STATISTICAL THERMODYNAMICS OF MIXTURES
A NEW VERSION FOR THE THEORY OF CONFORMAL SOLUTION
Statistical Thermodynamics of Mixtures
A New Version for the Theory of Conformal Solution

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A new method for the calculation of thermodynamic properties of simple fluid mixtures constitutes an extension of the approach defined earlier as the "van der Waals" conformal solution theory. This extension is made possible by advances in the analytical representation of the thermodynamic properties of a mixture of hard spheres which permit the properties to be calculated directly, without the use of a reference fluid. A new hard-sphere excess function, defined as a property of the mixture less the value of this property for the hard-sphere mixture, is obtained by a new conformal solution theory using a single pure fluid as a reference substance. Although the reference substance properties could be experimentally measured values, this work obtains them from an analytical form of the Barker-Henderson perturbation theory.

This new method improves prediction of the effects of large molecular size differences on the excess properties of the mixture. It uses the reference fluid to account for most of the temperature dependence of the cut-off parameter needed to define the molecular diameters in the direct hard-sphere mixture calculations and the calculations need only the high temperature limit of the cut-off parameters, even far below the critical temperature. The new method extends the original vdW conformal solution method to lower temperatures and provides an opening for inclusion of three-body interactions.

Conventional excess mixing functions for several binary liquid mixtures calculated by the new method are compared with the predictions of other theories and with both experimental and Monte Carlo data.

The most successful theories for the prediction of equilibrium excess thermodynamic properties of simple liquid solutions have been the corresponding states, or conformal solution theories,1-6 which predict mixture properties from the experimentally measured properties of one or more pure reference substances. A recent example is the "van der Waals" approximation.4, 5 However, considerable progress has been made recently in the development of rigorous predictive methods which do not require extensive experimental data for pure component properties. The most significant of these are the variational7 and perturbational8 theories. Although these cannot as yet compete with the corresponding states methods which use experimental data, they are important steps in the development of rigorous analytical expressions for the equilibrium thermodynamic properties of liquid mixtures. Both the perturbational and variational methods seek to define the effective hard-sphere diameter which most accurately represents the contribution of the repulsive portion of a given intermolecular potential function.

The variational method7 gives an analytical expression for the upper bound of the Helmholtz free energy in terms of the effective hard-sphere diameter. The technique then finds the diameter which minimizes the numerical value of this upper bound. In principle this procedure is readily extended to mixtures. However, its application to a binary mixture, for example, requires the determination of two effective diameters by the minimization of a function of two variables. This increases the complexity of the calculation and presents a formidable computational task with multicomponent systems.

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The perturbation procedure for pure components leads to a direct analytical equation for the Helmholtz free energy in terms of the Laplace transform of the reference hard-sphere radial distribution function. For mixtures, however, the technique requires the inversion of the Laplace transform of the radial distribution functions of the hard-spheres reference mixture with different effective diameters, resulting in the loss of a closed analytical expression.

This work presents a means of avoiding these difficulties in an analytical theory for mixtures by using an improved conformal solution method with the pure fluid perturbation equation as a reference. The result is a conformal solution theory completely free of experimentally measured reference fluid properties.

THE HSE CONFORMAL SOLUTION METHOD

The essential concept in developing this conformal solution theory for dense fluid mixtures is that of expanding the radial distribution function about its value for a hard-sphere fluid. This procedure is designated here as the HSE or hard-sphere expansion technique. To illustrate, consider the radial distribution function in a pure fluid:

\[
g^{(2)}(r) = \frac{V^2}{N^2(N-2)!} \frac{1}{Q} \int \ldots \int \exp(-U/kT) \, dr_3 \ldots dr_N. \tag{1}
\]

The total intermolecular potential \( U \) in eqn (1) is divided into a hard-sphere potential \( U_0 \) and a residual \( U_1 = (U - U_0) \). The residual includes contributions from the attractive potential and from the finite slope of a soft-sphere repulsive potential function. In the integrand of eqn (1) and likewise in the configurational partition function, \( Q \), the exponential term is expanded in terms of the residual potential \( U_1 \) to give:

\[
\exp(-U/kT) = \exp(-U_0/kT) \left[ 1 - (U_1/kT) + \frac{1}{2!} (U_1/kT)^2 \ldots \right] \tag{2}
\]

As in any conformal solution theory it is necessary to assume that \( U_1 \) can be factorized into the product of an energy parameter and a function of \((r_i/\sigma)\). In this work we assume that \( U \) can be expressed as a sum of two- and three-body interactions in the form:

\[
U = \sum_{j>i=1}^N u(r_{ij}) + \sum_{j>i=1}^N w(r_{ij}, r_{ik}, r_{jk}). \tag{3}
\]

The hard-sphere potential is expressed as a sum of pair potentials.

\[
U_0 = \sum_{j>i=1}^N u_0(r_{ij}) \quad \text{where} \quad u_0(r_{ij}) = \begin{cases} 0, & r_{ij} > \sigma \\ \infty, & r_{ij} \leq \sigma. \end{cases} \tag{4}
\]

The residual potential \( U_1 \) given by the difference between eqn (3) and (4) is represented by

\[
U_1 = \sum_{j>i=1}^N u_1(r_{ij}) + \sum_{k>j>i=1}^N w(r_{ij}, r_{ik}, r_{jk}). \tag{5}
\]

where \( u_1(r_{ij}) = u(r_{ij}) - u_0(r_{ij}) \). The three-body interaction \( w(r_{ij}, r_{ik}, r_{jk}) \) is defined so that it vanishes entirely whenever one member of the triplet is moved an infinite distance from the other two.

It is assumed that eqn (5) may be factorized to give:

\[
U_1 = \varepsilon \sum_{j>i=1}^N f_1(r_{ij}/\sigma) + (v\sigma^{-9}) \sum_{k>j>i=1}^N f_3' \frac{r}{\sigma}, r_{ik}/\sigma, r_{jk}/\sigma. \tag{6}
\]
Eqn (6) for $U_1$ is now substituted into eqn (2) and the result is placed in eqn (1), in both $Q$ and in the integrand. The resulting expansions of the integral and $Q$ in (1) are each divided by $Q_0$, the configurational integral for a hard-sphere fluid. The result can then be expressed in the form:

$$g(r) = g_0(r/\sigma, \rho \sigma^3) + \left( \frac{\epsilon}{kT} \right) \left[ \psi_1(r/\sigma, \rho \sigma^3) \right] + \left( \frac{\nu \sigma^{-9}}{kT} \right) \left[ \Gamma_1(r/\sigma, \rho \sigma^3) \right] + \left( \frac{\epsilon}{kT} \right)^2 \left[ \psi_2(r/\sigma, \rho \sigma^3) \right] + \left( \frac{\nu \sigma^{-9}}{kT} \right)^2 \left[ \Gamma_2(r/\sigma, \rho \sigma^3) \right] + \ldots \quad (7)$$

The $g_0(r/\sigma, \rho \sigma^3)$ term represents the pair distribution function for a fluid of hard spheres of diameter $\sigma$. The functions $\Psi$ and $\Gamma$ are sums of complicated integrals, but in a conformal solution approach they need not be evaluated. It is only necessary to show that the coefficients of the powers of $1/kT$ depend only on $r/\sigma$ and $\rho \sigma^3$, and that effects of both the attraction and soft-sphere repulsion may be taken into account by a power series in $1/kT$.

The equation of state for a pure fluid with a total potential in the form of eqn (3) can be written in terms of distribution functions as follows:

$$Z = \frac{PV}{NkT} = 1 - \frac{2\pi \rho}{3kT} \int_0^\infty r_{12}^3 u'(r_{12}) g^{(2)}(r_{12}) \, dr_{12} - \frac{\rho^2}{6kT} \int \int g^{(3)}(123) w'(123) \, dr_{12} \, dr_{13}. \quad (8)$$

In eqn (8) the $u'(r_{12})$ term is the first derivative of the two-body pair potential with respect to $r_{12}$ and

$$w'(123) = \sum_{j>i=1}^3 r_{ij} \frac{\partial w(123)}{\partial r_{ij}} \quad (9)$$

The $g^{(2)}(r_{12})$ and $g^{(3)}(123)$ terms are the pair and triplet distribution functions, respectively.

Substituting the expanded distribution function in eqn (7) and the separated potentials in eqn (4) and (5) into eqn (8) produces an expansion of the equation of state about a hard-sphere value in powers of $1/kT$. In this work we wish to retain the leading terms in the coefficients of $(1/kT)^2$ for two-body interactions and the coefficients of $(1/kT)$ for three-body effects. By substituting the expanded pair distribution function into eqn (8), one can show that terms which effect the distribution function to the order of $(1/kT)$ will affect the equation of state to the order of $(1/kT)^2$. Furthermore, it will be shown that when the effects of three-body interactions are described by means of only one additional parameter, $\nu$ as in eqn (6), then three-body effects of the order of $(1/kT)^2$ and higher cannot be considered in a conformal solution approach. Their inclusion would require additional parameters in the description of the three-body potential. The triplet interaction effects to the order of $(1/kT)$, will then enter only through the $w'(123)$ term in the second integral of eqn (8) neglecting any three-body potential effects on the pair distribution function in the first integral. Consequently, in the two-body term represented by the first integral in eqn (8), the radial distribution function will be truncated after the second term on the right hand side of eqn (7) with the $\Gamma_1$, $\Psi_2$, $\Gamma_2$, and all higher order functions omitted. To introduce three-body effects to the order of $1/kT$ in the equation of state the triplet distribution function is

$$g^{(3)}(123) = g_0(r_{12}/\sigma, \rho \sigma^3)g_0(r_{13}/\sigma, \rho \sigma^3)g_0(r_{23}/\sigma, \rho \sigma^3) + \mathcal{O}(1/kT) \quad (10)$$
where the leading term is obtained from the hard-sphere terms in the pair distribution
expansions using the superposition approximation. When these truncations of
eqn (7) and (10) are substituted into (8) and the derivative of the pair potential is
replaced with
\[ u'(r_{12}) = u'_0(r_{12}) + u'_1(r_{12}), \] (11)
an expanded equation of state is produced which begins with the equation of state
for hard-sphere fluid followed by higher order terms up to and including the \((1/kT)^2\)
term due to two-body forces.

