Lawrence Berkeley National Laboratory
Recent Work

Title
EQUATIONS OF STATE FOR STRONGLY NONIDEAL FLUID MIXTURES. APPLICATION OF LOCAL-COMPOSITIONS TOWARD DENSITY-DEPENDENT MIXING RULES

Permalink
https://escholarship.org/uc/item/7fh2z3wc

Authors
Whiting, W.B.
Prausnitz, J.M.

Publication Date
1982-02-01
EQUATIONS OF STATE FOR STRONGLY NONIDEAL FLUID MIXTURES. APPLICATION OF LOCAL-COMPOSITIONS TOWARD DENSITY-DEPENDENT MIXING RULES

Wallace B. Whiting and John M. Prausnitz

February 1982

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks.
For a personal retention copy, call Tech. Info. Division, Ext. 6782
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
EQUATIONS OF STATE FOR STRONGLY NONIDEAL FLUID MIXTURES.
Application of Local-Compositions Toward
Density-Dependent Mixing Rules

Wallace B. Whiting* and John M. Prausnitz

Lawrence Berkeley Laboratory and
Department of Chemical Engineering
University of California
Berkeley, California 94720

ABSTRACT

A local-composition, two-fluid model has been developed for equation-of-state calculation of fluid-phase equilibria for asymmetric mixtures; it is applicable to any equation of state of the van der Waals form. A modification of the quasi-chemical theory of Guggengheim is applied to mixtures at all fluid densities. Desirable boundary conditions are met at low densities, at high densities, and at high temperatures.

In effect, the local-composition model uses density-dependent mixing rules. It contains no new adjustable binary parameters and can be extended to multicomponent mixtures without ternary (or higher) parameters. It appears that, when compared to conventional one-fluid models, significant improvement may be obtained for vapor-liquid equilibria of typical asymmetric mixtures.

*current address: Department of Chemical Engineering, West Virginia University, Morgantown, WV 26506
For representing thermodynamic properties of mixtures, including phase equilibria, it is desirable to use an equation of state valid at all fluid densities. When such an equation of state is available, mixtures containing supercritical components can be described without the use of hypothetical standard states. In this work, we discuss a new procedure for extending to mixtures an equation of state for pure fluids. Our work is similar in concept, but not in detail, to that of Mollerup (1981).

While much attention has been given toward establishing new equations of state for pure fluids, much less attention has been given toward extending these equations to mixtures. With few exceptions, the general procedure today for such extension is to use the "one-fluid" method proposed by van der Waals (1890) nearly a century ago: we suppose that the properties of a fluid mixture at temperature $T$, pressure $P$, and composition $x$ are the same as those of a hypothetical pure fluid (at the same $T$ and $P$) whose characteristic parameters (constants) are functions of composition $x$. These functions, called mixing rules, are quadratic in mole fraction; if $C_{ij}$ stands for any constant in the equation of state for pure component $i$, then for the mixture ($M$) containing $m$ components:

$$C_M = \sum_{i=1}^{m} \sum_{j=1}^{m} x_i x_j C_{ij},$$

where $x_i$ is the mole fraction of component $i$. In the special case where
\[ C_{ij} = (C_i + C_j) / 2 \]  
Equation 1 reduces to

\[ C_M = \sum_{i=1}^{m} x_i C_{ii} \]  

For many years, it has become common practice to use Equation 3 for the constant that characterizes molecular size (van der Waals' \( b \)). For the constant that characterizes intermolecular attraction (van der Waals' \( a \)), Equation 1 is commonly used with

\[ C_{ij} = (C_{ii} C_{jj})^{0.5} (1 - k_{ij}) \]  

where \( k_{ij} \) is a binary parameter, usually positive and, for simple mixtures, of order \( 10^{-2} \). During the last 20 years, much attention has been given to this binary parameter but little attention has been given to the one-fluid theory and Equation 1.

In an equation of state of the van der Waals form (e.g., equations of Redlich-Kwong [1949], Soave [1972], Peng-Robinson [1976]), it is necessary that Equation 1 hold at low density because the second virial coefficient of a mixture must be a quadratic function of mole fraction. While this theoretically necessary result holds at low densities, it does not, however, follow that a quadratic dependence must hold at high (liquid-like) densities. Indeed, empirical evidence clearly shows that, for non-simple liquid mixtures, the quadratic mole-fraction rule is in error, often very much so.

For example, the liquid-phase excess Gibbs energy, \( G^E \),
is related to the equation of state through

\[ G^E = A^E + pV^E \]  \hspace{2cm} (5)

\[ A^E = \Delta A_{\text{mixing}} - RT \sum_{i=1}^{m} N_i \ln x_i \]  \hspace{2cm} (6)

\[ \Delta A_{\text{mixing}} = \int_{V_M}^{\infty} \left[ \frac{p-NRT}{V} \right] dV - \sum_{i=1}^{m} \int_{V_i}^{\infty} \left[ \frac{p-N_iRT}{V} \right]_{\text{pure}} dV \]

\[ + RT \sum_{i=1}^{m} N_i \ln \left[ \frac{V_i}{V_M} \right] \]  \hspace{2cm} (7)

where \( V_M \) is the volume of the mixture, \( V_i \) is the volume of pure \( i \), \( \Delta A_{\text{mixing}} \) is the Helmholtz energy of mixing of a mixture containing \( N_1 \) moles of component 1, \( N_2 \) moles of component 2, etc. (For liquid mixtures at low or modest pressures, the term \( pV^E \) is negligible.) Without going into details here, it is clear that liquid-mixture data for \( G^E \) (through experimentally-determined activity coefficients) can give information on the best mixing rules for an equation of state at high densities, as pointed out by Wilson (1972). Unfortunately, Wilson's suggestion was not followed until Huron and Vidal (Vidal, 1978; Huron and Vidal, 1979) and Won (1981) proposed empirical, non-quadratic mixing rules suggested by liquid-state activity-coefficient data. While these rules necessarily give good results at high densities, they are in error at low densities because they are in conflict with the theoretical second-virial-coefficient requirement. For calculating vapor-liquid equilibria at low
or moderate pressures, this conflict often has little practical significance because, at such pressures, essentially all nonideality is in the liquid phase. However, an incorrect mixing rule at low densities is nevertheless a serious disadvantage because, as shown in Equation 7, the liquid-phase excess function depends on an integral that extends from the liquid-phase volume to the ideal-gas state; therefore, if an incorrect mixing rule is used in performing the integration, the resulting expression may have empirical value, but the empirically-determined constants do not have any clear physical significance. However, it is precisely this significance that we need when we try to correlate measured phase equilibria toward predicting behavior of systems where experimental data are not available.

It would be desirable to utilize binary constant $k_{ij}$ (Equation 4), obtained from second-virial coefficient ($B_{ij}$) data, toward predicting vapor-liquid equilibria. This cannot be done if the mixing rule, obtained from liquid-phase data, is invalid at low densities.

Since theory demands a quadratic mixing rule at low densities, while experiment shows that this rule is not reliable at high densities, we require density-dependent mixing rules. Our procedure for deriving such rules is based on our knowledge at the two density limits. At low densities, we want to satisfy the second-virial coefficient requirement. At high densities, we want a result similar to that given by recent equations for the excess Gibbs energy;
these equations are based on the two-fluid theory coupled with the local-composition concept (Maurer, 1978; Kemeny and Rasmussen, 1981).

