f_{ix}h_{ix} = \sum_jx_jf_{ij}h_{ij} \quad (56)$$

This equation is actually the second van der Waals multi-fluid mixing rule. Also by replacing eq.(55) in (36) an additional mixing rule will be produced,

$$|B^*|/\rho RT\kappa_{Tix} = \sum_jx_j|B^*|_{ij}. \quad (57)$$

where $|B^*|_{ij} = x_i\{\delta_{ij} + (x_jh_{ij}/2)[(\rho RT\kappa_{Tix}-1)/h_{ix}+(\rho RT\kappa_{Txj}-1)/h_{xj}]\}$.

Eq.(57) is a new mixing rule for h_{ix} . By using the hard-sphere potential [by replacing eq.(55) in (36)] we will derive the following mixing rule

$$h_{ix} = \sum_j x_j h_{ij} \quad (58)$$

This mixing rule is the first multi-fluid van der Waals mixing rule which, in conjunction with eq.(56) is usually used for calculation of mixture thermodynamic properties.

Multi-Fluid HSE for Mixtures: In a similar manner as the one-fluid case we can derive the mixing rules reported in Table II. These mixing rules are used for calculation of excess properties of a mixture over the hard-sphere mixture.

Multi-Fluid DEX Approximation: In a similar manner as the one-fluid case we can derive the mixing rules reported in Table II.

In Table II the mixing rules for conformal parameters f & h derived by different multi-fluid CST approximations of RDF are reported.

TABLE II

Multi-Fluid Conformal Solution Mixing Rules According to Different Theories

APM

$$f_{ix} h_{ix} = [\sum_j x_j f_{ij} h_{ij}^2]^{3/2} / [\sum_j x_j f_{ij} h_{ij}^4]^{1/2}$$

$$h_{ix} = [\sum_j x_j f_{ij} h_{ij}^4 / \sum_j x_j f_{ij} h_{ij}^2]^{1/2}$$

vdW

$$f_{ix} h_{ix} = \sum_j x_j f_{ij} h_{ij}$$

$$h_{ix} = \sum_j x_j h_{ij}$$

HSE

$$f_{ix} h_{ix} = \sum_j x_j f_{ij} h_{ij}$$

$$h_{ix} = [\sum_j x_j f_{ij} h_{ij}]^2 / \sum_j x_j f_{ij}^2 h_{ij}$$

DEX

$$f_{ix} h_{ix} = \sum_j x_j f_{ij} h_{ij} \{1 - (f_{ij}/f_{ix} - 1)[u - u_{ig}]/kT + T(C_v - C_{v,ig})/(u - u_{ig})\}$$

$$h_{ix} = \sum_j x_j h_{ij}$$

CSA

$$f_{ix} h_{ix} = \sum_j x_j f_{ij} h_{ij}$$

$$1 + \Delta_{ix} = |B^*| / \sum_j x_j |B^*|_{ij}; \quad B^*_{ij} = x_i (\delta_{ij} + x_j \Delta_{ix} h_{ij} / h_{ix})$$

$$\Delta_{ix} = \rho RT \kappa_{Tx}; \quad \kappa_T = -(1/V)(\partial V / \partial P)_T$$

APPLICATION OF MIXING RULES FOR EQUATIONS OF STATE

The mixing rules for conformal parameters based on different theories are tabulated in Tables I and II. These can be directly used in equations of state in which the parameters are actually intermolecular potential parameters. In order to apply these mixing rules for other equations of state one has to express their parameters with respect to the conformal parameters h and f . As an example we demonstrate here the use of these mixing rules and combining rules for a generalized three-parameter cubic equation of state of the form

$$Z = Pv/RT = v/(v - b) - (av/RT)/[T^\theta(v^2 + \alpha cv + \beta c^2)] \quad (59)$$

This equation can reduce to the commonly used cubic equations of state using proper values for θ , α and β as demonstrated in Table III.

TABLE III

Parameters of the generalized equation of state $Z = v/(v - b) - (av/RT) / [T^\theta(v^2 + \alpha cv + \beta c^2)]$ according to different cubic equations.