It is now necessary to consider the possibility of developing a similar expansion
of the equation of state for a mixture of conformal components. For an \(m\)-component mixture the equation of state analogous to eqn (8) is:
\[
Z = \frac{PV}{nkT} = 1 - \frac{2\pi\rho}{3kT} \sum_{a=1}^{m} x_a x_b \int_{0}^{\infty} r_{12}^3 u_{a\beta}^*(r_{12}) g_{a\beta}^{(2)}(r_{12}) \, dr_{12} -
\]
\[
\frac{\rho^2}{6kT} \sum_{a=1}^{m} x_a x_b x_c \int_{0}^{\infty} \int_{0}^{\infty} r_{12}^3 r_{13}^3 \, g_{a\beta,\gamma}^{(3)}(r_{123}) w_{a\beta,\gamma}(r_{123}) \, dr_{12} \, dr_{13}. \] (12)

A one-fluid conformal solution theory attempts to find a pure reference substance
which has the same dimensionless thermodynamic properties as the mixture when
each are at the same temperature and density. This can be done by using the expansion
of eqn (8) for the pure reference and equating it to eqn (12) for the mixture. If
the mixture equation could be expanded in powers of \(1/kT\) like the equation for the
pure reference, then the coefficients of the like powers of \(1/kT\) must be the same in
each expansion, if the two equations are to be equal at all temperatures, densities,
and compositions. From the relationships created by equating these coefficients
one obtains the potential parameters of the pure reference substance as functions of
the composition and potential parameters of the components in the mixture. The
principal difficulty in the hard-sphere expansion of eq (12) is that almost nothing is
known about the analytical representation of the radial distribution function for a
pair in a mixture. However, this expansion can be done in the same manner as for
a pair in a pure component if some important simplifying assumptions are made
concerning the composition dependence of the distribution function in the mixture.

For example, let \(\tilde{\varepsilon}, \tilde{\sigma}^3\) and \(\tilde{\nu}\) be the potential parameters of the pure reference
which would give the compressibility factor of the mixture when substituted in place
of \(\varepsilon, \sigma^3,\) and \(\nu\) in eqn (8) at the mixture temperature and density. When these reference
fluid parameters are used in the total potential of eqn (3) and substituted in (1), the
resulting \(g^{(2)}(r)\) value for the pure reference fluid depends on four dimensionless
variables:
\[
g^{(2)}(r) = f\left(\frac{r}{\tilde{\sigma}^3}, \frac{\tilde{\varepsilon}}{kT}, \frac{\tilde{\nu} \tilde{\sigma}^{-3}}{kT}, \rho \tilde{\sigma}^3\right). \] (13)

In a mixture the assumption made for the pair distribution of a molecule of species
\(\alpha\) and another of species \(\beta\) is that, neglecting three-body effects, it can be approximated
by the same function as in eqn (13) but evaluated with different dimensionless variables
as shown below.
\[
g^{(2)}(r) = f\left(\frac{r}{\sigma_{\alpha\beta}}, \frac{\varepsilon_{\alpha\beta}}{kT}, \rho \tilde{\sigma}^3\right). \] (14)

The true distribution function for a pair in a mixture actually depends not only
on the parameters characteristic of the \(\alpha\beta\) pair, but also on the parameters describing
the total interaction of each member of the pair with all the molecules in the mixed
environment surrounding them. The assumptions in eqn (14) replace the effect of the true environment around the \( \alpha \beta \) pair with that of an average. This average is the environment produced by an imaginary pure component with pair interactions equal to those of an \( \alpha \beta \) pair and with a dimensionless density equal to \( \rho \bar{\sigma}^3 \). The nature of this approximation can be illustrated further by substituting the parameters \( \varepsilon_{\alpha \beta}, \sigma_{\alpha \beta} \), with \( v = 0 \) into the total potential in eqn (3) and substituting the result into the formal definition of \( g^{(2)}(r) \) for a pure component in eqn (1). This procedure shows that the dimensionless groups in eqn (14) are produced when the density of the pure component in eqn (1) is set equal to \( \rho^0 \) where

\[
\rho^0 = \left( \frac{\sigma_{\alpha \beta}^3}{\sigma_{\alpha \beta}} \right)^{3/3}
\]  

and the average environment around the \( \alpha \beta \) pair is that of a pure fluid with all interactions equal to those of an \( \alpha \beta \) pair compressed to the density \( \rho^0 \).

As was the case for the pure fluid, three-body effects on the mixture equation of state are to be considered only to the order of \( (1/kT) \) to the first power. To achieve this no three-body effects need be included in eq (14). Consequently, the expansion of the pair distribution in the mixture can be carried out in the same manner as for the distribution in a pure component. The result is:

\[
g^{(2)}_{\alpha \beta}(r) = g_0 \left( \frac{r}{\sigma_{\alpha \beta}}, \rho \bar{\sigma}^3 \right) + \left( \frac{\varepsilon_{\alpha \beta}}{kT} \right) \psi_1 \left( \frac{r}{\sigma_{\alpha \beta}}, \rho \bar{\sigma}^3 \right) + \varnothing \left( \frac{1}{kT} \right)^2
\]  

where the \( g_0 \) and \( \psi_1 \) functions are the same as those in eqn (7) for the pure fluid. Eqn (16) considerably simplifies the complex composition dependence of the pair distribution in the mixture. The composition dependence in eqn (16) enters only through \( \bar{\sigma}^3 \).

The expansion of \( g^{(3)}_{\alpha \beta \gamma}(123) \) for a three-body distribution in the mixture may also be obtained using the superposition approximation and eqn (16). As in the case of the pure fluid, only the leading term is retained so that

\[
g^{(3)}_{\alpha \beta \gamma}(123) = g_0 \left( \frac{r_{12}}{\sigma_{\alpha \beta}}, \rho \bar{\sigma}^3 \right) g_0 \left( \frac{r_{13}}{\sigma_{\alpha \gamma}}, \rho \bar{\sigma}^3 \right) g_0 \left( \frac{r_{23}}{\sigma_{\beta \gamma}}, \rho \bar{\sigma}^3 \right) + \varnothing \left( \frac{1}{kT} \right)^3
\]  

An expanded equation of state for the mixture is then obtained by substituting eqn (16) and (17) into (12) with the potential separated into the hard-sphere and residual portions. From this expanded equation, one may subtract the analogous expansion for the pure reference in terms of the reference parameters \( \varepsilon, \bar{\sigma}^3, \) and \( v \). If the pure reference is to represent the mixture at all temperatures, densities, and compositions, the result must equal zero with coefficients of like powers of \( 1/kT \) vanishing. This is shown in eqn (18).

\[
(Z_M - Z_R) = \sum_{\alpha, \beta} x_{\alpha} x_{\beta} \rho_o \sigma_{\alpha \beta}^3 \bar{\sigma}^3 - \frac{2\pi \rho}{3} \int_0^\infty y^3 \frac{\partial u_0(y)}{\partial y} g_0(y, \rho \bar{\sigma}^3) \, dy + \frac{1}{kT} \left[ \sum_{\alpha, \beta} x_{\alpha} x_{\beta} \rho_o \sigma_{\alpha \beta}^3 \bar{\sigma}^3 \varepsilon - \frac{2\pi \rho}{3} \right] \int_0^\infty y^3 \frac{\partial f_1(y)}{\partial y} g_0(y, \rho \bar{\sigma}^3) \, dy + \frac{1}{kT} \left[ \sum_{\alpha, \beta} x_{\alpha} x_{\beta} \rho_o \sigma_{\alpha \beta}^3 \bar{\sigma}^3 \varepsilon^2 - \frac{2\pi \rho}{3} \right] \int_0^\infty y^3 \frac{\partial f_1(y)}{\partial y} \psi_1(y, \rho \bar{\sigma}^3) \, dy + \frac{1}{kT} \left[ \sum_{\alpha, \beta, \gamma} x_{\alpha} x_{\beta} x_{\gamma} \rho_o \sigma_{\alpha \beta} \sigma_{\alpha \gamma} \sigma_{\beta \gamma} \phi_1(y, \rho \bar{\sigma}^3) \, dy + \ldots \right]
\]

\[
g_0(y_1, \rho \bar{\sigma}^3) g_0(y_2, \rho \bar{\sigma}^3) g_0(y_3, \rho \bar{\sigma}^3) y_1 y_2 y_3 \frac{4\pi^2 \rho^2}{3} \int_0^\infty \int_0^\infty \int_0^\infty \sum_{i=1}^3 y_i \frac{\partial f_2(y_1, y_2, y_3)}{\partial y_i} g_0(y_1, \rho \bar{\sigma}^3) g_0(y_2, \rho \bar{\sigma}^3) g_0(y_3, \rho \bar{\sigma}^3) y_1 y_2 y_3 \, dy_1 \, dy_2 \, dy_3 + \ldots = 0
\]  

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From equating the coefficient of \( \frac{1}{kT} \) to zero in eqn (18):

\[ \bar{\sigma}^3 = \sum_{a,b=1}^{m} x_a x_b \sigma_{a,b}^3. \]  

From equating the coefficient of \( \frac{1}{kT} \) to zero in eqn (18):

\[ \bar{\varepsilon} \bar{\sigma}^3 = \sum_{a,b=1}^{m} x_a x_b \bar{\varepsilon}_{a,b} \sigma_{a,b}^3. \]  

From equating the coefficient of \( (1/kT)^2 \) to zero:

\[ \bar{\varepsilon}^2 \bar{\sigma}^3 = \sum_{a,b=1}^{m} x_a x_b \bar{\varepsilon}_{a,b}^2 \sigma_{a,b}^3 \quad \text{etc.} \]

With only three parameters not all of the eqn (19) to (22), with the higher order ones, can be satisfied. With the parameters \( \bar{\varepsilon}, \bar{\sigma}^3 \) and \( \bar{\nu} \) only three in the set can be satisfied; those which cannot indicate the orders of \( 1/kT \) which are beyond the scope of the theory. The effects of the unsatisfied equations are more serious with decreasing temperature and with increasing dissimilarity among the potential parameters of the mixture components. In the original utilization of this set of equations, only the first two eqn (19) and (20) were considered. This requires the neglect of all three-body effects and the neglect of the consequences of any difference in the coefficients of \( (1/kT)^2 \) terms between the reference and the mixture. Eqn (19) and (20) are exactly the relations which van der Waals assumed in the generalization of his equation of state to mixtures; accordingly the conformal solution theory based upon them was called the van der Waals (vdW) approximation.