Before deriving density-dependent mixing rules, it is useful to reflect on the physical need for such rules. At low densities, molecules are relatively free in the sense that they do not seriously interfere with each other's motion, position, or orientation. Therefore, at low densities, the distribution of molecules in space is essentially random, that is, a particular molecule does not exercise any preference in its choice of partner in a two-body collision; that choice is dictated primarily by availability (that is, composition) rather than by intermolecular forces. At low densities, then, we have a state described by the word randomness.

At high densities, however, the motion, position, and orientation of a given molecule are strongly affected by the close presence of other molecules, that is, by intermolecular forces. In a mixture, there are several types of molecules available, and, therefore, a given molecule may well "prefer" to surround itself with one type rather than another. This preference is described by the word nonrandomness.

The task of density-dependent mixing rules is to describe in a continuous manner how the structure of a mixture changes from randomness at low densities to nonrandomness at high densities. We have no theoretically rigorous
method for describing this transition; in effect we can only interpolate between desired limits. Such interpolation is described here.

An alternate method to introduce nonrandomness is through a "chemical" hypothesis where we assume the existence of new species (e.g., dimers) whose concentrations are calculated through an empirically-determined equilibrium constant. This method has a long history, having been used extensively, for example, for strongly nonideal vapors (e.g., acetic acid) and for strongly nonideal liquid mixtures (e.g., alcohols in hydrocarbons). More recently, a unified treatment, where chemical equilibria are superimposed on a van-der-Waals-like equation of state, was described by several authors, e.g., Gmehling et al. (1979) and Baumgärtner, Rupp, and Wenzel (1979). The disadvantage of this procedure follows from arbitrariness in deciding what associated species are present and, more serious, from computational complexity for systems containing more than two components.

Before discussing our procedure for taking into account nonrandomness due to attractive intermolecular forces, we discuss first our procedure for calculating the properties of our athermal reference system.

ATHERMAL ENTROPY OF MIXING

Our description of nonrandomness uses a perturbation about an athermal reference system. For our purposes here,
we assume that the properties of a mixture of molecules interacting with purely repulsive potentials (our reference system) is well described by some simple model, for example, one-fluid theory applied to the Carnahan-Starling (1969) equation of state for hard spheres. We then perturb our reference system by adding corrections for nonrandomness due to the presence of attractive intermolecular potentials.

For the athermal entropy of mixing (chain-like) large and small molecules, it is better to use the Flory-Huggins (Flory, 1941; Huggins, 1941) expression (or a modification thereof) than that corresponding to ideal mixing. For liquid-state activity-coefficient models, it is convenient to use the Flory-Huggins expression, which uses volume fractions, an appropriate measure of composition at high densities. Equations of state, however, must meet the low-density limit of ideal mixing, which uses mole fractions.

To test the one-fluid athermal model, we have calculated the high-density entropy of mixing using the (hard-sphere) Carnahan-Starling equation of state. Figure 1 shows a comparison between this entropy of mixing and that calculated from the Flory-Huggins expression. (Appendix A shows what assumptions must be made to recover the Flory-Huggins result from the repulsive part of the van der Waals equation.) Although the Carnahan-Starling entropy of mixing is greater than that for ideal-mixing, it is far short of the Flory-Huggins result for a binary mixture of molecules with a size ratio of 10:1. In a later section, we briefly dis-
cuss a method for achieving the Flory-Huggins result at high density, while retaining the proper low-density limit.

For the calculation shown in Figure 1, we use the (one-fluid) Carnahan-Starling equation of state:

\[ P = \rho RT \left[ 1 + \frac{\xi}{2} - \frac{\xi^2}{12} \right] \]

where

\[ \xi = \frac{b\rho}{4} \]

and \( \rho \) is the molar density. Parameter \( b \) is calculated using Equation 1 with cross term \( b_{ij} \) calculated using the Lorentz (cube-root) rule. The molar entropy of mixing for this equation of state is:

\[
\Delta s_{\text{mixing}} = -R \sum_{i=1}^{m} x_i \ln \left( \frac{x_i \rho}{\rho_i^{\text{pure}}} \right) \\
\quad + R \left[ \xi_i (3\xi_i - 4) \right] - R \sum_{i=1}^{m} x_i \left[ \frac{\xi_i (3\xi_i - 4)}{(1-\xi_i)^2} \right],
\]

where

\[ \xi_i = \frac{b_i \rho_i^{\text{pure}}}{4} \]

We have also calculated \( \Delta s_{\text{mixing}} \) with the Mansoori et al. (1971) equation; the results are essentially the same as those obtained from Equation 10, even for a binary system with a size ratio of 10:1. We prefer to use the one-fluid model for our reference system because it allows us, if necessary, to use a binary parameter (to account for the nonadditivity of molecular diameters), to correlate experimental data. However, we have not used that binary parame-
TWO-FLUID THEORY AND LOCAL COMPOSITION

We assume that some nonrandomness occurs in mixtures of nearly equal-sized molecules if their intermolecular potentials are significantly different. Further, we assume that this nonrandomness exists, to some extent, at all densities greater than zero.

For simplicity, we first consider mixtures containing molecules of nearly equal size. However, the results can be generalized to mixtures of molecules that differ appreciably in size by redefining the characteristic energy, as indicated later.

First, we separate the residual Helmholtz energy into a repulsive (hard-sphere) part and an attractive part:

\[ A - A^{\text{id}} = A^{\text{rep}} + A^{\text{attr}}, \]  

where superscript id stands for the ideal-gas contribution.

The repulsive contribution to the Helmholtz energy of the mixture is calculated with a one-fluid model which is known to represent well the properties of mixtures of molecules interacting solely with repulsive potentials (Henderson and Leonard, 1970). Although much of the structure of the fluid is determined by the repulsive part of the intermolecular potentials (cf. Chandler, 1978), our goal is to calculate the effects of the attractive potential on the nonrandomness of the mixture.

For a binary mixture, we consider two representative
fluid regions, as shown in Figure 2. One region centers around a type-1 molecule, and the other centers around a type-2 molecule. The local compositions in these two types of regions are not the same. As suggested by quasi-chemical theory (Guggenheim, 1935; Renon, 1968), we approximate these local compositions through Boltzmann factors of a function with units of energy, $\alpha E_{ij} \ (i=1,2; \ j=1,2)$, characteristic of the like and unlike two-body interactions. For hypothetical fluid (1), local mole fractions $x_{11}$ and $x_{21}$ are related to mole fractions $x_1$ and $x_2$ through

$$\frac{x_{21}}{x_{11}} = \frac{x_2 \exp(-\alpha E_{21}/RT)}{x_1 \exp(-\alpha E_{11}/RT)} \quad (13)$$

and $x_{21} + x_{11} = 1$. Similarly, for hypothetical fluid (2),

$$\frac{x_{12}}{x_{22}} = \frac{x_1 \exp(-\alpha E_{12}/RT)}{x_2 \exp(-\alpha E_{22}/RT)} \quad (14)$$

Equations 13 and 14 indicate that the local mole fraction of i molecules around a central j molecule is proportional to the total number of i molecules and proportional to the Boltzmann factor whose argument contains $\alpha E_{ij}$, which is characteristic of the attractive ij interaction. Unlike Guggenheim, we allow $\alpha E_{ij}$ to depend on density.