Equation of State	θ	α	β
Van der Waals	0	0	0
Bethelot	1	0	0
Clausius	1	2	1
Heyen	0	$(b+c)/c$	$-b/c$
Keys	0	-2	1
Peng-Robinson	0	$2b/c$	$-b^2/c^2$
Redlich-Kwong	1/2	b/c	0
Yu-Lu	0	$(3b+c)/c$	b/c

parameters (b) and (c) in this equation are proportional to molecular volume ($b \propto h$, $c \propto h$) while parameter (a) is proportional to (molecular volume) \times (molecular energy) $^{1+\theta}$ or ($a \propto h \cdot f^{1+\theta}$). By considering these proportionalities we can apply the mixing rules of Table I for parameters a , b , & c of eq.(59) to derive the one-fluid mixing rules as reported in Table IV.

TABLE IV

One-Fluid Mixing Rules for the Generalized Cubic Equation of State

$$Z_x = Pv/RT = v/(v - b_{xx}) - (a_{xx}v/RT) / [T^\theta (v^2 + \alpha_{xx}c_{xx}v + \beta_{xx}c_{xx}^2)]$$

According to Different Theories

RMA

$$a_{xx} = [\sum_i \sum_j x_i x_j b_{ij} \Psi_{ij}]^{(3/2+2\theta)} / [\sum_i \sum_j x_i x_j b_{ij}^3 \Psi_{ij}]^{(1/2+\theta)}$$

$$b_{xx} = [\sum_i \sum_j x_i x_j b_{ij}^3 \Psi_{ij} / \sum_i \sum_j x_i x_j b_{ij} \Psi_{ij}]^{1/2}$$

$$c_{xx} = [\sum_i \sum_j x_i x_j c_{ij}^3 \mu_{ij} / \sum_i \sum_j x_i x_j c_{ij} \mu_{ij}]^{1/2}$$

vdW

$$a_{xx} = [\sum_i \sum_j x_i x_j \Psi_{ij}]^{(1+\theta)} / [\sum_i \sum_j x_i x_j b_{ij}]^\theta$$

$$b_{xx} = \sum_i \sum_j x_i x_j b_{ij}$$

$$c_{xx} = \sum_i \sum_j x_i x_j c_{ij}$$

HSE

$$a_{xx} = [\sum_i \sum_j x_i x_j \Psi_{ij}]^{(1-\theta)} [\sum_i \sum_j x_i x_j \Psi_{ij}^2 / b_{ij}]^\theta$$

$$b_{xx} = [\sum_i \sum_j x_i x_j \Psi_{ij}]^2 / \sum_i \sum_j x_i x_j \Psi_{ij}^2 / b_{ij}$$

$$c_{xx} = [\sum_i \sum_j x_i x_j \mu_{ij}]^2 / \sum_i \sum_j x_i x_j \mu_{ij}^2 / c_{ij}$$

DEX

$$a_{xx} = [\sum_i \sum_j x_i x_j b_{ij}]^{-\theta} \left[\sum_i \sum_j x_i x_j \Psi_{ij} \left\{ 1 - [(a_{ij} b_{xx} / a_{xx} b_{ij})^{1/(1+\theta)} - 1] [u - u_{ig}] / kT + T(C_v - C_{v,ig}) / (u - u_{ig}) \right\} \right]^{(1+\theta)}$$

$$b_{xx} = \sum_i \sum_j x_i x_j b_{ij}$$

$$c_{xx} = \sum_i \sum_j x_i x_j c_{ij}$$

CSA

$$a_{xx} = [\sum_i \sum_j x_i x_j \Psi_{ij}]^{(1+\theta)} / b_{xx}^\theta$$

$$1 + \Delta_{xx1} = |B^*| / \sum_i \sum_j x_i x_j |B^*|_{ij}; \quad B^*{}_{ij} = x_i (\delta_{ij} + x_j \Delta_{xx1} b_{ij} / b_{xx}) \quad 1 + \Delta_{xx2} = |B^*| / \sum_i \sum_j x_i x_j |B^*|_{ij}; \quad B^*{}_{ij} = x_i (\delta_{ij} + x_j \Delta_{xx2} c_{ij} / c_{xx})$$

$$\Psi_{ij} = b_{ij} (a_{ij} / b_{ij})^{1/(1+\theta)}$$

$$\mu_{ij} = c_{ij} (a_{ij} / c_{ij})^{1/(1+\theta)}$$

Similarly, we can apply the mixing rules of Table II for parameters a, b, & c of eq.(59) to derive the multi-fluid mixing rules as reported in Table V with the understanding the mixture equation of state will be

$$Z_x = \sum_i x_i Z_i = \sum_i x_i v / (v - b_{ix}) - \sum_i x_i (a_{ix} v / RT) / [T^\theta (v^2 + \alpha_{ix} c_{ix} v + \beta_{ix} c_{ix}^2)] \quad (60)$$

