

## STATISTICAL MECHANICAL THEORY OF LOCAL COMPOSITIONS \*

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### ABSTRACT

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The concept of local composition has received much attention during the past few years, much of which has been devoted to justifying the empirical model proposed by Wilson in 1964. In this report the concept of local composition is defined on statistical mechanical grounds and expressions relating these compositions to thermodynamic properties of equilibrium fluid mixtures are derived. In particular, different local composition approximations are presented and new approximations based on molecular theories of mixtures are derived. Sets of mixing rules consistent with these different local composition approximations result, some of which are density and temperature dependent. Also, relations for partial molar properties in terms of local compositions are derived from the Kirkwood–Buff solution theory. Finally the radius of the sphere of influence of local compositions is formulated on statistical mechanical grounds.

### INTRODUCTION

There has been a great deal of interest during the past few years in the concept of local composition and its relationship to molecular characteristics and macroscopic thermodynamic properties of mixtures (Wilson, 1964; Renon and Prausnitz, 1968; Prausnitz, 1969; McDermott and Ashton, 1977;

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Nakanishi, 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 Nakanashi, 1984; Hoheisel and Kohler, 1984). Many of these analyses have been based on lattice theories of fluids and/or empirical interpretation of local composition (LC) and its relationship to the internal and excess Gibbs energy. An exception to the lattice theory approach is the recent work of Lee et al. (1983) which related liquid theory distribution functions and related potentials of mean force to the local composition model of Wilson (1964). In addition, the computer simulation studies of Hoheisel and Kohler (1984) and Nakanishi et al., (1979, 1982, 1983) avoid any reference to a particular theoretical model and provide data for molecules interacting with the Lennard-Jones potential which can be used to test and improve LC models.

In this report, the statistical mechanical radial distribution function approach is used to relate the concept of local compositions to various thermodynamic properties. This work differs from that of Lee et al. (1983) in that rigorous statistical mechanical expressions for the internal energy, compressibility factor and isothermal compressibility are derived in terms of local particle numbers (number of particles of a certain type within a volume) which are closely related to local mole fractions. It will be shown that the local particle numbers are the quantities which are of prime importance in studying "local composition" effects on thermodynamic properties. No particular effort is made to derive or justify the Wilson expression in terms of these theoretical results. We do show, however, how common liquid theory approximations such as the van der Waals one-fluid approximation can lead to different local composition expressions.

To summarize, the purpose of this report is to present a unified, theoretically consistent treatment of the local composition concept as applied to fluid mixtures. In particular, the section entitled, definition of local composition, presents the basic definitions which relate local compositions to radial distribution functions and to each other. The third section entitled, statistical mechanical expressions, deals with the incorporation of the LC concept in a theoretically rigorous manner. The method presented in that section provides explicit relations for the internal energy, equation of state and isothermal compressibility in terms of the local particle numbers. These results are rigorous apart from the assumption of pairwise additivity in the intermolecular potential. In the fourth section entitled, local composition approximations, different phenomenological and statistical mechanical approximations to local compositions are presented and compared. The fifth section headed, development of mixing rules based on local composition approximations, addresses the development of mixing rules for different LC approximations. These mixing rules are derived by introducing the LC approximations

discussed in the fourth section into the mixture equations derived in the third section and equating the results to equivalent expressions for hypothetical pure fluid(s). In the sixth section entitled, partial molar properties and local composition approximations, expressions for the partial molar volume and chemical potential of a mixture component in terms of local particle numbers are derived. These expressions are obtained without recourse to mixing rules or additional assumptions. Finally, in the seventh section entitled, the radius of the sphere of influence of local composition, a discussion of the "cut-off" parameter of "radius of sphere of influence" of local compositions and its role in the calculation of mixture thermodynamic properties is presented.

#### DEFINITION OF LOCAL COMPOSITION

According to statistical mechanical theory, 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  $g_{ij}(r, [\rho_k], T, [\sigma_{kl}], [\epsilon_{kl}])$  which is proportional to the probability of observing a molecule of type  $i$  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  $[\epsilon_{kl}]$  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 (Hill, 1956)

$$n_{ij}(R_{ij}) = \frac{N_i - \delta_{ij}}{V} \int_0^{R_{ij}} g_{ij}(r, [\rho_k], T, [\sigma_{kl}], [\epsilon_{kl}]) 4\pi r^2 dr \quad (1)$$

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 eqn. (1) so that  $N_i - \delta_{ij} \sim N_i$ .

As mentioned above, eqn. (1) 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. In this work, we have taken advantage of the previous results (Lebowitz and Percus, 1983; Massih and Mansoori, 1983) which indicate that one can effectively represent the properties of polar molecules through angle averaging techniques which provide an effective spherical potential.

With these definitions in mind, the local composition about a central  $j$  molecule is defined in terms of eqn. (1), viz.

$$x_{ij}(R_{ij}) = n_{ij}(R_{ij}) / \sum_{k=1}^c n_{kj}(R_{ij}) \quad (2)$$

where  $c$  is the number of components in the mixture.

Exact relationships between the  $x_{ij}$  and  $x_{ji}$  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 known. It is possible, however, to derive several relations between the local and bulk mole fractions and local particle numbers which will be of use in later sections of the manuscript.

