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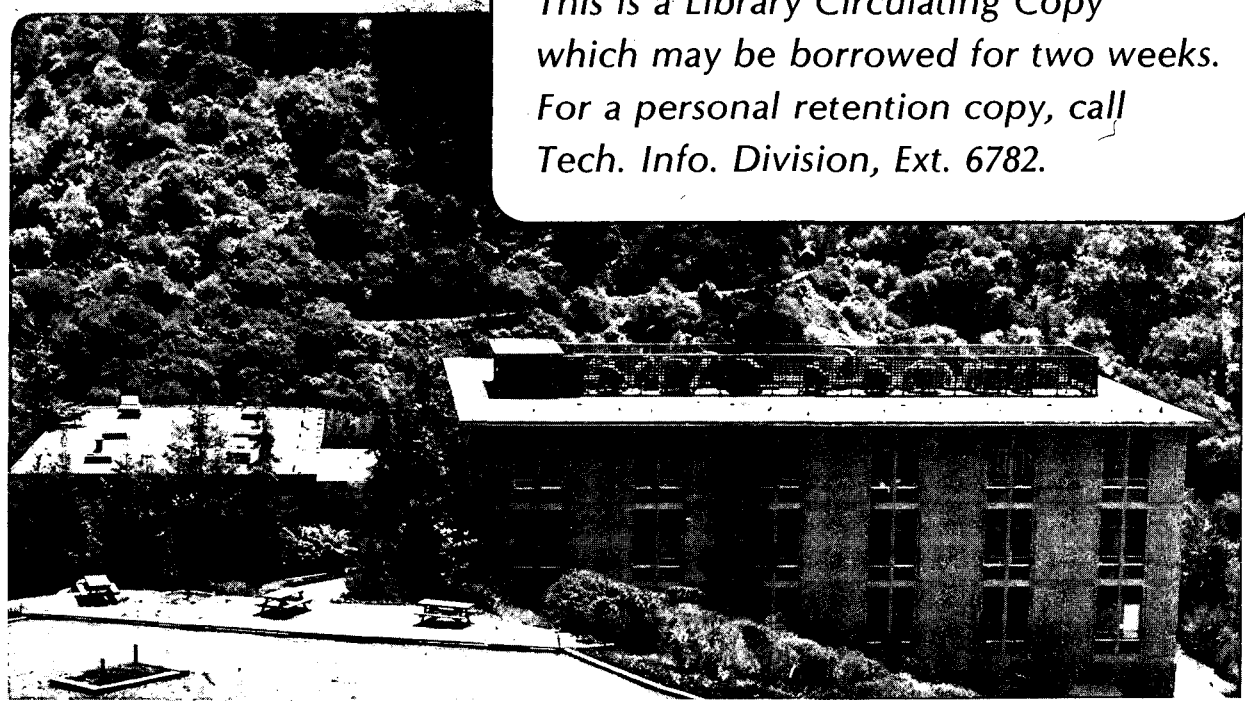## Materials & Molecular Research Division

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CONTAINING MOLECULES THAT DIFFER IN SIZE AND
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MOLECULAR THERMODYNAMICS OF FLUID MIXTURES CONTAINING MOLECULES THAT DIFFER IN SIZE AND POTENTIAL ENERGY

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MOLECULAR THERMODYNAMICS OF FLUID MIXTURES CONTAINING MOLECULES

THAT DIFFER IN SIZE AND POTENTIAL ENERGY

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ABSTRACT

Recent computer-simulation work by Shing and Gubbins for binary mixtures has shown that common semi-empirical models (van der Waals n-fluid models) are in error when the molecules of the two components differ appreciably in size; the error is most severe in the dilute region. While perturbation theories are much better they, like computer simulations, are not as yet useful for engineering work because of prohibitive computer requirements.