The proper way to evaluate $\alpha E_{ij}$ is unclear. Equations 13 and 14 reduce to the quasi-chemical theory (Guggenheim, 1935 and 1952) if $\alpha E_{ij}$ is the energy of interaction (per mole) between a j molecule and an i molecule which are nearest neighbors on a lattice. (See Appendix B.) On the other hand, Equations 13 and 14 give the local mole frac-
tions in UNIQUAC if $\alpha E_{ij}$ is the energy (per mole) of a fluid whose molecules interact with an $ij$ type potential, i.e., if $\alpha E_{ij}$ is $(z/2)$ times the energy of interaction (per mole) of nearest-neighbor molecules of type $i$ and $j$, where $z$ is the coordination number of the lattice (Maurer and Prausnitz, 1978). Given this discrepancy, we consider $E_{ij}$ to be some molar energy of a fluid in which the molecules interact with an $ij$ potential and $\alpha$ a proportionality factor of order unity. If $\alpha$ is unity, the UNIQUAC expression is recovered; if $\alpha$ equals $(2/z)$ (e.g., $1/6$ for hexagonal close packing), we obtain quasi-chemical theory. In our work, we have somewhat arbitrarily used $\alpha = 0.5$.

It would be tempting to use $\alpha$ as a binary parameter; however, as explained later, we cannot extend local-composition theory to multicomponent mixtures unless $\alpha$ is a universal constant.

As argued by Guggenheim (1966), $E_{ij}$ should be a free (Helmholtz) energy, because both the entropy and potential energy of a configuration contribute to its probability. We, therefore, define $E_{ij}$ as the attractive Helmholtz energy (per mole) of a fluid in which the molecules interact with an $ij$ potential.

In previous liquid-state models, $E_{ij}$ was considered independent of density and temperature because, by implication, the molecules were confined to sites on a quasi-lattice. For liquids, this simplification may be reasonable, but, for lower densities, we expect $E_{ij}$ to be a strong
function of density and a weak function of temperature. For any equation of state of the van der Waals type, we can calculate $E_{ij}$ as a function of density and temperature from the equation of state; $E_{ij}$ is the attractive Helmholtz energy of a system whose molecules interact with an $ij$ intermolecular potential.

Assuming additivity, the total attractive internal energy of the fluid mixture is given by the sum of contributions from all types of regions:

$$u_{\text{attr}} = N_1(x_{21}u_{21} + x_{11}u_{11}) + N_2(x_{12}u_{12} + x_{22}u_{22}) , \quad (15)$$

where $u_{ij}$ is the molar attractive energy of a fluid whose molecules interact according to the $ij$ potential. Equation 15 can be integrated with respect to temperature (at constant density and composition) to obtain the attractive Helmholtz energy of the mixture. This Helmholtz energy is then differentiated with respect to density to produce an equation of state for the mixture. This procedure is demonstrated below for the van der Waals equation. But it is important to emphasize that the same procedure can be applied to any equation of state of the van der Waals type, that is, to any equation of state that separates the repulsive and attractive contributions to the residual Helmholtz energy (Equation 12).
EXAMPLE. Extension of van der Waals' Equation to a Binary Mixture

The simplest reasonable equation of state for fluids is the van der Waals (1873) equation,

\[ p = p^{\text{rep}} - a\rho^2, \quad (16) \]

which we use here for illustration. For \( p^{\text{rep}} \), van der Waals suggested

\[ p^{\text{rep}} = \frac{eRT}{1 - b\rho}, \quad (16a) \]

but this particular choice is not important here. For illustrative purposes, we assume that \( a \) is independent of temperature. (As a result of this assumption, the attractive free energy is the same as the attractive energy.) By integrating the equation of state with respect to density, we obtain an expression for the total Helmholtz energy:

\[ A - A(T, \rho, \text{ideal-gas state}) = N \int_0^\rho \frac{p}{\rho^2} \, d\rho = A^{\text{rep}} + A^{\text{attr}}, \quad (17) \]

where

\[ A^{\text{attr}} = -N4a\xi/b \quad (18) \]

and \( b \) is calculated as in Equation 10 and \( \xi = b\rho/4 \). To obtain the attractive part of the internal energy, we apply the relation,

\[ \left[ \frac{\partial (A/T)}{\partial (1/T)} \right]_{N,V} = u, \quad (19) \]

to the attractive Helmholtz energy:

\[ U^{\text{attr}} = \frac{\partial (-N\rho p/T)}{\partial (1/T)} = -N\rho \quad (20) \]

The local compositions are now given by
\[ x_{ij} = \frac{x_i}{x_j} \exp \left[ \frac{a(a_{ii}b_{ji} - a_{ji}b_{ij})4\xi_i}{RT} \right] \quad (21) \]

where \( \xi_i = \frac{b_{ii}\rho}{4} \).

Equation 21 shows an important feature of the local-composition model: the local mole fractions become identical to the respective bulk mole fractions at infinite temperature and, more important, at the low-density limit. Any consistent treatment of non-randomness must meet this boundary condition. To do so, any equation of state may be used provided that the attractive internal energy is proportional to the density in the low-density limit. All reasonable equations of state have such a density dependence.

Combining Equations 13, 14, 15, and 21, for a binary mixture, we obtain the attractive internal energy of the mixture:

\[ U_{\text{attr}} = -\frac{2}{N} \sum_{i=1}^{2} x_i \left[ \sum_{j=1} a_{ii} \frac{4\xi_i}{RT} \exp \left[ \frac{a(a_{ii}b_{ji} - a_{ji}b_{ij})4\xi_i}{RT} \right] \right]. \quad (22) \]

We now integrate \( U_{\text{attr}} \), using Equation 19, to obtain the attractive Helmholtz energy of the mixture:

\[ A_{\text{attr}} = -\frac{RT}{a} \sum_{i=1}^{2} x_i \ln \sum_{j=1}^{2} x_j \exp \left[ \frac{a(a_{ii}4\xi_i)}{RTb_{ji}} \right]. \quad (23) \]

This expression for \( A_{\text{attr}} \) can be differentiated with respect to mole number to obtain the attractive chemical potential.
of either component. Further, it can be differentiated with respect to density to obtain the attractive pressure. The equation of state is

\[ p = p_{rep} + \text{pattr}, \]  

(24)

where

\[ \text{pattr} = -\rho^2 \sum_{i=1}^{2} \sum_{j=1}^{2} x_i x_j \left[ \frac{a_{ij} 4 \zeta_i}{b_{ij}} \right] \exp \left[ \frac{a_{ij} 4 \zeta_i}{R T b_{ij}} \right] \]  

(25)

Equation 25 is the attractive contribution to the equation of state for a binary mixture using the local-composition model with the van der Waals equation. To compare this contribution to that of the one-fluid van der Waals model, we define \( a_M \) (the effective van der Waals \( a \) for the mixture) by

\[ a_M = -\frac{\text{pattr}}{\rho^2}, \]  

(26)

where \( \text{pattr} \) is given by Equation 25. Figure 3 shows \( a_M \) as a function of composition for two densities. For the local-composition model, \( a_M \) differs from that for the one-fluid model only at the higher density, as expected. Of particular interest is the difference between the slopes of the two curves. These slopes are directly related to the chemical potentials of the components of the mixture; the different slopes suggest that phase equilibria calculated using the new two-fluid theory are significantly different from those calculated using conventional one-fluid theory.
LOW-DENSITY LIMIT

At low densities, every equation of state for a mixture should give a second virial coefficient with a quadratic mole-fraction dependence (Reed and Gubbins, 1977). By differentiating Equation 24 (using a reasonable expression for \( p_{\text{ref}} \)), the second virial coefficient for a binary mixture is

\[
B = \frac{1}{RT} \left[ \frac{\partial (P/\rho)}{\partial \rho} \right]_{T,x,p} \rightarrow 0 = \sum_{i=1}^{2} \sum_{j=1}^{2} x_i x_j (b_{ij} - \frac{a_{ij} b_{ij}}{RT b_{ij}})
\]

which is quadratic in mole fraction. Any equation of state for which the attractive Helmholtz energy is proportional to the density in the low-density limit can be used with the local-composition model to give the proper second-virial-coefficient limit.