Generally  $R_{ij}$  is a function of  $\rho$  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

$$n_{ij}(R_{ij})/n_{ji}(R_{ij}) = x_i/x_j \quad (3)$$

$$n_{ij}(R_{ij})/n_{jj}(R_{jj}) = x_{ij}/x_{jj} \quad (4)$$

and combining (3) and (4) we find

$$n_{ii}(R_{ii})/n_{jj}(R_{jj}) = (x_{ii}/x_{jj})(x_{ij}/x_{ji})(x_j/x_i) \quad (5)$$

Finally, differentiating eqn. (1) and rearranging terms one obtains

$$g_{ij}(R_{ij}) = \frac{V}{4\pi N_i} \frac{1}{R_{ij}^2} \frac{dn_{ij}}{dR_{ij}} \quad (6)$$

## STATISTICAL MECHANICAL EXPRESSIONS

Equation (6) can be used to re-express thermodynamic properties of multicomponent mixtures which were originally defined with respect to radial distribution functions. The statistical mechanical equations considered here are the energy, virial and compressibility relations. In the case of the internal energy, we start with the standard expression (Hill, 1956; McQuarrie, 1976)

$$\frac{U - U^0}{N_a k T} = \frac{\rho}{2kT} \sum_{i=1}^c \sum_{j=1}^c x_i x_j \int_0^\infty g_{ij}(r) u_{ij}(r) 4\pi r^2 dr \quad (7)$$

In this equation  $U^0$  is the ideal gas internal energy of the mixture,  $\rho$  is the molecular number density,  $k$  is the Boltzmann constant,  $N_a$  is Avogadro's number,  $x_i$  is the bulk mole fraction of component  $i$  and  $u_{ij}(r)$  is the pair

intermolecular potential energy function for molecules of kinds  $i$  and  $j$ . This "energy equation" can be re-expressed with respect to local particle numbers with the following result

$$\frac{U - U^0}{N_a kT} = -\frac{1}{2} \sum_{i=1}^c \sum_{j=1}^c x_j \int_0^{\infty} n_{ij}(r) u'_{ij} dr \quad (8)$$

where the prime indicates differentiation with respect to the intermolecular separation. In deriving this relation, eqn. (6) is substituted into (7) followed by integration by parts.

A similar procedure for the virial equation yields

$$Z = 1 + \frac{1}{6kT} \sum_{i=1}^c \sum_{j=1}^c x_j \int_0^{\infty} n_{ij}(r) (u'_{ij} + ru''_{ij}) dr \quad (9)$$

where  $Z$  is the compressibility factor  $pV/N_a kT$ .

The compressibility equation is somewhat more complex. Kirkwood and Buff (1951) expressed the isothermal compressibility  $K_T = (1/\rho)(\partial\rho/\partial p)_T$ , of a multicomponent mixture with respect to the mixture distribution radial distribution functions by the following equation

$$\frac{1}{\rho kT K_T} = \frac{\rho}{|B|} \sum_{i=1}^c \sum_{j=1}^c x_i x_j |B|_{ij} \quad (10)$$

where  $B$  symbolizes a  $c \times c$  matrix with its elements  $B_{ij}$  defined by

$$B_{ij} = \rho x_i [\delta_{ij} + x_j \rho G_{ij}] \quad (11)$$

and  $|B|_{ij}$  is the cofactor of  $B_{ij}$  in the determinant  $|B|$ . In eqn. (11),  $\delta_{ij}$  is the Kronecker delta and  $G_{ij}$  is defined with respect to the radial distribution function  $g_{ij}$

$$G_{ij} = \int_0^{\infty} [g_{ij}(r) - 1] 4\pi r^2 dr \quad (12)$$

Equation (10) is commonly called "the compressibility equation" in statistical mechanics. Note that while the expressions for the compressibility factor and internal energy with respect to  $g_{ij}(r)$  are based on the assumption of pairwise additivity of the intermolecular potential energy function, expression of the isothermal compressibility, eqn. (10) is independent of such an assumption.

To express  $K_T$  with respect to the local particle numbers we write eqn. (12) in the following form

$$G_{ij} = \int_0^{R_{ij}} (g_{ij} - 1) 4\pi r^2 dr + \int_{R_{ij}}^{\infty} (g_{ij} - 1) 4\pi r^2 dr$$

Substituting eqn. (6) in the first integral and subsequent integration yields

$$G_{ij} = \frac{1}{\rho x_i} [n_{ij}(R_{ij}) - \langle n_i(R_{ij}) \rangle] + \int_{R_{ij}}^{\infty} (g_{ij} - 1) 4\pi r^2 dr \quad (13)$$

where  $\langle n_i(R_{ij}) \rangle = 4\pi\rho x_i R_{ij}^3/3$  is the average number of molecules of type  $i$  in a spherical volume of radius  $R_{ij}$ . To simplify further this expression one must make some assumption about the magnitude of  $R_{ij}$ . In this work we will assume that  $R_{ij}$  is chosen such that the integral remaining in eqn. (13) vanishes. The details of this choice are given in the section entitled, the radius of the sphere of influence of local compositions. We find, therefore, that

$$G_{ij} = \frac{1}{\rho x_i} \Delta n_{ij}(R_{ij}) \quad (14)$$

where  $\Delta n_{ij}(R_{ij}) = n_{ij}(R_{ij}) - \langle n_i(R_{ij}) \rangle$ . Note that for a pure fluid eqns. (10–14) result in

$$\begin{aligned} \rho kT K_T &= 1 + \rho G \\ &= 1 + \Delta n_x(R) \end{aligned}$$

where the subscript  $x$  denotes a pure fluid. Substituting eqn. (14) into (11) one finds

$$B_{ij} = \rho x_i \left[ \delta_{ij} + \frac{x_j}{x_i} \Delta n_{ij}(R_{ij}) \right] \quad (15)$$

Equations (10) and (15) 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 Kirkwood–Buff theory of solutions (see Kirkwood and Buff, 1951; Buff and Brout, 1955) the partial molar volume of component  $i$  of a  $c$ -component mixture is given by the following equation

$$\bar{V}_i = \frac{1}{\rho} \frac{\sum_{j=1}^c x_j |B|_{ij}}{\sum_{j=1}^c \sum_{k=1}^c x_j x_k |B|_{jk}} \quad (16)$$

Likewise, the chemical potential of a component of the mixture can be

expressed through the Kirkwood–Buff theory of solutions in the following form

$$\left( \frac{\partial \mu_i}{\partial N_j} \right)_{T,P,N_{k \neq j}} = \frac{kT}{\rho x_i x_j} \frac{|\underline{\Delta}|_{ij}}{|\underline{\Delta}|} \quad (17)$$