The purpose of this paper is to show how it is possible to extend this theory to allow consideration of the leading terms in the three-body contribution to the mixture properties. This extension includes eqn (21) and also eqn (22), which represents the leading term in the contribution of the \( (1/kT)^2 \) coefficients. This should improve the theory at lower temperatures and give better results when there are large dissimilarities among the potential parameters of the molecular species in the mixture.

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Among the equations in the set (19) to (22), undoubtedly the most important for the prediction of mixture properties is eqn (19). As pointed out previously, the structure of a fluid, even at low temperatures, is determined mainly by the repulsive part of the intermolecular potential. The attractive portion merely produces the internal pressure needed to maintain the high density. In view of this importance, a significant improvement in the conformal solution technique should result from
utilizing recent developments which give a very accurate analytical representation of the hard-sphere properties of both pure fluids and mixtures. Consequently, the hard-sphere contributions to mixing properties can be entirely eliminated from the corresponding states procedure and replaced with a direct analytical calculation. The corresponding states principle is then used to predict only a new type of excess function. Conformal solution theories in the past have aimed at the prediction of the traditional excess functions over the well-known ideal gas properties. The procedure proposed in this work defines an excess over the hard-sphere behaviour and predicts this excess from the corresponding property of a pure reference.

This version of the conformal solution theory thus relaxes the necessity for satisfying eqn (19). The three parameters $\bar{\sigma}^3$, $\bar{\epsilon}$ and $\bar{\nu}$ are defined to satisfy eqn (20) to (22), and are subsequently used only to predict the excess over the hard-sphere properties of the mixture. The total mixture properties are then obtained by adding to this excess the properties of the hard-sphere mixture obtained by direct analytical computation. In a mixture of $m$ components the parameters $\bar{\sigma}^3$, $\bar{\epsilon}$ and $\bar{\nu}$ defined in this manner are:

\begin{align*}
\bar{\sigma}^3 &= \left[ \frac{\sum_{a} x_a x_\beta \sigma_{a\beta}^3 \sigma_{a\beta}^2}{\sum_{a} x_a x_\beta \sigma_{a\beta}^3 \sigma_{a\beta}^2} \right]^{\frac{1}{2}} \sum_{a} x_a x_\beta \sigma_{a\beta}^3 \sigma_{a\beta}^2 \\
\bar{\epsilon} &= \left[ \sum_{a} x_a x_\beta \sigma_{a\beta}^3 \sigma_{a\beta}^2 \right] / \bar{\sigma}^3 \\
\bar{\nu} &= \bar{\sigma}^3 \sum_{a} x_a x_\beta x_\gamma \left( \sigma_{a\beta \gamma} \sigma_{a\beta \gamma} \right)
\end{align*}

Not only should this procedure give better results for the hard-sphere contributions to mixture properties, but the inclusion of contributions from terms of the order $(1/kT)^2$ should greatly extend the temperature range of effectiveness of the conformal solution method. For identification purposes this procedure is referred to here as the HSE, or hard-sphere expansion conformal solution theory.

**Effects of the cut-off parameter**

The technique proposed here, of eliminating eqn (19) and replacing it with a direct calculation of hard-sphere mixture properties, carries with it one important disadvantage. This is the difficulty in defining the molecular diameter to be used in the direct calculation of the hard-sphere properties. In a completely conformal solution technique—such as the van der Waals solution theory—where eqn (19) is satisfied, this problem does not arise if the reference fluid and all mixture components are conformal. In this case, the slope of the repulsive potential at $r = \sigma$ is the same for the reference and for the mixture components. The effect of the deviation of this slope from the infinite value assumed in deriving eqn (19) is then predicted in the mixture by the corresponding effect on the properties of the reference so that the hard-sphere contributions of a finite potential slope at $r = \sigma$ exactly cancel on each side of eqn (19). A similar cancellation also occurs for the finite repulsion slope contributions to the higher powers of $1/kT$ in the remaining eqn (20), (21), etc., whenever the mixture components and the reference are all conformal.

However, when a direct calculation of the hard-sphere contribution is to be made, without recourse to the corresponding state of a reference fluid, then a precise definition of this molecular diameter is required. As shown by Zwanzig and by Frisch et al., the thermodynamic properties of the hard-sphere fluid are extremely sensitive to this definition. The studies by Rowlinson, Henderson and Davison; Barker,
Henderson and Smith\textsuperscript{23} and McQuarrie and Katz\textsuperscript{24} have all shown that the effective molecular diameter \(d\) is temperature dependent and may be written:

\[
d = c(T)\sigma
\]  \hspace{1cm} (26)

where \(\sigma\) is the value of the molecular centre separation distance when \(u(r) = 0\). The \(c(T)\) term is a dimensionless coefficient called the cut-off parameter. Its analytical formulation has been derived rigorously for several different potentials by Rowlinson.\textsuperscript{21}

One of the advantages of the HSE procedure is that it makes possible the utilization of direct hard-sphere calculations with a simplified definition of the cut-off parameter. This is because the bulk of its temperature dependence is accounted for by eqn (20) and (21) using conformal solution principles and a reference fluid. Only the high temperature limit must be considered in the hard-sphere calculations when using the HSE method. This may be illustrated by assuming expansions of the cut-off parameter about its high temperature limit as follows:

For an interaction in the mixture:

\[
c_{ij}(T) = c_0 + c_1(e_{ij}/kT) + c_2(e_{ij}/kT)^2 + \ldots \Theta(e_{ij}/kT)^3.
\]  \hspace{1cm} (27)

For an interaction in the reference:

\[
c(T) = c_0 + c_1(\bar{e}/kT) + c_2(\bar{e}/kT)^2 + \ldots \Theta(\bar{e}/kT)^3.
\]  \hspace{1cm} (28)

For conformal substances, which must all obey the same potential function, the coefficients \(c_0, c_1\) and \(c_2\) are the same for each fluid. Suppose one substitutes the appropriate diameter \(d\) from eqn (26) with its \(c(T)\) coefficient expanded as in eqn (27) and (28) in the place of each \(\sigma_{ij}\) and \(\bar{\sigma}\) term in eqn (18). Because eqn (18) was derived for an infinite slope repulsion, this substitution is needed to correct the equation for the existence of a finite slope repulsion. If one now reassembles like powers of \(1/kT\) and again equates the coefficients to zero, one finds that for conformal fluids the set of eqn (19) to (22) is generated exactly as in the infinite slope case. Consequently, all of the eqn (19) to (22) which are satisfied will include, to that order of \(1/kT\), all of the effects of a finite slope at \(r = \sigma\). In the HSE method, however, where eqn (19) is not satisfied, multiplying each \(\sigma\) term in eqn (18) by its expanded \(c(T)\) parameter does not cause the zeroth order \(1/kT\) term to vanish. This term still remains in the equation and contains the \(c_0\) portion of the cut-off parameter expansions in eqn (27) and (28). Consequently, in the directly calculated hard-sphere mixture contributions, which replace the first term in eqn (18), only the high temperature limit, \(c_0\), must be considered as a multiple of each \(\sigma\) value to obtain the effective hard-sphere diameter.

In order to evaluate \(c_0\) numerically, one might attempt to make use of the exact cut-off parameter function derived by Rowlinson\textsuperscript{21} for a Lennard-Jones type \((n,n/2)\) potential. However, this rigorous function clearly does not have an expansion in the form of eqn (27) or (28). It actually approaches a high temperature limit of zero as \((e/kT)\) becomes vanishingly small. If it is impossible for the molecules in a real fluid to coincide, this limit is a constant greater than zero, representing some minimum approach distance which cannot be decreased no matter how high the temperature becomes. In the case of the \((n,n/2)\) potential with a repulsion proportional to \((\sigma/r)^n\) the minimum separation distance approaches zero. However, even in this case, the repulsive contribution behaves, for all practical purposes, as though its value were infinitely large at separation distances considerably greater than zero and eqn (27) or (28) may be regarded as a polynomial approximation which reflects this aspect of its behaviour. The \(c_0\) coefficient, however, cannot be evaluated from any limiting value of the rigorous cut-off parameter function.
In this work a value of $c_0$ applicable to all Lennard-Jones (12,6) fluids was obtained as the constant which gave best agreement with the Monte Carlo excess free energy calculations of Singer and Singer\cite{27} for mixtures of these fluids. Although these calculations have considerable computational uncertainty, they do have the advantage of eliminating the uncertainty due to the form of the unlike molecular pair interactions and contributions of three-body interactions. Because $c_0$ is assumed to be constant it has no effect on the excess enthalpy of the mixtures, and because of the nearness of $c_0$ to unity the effect on the excess volume is negligibly small. The excess free energy, however, is very sensitive to the value of the cut-off parameter and was used in this study to test the assumption that the bulk of the cut-off parameter, and all of its temperature dependence, can be accounted for by the HSE conformal solution technique, leaving only a residual constant to be used directly in the hard-sphere calculations. The value of this constant which gave best results over the entire range of the Monte Carlo results\cite{27} was $c_0 = 0.98$. This result generally produced agreement within the reported experimental uncertainty at all conditions, except the case when the components of the mixture have the same $\varepsilon$ value. In this case best results were obtained with the value of $c_0 = 0.94$. The Monte Carlo results at these conditions, however, are very small in magnitude and many of them are subject to a high percentage experimental uncertainty.