HIGH-DENSITY LIMIT

For liquid-like densities, we desire that the local-composition model become identical to the liquid-state activity-coefficient model on which it is based. To compare these models, we must evaluate the molar excess Gibbs energy of a binary mixture, which can be calculated from an equation of state by

\[
\delta G = \mu^r - \sum_{i=1}^{2} x_i \mu_i^{\text{pure}} + RT \ln \rho - RT \sum_{i=1}^{2} x_i \ln \rho_i^{\text{pure}}
\]

where \( \rho \) is the molar density of the mixture at \((T,P,x)\) and where \( \rho_i^{\text{pure}} \) is the molar density of pure liquid \( i \) at the same \((T,P)\). These densities are used to calculate the respective residual chemical potentials from
\[
\mu_i^r = \frac{\partial}{\partial N} \left[ N \int_0^{\rho} \left( \frac{P - \rho RT}{\rho^2} \right) \rho \right]_{T, V, x},
\]
where the equation of state for pure component \(i\) is used to calculate \(\mu_i^r, \text{pure}\) and the equation of state for the mixture is used to calculate \(\mu_i^r\). It is important to note that Equation 28 is valid only when all components are subcritical, i.e., when the equation of state has a liquid-like density root for all pure components at \((T, P)\); otherwise, the excess Gibbs energy of the mixture is undefined. If Equation 24 is used in Equation 29, the high-density limit (for a binary mixture of equi-sized molecules) is:

\[
g_E = -\frac{RT}{a} \sum_{i=1}^{2} x_i \ln \sum_{j=1}^{2} x_j \exp \left[ \frac{a(a_{ij} - a_{ii})}{bRT} \right].
\]

The form of equation 30 is the same as that of the three-parameter Wilson (1964) equation for mixtures of components with equal molar volumes.

**Extension to Mixtures of Molecules of Unequal Size**

To extend our model to binary mixtures of molecules not nearly equal in size, we assume that each molecule of type \(i\) has an external surface area \(q_i\) (calculated by the method of Bondi [1968]); only this area is available for intermolecular attraction. If we designate the average attractive Helmholtz energy per unit surface area of an \(ij\) interaction as \(\eta_{ij}\), the attractive internal energy of a type 1 region is

\[
u^{(1)} = x_{11} q_1 \left[ \frac{\partial (\eta_{11}/T)}{\partial (1/T)} \right]_{\nu, x} + x_{21} q_1 \left[ \frac{\partial (\eta_{21}/T)}{\partial (1/T)} \right]_{\nu, x},
\]

where \(x_{ji}\) is the local mole fraction of type \(j\) molecules in
a type i region. A similar relation holds for $u^{(2)}$. For a binary mixture, the total attractive internal energy is the sum of the contributions from each type of region:

$$\frac{\Pi_{\text{attr}}}{N} = x_1 u^{(1)} + x_2 u^{(2)}.$$  \hfill (32)

To calculate the local mole fractions, we use Equations 13 and 14 with the new definition of characteristic energies in terms of the surface areas:

$$\frac{x_{21}}{x_{11}} = \frac{x_2}{x_1} \exp \left[-\frac{a q_1 (\eta_{21} - \eta_{11})}{RT}\right]$$  \hfill (33)

$$\frac{x_{12}}{x_{22}} = \frac{x_1}{x_2} \exp \left[-\frac{a q_2 (\eta_{12} - \eta_{22})}{RT}\right],$$  \hfill (34)

where $x_{21} + x_{11} = 1$ and $x_{12} + x_{22} = 1$.

Equations 31–34 are fundamentally different from similar equations used in the derivation of the UNIQUAC equation. Our equations use local mole fractions; those in UNIQUAC use local surface fractions. If local surface fractions had been used here, the necessary low-density limit would not have been met.

For the simple van der Waals equation, the attractive Helmholtz energy for pure i is

$$q_i \eta_{ii} = \frac{-a_i \xi_i}{b_{ii}}.$$  \hfill (35)

The attractive Helmholtz energy per unit surface area, $\eta_{ii}$, is a function of density and may be also a function of temperature. To calculate $\eta_{ji}$, we write
\[ q_{ij} = \frac{-a_{ij}^4 \xi_i}{b_{ij}}, \]  
\[ a_{ji} = q_i \left[ \frac{a_{ij}^4 \xi_i}{q_j q_i} \right]^{0.5} (1 - k_{ji}). \]  

We can now write an expression for the attractive contribution to the pressure for a binary mixture of molecules whose attractive forces are described by the simple van der Waals equation:

\[ \text{pattr} = -\rho \sum_{i=1}^{2} \sum_{j=1}^{2} x_i x_j \left[ \frac{a_{ij}^4 \xi_i}{b_{ij}} \right] \exp \left[ \frac{a_{ij}^4 \xi_i}{RT b_{ij}} \right] \]  

In general, for any equation of state of the van der Waals type, the appropriate expression for \( \eta_{ij} \) is determined from the equation of state with the pure-component parameters \((a_{ii}, b_{ii})\) replaced by the corresponding binary parameters \((a_{ji}, b_{ji})\).

For the van der Waals equation, our local-composition model reduces to the one-fluid model if the energy parameter per segment \((a/bq)\) is the same for each species in a mixture, regardless of molecular size. (In that event we have an athermal mixture.) Thus, we rely heavily on the reference system (i.e., the repulsive part of the mixture equation of state) to predict important entropic effects in mixtures of, for instance, a polymer with its monomer. Some deficiencies of the reference system can be corrected with the function \( F_{ji} \), discussed below.
VAN LAAR'S THEORY OF SOLUTIONS AND LOCAL-COMPOSITION THEORY

Early in this century, van Laar (1910) derived an expression for the excess Gibbs energy of a liquid solution using the van der Waals equation of state. Assuming that for a pure liquid \( v_i = b_i \) and that for the mixture \( v = x_1 b_1 + x_2 b_2 \), van Laar's equation is

\[
g^E = (x_1 b_1 + x_2 b_2) \bar{\omega}_i \left( \frac{a_{11}}{b_1^2} + \frac{2a_{12}}{b_1 b_2} + \frac{a_{22}}{b_2^2} \right),
\]

where \( \bar{\omega}_i \) is the volume fraction:

\[
\bar{\omega}_i = \frac{x_i v_i}{m} \sum_{j=1}^{m} x_j v_j
\]

and \( v_i \) is the molar volume of pure \( i \) at the same temperature and pressure.