In this equation  $|\underline{\Delta}|$  symbolizes the determinant of the  $c \times c$  matrix  $\underline{\Delta}$  with elements  $\Delta_{ij}$  given by

$$\Delta_{ij} = \frac{\delta_{ij}}{\rho x_i} + \frac{1}{\rho x_1} + G_{ij} + G_{11} - G_{1i} - G_{1j} \quad (18)$$

and  $|\underline{\Delta}|_{ij}$  is the cofactor of  $\Delta_{ij}$ . Substitution of eqn. (14) into (18) yields an expression for  $\Delta_{ij}$  in terms of the local particle numbers

$$\Delta_{ij} = \frac{1}{\rho x_i} \left\{ \delta_{ij} + \Delta n_{ij}(R_{ij}) + \frac{x_i}{x_1} \left[ 1 + \Delta n_{11}(R_{11}) - \Delta n_{1i}(R_{1i}) - \Delta n_{1j}(R_{1j}) \right] \right\} \quad (19)$$

It should be pointed out that the expressions for the partial molar volumes and chemical potentials of components of the mixture with respect to radial distribution functions are independent of the pairwise additivity assumption for the intermolecular potential energy functions.

#### LOCAL COMPOSITION APPROXIMATIONS

In this section the existing approximate expressions for local compositions are summarized and new approximations for  $n_{ij}$  (and thus  $x_{ij}$ ) based on the available approximations for  $g_{ij}$  are developed. This development enables one to derive (or re-examine) mixing rules to be used in conjunction with different theories of mixtures.

There are two well known direct approximations of  $n_{ij}/n_{jj}$ , one due to Wilson (1964) and the other due to Renon and Prausnitz (1968). Wilson's expression, which is given in Table 1, was the first attempt at defining the concept of local composition. Renon and Prausnitz's (1968) expression, which is also reported in Table 1, is based on an analogy with the quasichemical approximation of Guggenheim (1952) for lattice statistics. In addition to these two approximations for  $n_{ij}$  one can utilize eqn. (3) and theoretical approximations which exist for the radial distribution function to derive other expressions for  $n_{ij}/n_{jj}$  or equivalently  $x_{ij}/x_{jj}$ .

We have followed this procedure and the results obtained from four different common theoretical approximations for radial distribution functions are reported in Table 1. In the first of these, the random mixture approximation (RMA), it is assumed that all the radial distribution functions

TABLE I  
Approximations for local compositions based on different mixture theories

Approximation technique	$n_{ij}$	$\frac{x_i}{x_j} = \frac{n_{ij}}{n_{ji}}$ according to different techniques
Wilson (Wilson's Approximation) (c-fluid)	$A x_i e^{-\lambda_{ij}/kT}$	$\frac{x_i}{x_j} = \frac{n_{ij}}{n_{ji}}$ according to different techniques
RP (Renon-Prausnitz Approximation) (c-Fluid)	$A x_i e^{-\alpha_{ij} \lambda_{ij}/kT}$	$\frac{x_i}{x_j} e^{-(\alpha_{ij} \lambda_{ij} - \alpha_{ji} \lambda_{ji})/kT}$ $\lambda_{ij} = \lambda_{ji}$ $\alpha_{ij} = \alpha_{ji} \quad \lambda_{ij} = \lambda_{ji}$
RMA (Random Mixing Approximation) (one-fluid)	$x_i n_x(R_{ij})$	$\frac{x_i n_x(R_{ij})}{x_j n_x(R_{ji})}$
APM (Average Potential Model) (c-Fluid)	$\frac{1}{2} \left[ n_{xi}(R_{ij}) + \frac{x_i}{x_j} n_{xj}(R_{ij}) \right]$	$\frac{x_i}{x_j} \frac{1}{2} \left[ \frac{n_{xi}(R_{ij})}{n_{xj}(R_{ji})} \frac{x_j}{x_i} + \frac{n_{xj}(R_{ij})}{n_{xj}(R_{ji})} \right]$
CSA(1F) (Conformal Solution Approximation) (one-Fluid)	$x_i \sigma_{ij}^3 n_x(R_{ij}) / \sigma_x^3$	$\frac{x_i}{x_j} \left( \frac{h_{ij}}{h_{jj}} \right) \frac{n_x(R_{ij})}{n_x(R_{ji})}$
CSA(cF) (Conformal Solution Approximation) (c-Fluid)	$\frac{1}{2} x_i \sigma_{ij}^3 [n_{xi}(R_{ij}) / \sigma_{xi}^3 + n_{xj}(R_{ij}) / \sigma_{xj}^3]$	$\frac{1}{2} \frac{x_i}{x_j} \frac{h_{ij}}{h_{jj}} \left[ \left( \frac{h_{xi}}{h_{xi}} \right) \frac{n_{xj}(R_{ij})}{n_{xj}(R_{ji})} + \frac{n_{xj}(R_{ij})}{n_{xj}(R_{ji})} \right]$

in the mixture are identical (see Scott, 1956; Leland et al., 1969; McQuarrie, 1976)

$$g_{11}(r) = g_{22}(r) = g_{12}(r) = \dots = g_x(r) \quad (20)$$

or substituting into eqn. (1)

$$n_{ij} = x_i n_x(R_{ij})$$

where the subscript  $x$  denotes a pure fluid value. The second is the average potential model (APM) which assumes that the unlike radial distribution function is the average of the like values

$$\begin{aligned} g_{ij}(r) &= \frac{1}{2} [g_{ii}(r) + g_{jj}(r)] \\ &= \frac{1}{2} [g_{xi}(r) + g_{xj}(r)] \end{aligned} \quad (21)$$

or

$$n_{ij} = \frac{1}{2} [n_{xi}(R_{ij}) + (x_i/x_j)n_{xj}(R_{ij})]$$

In the one-fluid conformal solution approximation it is assumed that the radial distribution functions are equal to a universal pure fluid function (denoted by a subscript  $x$ ) of the reduced intermolecular separation evaluated at some mean or effective density

$$g_{ij}(r_{ij}^*) = g_{ii}(r_{ii}^*) = \dots = g_x(r^*) \quad (22)$$

where the reduced distance parameter is defined as  $r_{ij}^* = r_{ij}/\sigma_{ij}$  where  $\sigma_{ij}$  is the intermolecular potential distance parameter and  $x$  denotes a pure fluid. Substituting eqn. (22) into (1) we find