For real fluids, the process of evaluating the cut-off parameter from experimental data is much more difficult because of the uncertainties due to deviations from the Lorentz-Berthelot combination rules and uncertainties arising from the contribution of three-body interactions. The only case where there are sufficient data to take all these into account is the krypton-argon system. In this case, the unlike pair interactions have been determined accurately by Fender and Halsey\cite{31}; Bell and Kingston\cite{32} have also determined three-body parameters. Table 10 shows the results of considering both of these effects with the HSE method. Because real fluids probably have a repulsion exponent considerably greater than $n = 12$, one would expect their cut-off parameter limit to be nearer to unity than the $c_0 = 0.98$ value obtained for the (12-6) potential. As demonstrated by Rowlinson\cite{21} the cut-off parameter depends strongly on the value of $n$ and rapidly approaches unity as $n$ becomes large. However, in this work all fluids are assumed to be conformal with a 12-6 fluid reference and consequently $c_0 = 0.98$ was used also with real fluids.

**THE HSE METHOD FOR MIXTURES WITH FINITE SLOPE REPULSION POTENTIALS**

The extension of eqn (18) to mixtures with finite slope repulsion potentials is accomplished by multiplying each $\sigma$ term by the appropriate cut-off parameter function in eqn (27) or (28). When this is done, eqn (18) becomes:

$$[Z_M - Z_R(\bar{\sigma}^3, \bar{\varepsilon}, \bar{v})] = Z_{\text{MHS}}(c_0 \sigma_{ij}) - Z_{\text{RHS}}(c_0 \bar{\sigma}).$$  \hspace{1cm} (29)

The right side of eqn (29) represents that portion of eq (18) which remains after the cut-off parameters have been inserted and the coefficients of the $1/kT^2$ terms equated to zero by the choice of $\bar{\sigma}^3$, $\bar{\varepsilon}$ and $\bar{v}$. $Z_{\text{MHS}}(c_0 \sigma_{ij})$ is the directly calculated hard-sphere mixture compressibility factor with the effective diameter $(c_0 \sigma_{ij})$ for each interaction. $Z_{\text{RHS}}(c_0 \bar{\sigma})$ is the pure fluid hard-sphere compressibility factor at the molecular diameter $c_0 \bar{\sigma}$. It is convenient to express each term in eqn (29) as an expansion about a $c_0$ of unity, neglecting terms of higher order than $(c_0 - 1)$, when deriving thermodynamic properties from it.
Reduced hard-sphere densities for the reference and for the mixture, both with unit cut-off parameter, are defined:

\[ \xi = \frac{\pi}{6} \rho \sigma^3 \]  
\[ \xi_M = \frac{\pi}{6} \sum_{i=1}^{m} \alpha_i \rho \sigma_i^3. \]  

With these definitions the equation of state expanded about a unit cut-off parameter becomes:

\[ Z_M = Z_{\text{MHS}}(\sigma_{ij}) + \left[ Z_R(\bar{\sigma}, \bar{\varepsilon}, \bar{\eta}) - Z_{\text{RHS}}(\bar{\sigma}) \right]_{c_0=1} + 
\sum_{c_0=1} \left( \frac{\partial Z_{\text{MHS}}}{\partial \xi_M} \right)_{c_0=1} \bar{\varepsilon} \frac{\partial Z_{\text{RHS}}}{\partial \xi_M} \right)_{c_0=1} (c_0 - 1). \]  

The Helmholtz free energy of the mixture is given by:

\[ \left( \frac{A - A^*}{NkT} \right)_M = \left[ \frac{A(\sigma_{ij}) - A^*}{NkT} \right]_{\text{MHS}} + \left[ \left( \frac{A(\bar{\sigma}, \bar{\varepsilon}, \bar{\eta}) - A^*}{NkT} \right) \right]_{\text{RHS}} + \sum_{c_0=1} \left( Z_{\text{MHS}} - Z_{\text{RHS}} \right)_{c_0=1} (c_0 - 1). \]  

The internal energy of the mixture is obtained from:

\[ \left( \frac{U - U^*}{NkT} \right)_M = \left( \frac{U(\sigma, \varepsilon, \eta) - U^*}{NkT} \right) \]  

The \( A^* \) and \( U^* \) terms represent values of the Helmholtz free energy and internal energy which the fluid would have if it obeyed the ideal gas law at the given temperature and volume.

**Equations of State for Hard Sphere Fluids**

In order to evaluate properties from eqn (32), (33) and (34) one must have an analytical formulation of the equation of state for pure and mixed hard spheres to compute \( Z_{\text{MHS}} \) and \( Z_{\text{RHS}} \) and the other hard-sphere properties. For a pure component with a cut-off parameter of unity, the following form of the hard-sphere equation of state closely reproduces the machine calculated data.\(^{17}\) For the pure reference hard sphere fluid:

\[ Z_{\text{RHS}} = \left( \frac{PV}{NkT} \right)_{\text{RHS}} = \left[ 1 + \xi + \xi^2 - \xi^3 \right] \]  

where \( \bar{\varepsilon} \) is defined in eqn (30).

It has also been shown previously \(^{18}\) that the following equation of state is the best analytical representation of the hard-sphere equation of state for mixtures of \( m \) components with a unit cut-off parameter when \( \sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) \):

\[ Z_{\text{MHS}} = \left( \frac{PV}{NkT} \right)_{\text{MHS}} = \left[ 1 + (1 - 3y_1)\xi_M + (1 - 3y_2)\xi_M^2 - y_3\xi_M^3 \right] \]  

\[ \left( 1 - \xi_M \right)^3 \]
where $\xi_M$ is defined in eqn (31) and

$$
\begin{align*}
y_1 &= \sum_{j>1}^m \left( \Delta_{ij} \right) \left( \sigma_{ii} + \sigma_{jj} \right) \left( \sigma_{ij} \sigma_{jj} \right)^{-\frac{1}{2}} \\
y_2 &= \sum_{j>1}^m \left( \Delta_{ij} \right) \sum_{k=1}^m \frac{\xi_k}{\xi_M} \left( \sigma_{ij} \sigma_{jj} \right)^{\frac{1}{2}} \\
y_3 &= \left[ \sum_{i=1}^m \left( \frac{\xi_i}{\xi_M} \right)^{\frac{1}{2}} \right]^3 \\
\zeta_i &= \frac{\pi}{6} x_i \rho_i \sigma_{ii}^3 \\
\Delta_{ij} &= \frac{(\zeta_i \xi_j)^{\frac{1}{2}} (\sigma_{ii} - \sigma_{jj})^2}{\sigma_{ii} \sigma_{jj}} (x_i x_j)^{\frac{1}{2}}.
\end{align*}
$$

With the assumption of a constant cut-off parameter limit for each component in the mixture as defined by $c_0$ in eqn (28) and (29), differential $\partial Z_{\text{MHS}} / \partial \xi_M$ in eqn (32) is obtained by differentiating eqn (36) with the values of $y_1$, $y_2$ and $y_3$ held constant.

The hard-sphere equations for the Helmholtz free energy can be derived from eqn (36). The results are:

- For the pure reference fluid with diameter $\bar{a}$:
  $$
  \frac{\left( A(\bar{a}) - A^* \right)}{NkT} = \frac{4 - 3\xi}{(1 - \xi)^3}. 
  $$

- For the hard-sphere mixtures:
  $$
  \frac{\left( A(\sigma_{ij}) - A^* \right)}{NkT} = \left[ -\frac{3}{2} (1 - y_1 + y_2 + y_3) + (3y_2 + 2y_3)(1 - \xi_M)^{-1} + \right.
  \left. \frac{3}{2} (1 - y_1 - y_2 - \frac{1}{3}y_3)(1 - \xi_M)^{-2} + (y_3 - 1) \ln (1 - \xi_M) \right] 
  $$

where $y_1$, $y_2$, $y_3$ are defined in eqn (36).

**EQUATION OF STATE FOR THE REFERENCE FLUID**

Although any empirical equation of state tabulation of properties could be used for the reference, in this work it is desired to test the use of a theoretically based analytical equation of state for the pure reference fluid. For this purpose we have used the equation of state based on perturbation theory $^{23, 25}$ expressed in a completely analytical form in terms of known Laplace transforms of the radial distribution function for a hard-sphere system. $^9$ It has been shown previously $^9$ that for $T^* = (kT/\bar{a}) \leq \Theta(10^4)$ the Helmholtz free energy from the first order perturbation theory of Barker, Henderson and Smith $^{23}$ corrected for three-body effects can be written as in eqn (39) below, where it is applied to the pure reference fluid with parameters $\bar{a}^3$, $\bar{e}$ and $\bar{v}$.

$$
\frac{\left( A(\bar{a}^3, \bar{e}, \bar{v}) - A^* \right)}{NkT} = \left( \frac{A(\bar{a}) - A^*}{NkT} \right)_R + \frac{12 \bar{n}}{T^*} \int_0^{\infty} G(\bar{d}, s) U_1(\bar{c}, s) \, ds - \int_1^{1/\xi} g^{(1)}(\bar{d}, y) u(\bar{c}, y) y^2 \, dy + \left[ \frac{A(\bar{d}, T^*, \bar{v}^*)}{NkT} \right]_{3b} 
$$

\[39\]
where $\bar{\eta} = (\pi/6)p\bar{d}^3$, $\bar{T}^* = kT/\bar{\eta}$, $\bar{v}^* = \bar{v}/\bar{\eta}^3$, and $\bar{d}$ is the Barker-Henderson effective diameter defined in eqn (40) and (41). The $U_1(\bar{c}, s)$ term is the inverse Laplace transform of $zu(z)$ where $u(z)$ is the potential function in terms of $z = r/\bar{c}$ with $\bar{c}$ defined by eqn (41). $G(\bar{d}, s)$ is the Laplace transform of $r g_0(\bar{d}, r)$ and $g_0(d, r)$ is the radial distribution function of a hard-sphere fluid with an effective diameter $\bar{d}$. The $g_0^{(3)}(\bar{d}, r)$ term is the radial distribution function in the range ($\bar{d} < r < 2\bar{d}$). The parameter $y = r/\bar{d}$. The subscript HS refers to the hard-sphere contribution to the Barker-Henderson equation. It is evaluated from eqn (37) at $\bar{\eta}$ instead of $\bar{\eta}$. The subscript $3b$ refers to the contribution of three-body forces.