TABLE V

Multi-Fluid Mixing Rules for the Generalized Cubic Equation of State

$$Z_1 = Pv/RT = v/(v - b_{1x}) - (a_{1x}v/RT) / [T^\theta (v^2 + \alpha_{1x}c_{1x}v + \beta_{1x}c_{1x}^2)]$$

According to Different Theories

RMA

$$a_{1x} = [\sum_j x_j b_{1j} \psi_{1j}]^{(3/2+2\theta)} / [\sum_j x_j b_{1j}^3 \psi_{1j}]^{(1/2+\theta)}$$

$$b_{1x} = [\sum_j x_j b_{1j}^3 \psi_{1j} / \sum_j x_j b_{1j} \psi_{1j}]^{1/2}$$

$$c_{1x} = [\sum_j x_j c_{1j}^3 \mu_{1j} / \sum_j x_j c_{1j} \mu_{1j}]^{1/2}$$

vdW

$$a_{1x} = [\sum_j x_j \psi_{1j}]^{(1+\theta)} / [\sum_j x_j b_{1j}]^\theta$$

$$b_{1x} = \sum_j x_j b_{1j}$$

$$c_{1x} = \sum_j x_j c_{1j}$$

HSE

$$a_{1x} = [\sum_j x_j \psi_{1j}]^{(1-\theta)} [\sum_j x_j \psi_{1j}^2 / b_{1j}]^\theta$$

$$b_{1x} = [\sum_j x_j \psi_{1j}]^2 / \sum_j x_j \psi_{1j}^2 / b_{1j}$$

$$c_{1x} = [\sum_j x_j \mu_{1j}]^2 / \sum_j x_j \mu_{1j}^2 / c_{1j}$$

DEX

$$a_{1x} = [\sum_j x_j b_{1j}]^{-\theta} \left[\sum_j x_j \psi_{1j} \left\{ 1 - [(a_{1j} b_{1x} / a_{1x} b_{1j})^{1/(1+\theta)} - 1] [u - u_{1g}] / kT + T(C_v - C_{v1g}) / (u - u_{1g}) \right\} \right]^{(1+\theta)}$$

$$b_{1x} = \sum_j x_j b_{1j}$$

$$c_{1x} = \sum_j x_j c_{1j}$$

CSA

$$a_{1x} = [\sum_j x_j \psi_{1j}]^{(1+\theta)} / b_{1x}^\theta$$

$$1 + \Delta_{1x1} = |B^*| / \sum_j x_j |B^*|_{1j}; \quad B^*_{1j} = x_1 (\delta_{1j} + x_j \Delta_{1x1} b_{1j} / b_{1x})$$

$$1 + \Delta_{1x2} = |B^*| / \sum_j x_j |B^*|_{1j}; \quad B^*_{2j} = x_1 (\delta_{1j} + x_j \Delta_{1x2} c_{1j} / c_{1x})$$

$$\psi_{1j} = b_{1j} (a_{1j} / b_{1j})^{1/(1+\theta)} \quad \mu_{1j} = c_{1j} (a_{1j} / c_{1j})^{1/(1+\theta)}$$