$$n_{ij} = x_i \sigma_{ij}^3 n_x(R_{ij}) / \sigma_x^3$$

Finally, the  $c$ -fluid conformal solution approximation assumes that the following expression exists between the distribution functions with scaled distances

$$\begin{aligned} g_{ij}(r_{ij}^*) &= \frac{1}{2} [g_{ii}(r_{ii}^*) + g_{jj}(r_{jj}^*)] \\ &= \frac{1}{2} [g_{xi}(r^*) + g_{xj}(r^*)] \end{aligned} \quad (23)$$

or

$$n_{ij} = \frac{1}{2} x_i \sigma_{ij}^3 \left[ \frac{n_{xi}(R_{ij})}{\sigma_{xi}^3} + \frac{n_{xj}(R_{ij})}{\sigma_{xj}^3} \right]$$

Using these different approximations one can easily derive the local composition or  $n_{ij}/n_{jj}$  expressions reported in Table 1. Note that in Table 1 we have assumed, in the Wilson and Renon and Prausnitz cases, that

$$n_{ij} = A x_i e^{-\alpha_{ij} \lambda_{ij}}$$

where  $\lambda_{ij}$  is an energy parameter as defined by Wilson (1964),  $\alpha_{ij}$  is a nonrandomness parameter as defined by Renon and Prausnitz ( $\alpha_{ij} = 1$  for Wilson) and  $A$  is a universal constant. This particular form seems to be the simplest which is consistent with the  $x_{ij}/x_{jj}$  results presented by these authors, although there may be others. Also appearing in Table 1 are the conformal solution equivalent substance reducing ratios  $f_{ij}$  and  $h_{ij}$  defined as

$$f_{ij} = \epsilon_{ij}/\epsilon_0 \text{ and } h_{ij} = \sigma_{ij}^3/\sigma_0^3$$

where the intermolecular potential is assumed to be of the form

$$u_{ij} = f_{ij}u_0(r/h_{ij}^{1/3}) \quad (24)$$

and the 0 subscript indicates a pure reference fluid (see, for example, Massih and Mansoori (1983) for definitions and scaling of conformal solution parameters).

Expressions of  $n_{ij}/n_{ji}$  reported in Table 1 can be used to develop either mixing rules for conformal solution models or they can be used directly in the expressions for partial molar volumes, eqn. (16), and chemical potential, eqn. (17) to derive correlations for partial molar properties and activity coefficients of components in a multicomponent mixture. It is also possible to use the results of Table 1 in a model such as the Flory–Huggins model to develop activity coefficient expressions. It should be pointed out that in developing mixing rules from the local composition approximations given in Table 1, one does not need to make any other approximation. However, for calculation of partial molar volumes and activity coefficients of components of a mixture one needs to use expressions for a pure fluid radial distribution function.

#### DEVELOPMENT OF MIXING RULES BASED ON LOCAL COMPOSITION APPROXIMATIONS

Recent accurate examinations of conventional (e.g., van der Waals) mixing rules have indicated the inability of such expressions to predict accurately thermodynamic properties in varieties of state conditions (Vidal, 1978; McCarty, personal communication, 1984) and have led the investigators to search for density and temperature dependent mixing rules (Whiting and Prausnitz, 1982). Another indication of the need for density and temperature dependent mixing rules is that of the widespread use of combining rule interaction parameters which are temperature and density dependent—a result which is contrary to the theory of intermolecular interactions.

In developing mixing rules, our general procedure is that proposed by Henderson and Leonard (1971). In particular, one-fluid theory mixing rules based on eqns. (8)–(10) are derived by assuming that there exists a hypo-

thetical pure fluid with potential energy function  $u_x(r)$  and local particle number  $n_x(r)$  which can represent a mixture and can reproduce  $Z$ ,  $(U - U^0)/N_a kT$ , and  $\rho kT K_T$  of the mixture. This hypothetical pure fluid's potential energy function and local particle number, then, must satisfy the following three equations

$$\int_0^\infty n_x(r) u'_x(r) dr = \sum_{i=1}^c \sum_{j=1}^c x_j \int_0^\infty n_{ij}(r) u'_{ij}(r) dr \quad (25)$$

$$\int_0^\infty n_x(r) [u'_x(r) + r u''_x(r)] dr = \sum_{i=1}^c \sum_{j=1}^c x_j \int_0^\infty n_{ij}(r) [u'_{ij}(r) + u''_{ij}(r)] dr \quad (26)$$

and

$$\frac{1}{1 + \Delta n_x(r)} = \frac{\rho}{|B|} \sum_{i=1}^c \sum_{j=1}^c x_i x_j |B|_{ij} \quad (27)$$

where the prime indicates a derivative and the understanding that the  $B_{ij}$  terms of determinants  $|B|$  and  $|B|_{ij}$  are given by eqn. (15). Equation (25) is a result of equating reduced internal energy of the hypothetical pure fluid with that of the mixture, eqn. (26) is a result of equating compressibility factor of the hypothetical pure fluid with that of the mixture, and eqn. (27) is due to equality of the reduced isothermal compressibility of the hypothetical pure fluid and the mixture. By replacing the one-fluid theory expressions for  $n_{ij}$  for the RMA and CSA(1F) approximations, in the right-hand side of eqns. (25)–(27) one can derive mixing rules which are reported in Table 2.