This work proposes an algebraic expression for the Helmholtz energy of a mixture which gives results in very good agreement with those reported by Shing and Gubbins. This expression, using the local-composition concept, is based on a simplified but realistic picture of a fluid mixture: short-range order and long-range disorder. The proposed expression uses the Mansoori-Carnahan-Starling-Leland equation for the contribution of repulsive forces. For the contribution of attractive forces, it uses a new expression based on not one, but several radii for the first-neighbor shell, one radius for each component.

With reasonable simplifications, the resulting equation for the Helmholtz energy indicates that van der Waals "constant" a is a strict quadratic function of mole fraction only at very low densities; at advanced densities, there are small deviations from the quadratic mixing rule. For practical calculations, computer requirements are nearly the same as those for conventional engineering models.

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Since van der Waals' work on fluid mixtures of nonelectrolytes about 90 years ago, many authors have proposed models for the equilibrium properties of such mixtures. Most of these models follow from phenomenological, semi-empirical considerations leading, on the one hand, to variations on the original van der Waals equation of state [e.g. Redlich-Kwong (1949), Soave (1972), Peng-Robinson (1976)] and on the other, to variations on van Laar's equation for activity coefficients [e.g. Scatchard-Hildebrand (Hildebrand,1929), Wilson (1964), NRTL (Renon and Prausnitz,1968), UNIQUAC (Abrams and Prausnitz, 1975)]. At the same time, more fundamental models based on perturbation theory [e.g. Barker-Henderson (1967), Chandler-Weeks-Anderson (1970), Mansoori-Leland (1970)] have been proposed. More recently, with the increasing availability of large computers, it has become possible to avoid models entirely and to calculate thermodynamic properties of mixtures by computer simulation using Monte Carlo or molecular-dynamics techniques (Mansoori and Haile, 1983).

While semi-empirical methods often give good agreement with experiment, such agreement is obtained only through several adjustable binary parameters which in many cases can represent only one property (usually chosen to be the Gibbs energy) while failing for another property (e.g. enthalpy or density). Computer simulations have indicated that currently available semi-empirical models are fundamentally incorrect for mixtures of different sized molecules, especially in the dilute region (Shing and Gubbins, 1983).

For engineering work, semi-empirical methods are nevertheless used because good pertubation theories and computer simulation require excessive amounts of computer time. For a typical calculation of a chemical potential in a mixture, computer requirements for the modern methods are two or three orders of magnitude larger than those for the older, semi-empirical

techniques. For iterative design of equipment for separation operations, where thermodynamic properties must be calculated over and over again, presently available theoretical models are not economical.

In this work we present an algebraic expression for the Helmholtz energy A of a simple mixture; other desired thermodynamic properties are readily obtained by standard differentiation. Because it is algebraic, computer requirements for our expression are nearly the same as those for common semi-empirical models.

Our expression for A is based on a realistic but simplified picture of fluid mixtures including those where the components differ appreciably in molecular size. Although relatively simple (as dictated by low computer requirements), our expression is in good agreement with computer-simulation results reported by Shing and Gubbins (1983).

As derived in the following sections, our expression for A is limited to simple mixtures (i.e. those containing spherical molecules that interact predominantly through dispersion forces), not only because that is the simplest case, but also because it is only for such mixtures that we can compare our results with presently-available computer-simulation and perturbation-theory results. Our expression for A for simple mixtures, however, serves as a useful basis for a modified expression, suitable for more complex mixtures.

Molecular-Thermodynamic Framework

We seek an expression for Helmholtz energy A as a function of volume V , temperature T and mole numbers n_1, $n_2 \ldots n_k$. Similar to our previous work (Hu et al., 1983), we begin with the pure fluids in the standard state

(°) and we then subject these fluids to three steps, as discussed below. This procedure gives us an expression of the form

$$A = A° + \Delta A_I + \Delta A_{II} + \Delta A_{III} \tag{1}$$

The standard state is the pure, ideal-gas fluid at system temperature T and 1 bar.