In using the Barker-Henderson equation for the pure reference in this work, the effective diameter $\bar{d}$ is obtained from:

$$\bar{d} = \bar{c}\bar{\sigma}$$

(40)

where $\bar{\sigma}$ is the reference fluid parameter obtained from eqn (23) using the HSE conformal solution method. The $\bar{c}$ coefficient in the Barker-Henderson equation is

$$\bar{c} = \int_0^1 \left[ 1 - \exp \left( -\frac{\bar{f}(y)}{kT} \right) \right] dy$$

(41)

where $y = r/\bar{\sigma}$ and $\bar{f}(y) = u(r/\bar{\sigma})$.

To evaluate the three-body contribution, Barker, et al., used the Axilrod-Teller equation for the three-body attractive potential and the superposition approximation to obtain a triplet distribution function for a hard-sphere fluid. With these assumptions they developed a Padé approximant for the three-body contribution. For the pure reference fluid of this study the three-body contribution is:

$$\left[ \frac{A(\bar{d}, \bar{T}^*, \bar{v}^*)}{NkT} \right]_{3b} = \left( \frac{\bar{v}}{\bar{c}^3} \right) \left[ \frac{2.70797 + 1.68918(\rho\bar{d}^3) - 0.31570(\rho\bar{d}^3)^2}{1 - 0.59056(\rho\bar{d}^3) + 0.20059(\rho\bar{d}^3)^2} \right]$$

(42)

The compressibility of the reference fluid was obtained from eqn (39) to (42) by:

$$\left[ Z_R(\bar{\sigma}^3, \bar{\eta}, \bar{v}) - 1 \right] = \rho \frac{\partial \left( A(\bar{\sigma}^3, \bar{\eta}, \bar{v}) - A^* \right)}{\partial \rho}$$

(43)

Likewise, the internal energy for the pure reference fluid is

$$\left( \frac{U(\bar{\sigma}^3, \bar{\eta}, \bar{v}) - U^*}{NkT} \right)_R = -T \frac{\partial \left( A(\bar{\sigma}^3, \bar{\eta}, \bar{v}) - A^* \right)}{\partial T}$$

(44)

CALCULATION OF EXCESS FUNCTIONS OF MIXING

In applying eqn (32), (33) and (34), the hard-sphere and total fluid properties were obtained from eqn (35) to (44). In order to test these equations and the HSE method, the excess mixing functions of Lennard-Jones (12-6) fluids obtained from the Monte Carlo calculations of Singer and Singer were used to compare with results predicted by the HSE method. Because the reference fluid equations used are also for a fluid with a Lennard-Jones $(n, n/2)$ potential and because the same Lorentz-Berthelot combining rules for unlike pair interactions were used in both the HSE method definitions of $\bar{c}$ and $\bar{\sigma}$ and in the Monte Carlo calculations of Singer and Singer, the comparison should provide a sensitive test of the new mixing theory. In addition, the HSE method was also tested as to its ability to predict the experimentally measured excess properties for several real binary mixtures.
In computing excess volumes of mixing, the volume of the liquid mixture at zero pressure was obtained by solving eqn (32) for the smallest volume root when the mixture compressibility factor was set at zero. A similar procedure was used for the calculation of the liquid volumes of the pure components at zero pressure. For pure components, eqn (32) reduces to

\[ Z = Z_R(\sigma^3, \varepsilon, \nu) \]  

(45)

with \( Z_R \) obtained from eqn (43) and eqn (39) through (42) using the appropriate \( \sigma^3, \varepsilon \) and \( \nu \) values for the pure component.

The excess Gibbs free energy of mixing at constant temperature and at a constant zero pressure is obtained by first calculating the residual Helmholtz free energy \( (A - A^*)/NkT \) for the mixture from eqn (33) using eqn (37), (38) and (39) at the given temperature \( T \) and at the calculated liquid mixture molal volume \( V_M \) which corresponds to zero pressure. This residual free energy function is also calculated in this manner for each pure component at the temperature \( T \) and its pure liquid volume corresponding to a pressure of zero. The \( \Lambda^* \) value in this residual for the mixture is the ideal gas free energy of the mixture at \( T \) and a pressure \( P^* = RT/V_M \). Similarly, the \( \Lambda^* \) values in the residual Helmholtz free energies of each pure component are the ideal gas values at \( T \) and the ideal gas pressure corresponding to this temperature and the liquid volume of each pure component. However, to obtain the desired excess properties we need to calculate residuals with respect to an ideal gas \( \Lambda^* \) value at \( T \) and the constant zero pressure \( P_0 \) for the mixture and also for the pure components. This type of residual free energy is related to that obtained from eq (33) as follows. For the mixture:

\[ \left( \frac{A_{T,P_0} - A^*_{T,P_0}}{NkT} \right)_M = \left( \frac{A_{T,P_0} - A^*_{T,P_0}}{NkT} \right)_M - \ln \left( \frac{P_0}{RT} \right) - \ln V_M \]  

(47)

where \( V_M \) is the molal volume of the liquid mixture at \( T \) and \( P_0 \). The first term on the right side of eqn (47) is that obtained from eqn (33) using the HSE conformal solution method. Relations analogous to (47) exist between the two types of residuals for the pure components. The excess Helmholtz free energy of mixing at constant \( T \) and \( P_0 \) is:

\[ \frac{\Delta A^E_{T,P_0}}{NkT} = \Delta \left( \frac{A_{T,P_0} - A^*_{T,P_0}}{NkT} \right) - \ln \left( \frac{V_M}{V_1 V_2} \right) \]  

(48)

where \( V_1 \) and \( V_2 \) are the molal volumes of the pure liquids at \( T \) and the zero pressure \( P_0 \). The \( x_1 \) and \( x_2 \) terms are the mol fractions of each in the mixture.

The excess Gibbs free energy of mixing at \( T \) and the zero pressure \( P_0 \) is:

\[ \frac{\Delta G^E_{T,P_0}}{NkT} = \frac{\Delta A^E_{T,P_0}}{NkT} + \left( P_0 \Delta V^E_{T,P_0} \right)/NkT \]  

(49)

and because \( P_0 \) is zero the last term in eqn (49) vanishes.

RESULTS USING TWO-BODY INTERACTIONS ONLY

A series of comparisons between the predicted excess properties on mixing and those properties from experimental and Monte Carlo data was first carried out by neglecting all three-body interactions entirely. The three-body term in the pure fluid reference equations and the parameter \( \bar{v} \) determined in eqn (25) were both omitted. In table 1 the excess properties of an equimolar liquid mixture of argon
and krypton calculated using two-body forces only are compared with the machine-calculated Monte Carlo (MC) data of McDonald \(^{28}\) with some corrections by Henderson.\(^{29}\) The notation (vdW) refers to the original van der Waals conformal solution theory obtained from eqn (19) and (20). The notation (HSE) refers to the method developed in this paper. In table 1 the Lorentz-Berthelot combining rules for unlike pair interaction parameters were used throughout. As shown in the table, the excess properties calculated by the HSE procedure are in better agreement with the MC and experimental data than the predictions of the other theories presented.

**Table 1**.—Excess thermodynamic properties of equimolar liquid mixture of argon and krypton at \(P = 0\) and 115.8 K, calculated by different theories, considering only two-body forces and the experimental values. (For argon \(\epsilon/k = 119.8\) K, \(\sigma = 3.405\) Å, and for krypton \(\epsilon/k = 167.0\) K and \(\sigma = 3.633\) Å.) Lorentz-Berthelot combination rules used entirely

<table>
<thead>
<tr>
<th>method</th>
<th>(v^E) (\text{cm}^3) (\text{mol}^{-1})</th>
<th>(H^E) (\text{J}) (\text{mol}^{-1})</th>
<th>(G^E) (\text{J}) (\text{mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>APM(^a)</td>
<td>0.23</td>
<td>169</td>
<td>136</td>
</tr>
<tr>
<td>perturbational (^b)</td>
<td>-0.73</td>
<td>-48.5</td>
<td>32.7</td>
</tr>
<tr>
<td>variational (^c) (corrected)</td>
<td>-0.73</td>
<td>-31</td>
<td>46.7</td>
</tr>
<tr>
<td>vdW (^a)</td>
<td>-0.46</td>
<td>-12.6</td>
<td>42.3</td>
</tr>
<tr>
<td>vdW (^b)</td>
<td>-0.79</td>
<td>-45.4</td>
<td>42.2</td>
</tr>
<tr>
<td>vdW (^c)</td>
<td>-0.67</td>
<td>-42.5</td>
<td>36.94</td>
</tr>
<tr>
<td>HSE</td>
<td>-0.61</td>
<td>-45.9</td>
<td>{53 (c_0 = 1.0) (c_0 = 0.98) }</td>
</tr>
<tr>
<td>MC (^d)</td>
<td>-0.80 ± 0.16</td>
<td>-80 ± 34</td>
<td></td>
</tr>
<tr>
<td>MC (^e)</td>
<td>-0.54 ± 0.20</td>
<td>-34 ± 40</td>
<td>34 ± 10</td>
</tr>
<tr>
<td>experimental</td>
<td>-0.52</td>
<td>(84)</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) Taken from ref. (8). Calculated using McDonald's MC curve for the reference system.

\(^{b}\) Calculated using the experimental curves of Bellemans \(\textit{et al.}\) for the reference system.\(^8\)

\(^{c}\) Calculated using eqn (39) for the reference system (two-body potentials only).

\(^{d}\) Taken from ref. (28).