In developing mixing rules from  $c$ -fluid theories we assume that there exist  $c$  hypothetical pure fluids with potential energy functions  $u_{x1}, u_{x2}, \dots, u_{xc}$  and local particle numbers  $n_{x1}, n_{x2}, \dots, n_{xc}$  which collectively can represent  $Z$ ,  $(U - U^0)/N_a kT$ ,  $\rho kT K_T$  of a mixture of  $c$ -components through the expressions

$$Z_m = \sum_{i=1}^c x_i Z_{xi}, \quad \frac{U_m - U_m^0}{RT} = \sum_{i=1}^c x_i \frac{U_{xi} - U_{xi}^0}{RT}, \quad \frac{1}{K_{Tm}} = \sum_{i=1}^c \frac{x_i}{K_{Tx_i}}$$

The local particle numbers and intermolecular potential energy functions of the  $c$  hypothetical pure fluids, then, must be chosen to satisfy the following three equations

$$\sum_{i=1}^c x_i \int_0^\infty n_{xi}(r) u'_{xi}(r) dr = \sum_{i=1}^c \sum_{j=1}^c x_j \int_0^\infty n_{ij}(r) u'_{ij}(r) dr \quad (28)$$

$$\begin{aligned} & \sum_{i=1}^c x_i \int_0^\infty [n_{xi}(r) u'_{xi}(r) + r u''_{xi}(r)] dr \\ & = \sum_{i=1}^c \sum_{j=1}^c x_j \int_0^\infty n_{ij}(r) [u'_{ij}(r) + u''_{ij}(r)] dr \end{aligned} \quad (29)$$

and

$$\sum_{i=1}^c \frac{x_i}{1 + n_{xi}(r)} = \frac{\rho}{|B|} \sum_{i=1}^c \sum_{j=1}^c x_i x_j |B|_{ij} \quad (30)$$

Substituting the  $c$ -fluid theory approximation expressions for  $n_{ij}$  given previously in eqns. (28)–(30) one obtains the mixing rules reported in Table 2. According to Table 2 all the mixing rules which are derived from the energy and virial equations are only dependent upon composition, while those based on the compressibility equation are generally composition, density, and temperature dependent. The Wilson, RP, RMA, and APM mixing rules based on energy and virial equations all depend upon the exact functional forms of the intermolecular potential energy functions. The CSA(1F) and CSA( $c$ F) mixing rules based on energy and virial equations are derived with the assumption that the potential energy function is of the form given in eqn. (23). It should be pointed out that all the mixing rules which are derived based on the compressibility equation are independent of the nature and form of the potential energy function.

Note that in Table 2 (as well as the remainder of this report) that there is no distinction between the Wilson and Renon and Prausnitz mixing rules which are collectively referred to as WRP. This is the case since the Wilson local composition expression is merely a special case of the Renon and Prausnitz expression, namely that with  $\alpha_{ij} = 1$ . In other words, the  $\alpha_{ij}$  parameter can only have significance in conjunction with the lattice model used to derive the activity coefficient expressions.

Another important observation about the mixing rules in Table 2 is that energy and virial equations produce only one mixing rule for CSA(1F) and CSA( $c$ F) theories, which in the CSA(1F) case is identical to the second van der Waals mixing rule. They produce two mixing rules for the other theories. The compressibility equation does not yield any mixing rules for the RMA and APM theories since the corresponding local particle number expressions are independent of the intermolecular potential. Overall, the RMA, APM, CSA(1F), and CSA( $c$ F) theories each yield two mixing rules while the Wilson and RP theories give up to three mixing rules. As a result, the RMA, APM, CSA(1F), and CSA( $c$ F) mixing rules seem to be suitable for pair potential energy functions having two parameters (such as the Lennard–Jones potential) while the WRP rules will pose a dilemma when applied with such potential energy functions.

To further investigate the mixing rules of Table 2, we report here specific forms of these mixing rules which can be derived by assuming different model intermolecular potentials. In particular, Table 3 summarizes hard-sphere fluid mixing rules obtained from the different theories. Note that the

TABLE 2  
 Various sets of mixing rules according to different theories of mixtures (or different local composition approximations)

Approximation technique	Virial and/or energy equations	Compressibility equation
WRP	$u'_{xi} = \sum_j x_j u'_{ij} e^{-(\alpha_{ij}\lambda_{ij} - \alpha_{ij}\lambda_{xi})/kT}$	$(1 + \Delta_{xi})^{-1} =  B^* ^{-1} \sum_j x_j  B^* _{ij}$
RMA	$u'_{xx} = \sum_i \sum_j x_i x_j u'_{ij}$	$B^*_{ij} = x_i \left[ \delta_{ij} + x_j \Delta_{xj} e^{-(\alpha_{ij}\lambda_{ij} - \alpha_{ij}\lambda_{xj})/kT} \right]$
APM	$u'_{xi} = \sum_j x_j u'_{ij}$	-
CSA(1F)	$h_x f_x = \sum_i \sum_j x_i x_j h_{ij} f_{ij}$	$u'_{xx} = \sum_i \sum_j x_i x_j u''_{ij}$
		$u'_{xi} = \sum_j x_j u''_{ij}$
		$(1 + \Delta_x)^{-1} =  B^* ^{-1} \sum_i \sum_j x_i x_j  B^* _{ij}$
CSA(cF)	$h_{xi} f_{xi} = \sum_j x_j h_{ij} f_{ij}$	$B^*_{ij} = x_i \left[ \delta_{ij} + x_j \frac{h_{ij}}{h_x} \Delta_x \right]$
		$(1 + \Delta_{xi})^{-1} =  B^* ^{-1} \sum_j x_j  B^* _{ij}$
		$B^*_{ij} = x_i \left[ \delta_{ij} + \frac{x_j h_{ij}}{2} \left( \frac{\Delta_{xi}}{h_{xi}} + \frac{\Delta_{xj}}{h_{xj}} \right) \right]$
		$\Delta_x = \rho k T K_{Tx}^{-1}$
		$\Delta_{xi} = \rho k T K_{Tx_i}^{-1}$

TABLE 3

Hard-sphere potential mixing rules according to various local composition approximations