Van Laar assumed that the repulsive part of the equation of state does not affect the excess Gibbs energy, and, thus, he was concerned only with what we call \( g^E, \text{attr} \), the contribution to the excess Gibbs energy from the attractive part of the intermolecular potential. For any equation of state of the van der Waals type, we can calculate this quantity, and, for most of these equations, it has the form:

\[
g^E, \text{attr} = -\frac{a}{v} \Theta(\xi) + \frac{a_{11}}{v_1 x_1 \Theta(\xi_1)} + \frac{a_{22}}{v_2 x_2 \Theta(\xi_2)}
\]

where the reduced density \( \xi = b/4v \), \( a \) is a quadratic function of mole fraction (and may be temperature-dependent), and \( \Theta(\xi) \) is some function of reduced density. Table I shows \( \Theta(\xi) \) for three popular equations of state.
To calculate $g_{E, attr}$, we need not make van Laar's stringent assumptions. Instead, we assume that for each component the molar volume is proportional to $b$,

$$\xi = \xi_1 = \xi_2,$$  \hspace{1cm} (42)

where

$$\xi_i = \frac{b_i}{4v_i},$$ \hspace{1cm} (43)

and we assume that for the mixture $b = x_1b_1 + x_2b_2$. It follows directly that

$$g_{E, attr} = \Theta(\xi)\frac{1}{v_1v_2} \left[ \frac{a_{11}}{v_1^2} - \frac{2a_{12}}{v_1v_2} + \frac{a_{22}}{v_2^2} \right],$$  \hspace{1cm} (44)

where $\Theta(\xi)$ is a function only of reduced density. Thus, for many equations of state, we can derive a result similar to the van Laar form that has been shown empirically to correlate well liquid-state activity coefficients.

Appendix C shows that the local-composition theory for an equation of the van der Waals type approaches the van Laar result at conditions where random mixing prevails, i.e., when the local compositions become equal to the respective bulk compositions.

To show the effect of local-composition theory on the attractive contribution to the excess Gibbs energy, we have calculated this function for several model mixtures. In each case, we made the calculations for the mixture at $0^\circ C$ and 200 bar. This pressure is above the vapor pressure of the most volatile component.
Figure 4 shows the effect of energy parameter $a$. In this case, the size and surface-area parameters, $b$ and $q$, are the same for both components. The local-composition curve is always lower than the corresponding one-fluid curve because the molecules are in more energetically favorable, nonrandom configurations. The effect of local-composition theory increases with the difference between the energy parameters; again, this effect is to be expected because higher asymmetry leads to increased nonrandomness.

Figure 5 shows the effect of molecular-size differences. Results using local-composition theory differ only moderately from those using one-fluid theory, primarily because we include only the effect of the attractive part of the intermolecular potential in calculating local compositions. Since the major effect of molecular-size differences on mixture properties is due to the repulsive (reference) part of the intermolecular potential, it does not appear in $g_{E,attr}$.

The binary parameter, $k_{ij}$, has a large effect on calculated mixture properties, as shown in Figure 6 for a mixture of molecules where both size and energy parameters are different. Again, the local-composition theory predicts an excess Gibbs energy lower than that predicted by one-fluid theory. For $k_{12} = 0.05$, we have also calculated the excess enthalpy and excess entropy of the mixture, as shown in Figure 7. The larger contribution to the excess Gibbs energy comes, as expected, from the excess enthalpy.
To show the effect of the local-composition model on calculated phase equilibria, we consider several asymmetric systems. We have chosen a very simple equation of state for our example: the repulsive part is given by the expression of Carnahan and Starling (1969), and the attractive part is given by the van der Waals term:

$$P = \rho RT \left[ 1 + \frac{\xi^2 - 2\xi^3}{(1 - \xi)} \right] - \alpha \rho^2 ,$$  \hspace{1cm} (45)

where the reduced density is

$$\xi = \frac{\rho_0}{\rho} .$$  \hspace{1cm} (46)

We have used the following one-fluid mixing rule for the repulsive contributions to mixture properties:

$$b_M = \sum_{i=1}^{2} \sum_{j=1}^{2} x_i x_j b_{ij} ,$$  \hspace{1cm} (47)

where

$$b_{ij} = \left[ \frac{\rho_i^{1/3} + \rho_j^{1/3}}{2} \right]^3 .$$  \hspace{1cm} (48)

To determine pure-component parameters for subcritical components, we use experimental values for the vapor pressure and the density of the saturated liquid at the temperature of interest. For the components which are supercritical at the temperatures considered, we used experimental values for the fugacity and the density at the desired temperature and at an arbitrarily chosen high pressure.
bar). From these pure-component data, unique parameters a and b were determined, as shown in Table II.

The binary interaction parameter $k_{ij}$ was found, at the temperature of interest, from cross-second-virial-coefficient data for each binary pair (Table III). In the low-density limit, both the random-mixing and the local-composition models give the same second virial coefficient; therefore, we use the same value for $k_{ij}$ for both models.

Figure 8 shows calculated and experimental vapor-liquid equilibria for methane/water at $150^\circ$C. Although both models predict the vapor-phase composition reasonably well, the local-composition model predicts the solubility of methane in the liquid phase much better. (Note that the scale for the mole fraction methane at low concentrations is logarithmic.) The improvement in the fit of the methane/water data by use of the local-composition model is not at the expense of another binary parameter.

Table IV shows the effect of local-composition theory on predicted Henry's constants, $H_i$, for several systems. Although the predicted vapor-phase composition was not much affected by the new mixing rules, in each case, the calculated liquid-phase compositions were shifted in the proper direction, often dramatically so.

EXTENSION TO MULTICOMPONENT MIXTURES

We extend the local-composition model to multicomponent mixtures by considering $m$ different types of regions in the
fluid, where \( m \) is the number of components. Each type of region contains a molecule of type \( i (i=1,2,\ldots, m) \) at its center.

To calculate thermodynamic properties, we again sum the contributions to the attractive internal energy of all the regions:

\[
\frac{\Pi_{\text{attr}}}{N} = \sum_{i=1}^{m} x_i u(i),
\]

where

\[
u(i) = \sum_{j=1}^{m} x_{ji} \left[ \frac{\partial \eta_{ij}/T}{\partial (1/T)} \right]_{\rho,x}
\]

and where the local compositions are given by

\[
\frac{x_{ii}}{x_i} = \frac{x_i \exp \left[ \frac{-aq_i(\eta_{ii}-\eta_{ii})}{RT} \right]}{x_i}
\]

\[
\sum_{j=1}^{m} x_{ji} = 1, \text{ for all } i.
\]

Substituting Equations 50–52 into Equation 49, we obtain

\[
\frac{\Pi_{\text{attr}}}{N} = \sum_{i=1}^{m} x_i \left[ \frac{\partial \eta_{ii}/T}{\partial (1/T)} \right]_{\rho,x} \exp \left[ \frac{-aq_i\eta_{ii}}{RT} \right]
\]

To calculate the attractive Helmholtz energy, we integrate \( \Pi_{\text{attr}}/T \) with respect to \( 1/T \) and obtain

\[
\frac{\Delta_{\text{attr}}}{NRT} = \frac{1}{a} \sum_{i=1}^{m} x_i \ln \sum_{j=1}^{m} x_j F_{ij} \exp \left[ \frac{-aq_{ij}\eta_{ij}}{RT} \right]
\]

where
\[ \frac{R}{a} \sum_{i=1}^{m} x_i \ln \sum_{j=1}^{m} F_{ji} = \lim_{T \to \infty} \left( \frac{S^E}{N} \right), \]  

(55)

where \( S^E \) is the excess entropy of the mixture. This term arises from the lower limit of integration, which is \( T \to \infty \).

For the present, we assume that \( F_{ji} \) is unity. This is equivalent to assuming that the athermal entropy of mixing is adequately given by the repulsive part of the equation of state (see the following section). If, however, we had assumed that

\[ F_{ji} = \frac{\nu_i}{\nu_i}, \]

(56)

where \( \nu_i \) is the molar volume of component \( i \) in the mixture, we would have recovered the three-parameter Wilson (1964) equation for unequal-sized molecules provided that there is no excess volume.