The combining rules for a_{ij} , b_{ij} and c_{ij} ($i \neq j$) of this equation of state, consistent with eqs.(32) will be

$$a_{ij} = (1 - k_{ij}) (a_{ii} a_{jj})^{1/2} [b_{ij} / (b_{ii} b_{jj})^{1/2}]^{\theta+1} \quad (61)$$

$$b_{ij} = (1 - \ell_{ij}) [(b_{ii}^{1/3} + b_{jj}^{1/3}) / 2]^3 \quad (62)$$

$$c_{ij} = (1 - m_{ij}) [(c_{ii}^{1/3} + c_{jj}^{1/3}) / 2]^3 \quad (63)$$

It should be pointed out that in some equations of state one or more of the parameters (a , b , c) are not constants, but functions of temperature (or

volume). In such a case one has to write the mixing rules for the constants of the parameter involved. One such example is the Peng - Robinson equation of state in which parameter a is a function of temperature,

$$a(T) = a_c \{1 + \theta [1 - T/T_c]^{1/2}\}^2 \quad (64)$$

where $a_c = 0.45724R^2T_c^2/P_c$; $\theta = 0.37464 + 1.54226\omega - 0.26992\omega^2$, T_c and P_c are the critical temperature and pressure, respectively; and ω is the acentric factor. In order to utilize the mixing rules for this equation of state we first separate thermodynamic variables from constants of parameter a and re-write it in the following form

$$a(T) = a_1/RT + a_2 - 2(a_1a_2/RT)^{1/2}, \quad a_1 = a_c(1+\theta)^2, \quad a_2 = a_c\theta^2/RT_c \quad (65)$$

As a result there exist three independent parameters (a_1 , a_2 , b) in the PR equation. Parameters (a_2) and (b) are proportional to the molecular volume ($a_2 \propto h$; $b \propto h$) while parameter (a_1) is proportional to (molecular volume)(molecular energy) or ($a_1 \propto f \cdot h$). Then, by replacing $a \rightarrow a_1$ and $c \rightarrow a_2$ we can use the mixing rules of Tables IV and V and combining rules given by eqs. (61-63) for this equation.

THE ROLE OF THREE-BODY INTERACTIONS

In the mixture models presented above basically two principles are considered. One is the choice of mixing rules and the other is the choice of an equation of state for a reference pure system. The unlike-interaction parameters of the mixing rules are then fitted to the binary mixture data. When the resulting equations of state are used for prediction of multicomponent mixtures sometimes certain deviations are observed in predicting their properties which indicates an inconsistency in the mixture models. Our studies indicate that some of the inconsistencies of mixture equations of state in simultaneous prediction of binary and multicomponent mixtures is due to the lack of consideration of the three-body interaction energies in the theory of mixtures. Such problems are not expected to arise in a rigorous statistical mechanical equation of state in which the three-body effects are incorporated in its formulation [Benmekki and Mansoori, 1988].

The three-body potential between three different molecules can be effectively approximated to the Axilrod and Teller triple-dipole interaction energy as the following [Lan and Mansoori, 1977]

$$W_{123} = v_{123} [3 \cos \delta_1 \cos \delta_2 \cos \delta_3] / (r_{12} r_{13} r_{23})^3 \quad (66)$$

Where δ_i is the angle between sides r_{ij} and r_{ik} , and v_{123} is a positive quantity.

Bell and Kingston have demonstrated that the unlike-three-body interaction is the largest part of the three-body interaction. Contribution of triple-dipole three-body interactions to the thermodynamic properties of dense fluids are calculated using the perturbation theory of statistical mechanics [Barker et al., 1968]. Contribution of the unlike-three-body interaction to the Helmholtz free energy of the mixture is as the following [Benmekki and Mansoori, 1988]

$$A_{(3b)} = x_1 x_2 x_3 v_{123} (f_1/f_2) \quad (67)$$

Where x_i is mole fraction of component i , and f_1 and f_2 are analytic functions dependent on density and molecular diameters of the three molecules under consideration [Barker et al., 1968].

It should be pointed out that in the mixture models based on pairwise-additivity equations of state only the unlike-three-body interaction term is missing. The other three-body effects are accounted for through fitting the unlike-pair interaction parameters to binary mixture data [Benmekki and Mansoori, 1988]. In this case it is possible to correct the mixture model by properly adding the unlike three-body interaction term. For example the mixture van der Waals equation of state can be corrected to the following form:

$$P = P_{vdW} + c_1 c_2 x_1 x_2 x_3 (\theta/b^2 v) (f_1' f_2 - f_1 f_2') / f_2^2 \quad (68)$$

Where $c_1 = (8/27) \pi^3 N_0^4 v_{123}$, $c_2 = (b_{12} b_{13} b_{23})^{-1/3}$. Other thermodynamic properties can be readily derived from this equation.