Approximation technique	From virial equation	From compressibility equation
WRP	$h_{xi}^{1/3} = \sum_j x_j h_{ij}^{1/3}$	-
RMA	$h_x^{1/3} = \sum_i \sum_j x_i x_j h_{ij}^{1/3}$	-
APM	$h_{xi}^{1/3} = \sum_j x_j h_{ij}^{1/3}$	-
CSA(1F)	$h_x = \sum_i \sum_j x_i x_j h_{ij}$	$(1 + \Delta_x)^{-1} =  B^* ^{-1} \sum_i \sum_j x_i x_j  B^* _{ij}$ $B_{ij}^* = x_i \left( \delta_{ij} + x_j \frac{h_{ij}}{h_{xx}} \Delta_x \right)$
CSA(cF)	$h_{xi} = \sum_j x_j h_{ij}$	$(1 + \Delta_x)^{-1} =  B^* ^{-1} \sum_j x_j  B^* _{ij}$ $B_{ij}^* = x_i \left[ \delta_{ij} + \frac{x_j h_{ij}}{2} \left( \frac{\Delta_{xi}}{h_{xi}} + \frac{\Delta_{xj}}{h_{xj}} \right) \right]$

energy equation vanishes in the case of the hard-sphere fluid. In deriving the WRP mixing rules for hard spheres, the energy parameters  $\lambda_{ij}$  were set equal to zero. As shown in Table 3, the WRP and APM mixing rules resulting from the virial equation are identical. The compressibility equation produces no mixing rules for the WRP, RMA, and APM approximations while it produces mixing rules for the conformal solution models. The first mixing rules produced by the CSA(1F) and CSA(cF) theories and the virial equation are equivalent to the van der Waals one-fluid, and van der Waals *c*-fluid theories, respectively.

According to Table 3 there are six different mixing rules for the hard-sphere mixture. Four of these mixing rules are only composition dependent. The two mixing rules due to the CSA(1F) and CSA(cF) theories based on the compressibility equation are composition and density dependent. To make further observations on the hard-sphere mixing rules based on compressibility equation we write them here for a binary mixture. The CSA(1F) mixing rule based on compressibility equation for a binary system reduces to the following form after expansion of the determinants and simplification of the resulting equation

$$h_x = \frac{x_1^2 h_{11} + x_2^2 h_{22} + 2 x_1 x_2 h_{12} + \frac{\Delta_x}{h_x} x_1 x_2 (h_{11} h_{22} - h_{12}^2)}{1 + \frac{\Delta_x}{h_x} x_1 x_2 (h_{11} + h_{22} - 2 h_{12})} \quad (31)$$

Solving for  $h_x$ , one finds

$$h_x = \frac{1}{2} \left\{ h_x^{\text{vdw}} - B\Delta_x x_1 x_2 + \left[ \left( h_x^{\text{vdw}} - B\Delta_x x_1 x_2 \right)^2 + 4A\Delta_x x_1 x_2 \right]^{1/2} \right\} \quad (32)$$

where  $h_x^{\text{vdw}}$  is the van der Waals mixing rule for the binary hard-sphere mixture

$$h_x^{\text{vdw}} = x_1^2 h_{11} + x_2^2 h_{22} + 2x_1 x_2 h_{12}$$

and coefficients  $A$  and  $B$  are defined by the following expressions

$$A = h_{11} h_{22} - h_{12}^2$$

$$B = h_{11} + h_{22} - 2 h_{12}$$

The CSA(cF) mixing rule based on compressibility equation for a two-component mixture will be converted to a set of two equations

$$\frac{1}{1 + \Delta_{x1}} = \frac{\left( 1 + x_2 \frac{h_{22}}{h_{x2}} \Delta_{x2} \right) - \frac{x_2}{2} h_{12} \left( \frac{\Delta_{x1}}{h_{x1}} + \frac{\Delta_{x2}}{h_{x2}} \right)}{\left( 1 + x_1 \frac{h_{11}}{h_{x1}} \Delta_{x1} \right) \left( 1 + x_2 \frac{h_{22}}{h_{x2}} \Delta_{x2} \right) - \frac{x_1 x_2}{4} h_{12}^2 \left( \frac{\Delta_{x1}}{h_{x1}} + \frac{\Delta_{x2}}{h_{x2}} \right)^2} \quad (33)$$

and a corresponding equation for fluid 2 with the subscripts 1 and 2 reversed. These two equations can be solved simultaneously for  $h_{x1}$  and  $h_{x2}$  in order to be applied in the two-fluid mixture computations. It should be again pointed out that the CSA(1F) and CSA(2F) mixing rules presented above are composition and density dependent. The density dependence of these mixing rules is due to the presence of the function  $\Delta = \rho k T K_T - 1$  which is density dependent. For example, if one uses the Carnahan–Starling pure hard-sphere equation of state (Carnahan and Starling, 1969) the following analytic expression for  $\Delta_x$  function will be produced

$$\Delta_x = \frac{2\eta_x (\eta_x - 4)}{1 + 4\eta_x + 4\eta_x^2 - 4\eta_x^3 + \eta_x^4} \quad (34)$$

Similar expressions for  $\Delta_{xi}$  can be written in the case of the  $c$ -fluid theory of mixtures.

In Table 4 the Lennard–Jones mixing rules for different mixture theories based on virial, energy, and compressibility equations are reported. According to this table the WRP approximation produces three mixing rules while the other theories produce two. Considering that the mixture parameters to be specified for a  $c$ -fluid theory are  $h_{xi}$ ,  $f_{xi}$  with  $i = 1, 2, \dots, c$ , the WRP model indicates that there will be  $3c$  expressions for  $2c$  parameters while the other approximations produce  $2c$  expressions for  $2c$  parameters. Also, the mixing rule expressions based on the virial and/or energy equations are all

TABLE 4  
Lennard-Jones potential mixing rules according to various local composition approximations