The function \( F_{ji} \) is, in general, density dependent and may require binary parameters. It must meet the following conditions:

\[ F_{ii} = 1 \]

(57)

\[ \lim_{\rho \to 0} F_{ji} = 1 \]

(58)

\[ \left[ \frac{\partial F_{ii}}{\partial T} \right]_{\rho} = 0 \].

(59)

Unfortunately, there is no unambiguous way to calculate \( F_{ji} \) as a function of density. Although Equation 47 is a tempting choice for \( F_{ji} \) (since it reduces to the Flory-Huggins
result at high-density), it cannot be used in practice because Equation 59 is not satisfied.

The integral of \( U_{\text{attr}} \) (Equation 53) with respect to \( 1/T \) cannot be solved analytically if \( a \) is a binary parameter. We have here set \( a = 0.5 \), but, as experience grows, this value may well change.

For the molar excess Gibbs energy of a mixture of unequal-sized van der Waals molecules, the local-composition model gives

\[
g_E = -T_s E_{\text{rep}} - \frac{RT}{a} \sum_{i=1}^{m} x_i \ln \sum_{j=1}^{m} x_j \frac{[aa_i i^4 \zeta_i]}{RTb_{ij}}
\]

\[
- \sum_{i=1}^{m} \sum_{j=1}^{m} x_i x_j \frac{[aa_i i^4 \zeta_i]}{RTb_{ij}} \exp \frac{[aa_i i^4 \zeta_i]}{RTb_{ij}}
\]

\[
+ 2 \sum_{i=1}^{m} x_i a_{iii}^{\text{pure}}
\]

where \( s_{E, \text{rep}} \) is the contribution to the excess entropy from the repulsive part of the equation of state and where \( a_{ji} \) is given by Equation 36. Equation 60 is not identical to the UNIQUAC equation, although similarities are evident. The first term in Equation 60 is dependent on the chosen repulsive equation of state; it is not the Staverman (1950) form for the combinatorial excess Gibbs energy, as in UNIQUAC. However, the Staverman equation could be recovered here with the appropriate function \( F_{ij} \). The second term is more com-
licated (in part, because equations of state, in general, predict a nonzero excess volume) and uses only mole fractions, whereas the UNIQUAC equation uses surface fractions. Had we used volume fractions, we would not have met the low-density, second-virial-coefficient boundary condition.

The excess entropy arising from repulsive forces can be calculated from any desired model. One example for $s_{E,\text{rep}}$ is provided by the one-fluid Carnahan-Starling equation of state for hard spheres:

$$s_{E,\text{rep}} = -R \sum_{i=1}^{m} x_i \ln \left( \frac{\rho}{\rho_i^{\text{pure}}} \right)$$

$$+ R \left[ \frac{\xi(3\xi-4)}{(1-\xi)^2} \right] - R \sum_{i=1}^{m} x_i \left[ \frac{\xi_i(3\xi_i-4)}{(1-\xi_i)^2} \right] ,$$

(61)

where

$$\xi = \frac{b \rho}{4}$$

(62)

$$\xi_i = \frac{b_i \rho_i^{\text{pure}}}{4} .$$

(63)

Here, $\rho$ is the molar density of the mixture at $(T,P,x)$, and $\rho_i^{\text{pure}}$ is the molar density of pure $i$ at $(T,P)$. For the mixture, $b$ is found by a classical mixing rule, e.g., Equation 1.

CONCLUSIONS

The local-composition model may be used to extend to mixtures any one of many currently popular equations of state. This model incorporates the effect of nonrandomness
and, thereby, extends applicability of equations of state to calculation of vapor-liquid equilibria for asymmetric mixtures. No new binary parameters are introduced. For engineering applications, it is important that the complexity of the computations is much less than that for chemical-theory models. The local-composition model for nonrandomness in fluid mixtures is internally consistent and meets the necessary low- and high-density boundary conditions.

The approach we have taken is to account for nonrandomness due to the attractive part of the potential. In this perturbation-type approach, we have assumed that nonrandomness caused by repulsive potentials is adequately represented by our reference system, the one-fluid model. The choice of reference system, however, remains open. Any desired reference system may be used with the local-composition perturbation presented here.

In this work, we have only indicated the general ideas and outlined the calculational procedure. Comparison with experimental data requires a particular equation of state more realistic than the van der Waals equation used here only for illustrative purposes. Such comparison is given in another publication (Whiting and Prausnitz, 1982).

ACKNOWLEDGMENT

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical
Sciences Division of the U.S. Department of Energy under contract number W-7405-ENG-48.
LIST OF SYMBOLS

\( a = \) energy parameter in the van der Waals equation

\( a_M = \) effective van der Waals parameter \( a \) for a mixture

\( A = \) total Helmholtz energy

\( b = \) size parameter in the van der Waals equation

\( B = \) second virial coefficient

\( C = \) a constant appearing in some equation of state

\( E_{ij} = \) function with units of energy characteristic of an \( ij \) interaction

\( F_{ji} = \) function related to the infinite-temperature limit of the excess entropy and defined by Equation 41

\( g = \) molar Gibbs energy

\( G = \) total Gibbs energy

\( H_i = \) Henry's constant \[ \lim_{x_i \to 0} \frac{f_i}{x_i} \]

\( k = \) Boltzmann's constant

\( k_{ij} = \) energy interaction parameter for the \( ij \) binary

\( K = \) a proportionality factor

\( m = \) number of components
\[ N = \text{total number of moles} \]

\[ N_{\text{Av}} = \text{Avogadro's number} \]

\[ N_i = \text{number of moles of component } i \]

\[ p = \text{pressure} \]

\[ q_i = \text{external surface area of an } i \text{ molecule} \]

\[ R = \text{ideal-gas constant} \]

\[ s = \text{molar entropy} \]

\[ S = \text{total entropy} \]

\[ T = \text{absolute temperature} \]

\[ u = \text{molar internal energy} \]

\[ U = \text{total internal energy} \]

\[ v = \text{molar volume} \]

\[ v_i = \text{molar volume of pure } i \]

\[ V = \text{total volume} \]

\[ w = \text{Guggenheim's interchange energy} \]

\[ x_i = \text{mole fraction of component } i \]

\[ x_{ij} = \text{local composition of } i \text{ molecules around a } j \text{ molecule} \]

\[ X = \text{a variable used in quasi-chemical theory} \]
z = coordination number of a lattice

α = degree-of-randomness perturbation parameter,
   equal to 0.5 in this work

ΔA_{mixing} = Helmholtz energy change of mixing

ΔS_{mixing} = molar entropy of mixing

ε_{ij} = energy of interaction between an i molecule and a
        j molecule that are nearest neighbors on a lattice

η_{ij} = attractive Helmholtz energy per unit surface area for
        an ij interaction

μ = chemical potential

N_i = volume fraction of component i

ρ = density (N/V)

Θ = a function of reduced density only

ζ = reduced density

ζ_i = reduced density of pure i

Superscripts

attr = attractive

E = excess (beyond the ideal-mixing contribution)

(i) = region i
id = ideal gas

pure = pure component

r = residual (i.e., without the ideal-gas part)

rep = repulsive

Subscripts

ij = the interaction between an i molecule and a j molecule

M = mixture
REFERENCES


Won, K. W., 1981. "Vapor-Liquid Equilibria of High-Boiling Organic Solutes in Compressed Supercritical Fluids."
Equation of State with New Mixing Rule"; presented at the Annual Meeting of the American Institute of Chemical Engineers, New Orleans, November 8-12.