\(^{e}\) Unpublished results of McDonald \(^8\) using longer runs than those for \(d\).

* The authors are indebted to D. Henderson for assistance in preparing this table.

The importance of the combining rule and the conformal solution theory used is shown in fig. 1 and 2 for argon-krypton mixtures. The (LB) notation indicates results using the Lorentz-Berthelot rules and the (FH) symbol indicates the use of an improved \(\epsilon_{12}\) value designed specifically for Ar-Kr and Ar-Xe pairs by Fender and Halsey,\(^{31}\) in the form:

\[
\epsilon_{12} = \left( \frac{2\epsilon_{11}\epsilon_{22}}{\epsilon_{11} + \epsilon_{22}} \right)
\]  

Use of eqn (50) causes a definite improvement in the calculated excess properties. With the same combining rule and the same reference fluid equation, however, the HSE method produces better results than the van der Waals theory. Fig. 1 and 2 are based entirely on the use of the theoretical Barker-Henderson equation for a pure (12,6) fluid as the reference.

In table 3 the excess mixing properties of eight different binary systems are presented at different temperatures for equimolar mixtures. In this table the experimental results are compared with the average potential model (APM) of Bellemans, \(\textit{et al.}\),\(^3\) and with the one-fluid model of the van der Waals (vdW) approximation, both using the experimental equations of Bellemans, \(\textit{et al.}\)\(^3\) for the pure reference properties. Also presented in table 3 are the results for the perturbational theory
for mixtures along with the results of this HSE method again using the theoretical Barker-Henderson perturbation equation as the pure reference. For all like pair interactions in table 3 the interaction parameters are given in table 2. As base values, those of argon, \( e/k = 119.8 \) K and \( \sigma = 3.405 \) Å were used to obtain the other parameters in table 2. The Lorentz-Berthelot rules were used exclusively in table 3. The favourable performance of the HSE method is especially noteworthy in view of the purely theoretical reference fluid equation used.

![Excess Gibbs free energy of Ar-Kr liquid mixtures at zero pressure predicted by the HSE and vdW methods both using the same Barker-Henderson Equation for the pure reference fluid. LB refers to the Lorentz-Berthelot rule and FII to the Fender-Halsey rule for the unlike interaction parameters. Kr-Ar mixtures \( T = 115.8 \) K: ---, 2-body interactions included; ---, 3-body interactions included.](image)
In table 5 the excess mixing properties of CH₄ and CF₄ are calculated by different methods and compared with experimental results. The pair interaction parameters determined by Douslin, et al.³⁰ were used and are presented in table 4.

Fig. 2.—Excess volume of Ar-Kr liquid mixtures at zero pressure predicted by the HSE and vdW methods both using the same Barker-Henderson Equation for the pure reference fluid. Kr-Ar mixtures \( T = 115.8 \text{ K} \); ---, 2-body interactions only; ----, 3-body interactions included.

Tables 6, 7 and 8 show the calculations of different theories in comparison with the Monte Carlo data obtained by Singer and Singer ²⁷ for liquid mixtures with a Lennard-Jones (12,6) potential. These tables give the difference in \( G_M \), \( H_M \) and \( V_M \)

### Table 2.—Like pair-interaction parameters used in table 3.

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \epsilon/\epsilon ) (argon)</th>
<th>( \sigma/\sigma ) (argon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>argon</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>krypton</td>
<td>1.387</td>
<td>1.070</td>
</tr>
<tr>
<td>nitrogen</td>
<td>0.836</td>
<td>1.063</td>
</tr>
<tr>
<td>oxygen</td>
<td>1.022</td>
<td>0.995</td>
</tr>
<tr>
<td>carbon monoxide</td>
<td>0.881</td>
<td>1.070</td>
</tr>
<tr>
<td>methane</td>
<td>1.266</td>
<td>1.099</td>
</tr>
<tr>
<td>carbon tetrafluoride</td>
<td>1.288</td>
<td>1.365</td>
</tr>
</tbody>
</table>
Table 3.—Comparison of the experimental and theoretical values of excess thermodynamic properties at $P = 0$ and $x_1 = x_2 = 0.5$ for different systems of binary mixtures. $G^e$ and $H^e$ are in $J \text{ mol}^{-1}$ and $V^e$ is in $cm^3 \text{ mol}^{-1}$. $\sigma_{12} = (\sigma_{11} + \sigma_{22})/2$.

<table>
<thead>
<tr>
<th>System</th>
<th>Property</th>
<th>Expt.</th>
<th>APM</th>
<th>vdW</th>
<th>Pert.</th>
<th>HSE $c_0 = 1.0$</th>
<th>HSE $c_0 = 0.98$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar+Kr</td>
<td>$G^e$</td>
<td>84</td>
<td>170</td>
<td>37</td>
<td>28</td>
<td>53</td>
<td>38</td>
</tr>
<tr>
<td>(115.8 K)</td>
<td>$H^e$</td>
<td></td>
<td></td>
<td>-0.50</td>
<td>-0.44</td>
<td>-0.78</td>
<td>-0.72</td>
</tr>
<tr>
<td></td>
<td>$V^e$</td>
<td></td>
<td></td>
<td>-0.44</td>
<td>-0.78</td>
<td>-0.72</td>
<td>-0.72</td>
</tr>
<tr>
<td>Ar+N2</td>
<td>$G^e$</td>
<td>34</td>
<td>80</td>
<td>40</td>
<td>32</td>
<td>42</td>
<td>37</td>
</tr>
<tr>
<td>(84 K)</td>
<td>$H^e$</td>
<td>51</td>
<td>105</td>
<td>43</td>
<td>27</td>
<td>42</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>$V^e$</td>
<td>-0.18</td>
<td>-0.77</td>
<td>-0.32</td>
<td>-0.33</td>
<td>-0.24</td>
<td>-0.24</td>
</tr>
<tr>
<td>Ar+CO</td>
<td>$G^e$</td>
<td>57</td>
<td>26</td>
<td>18</td>
<td>28</td>
<td>24.5</td>
<td></td>
</tr>
<tr>
<td>(84 K)</td>
<td>$H^e$</td>
<td>32</td>
<td>14</td>
<td></td>
<td>38</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$V^e$</td>
<td>0.10</td>
<td>-0.20</td>
<td>-0.25</td>
<td>-0.14</td>
<td>-0.14</td>
<td></td>
</tr>
<tr>
<td>Ar+CH4</td>
<td>$G^e$</td>
<td>74</td>
<td>170</td>
<td>-19</td>
<td>-29</td>
<td>-8</td>
<td>-21</td>
</tr>
<tr>
<td>(91 K)</td>
<td>$H^e$</td>
<td>103</td>
<td>240</td>
<td>-53</td>
<td>-77</td>
<td>-46</td>
<td>-46</td>
</tr>
<tr>
<td></td>
<td>$V^e$</td>
<td>0.17</td>
<td>0.72</td>
<td>-0.31</td>
<td>-0.36</td>
<td>-0.16</td>
<td>-0.16</td>
</tr>
<tr>
<td>O2+Ar</td>
<td>$G^e$</td>
<td>37</td>
<td>1</td>
<td>0.5</td>
<td>0.5</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>(84 K)</td>
<td>$H^e$</td>
<td>60</td>
<td>2</td>
<td>0.5</td>
<td>0.1</td>
<td>0.45</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>$V^e$</td>
<td>0.14</td>
<td>0.01</td>
<td>-0.00</td>
<td>-0.00</td>
<td>-0.00</td>
<td>-0.00</td>
</tr>
<tr>
<td>O2+N2</td>
<td>$G^e$</td>
<td>42</td>
<td>65</td>
<td>51</td>
<td>40</td>
<td>53</td>
<td>45</td>
</tr>
<tr>
<td>(78 K)</td>
<td>$H^e$</td>
<td>44</td>
<td>85</td>
<td>54</td>
<td>34</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>$V^e$</td>
<td>-0.21</td>
<td>-0.11</td>
<td>-0.32</td>
<td>-0.34</td>
<td>-0.25</td>
<td>-0.25</td>
</tr>
<tr>
<td>N2+CO</td>
<td>$G^e$</td>
<td>23</td>
<td>1</td>
<td>0.5</td>
<td>1.7</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>(84 K)</td>
<td>$H^e$</td>
<td></td>
<td></td>
<td>-0.4</td>
<td>-0.9</td>
<td>-4.3</td>
<td>-4.3</td>
</tr>
<tr>
<td></td>
<td>$V^e$</td>
<td>0.13</td>
<td></td>
<td>-0.02</td>
<td>-0.02</td>
<td>-0.01</td>
<td>-0.01</td>
</tr>
<tr>
<td>CO+CH4</td>
<td>$G^e$</td>
<td>115</td>
<td>105</td>
<td>75</td>
<td>66</td>
<td>78</td>
<td>56</td>
</tr>
<tr>
<td>(91 K)</td>
<td>$H^e$</td>
<td>105</td>
<td>80</td>
<td>23</td>
<td>22</td>
<td>-2.4</td>
<td>-2.4</td>
</tr>
<tr>
<td></td>
<td>$V^e$</td>
<td>-0.32</td>
<td>-0.50</td>
<td>-0.85</td>
<td>-0.63</td>
<td>-0.64</td>
<td>-0.64</td>
</tr>
</tbody>
</table>

See ref. (3), (4) and (8) for the origin of the data and the methods of calculation of the results of theories presented in this table.

Table 4.—Pair interaction parameters for CH$_4$+CF$_4$

<table>
<thead>
<tr>
<th>$\epsilon/(CH_4)$</th>
<th>$\sigma/(CH_4)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$+CH$_4$</td>
<td>1.000</td>
</tr>
<tr>
<td>CF$_4$+CH$_4$</td>
<td>0.917</td>
</tr>
<tr>
<td>CF$_4$+CF$_4$</td>
<td>1.017</td>
</tr>
</tbody>
</table>

Table 5.—Comparison of the theoretical and experimental values of excess properties for the system CH$_4$+CF$_4$ at $p = 0$, 111 K, $x_1 = x_2 = 0.5$ with parameters from Tables 2 and 4.