Approx. technique	From virial and/or energy equations	From compressibility equation
WRP	$h_{xi}^2 f_{xi} = \sum_j x_j h_{ij}^2 f_{ij} e^{-(\alpha_j \lambda_j)^i - \alpha_{ix} \lambda_{xi}} / kT$	$1 + \Delta_{xi} =  B^*  / \sum_j x_j  B^* _{ij}$
RMA	$h_x^2 f_x = \sum_i \sum_j x_i x_j h_{ij}^2 f_{ij}$	$B_{ij}^* = x_i [\delta_{ij} + x_j \Delta_{xj} e^{-(\alpha_j \lambda_j)^i - \alpha_{ix} \lambda_{xi}} / kT]$
APM	$h_{xi}^2 f_{xi} = \sum_j x_j h_{ij}^2 f_{ij}$	-
CSA(1F)	$h_x f_x = \sum_i \sum_j x_i x_j h_{ij} f_{ij}$	$1 + \Delta_{xx} =  B^*  / \sum_i \sum_j x_i x_j  B^* _{ij}$
CSA(cF)	$h_{xi} f_{xi} = \sum_j x_j h_{ij} f_{ij}$	$B_{ij}^* = x_i \left( \delta_{ij} + x_j \frac{h_{ij}}{h_x} \Delta_x \right)$ $1 + \Delta_{xi} =  B^*  / \sum_j x_j  B^* _{ij}$ $B_{ij}^* = x_i \left( \delta_{ij} + \frac{x_j h_{ij}}{2} \left[ \frac{\Delta_{xi}}{h_{xi}} + \frac{\Delta_{xj}}{h_{xj}} \right] \right)$

explicit with respect to mixture parameters while the ones based on the compressibility equation are not generally explicit with respect to mixture parameters.

To make further observations on the compressibility equation based mixing rules we can write them for two-component mixtures. For example, the WRP mixing rules, based on compressibility equation, for a two-component mixture are

$$\frac{1}{1 + \Delta_{x1}} = \frac{1 + x_2 \Delta_{x2} - x_2 \Delta_{x1} e_{12}}{1 + x_1 \Delta_{x1} + x_2 \Delta_{x2} + x_1 x_2 \Delta_{x1} - \Delta_{x2} (1 - e_{12} e_{21})} \quad (35)$$

and a comparable equation for fluid 2 with the subscripts 1 and 2 reversed.

In these equations  $e_{ij} = e^{-(\alpha\lambda_{ji} - \alpha\lambda_{jj})/kT}$ .

Knowing that the compressibilities  $\Delta_{x1}$  and  $\Delta_{x2}$  are in general functions of  $h_{x1}$ ,  $f_{x1}$ , and  $h_{x2}$ ,  $f_{x2}$ , respectively, the above two equations must be solved simultaneously with two additional equations in order to calculate mixing parameters for every given temperature, density and composition. The CSA mixing rules based on the compressibility equation for the Lennard-Jones fluid mixture, and for any other potential energy function, will be the same as the ones reported for the hard-sphere mixture, eqn. (33).

In utilizing the composition, density and temperature dependent mixing rules which are introduced in this report for mixture calculations, one has to formulate thermodynamically consistent expressions for all the mixture properties in conjunction with the conformal solution theory of mixtures. This subject matter will be addressed in detail in a separate publication.

#### PARTIAL MOLAR PROPERTIES AND LOCAL COMPOSITION APPROXIMATIONS

Equation (16) provides an expression for the partial molar volume with respect to local particle numbers as does eqn. (17) for the chemical potential (and fugacity and activity coefficient). If eqn. (16) is written in dimensionless form it becomes

$$\frac{\bar{V}_i}{V} = \frac{\sum_{j=1}^c x_j |B|_{ij}}{\sum_{j=1}^c \sum_{k=1}^c x_j x_k |B|_{jk}} \quad (36)$$

For the one-fluid theories of mixtures (such as RMA and CSA(1F)) the above expression coupled with eqn. (10) can be written as

$$\frac{\bar{V}_i}{V} = \rho^2 kT K_{Tx} \frac{\sum_{j=1}^c x_j |B|_{ij}}{|B|} \quad (37)$$

TABLE 5  
Simplified forms of  $\Delta_{ij}^*$  (a representative term of determinant  $|\Delta^*|$  according to different local composition approximations)

Approximation technique	$\Delta_{ij}^* = \frac{1}{x_i} \left( \delta_{ij} + \frac{x_i}{x_1} \right) + \frac{1}{x_1} \left( \frac{x_1}{x_i} \Delta n_{ij} + \Delta n_{11} - \Delta n_{1i} - \Delta n_{1j} \right)$
WRP	$\Delta_{ij}^* = \frac{1}{x_i} \left( \delta_{ij} + \frac{x_i}{x_1} \right) + \frac{\Delta n_{11}}{x_1} - \frac{\Delta n_{ii}}{x_i} e_{ii} + \frac{\Delta n_{jj}}{x_j} (e_{ij} - e_{ij}); e_{ij} = e^{-(\alpha_j \lambda_{ij} - \alpha_j \lambda_{ij})/kT}$
RMA	$\Delta_{ij}^* = \frac{1}{x_i} \left( \delta_{ij} + \frac{x_i}{x_1} \right)$
APM	$\Delta_{ij}^* = \frac{1}{x_i} \left( \delta_{ij} + \frac{x_i}{x_1} \right)$
CSA(1F)	$\Delta_{ij}^* = \frac{1}{x_i} \left( \delta_{ij} + \frac{x_i}{x_1} \right) + \frac{\Delta n_{11}}{x_1} \left( \frac{h_{ij} - h_{1i} + h_{11} - h_{1j}}{h_{11}} \right)$
CSA(cF)	$\Delta_{ij}^* = \frac{1}{x_i} \left( \delta_{ij} + \frac{x_i}{x_1} \right) + \frac{\Delta n_{11}}{x_1} \left( 1 - \frac{h_{ii} - h_{ij}}{2h_{11}} \right) + \frac{\Delta n_{ij}}{x_i} \left( \frac{h_{ij} - h_{1i}}{2h_{ii}} \right) + \frac{\Delta n_{ij}}{x_j} \left( \frac{h_{ij} - h_{1j}}{2h_{jj}} \right)$

For *c*-fluid theories of mixture (RPM, APM, and CSA(cF)), eqn. (36) will reduce to the following

$$\frac{\bar{V}_i}{\bar{V}} = \sum_{j=1}^c x_j \frac{K_{Tx_i}}{K_{Tx_j}} \quad (38)$$

With use of appropriate pure fluid equations of state and application of a local composition model the above equations can be used for calculation of partial molar volumes of components of a mixture.