APPENDIX A. **Entropy of Mixing from the Repulsive Part of the van der Waals Equation**

The repulsive part of the van der Waals equation is

\[ p = \frac{RT}{v - b} \quad \text{(A1)} \]

The entropy of mixing for Equation A1 is

\[ \Delta s_{\text{mix}} = -R \sum_{i=1}^{m} x_i \ln \left( \frac{x_i v_{i\text{pure}}}{v} \right) + R \ln(1 - b/v) \]

\[ - R \sum_{i=1}^{m} x_i \ln \left( 1 - \frac{b_i}{v_i} \right) \quad \text{(A2)} \]

where \( v_{i\text{pure}} \) is the molar volume of pure \( i \) at the same pressure and temperature as those of the mixture and \( v \) is the molar volume of the mixture.

If we solve Equation A1 for \( v \),

\[ v = \frac{RT}{p} + b \quad \text{(A3)} \]

we get, upon substituting Equation A3 into Equation A2,

\[ \Delta s_{\text{mix}} = -R \sum_{i=1}^{m} x_i \ln x_i \quad \text{(A4)} \]

the ideal-mixing result.

Instead of using Equation A3, we could assume that at high pressure

\[ \frac{v}{b} = \frac{v_i}{b_i} \quad \text{for all } i, \quad \text{(A5)} \]

i.e., the reduced densities of all the pure components and of the mixture are equal to each other at the same pressure and temperature. We then obtain
APPENDIX B. Derivation of Local-Compositions from Quasi-Chemical Theory

The quasi-chemical theory of Guggenheim (1935, 1952) is a lattice theory in which nonrandomness is introduced through the numbers of different types of "pairs" of molecules. Two molecules form a pair if they are nearest neighbors on the lattice. The central equation of Guggenheim's theory is

\[
\frac{x^2}{(N_A - x)(N_B - x)} = \exp(-2w/zkT) \tag{B1}
\]

where \( z \) is the coordination number of the lattice, \( w \) is the interchange energy, \(^\dagger\) and \( zX \) is defined as the number of AB pairs in the configuration.

If we use the two-fluid theory of Scott (1956) to calculate the total number of AB, AA, and BB pairs, in terms of local compositions, we obtain

\[
\frac{x^2}{(N_A - x)(N_B - x)} = \frac{x_{AB}x_{BA}}{x_{BB}x_{AA}} \tag{B2}
\]

where the local composition \( x_{ij} \) is the composition of component \( i \) in the neighborhood of a type-\( j \) molecule. In terms of the molar energy of interaction, \( E_{ij} \), the interchange energy is

\[
wN_{Av} = E_{BA} + E_{AB} - E_{AA} - E_{BB} \tag{B3}
\]

Substituting Equations B2 and B3 into Equation B1, we obtain
where \( \alpha = 2/z \). We assume that Equation B4 can be factored into two parts; one part pertains only to a type-A region, and the other part pertains only to a type-B region. Factoring Equation B4 in this way, we obtain two relations, one for each region:

\[
\frac{x_{AB}^x}{x_{BB}^x} = K \exp \left[ -\alpha \frac{(E_{AB} + E_{BA} - E_{BB} - E_{AA})}{RT} \right],
\]

(B4)

\[
\frac{x_{BA}^x}{x_{AA}^x} = \frac{1}{K} \exp \left[ -\alpha \frac{(E_{BA} - E_{AA})}{RT} \right],
\]

(B5)

where \( K \) is some proportionality constant depending only on composition. To evaluate this constant, we consider the randomness limit. For any conditions at which the exponentials in Equations B5 and B6 approach unity, the local compositions are equal to their respective bulk compositions, i.e.,

\[
x_{ji} = x_j
\]

(B7)

for \( i, j = 1 \) or 2. Thus,

\[
K = \frac{x_A}{x_B}.
\]

(B8)

Substitution of Equation B8 into Equations B5 and B6 yields the expressions for the local compositions (Equations 13 and 14).

---

*Interchange energy \( w \) is related to molecular pair energy \( \epsilon_{ij} \) by*
\[ w = \frac{\mathbb{E}}{2} (\varepsilon_{AB} + \varepsilon_{BA} - \varepsilon_{AA} - \varepsilon_{BB}) \].

Therefore, coordination number \( z \) cancels out in the exponential of Equation B1.
APPENDIX C. Attractive Excess Gibbs Energy from Local-Composition Theory. Limit for Random Mixing

To investigate the randomness limit of local-composition theory, we here consider \( \alpha \) to be a perturbation parameter in the Boltzmann factor for the local compositions. For an equation of state of the van der Waals form,

\[
\frac{x_{ii}}{x_{ii}^*} = \frac{x_i}{x_i^*} \exp \left[ \frac{a(a_{ij}/b_{ij} - a_{ii}/b_{ii})4\xi_i \Theta(\xi_i)}{RT} \right],
\]

where \( \xi_i = b_{ii} \rho_i / 4 \), \( \rho \) is the density of the mixture, and \( \Theta(\xi_i) \) is given in Table I for several equations of state and where

\( \alpha > 0 \) for nonrandom mixing

and

\( \alpha \rightarrow 0 \) for random mixing.

As discussed in the text, the attractive excess Gibbs energy is:

\[
g_E,\text{attr} = \frac{-RT}{\alpha} \sum_{i=1}^{m} x_i \ln \sum_{j=1}^{m} x_j \exp \left[ \frac{a_{ii}4\xi_i f(\xi_i)}{RTb_{ij}} \right] \\
+ \sum_{i=1}^{m} x_i f(\xi_i^\text{pure}) \frac{a_{ii}4\xi_i^\text{pure}}{b_{ii}},
\]

where \( \xi_i^\text{pure} = b_{ii} \rho_i^\text{pure} / 4 \) and \( \rho_i^\text{pure} \) is the liquid density of pure \( i \) at the same temperature and pressure as the mixture.

Using L'Hôpital's rule, we obtain

\[
\lim_{\alpha \to 0} g_E,\text{attr} = -\sum_{i=1}^{m} \sum_{j=1}^{m} x_i x_j \left[ \frac{a_{ii}4\xi_i \Theta(\xi_i)}{b_{ij}} \right]
\]
\[ + \sum_{i=1}^{m} x_i \theta(\xi_i^{\text{pure}}) \frac{a_{ii}4 \xi_i^{\text{pure}}}{\xi_{ii}} \]  

which is Equation 41 of the text. Algebraic rearrangement gives van Laar's result.
### TABLE I. The Function $\Theta(\xi)$ for Three Equations of State.

<table>
<thead>
<tr>
<th>Equation of State</th>
<th>$\text{pattr}$</th>
<th>$\Theta(\xi)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>van der Waals</td>
<td>$-\frac{a}{v^2}$</td>
<td>1</td>
</tr>
<tr>
<td>Redlich-Kwong</td>
<td>$-\frac{a}{v(v+b)}$</td>
<td>$\frac{\ln(1+4\xi)}{4\xi}$</td>
</tr>
<tr>
<td>Peng-Robinson</td>
<td>$-\frac{a}{v(v+b) + b(v-b)}$</td>
<td>$\frac{(2)^{0.5}}{16\xi} \ln \left[ \frac{1 + 4(1+(2)^{0.5})\xi}{1 + [1-(2)^{0.5}]\xi} \right]$</td>
</tr>
</tbody>
</table>

where $\xi = \frac{b}{4v}$
TABLE II. Pure-Component Parameters for Equation 45.