<table>
<thead>
<tr>
<th>Property</th>
<th>Expt.</th>
<th>APM</th>
<th>vdW</th>
<th>Pert.</th>
<th>HSE $c_0 = 0.98$</th>
<th>Var.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G^e/(J \text{ mol}^{-1})$</td>
<td>360</td>
<td>870</td>
<td>279</td>
<td>209</td>
<td>212</td>
<td>424</td>
</tr>
<tr>
<td>$H^e/(J \text{ mol}^{-1})$</td>
<td>482</td>
<td>259</td>
<td>403</td>
<td>770</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V^e/(cm^3 \text{ mol}^{-1})$</td>
<td>0.88</td>
<td>7.1</td>
<td>0.90</td>
<td>-0.97</td>
<td>0.52</td>
<td>3.13</td>
</tr>
</tbody>
</table>

See ref. (3), (4) and (8) for the origin of the experimental data and the results of the APM, vdW, and perturbational theories reported in this table. The var. column is the variational method of ref. (7) corrected for a computational error.
for a mixture and the values \( G_{12} \), \( H_{12} \) and \( V_{12} \) of these properties for an imaginary pure component with pair potential parameters \( \varepsilon_{12} = \sqrt{\varepsilon_{11} \varepsilon_{22}} \) and \( \sigma_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22}) \). In the notation of Singer and Singer these tables report values of

\[
\begin{align*}
g^{III} &= \frac{(G - G_{12})_{T,P_0}}{NkT} \quad (51) \\
h^{III} &= \frac{(H - H_{12})_{T,P_0}}{NkT} \quad (52) \\
\Delta V^{III} &= \frac{(V - V_{12})_{T,P_0}}{NkT} \quad (53)
\end{align*}
\]

The properties defined in eqn (51), (52) and (53) are particularly sensitive to the mixing theory alone and in tables 6, 7 and 8, the effects caused by varying molecular

### Table 6.—Variation of \( g^{III} = 10^3 \) of the equimolar binary mixture of Lennard-Jones fluids with respect to the ratios of the molecular potential parameters of the two components at \( P = 0 \), 97 K and for \( \sigma_{12} = \frac{1}{2} (\sigma_{11} + \sigma_{22}) = 3.596 \) Å and \( \varepsilon_{12}/k = (\varepsilon_{11} \times \varepsilon_{22})/k = 133.5 \) K. Effects of varying the cut-off parameter limit, \( c_0 \), are shown for the HSE method

<table>
<thead>
<tr>
<th>( \sigma_{11}/\sigma_{12} )</th>
<th>( \varepsilon_{11}/\varepsilon_{12} )</th>
<th>MC (^{27} )</th>
<th>vdW (^{a} )</th>
<th>variational (^{7} )</th>
<th>HSE ( c_0 = 1.0 )</th>
<th>HSE ( c_0 = 0.98 )</th>
<th>HSE ( c_0 = 0.94 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>1.00</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>1.02</td>
<td>1.00</td>
<td>-1 ± 1</td>
<td>-0.6</td>
<td>-0.1</td>
<td>1.1</td>
<td>0.7</td>
<td>-0.1</td>
</tr>
<tr>
<td>1.04</td>
<td>1.00</td>
<td>-3 ± 2</td>
<td>-2.4</td>
<td>-0.3</td>
<td>4.2</td>
<td>2.6</td>
<td>-0.7</td>
</tr>
<tr>
<td>1.06</td>
<td>1.00</td>
<td>-4 ± 2</td>
<td>-5.4</td>
<td>-0.6</td>
<td>9.6</td>
<td>5.9</td>
<td>-1.4</td>
</tr>
<tr>
<td>1.08</td>
<td>1.00</td>
<td>-5 ± 3</td>
<td>-9.5</td>
<td>-1.1</td>
<td>16.9</td>
<td>10.4</td>
<td>-2.4</td>
</tr>
<tr>
<td>1.10</td>
<td>1.00</td>
<td>-6 ± 3</td>
<td>-14.9</td>
<td>-1.6</td>
<td>26.0</td>
<td>16.1</td>
<td>-3.8</td>
</tr>
<tr>
<td>1.12</td>
<td>1.00</td>
<td>-7 ± 3</td>
<td>-21.5</td>
<td>-2.4</td>
<td>37.0</td>
<td>23.0</td>
<td>-4.9</td>
</tr>
<tr>
<td>1.00</td>
<td>1.111</td>
<td>-27 ± 3</td>
<td>-23.1</td>
<td>-2.7</td>
<td>-17.0</td>
<td>-24.3</td>
<td>-38.8</td>
</tr>
<tr>
<td>1.03</td>
<td>0.90</td>
<td>5 ± 3</td>
<td>15.0</td>
<td>10.9</td>
<td>21.7</td>
<td>13.5</td>
<td>-2.8</td>
</tr>
<tr>
<td>1.03</td>
<td>1.00</td>
<td>-2 ± 2</td>
<td>-1.3</td>
<td>-0.1</td>
<td>2.4</td>
<td>1.4</td>
<td>-0.4</td>
</tr>
<tr>
<td>1.03</td>
<td>1.111</td>
<td>-65 ± 3</td>
<td>-64.1</td>
<td>-59.5</td>
<td>-50.9</td>
<td>-59.1</td>
<td>-75.5</td>
</tr>
<tr>
<td>1.06</td>
<td>0.9</td>
<td>38 ± 5</td>
<td>50.1</td>
<td>45.5</td>
<td>64.6</td>
<td>53.9</td>
<td>32.5</td>
</tr>
<tr>
<td>1.06</td>
<td>1.11</td>
<td>-101 ± 5</td>
<td>-107.6</td>
<td>-94.9</td>
<td>-79.7</td>
<td>-90.8</td>
<td>-112.5</td>
</tr>
</tbody>
</table>

\(^{a}\) Calculated based on the machine-calculated results for pure Lennard-Jones fluid (ref. (27)).

### Table 7.—Variation of \( h^{III} \times 10^3 \) with respect to the ratios of the molecular potential parameters at the same conditions as Table 6.

<table>
<thead>
<tr>
<th>( \sigma_{11}/\sigma_{12} )</th>
<th>( \varepsilon_{11}/\varepsilon_{12} )</th>
<th>MC (^{27} )</th>
<th>vdW (^{a} )</th>
<th>variational (^{7} )</th>
<th>HSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>1.00</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0</td>
</tr>
<tr>
<td>1.02</td>
<td>1.00</td>
<td>3 ± 15</td>
<td>0</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>1.04</td>
<td>1.00</td>
<td>13 ± 15</td>
<td>0</td>
<td>0</td>
<td>13</td>
</tr>
<tr>
<td>1.06</td>
<td>1.00</td>
<td>30 ± 18</td>
<td>0</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>1.08</td>
<td>1.00</td>
<td>54 ± 20</td>
<td>0</td>
<td>19</td>
<td>52</td>
</tr>
<tr>
<td>1.10</td>
<td>1.00</td>
<td>86 ± 25</td>
<td>0</td>
<td>29</td>
<td>81</td>
</tr>
<tr>
<td>1.12</td>
<td>1.00</td>
<td>126 ± 30</td>
<td>0</td>
<td>48</td>
<td>117</td>
</tr>
<tr>
<td>1.00</td>
<td>1.111</td>
<td>-26 ± 20</td>
<td>-31</td>
<td>-39</td>
<td>-36</td>
</tr>
<tr>
<td>1.03</td>
<td>0.90</td>
<td>20 ± 20</td>
<td>23</td>
<td>19</td>
<td>26</td>
</tr>
<tr>
<td>1.03</td>
<td>1.00</td>
<td>7 ± 15</td>
<td>0</td>
<td>0</td>
<td>7</td>
</tr>
<tr>
<td>1.03</td>
<td>1.111</td>
<td>-83 ± 20</td>
<td>-84</td>
<td>-87</td>
<td>-83</td>
</tr>
<tr>
<td>1.06</td>
<td>0.90</td>
<td>86 ± 25</td>
<td>76</td>
<td>78</td>
<td>102</td>
</tr>
<tr>
<td>1.06</td>
<td>1.111</td>
<td>-118 ± 25</td>
<td>-137</td>
<td>-116</td>
<td>-114</td>
</tr>
</tbody>
</table>

\(^{a}\) Calculated based on the machine-calculated results for pure Lennard-Jones fluid (ref. (27)).
sizes are emphasized. The HSE method is exceptionally good in the prediction of $h^{III}$ and $\Delta V^{III}$. For these properties, it is better than the van der Waals theory using the machine calculated results of a pure Lennard-Jones fluid as the reference. This

### Table 8.—Variation of $\Delta V^{III}$ in cm$^3$ mol$^{-1}$ with respect to the ratios of the molecular potential parameters at the same conditions as Table 6.