CONCLUSION AND DISCUSSION

In general applicability of a mixture model to a certain class of mixtures and its accuracy has to do with the kind of approximations used in deriving its mixing rules and accuracy of its pure equation of state. Discussion about pure equations of states is outside of the scope of the present paper.

In previous studies superiority of the one-fluid and multi-fluid vdW mixing rules over the RMA and APM mixing rules, respectively, are well established [Leland et al., 1968; Mansoori, 1972b; Mansoori, 1977]. It is also demonstrated that the HSE mixing rules are more accurate than the vdW mixing rules specially for asymmetric mixtures [Hu et al., 1983; Lan and Mansoori, 1977; Mansoori and Leland, 1972]. Studies on the DEX mixing rules also indicate their superiority over the vdW mixing rules when they are applied to dilute asymmetric mixtures [Mansoori and Ely, 1985a]. DEX, CSA, and HSE mixing rules exhibit little differences when they are applied for calculation of properties of simple mixtures.

Accuracy of mixing rules can be theoretically evaluated by examining the approximations used in the theories on which they are based upon. They can be also compared using computer simulation data of mixtures with known

model potentials such as the data on Lennard-Jones Mixtures produced by Huber and Ely (1989). On statistical mechanical grounds it is well established that [Leland et al. 1968] one-fluid mixing rules are generally superior to the multi-fluid mixing rules in predicting mixture behaviors. There are cases where, because of limitations in the availability of a general pure equations of state for all the components of the mixture, we are bound to use the multi-fluid mixing rules instead of one-fluid mixing rules.

From the approximations used in the mixture RDFs for deriving the mixing rules we may make a number of general conclusions about the range of applicability of mixing rules:

(i) In deriving the RMA mixing rules it is assumed that all the RDFs in a mixture are identical, eq.(37). This assumption is accurate for molecules of similar sizes and energetics. Application of the RMA for mixture calculations indicate that it is most accurate when the differences in potential energy parameters of the components of the mixture are small. A similar argument can be made for APM mixing rules, which are the multi-fluid version of the RMA.

(ii) The vdW mixing rules are based on the assumption of equality of the scaled mixture RDFs (CSA approximation), eq.(39). This assumption is generally valid so long that there are no drastic deviations in the sizes and natures of the components in the mixture. This is probably the underlying reason for universal success of the vdW mixing rules in predicting the behaviors of non-associating and non-asymmetric mixtures.

(iii) The HSE mixing rules are based on the assumption that we treat the hard-sphere part of the radial distribution function accurately, eq.(54). From statistical mechanics we know that configurational properties of fluids are mostly based on hard-sphere part of the intermolecular potential energy function. Since the hard-sphere part of the mixtures are accurately accounted for in the HSE theory it is no accident this mixture model has been widely successful in predicting properties of mixtures of non-associating molecules [Hu et al., 1983; Lan and Mansoori, 1977; Mansoori and Leland, 1972].

(iv) The DEX mixing rules are based on a virial expansion of the mixture RDFs, eqs. (46 & 59). As a result these mixing rules are expected to work well in dense gaseous state. The calculations performed and reported, so far, for these mixing rules indicate their accuracy in dense gas mixture calculations and supercritical fluid states.

(v) The CSA mixing rules have a similar approximation base as the vdW mixing rules. However, they are based on compressibility equation of statistical mechanics. Calculations on these mixing rules indicate that they have a similar (with opposite-sign) deviation from exact mixture data as the vdW mixing rule have. It is demonstrated that a set of mixing rules based on an average of the CSA and vdW mixing rules is superior to either CSA or vdW mixing rules [Hamad et al., 1987].

(vi) Another approach for dealing with mixtures containing species with large molecular size and intermolecular energy differences is the application

of the dense fluid theory of mixtures [Hamad and Mansoori, 1987]. In this work a dense fluid mixture theory, which is similar to the mixture virial expansion theory of imperfect gases, is introduced. This theory is shown to be applicable for mixtures of molecules with large size and energy differences.

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