<table>
<thead>
<tr>
<th>Component</th>
<th>T(°C)</th>
<th>(a(\text{dJ} \cdot \text{m}^3/\text{mol}^2))</th>
<th>(b(\text{cm}^3/\text{mol}))</th>
<th>(q)</th>
<th>Data Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>150</td>
<td>2.215</td>
<td>51.42</td>
<td>1.16</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>2.054</td>
<td>48.90</td>
<td>1.16</td>
<td>2</td>
</tr>
<tr>
<td>CH(_3)OH</td>
<td>25</td>
<td>12.009</td>
<td>79.42</td>
<td>1.43</td>
<td>1, 8</td>
</tr>
<tr>
<td>C(_2)H(_6)</td>
<td>300</td>
<td>5.782</td>
<td>84.22</td>
<td>1.70</td>
<td>7</td>
</tr>
<tr>
<td>C(_3)H(_8)</td>
<td>121</td>
<td>10.324</td>
<td>120.80</td>
<td>2.24</td>
<td>6</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>25</td>
<td>3.869</td>
<td>55.05</td>
<td>1.12</td>
<td>5</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>121</td>
<td>6.150</td>
<td>34.96</td>
<td>1.40</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>5.987</td>
<td>34.36</td>
<td>1.40</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>5.307</td>
<td>32.50</td>
<td>1.40</td>
<td>4</td>
</tr>
<tr>
<td>N(_2)</td>
<td>38</td>
<td>1.271</td>
<td>46.62</td>
<td>0.91</td>
<td>3</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>38</td>
<td>4.485</td>
<td>43.70</td>
<td>1.28</td>
<td>5</td>
</tr>
</tbody>
</table>

Data References


TABLE III. Binary Parameters for Equation 37 from Cross-Second-Virial-Coefficient Data.

<table>
<thead>
<tr>
<th>System</th>
<th>T(°C)</th>
<th>$k_{12}$</th>
<th>Data Ref. for $B_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄/H₂O</td>
<td>150</td>
<td>0.382</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.299</td>
<td>5</td>
</tr>
<tr>
<td>C₂H₆/H₂O</td>
<td>300</td>
<td>0.103</td>
<td>1</td>
</tr>
<tr>
<td>C₃H₆/H₂O</td>
<td>121</td>
<td>0.425</td>
<td>3</td>
</tr>
<tr>
<td>CO₂/CH₃OH</td>
<td>25</td>
<td>0.398</td>
<td>2</td>
</tr>
<tr>
<td>N₂/NH₃</td>
<td>38</td>
<td>0.657</td>
<td>4</td>
</tr>
</tbody>
</table>

Data References for $B_{12}$

TABLE IV. Henry's Constants for Asymmetric Mixtures Predicted Using Binary Parameters from Second-Virial-Coefficient Data (Table III).

<table>
<thead>
<tr>
<th>System</th>
<th>T(°C)</th>
<th>(\ln H_1) (bar)</th>
<th>Data Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td><strong>one-fluid</strong></td>
<td><strong>local-composition</strong></td>
</tr>
<tr>
<td>(\text{CH}_4/\text{H}_2\text{O})</td>
<td>150</td>
<td>15.90</td>
<td>12.04</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>10.89</td>
<td>9.68</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_6/\text{H}_2\text{O})</td>
<td>300</td>
<td>9.49</td>
<td>8.48</td>
</tr>
<tr>
<td>(\text{C}_3\text{H}_8/\text{H}_2\text{O})</td>
<td>121</td>
<td>23.02</td>
<td>17.41</td>
</tr>
<tr>
<td>(\text{CO}_2/\text{CH}_3\text{OH})</td>
<td>25</td>
<td>10.31</td>
<td>5.63</td>
</tr>
<tr>
<td>(\text{N}_2/\text{NH}_3)</td>
<td>38</td>
<td>12.64</td>
<td>9.75</td>
</tr>
</tbody>
</table>

**Data References**

Figure 1.

Athermal Entropy of Mixing for Hard Spheres

\[ \frac{\Delta s_{\text{mixing}}}{R} \]

\[ \xi_1 = 0.25, \xi_2 = 0.519 \]

\[ \frac{b_2}{b_1} = 10 \]

Flory-Huggins

One-Fluid Carnahan-Starling

Ideal Mixing

\[ x_1 \]

ATHERMAL ENTROPY OF MIXING FOR HARD SPHERES

XBL 819-6586
TWO-FLUID THEORY FOR A BINARY MIXTURE

TYPE-1 REGION

\[ u^{(1)} = x_{21}u_{21} + x_{11}u_{11} \]

TYPE-2 REGION

\[ u^{(2)} = x_{12}u_{12} + x_{22}u_{22} \]

FOR THE MIXTURE:

\[ \frac{U_{\text{attr.}}}{N} = x_1u^{(1)} + x_2u^{(2)} \]

\( u^{(i)} \) = molar attractive internal energy of hypothetical fluid \( i \)

\( i = 1 \) or \( 2 \)

\( x_i \) = mole fraction of component \( i \)

\( x_{ij} \) = local mole fraction of component \( i \) about a central molecule \( j \)

\( u_{ij} \) = attractive internal energy per mole for a hypothetical fluid

where all molecules interact according to an \( ij \) potential

\( N \) = total number of moles

Figure 2.
DENSITY = 0.40 mol/dm$^3$

DENSITY = 24 mol/dm$^3$

LOCAL COMPOSITION

ONE FLUID

EFFECTIVE VAN DER WAALS CONSTANT $a_M$ FOR A BINARY MIXTURE

$\text{AT } 0^\circ \text{C}$

$a_{11} = 0.40$, $a_{22} = 1.17$ J·m$^3$/mol$^2$; $b_{11} = 55$, $b_{22} = 121$ cm$^3$/mol; $k_{12} = 0.07$

Figure 3.
EXCESS GIBBS ENERGY FOR BINARY MIXTURES OF EQUISIZED MOLECULES.
EFFECT OF INTERMOLECULAR FORCES.

\[ a_{11} = 0.5 \text{ J} \cdot \text{m}^3/\text{mol}^2; \quad b_{11} = b_{22} = 50 \text{ cm}^3/\text{mol}; \quad b_1/q_1 = b_2/q_2; \]
\[ a_{12} = (a_{11} a_{22})^{1/2} \]

Figure 4.
EXCESS GIBBS ENERGY FOR BINARY MIXTURES OF NONEQUISIZED MOLECULES.
EFFECT OF MOLECULAR SIZE.

\[ a_{11} = a_{22} = a_{12} = 0.5 \, \text{J} \cdot \text{m}^3/\text{mol}^2; \quad b_{11} = 50 \, \text{cm}^3/\text{mol}; \quad b_{1}/q_1 = b_{2}/q_2 \]

Figure 5.
EXCESS GIBBS ENERGY FOR A BINARY MIXTURE: EFFECT OF DEVIATION FROM GEOMETRIC MEAN.

\[ a_{11} = 0.5, \quad a_{22} = 0.7 \text{ J} \cdot \text{m}^3/\text{mol}^2; \quad b_{11} = 50, \quad b_{22} = 60 \text{ cm}^3/\text{mol}; \quad b_1/q_1 = b_2/q_2; \]
\[ a_{12} = (a_{11} a_{22})^{1/2} (1 - k_{12}) \]

Figure 6.
Excess functions for a binary mixture

(pure-component parameters same as in Figure 6; \( k_{12} = 0.05 \))

Figure 7.
Phase equilibria for methane/water at 150°C
Predicted from cross-second-virial-coefficient data

Figure 8.
This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.