<table>
<thead>
<tr>
<th>$\sigma_{11}/\sigma_{12}$</th>
<th>$\epsilon_{11}/\epsilon_{12}$</th>
<th>MC$^{27}$</th>
<th>vdW</th>
<th>variational</th>
<th>HSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>1.00</td>
<td>0.0</td>
<td>0.00</td>
<td>0.00</td>
<td>0.0</td>
</tr>
<tr>
<td>1.02</td>
<td>1.00</td>
<td>0.03 ± 0.05</td>
<td>0.02</td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>1.04</td>
<td>1.00</td>
<td>0.15 ± 0.05</td>
<td>0.08</td>
<td>0.13</td>
<td>0.14</td>
</tr>
<tr>
<td>1.06</td>
<td>1.00</td>
<td>0.34 ± 0.05</td>
<td>0.18</td>
<td>0.30</td>
<td>0.31</td>
</tr>
<tr>
<td>1.08</td>
<td>1.00</td>
<td>0.62 ± 0.06</td>
<td>0.32</td>
<td>0.54</td>
<td>0.55</td>
</tr>
<tr>
<td>1.10</td>
<td>1.00</td>
<td>0.99 ± 0.08</td>
<td>0.50</td>
<td>0.84</td>
<td>0.86</td>
</tr>
<tr>
<td>1.12</td>
<td>1.00</td>
<td>1.43 ± 0.12</td>
<td>0.72</td>
<td>1.22</td>
<td>1.25</td>
</tr>
<tr>
<td>1.00</td>
<td>1.111</td>
<td>0 ± 0.06</td>
<td>-0.03</td>
<td>-0.06</td>
<td>-0.06</td>
</tr>
<tr>
<td>1.03</td>
<td>0.9</td>
<td>0.1 ± 0.06</td>
<td>0.07</td>
<td>0.07</td>
<td>0.09</td>
</tr>
<tr>
<td>1.03</td>
<td>1.111</td>
<td>0.0 ± 0.06</td>
<td>-0.04</td>
<td>-0.03</td>
<td>-0.04</td>
</tr>
<tr>
<td>1.06</td>
<td>0.9</td>
<td>0.39 ± 0.06</td>
<td>0.26</td>
<td>0.34</td>
<td>0.39</td>
</tr>
<tr>
<td>1.06</td>
<td>1.111</td>
<td>0.19 ± 0.06</td>
<td>0.05</td>
<td>0.15</td>
<td>0.13</td>
</tr>
</tbody>
</table>

*Calculated based on the machine-calculated results for pure Lennard-Jones fluid (ref. (27)).

Fig. 3.—Excess Gibbs free energy for an equi-molar mixture of Lennard-Jones 12-6 fluids. The data points are those of Singer and Singer.$^{27}$ The vdW curve uses the equations of Bellemans et al.$^{3}$ as the pure reference fluid.
marked improvement in $h^\text{III}$ over the van der Waals result is an excellent confirmation of the validity of including the $(1/kT)^2$ terms in deriving the HSE method. The value of $h^\text{III}$ does not depend at all on the hard sphere contributions so that the poorer results with the van der Waals theory are due to the fact that it neglects $(1/kT)^2$ contributions entirely.

Table 6 shows the effect of $c_0$ in the HSE method. All the Monte Carlo results are predicted within the reported uncertainty by a $c_0$ value of 0.98 except the very small $g^\text{III}$ values in the mixtures having the same $\epsilon$ values for both components. In this case, $c_0 = 0.94$ gives significantly better results, as shown in table 6. This

![Diagram](image)

Fig. 4.—Excess Gibbs free energy for an equi-molar mixture of Lennard-Jones 12-6 fluids. The data points are those of Singer and Singer. The curve labelled PERT is the result of the Barker-Henderson perturbation theory. The vdW curve uses the equations of Bellemans et al. as the pure reference fluid.

*undoubtedly reflects the approximate nature of eqn (27) and (28) and, rather than a universal constant, $c_0$ probably should be some function of the differences in $\epsilon$ values between the components. It should perhaps be 0.94 when the $\epsilon$ values are the same and rapidly approach 0.98 as they become dissimilar, although the large uncertainties in the very small Monte Carlo $g^\text{III}$ values at $\epsilon_{11}/\epsilon_{12} = 1.0$ would probably eliminate the possibility of any meaningful correlation of this type. Table 6 shows that it might
be possible to evaluate the $c_0$ term using the variational technique with the HSE method in which $c_0$ is a single variational parameter for the mixture.

Fig. 3 to 8 show the performance of several theories in predicting the complete excess functions for mixing Lennard-Jones 12-6 fluids. The van der Waals theory results plotted in these figures use the machine-computed values for a pure Lennard-Jones fluid as the reference. Fig. 3 and 4 show the importance of the $c_0$ value in the excess Gibbs free energy calculation with the HSE method. Although not shown on those figures, the variational method coincides almost exactly with the $c_0 = 1.0$ curves of the HSE method. The results for the HSE method show that $c_0 = 0.98$ gives an excellent representation of the overall $G$ curves despite the large deviations in the small $g^{III}$ values when $\sigma_{11}/\sigma_{12} = 1.0$. In this case the $c_0 = 0.98$ value in the HSE method predicts $G$ values of essentially zero until the size ratio $\sigma_{11}/\sigma_{12}$ becomes greater than about 1.03. With further increases in $\sigma_{11}/\sigma_{12}$ it becomes negative but much smaller in magnitude than the values reported by Singer and Singer.

![Diagram](image-url)

**Fig. 5.**—Excess enthalpy of the equimolar (12-6) Lennard-Jones mixture calculated also by the Average Potential Model (APM) and vdW both with Bellemans equations as the reference. The VAR curve is that calculated by the corrected variational procedure for mixtures.

It is surprising that fig. 5 for $H$ does not show a better performance of the HSE method at $\sigma_{22}/\sigma_{12} = 1.03$, in view of its good prediction of $H^{III}$ at these conditions. This indicates difficulties in predicting the pure component enthalpies from the Barker-Henderson reference equation. The Barker-Henderson perturbation theory for mixtures also gives results for $H$ at $\sigma_{22}/\sigma_{12} = 1.03$ which are poorer than one would expect in view of the good results it gives for $G$.
FIG. 6.—Excess enthalpy of the equi-molar (12-6) Lennard-Jones mixture calculated also by the same methods as in fig. 5.

FIG. 7.—Excess volumes of the equi-molar Lennard-Jones mixture calculated by various methods. The vdW and APM curves use the Bellemans equations for the reference. The other methods use the Barker-Henderson equation.
RESULTS CONSIDERING THREE-BODY FORCES

Although this work has developed a formalism for extending the conformal solution concept to include triplet interactions, with the exception of the monatomic gases there are no satisfactory data for three-body potential parameters. This is especially true in regard to the unlike triplet interaction parameters. The data for the rare gases are confined to the triplet dipole attraction term described by the Axilrod-Teller equation, which is probably the most important contributor. Table 9 gives these parameters for the argon-krypton system. Table 10 and fig. 1 and 2 give the excess mixing properties for argon and krypton in the case where two-body Lennard-Jones (12,6) potentials only are considered and show the comparison with the case where the three-body potential has been added. The consequences of the addition of the three-body effects are disappointing. The excess volume prediction becomes poorer than that predicted from two-body interactions alone.
The effects of the three-body calculations were inconclusive. There are not sufficient data at present to give enough three-body interaction parameters and unlike pair interaction potentials for a thorough study. A theory has been developed to serve as a starting point for introducing three-body effects into a conformal solution treatment of mixtures.

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The excess free energy is in very close agreement with the experimental result when two-body forces alone are considered and the value $c_0 = 0.98$ for the cut-off parameter limit is used. The addition of the three-body interactions makes the agreement poorer. One cause of this could be the fact that the Lennard-Jones potential is not strictly a pure pair potential but also accounts to some degree for the contribution of higher order interactions. If there were available true pair potentials for all like

<table>
<thead>
<tr>
<th>Property</th>
<th>Expt.</th>
<th>$e_{12} = (e_{11}e_{22})^{1/2}$</th>
<th>$e_1^{(2)} = (e_{11}+e_{22})^{1/2}$</th>
<th>$e_{12} = (e_1e_2)^{1/2}$</th>
<th>$e_{12} = (e_{11}+e_{22})^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G^e$</td>
<td>84</td>
<td>53</td>
<td>38</td>
<td>95</td>
<td>80</td>
</tr>
<tr>
<td>$H^e$</td>
<td>-0.52</td>
<td>-0.61</td>
<td>-0.50</td>
<td>-0.83</td>
<td>-0.66</td>
</tr>
<tr>
<td>$V^e$</td>
<td>-46</td>
<td>18</td>
<td>80</td>
<td>41</td>
<td>28</td>
</tr>
</tbody>
</table>

In this table for argon $\sigma = 3.405$ Å, $\epsilon/k = 119.8$ K, and for krypton $\sigma = 3.633$ Å and $\epsilon/k = 167$ K.

and unlike pair interactions in the system, such as the potential developed for argon-argon interactions by Barker and Pompe, for all interactions in the system, the inclusion of the three-body interactions might produce an improvement in all mixture and pure component calculations. Another reason for the difficulty is undoubtedly the limited accuracy of the $\nu$ values in table 9. They could be in error by as much as 10% according to Bell and Kingston.

**CONCLUSIONS**

This study shows that it is possible to improve the vdW conformal solution theory in the prediction of two-body contributions to mixture properties. The excess free energy predictions with the HSE method using the theoretical Barker-Henderson Equation as a reference and the best constant value of 0.98 determined for $c_0$ agree roughly with those of the vdW theory using empirical or experimental reference fluid properties. The excess enthalpy and especially the excess volume are generally predicted better by the HSE procedure in spite of the advantage of using an empirically fitted reference equation in the vdW procedure.

When the vdW and HSE procedures are both based on the same reference, as illustrated in fig. 1, the HSE method is clearly superior.

The results of the variational method presented in this work are those of ref. (7) with a computational error corrected. Ref. (7) unfortunately contains an error in converting excess functions at constant temperature and volume to excess functions at constant temperature and zero pressure. After this correction the variational method is nearly as good as the HSE method in computing the strictly mixing properties $h^{\text{III}}$ and $V^{\text{III}}$, and is as good or better for $G^{\text{III}}$. In computing the total excess properties from $g^{\text{III}}$, $h^{\text{III}}$ and $V^{\text{III}}$, the variational method was better than all others for $H^e$ and comparable to the HSE method for $G^e$. The HSE method was clearly superior only in the calculation of $V^e$. Further comparisons of the two methods need to be made. An exceptionally effective mixture theory should result from combining the HSE and variational methods using $c_0$ as a single variational parameter.
The effects of the three-body calculations were inconclusive. There are not sufficient data at present to give enough three-body interaction parameters and unlike pair interaction potentials for a thorough study. A theory has been developed to serve as a starting point for introducing three-body effects into a conformal solution treatment of mixtures.

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16 J. D. van der Waals, Die Continuität des Gasförmigen und Flüssigen Zustands (Barth, Leipzig, 1900), vol. 2, chap. 1.