The expression for chemical potential with respect to the local particle numbers eqn. (17), can be written as

$$\frac{1}{kT} \left( \frac{\partial \mu_i}{\partial N_j} \right)_{T,P,N_n} = \frac{1}{x_i x_j} \frac{|\Delta^*|_{ij}}{|\Delta^*|} \quad (39)$$

where  $N_j$  is the number of particles of type  $j$  and  $\Delta^*_{ij}$  is defined as

$$\Delta^*_{ij} = \rho \Delta_{ij} \text{ where } \Delta_{ij} \text{ is given in eqn. (19).}$$

Given the different approximations shown in Table 1,  $\Delta_{ij}$  can be calculated with the results which are reported in Table 5. According to Table 5, RMA and APM approximations provide ideal solution expressions for the chemical potential while the other theories lead to non-ideal expressions for the chemical potential of the mixture components. Note that to utilize the results of Table 5 for calculation of chemical potentials appropriate pure fluid equations of state must be available.

#### THE RADIUS OF THE SPHERE OF INFLUENCE OF LOCAL COMPOSITIONS

In the basic definition of the local particle numbers, eqn. (1),  $R$ , the radius of the sphere of influence of local compositions must be defined. In the statistical mechanical formulation which is provided in the previous sections of this report, no numerical value of this radius was specified for the sake of generality of the results. In developing the mixing rules based on different local composition approximations, knowledge of the value of this parameter was immaterial. However, 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 eqn. (14) from eqn. (13). According to this approximation the radius of the sphere of effectiveness of local composition can be defined by the following equation

$$\int_{R_{ij}}^{\infty} [g_{ij}(r) - 1] 4\pi r^2 dr = 0 \quad (40)$$

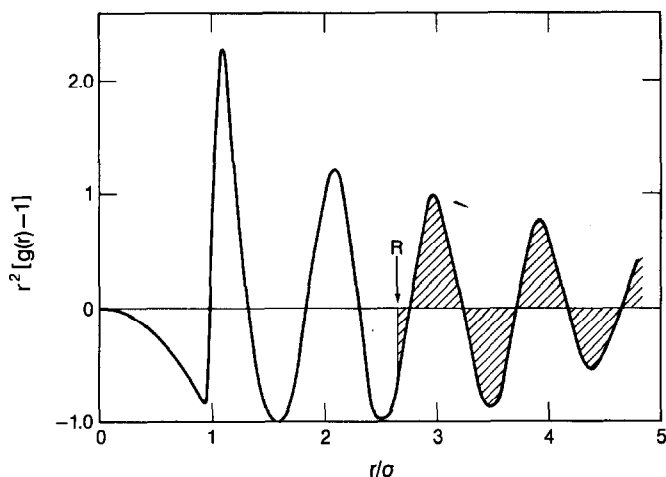


Fig. 1. Schematic diagram of the radial dependence of the compressibility integrand  $r^2[g(r) - 1]$  in a dense fluid. The approximate radius of influence of local compositions ( $R$ ) is shown as the point where the oscillations of  $g(r)$  about unity cancel each other.

This expression indicates that  $R_{ij}$  should be defined such that the dashed areas in Fig. 1 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  $R$  will also have to be a function of temperature, density, and composition. Since  $g_{ij}$  varies significantly with density it can be expected that  $R$  will be a strong function of density decreasing as the density increases.

It is certainly possible that eqn. (40) can have more than one solution and one must, therefore, impose some secondary constraint to obtain the correct value. Hanley and Evans (1981) showed for dense soft-spheres that 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, fig. 6 of the Hanley and Evans reference 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 eqn. (41) which is in the vicinity of 2-3 molecular diameters. Nonetheless, it is clear that in order to have a more quantitative knowledge about  $R$  one has to use accurate radial distribution function data, preferably, using computer simulation values. Unfortunately, relatively little detailed information concerning radial distribution functions has been published. 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 eqn. (40).

## CONCLUSION

The statistical mechanical approach presented here has allowed us to introduce a unified approach in formulating thermodynamic properties of mixtures with respect to the concept of local particle numbers and compositions—a topic which has been of interest to chemical engineering community in fluid phase equilibria calculation of multicomponent mixtures. This approach has produced a mechanism by which different phenomenological approximations to local compositions could be examined by statistical mechanics and could be compared with molecular theories of solutions. It has also provided a method of producing local composition approximation equivalents of molecular theories of mixtures. One significant result of this method is formulation of varieties of mixing rules according to different local composition approximations. Some of the mixing rules produced happen to be composition, density and temperature dependent which bring about a new perspective in mixture calculation and will require a new set of thermodynamic consistency conditions to be developed in the future. Incorporation of the local composition concept in the Kirkwood–Buff solution 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, eqn. (40), for the 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.

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## LIST OF SYMBOLS

$B_{ij}$	element of Kirkwood–Buff compressibility matrix $\underline{B}$
$c$	number of components
$e_{ij}$	exponential term in WRP models
$f$	conformal solution energy scaling parameter
$G_{ij}$	compressibility integral
$g_{ij}$	radial distribution function for $ij$ pair
$h$	conformal solution size scaling parameter
$k$	Boltzmann constant

$N_i$	number of particles of type $i$ in the mixture
$n_{ij}$	local number of particles of type $i$ about a central $j$
$R_{ij}$	radius of sphere of influence of local compositions
$T$	absolute temperature
$U$	internal energy
$u$	intermolecular potential function
$V$	system volume
$\bar{V}_i$	partial molar volume of component $i$
$x_{ij}$	local mole fraction of $i$ about $j$
$x_i$	bulk mole fraction of $i$
$Z$	compressibility factor $pV/NkT$
$\alpha_{ij}$	non-randomness parameter
$\delta_{ij}$	Kronecker delta function
$\Delta n_{ij}$	difference between local and average particle numbers
$\epsilon_{ij}$	intermolecular potential energy parameter
$K_T$	isothermal compressibility
$\lambda_{ij}$	energy parameter in WRP models
$\eta_i$	packing fraction of component $i$
$\rho_i$	number density of component $i$
$\mu_i$	chemical potential of component $i$

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