In the first step, we isothermally mix the pure ideal gases to form an ideal-gas mixture at system volume V,

$$\Delta A_I = \sum_{i=1}^{k} n_i RT \ln(n_i RT/V) \tag{2}$$

In the second step we isothermally and isometrically change the ideal-gas mixture to a hard-sphere mixture by inflating each molecule i to diameter σ_i . To find ΔA_{II} for this step, we use the expression of Mansoori-Carnahan-Starling-Leland (1971),

$$\Delta A_{II} = nRT\left[-3(1-\zeta_1+\zeta_2+\zeta_3)/2 + (3\zeta_2+2\zeta_3)(1-\xi)^{-1}\right. \tag{3}$$
$$\left. +3(1-\zeta_1-\zeta_2-\zeta_3/3)(1-\xi)^{-2}/2 + (\zeta_3-1)\ln(1-\xi)\right]$$

where

$$\xi = \sum_{i=1}^{k} \xi_i \qquad , \qquad \xi_i = \frac{\pi}{6}\frac{n_i N_{Av}}{V}\sigma_i^3$$

$$\zeta_1 = \sum_{j>i=1}^{k} \Delta_{ij}(\sigma_i+\sigma_j)(\sigma_i\sigma_j)^{-1/2}$$

$$\zeta_2 = \sum_{j>i=1}^{k} \Delta_{ij} \sum_{\ell=1}^{k} \left(\frac{\xi_\ell}{\xi}\right)\frac{(\sigma_i\sigma_j)^{1/2}}{\sigma_\ell}$$

$$\zeta_3 = \left[\sum_{i=1}^{k}(\xi_i/\xi)^{2/3}x_i^{1/3}\right]^3$$

$$\Delta_{ij} = \left[(\xi_i\xi_j)^{1/2}/\xi\right]\left[(\sigma_i-\sigma_j)^2/(\sigma_i\sigma_j)\right](x_i x_j)^{1/2}$$

Here N_{Av} is Avogadro's number. For comparison, it is useful to consider also expressions for ΔA_{II} based on van der Waals 1-, 2- and 3- fluid theories (Rowlinson and Swinton,1982); these are given in Appendix I.

In the third step, we "turn on" forces of intermolecular attraction and we allow for molecular softness. In other words, we charge the hard-sphere molecules with a potential. To obtain an algebraic expression for ΔA_{III} , we introduce a simplified but realistic physical picture for a dense fluid mixture as shown in Figure 1. For simplicity, that picture shows a binary mixture. However, the results derived below are given for a mixture of k components .

The essential idea in Figure 1 is that a dense fluid is described by short-range order and long-range disorder. Consider a molecule of species i which we arbitrarily select as our central molecule. This central molecule is surrounded by near neighbors that form a first coordination shell; some of these neighbors are of species i while others are of species j .

In the top section of Figure 1 we show only molecules of species i and in the middle section we show only molecules of species j , in addition to the central molecule. The lowest part of Figure 1 is the sum of the two other parts.

In the upper section, we see three neighbor molecules of species i in the first coordination shell. The center-to-center distance between the central molecule and any one of these three neighbors is r_{ii}^*. The distance between the center of the central molecule and the outer boundary of the shell formed by the neighbors is given by r_{ii}^{**}. These distances are shown by the dashed circles.

The middle section considers the dimensions of the first coordination shell formed by molecules j . The corresponding distances, again shown by the dashed circles, are r_{ji}^* and r_{ji}^{**} .

Consistent with this physical picture, we write

$$\Delta A_{III} = \Delta U_{III.SR} + \Delta U_{III.LR} - T\Delta S_{III.SR} \tag{4}$$

where SR designates the short-range (partially ordered) contribution and LR designates the long-range (random) contribution. Contribution ΔS_{IIILR} is zero.

To obtain an expression for ΔA_{III} we write

$$\Delta U_{III.SR} = \frac{1}{2} nN_{Av} \sum_{i=1}^{k} \sum_{j=1}^{k} x_i z_{(i)} x_{ji} \epsilon_{ji} (r_{ji}^*) \tag{5}$$

$$\Delta U_{III.LR} = \frac{1}{2} nN_{Av} \sum_{i=1}^{k} x_i \sum_{j=1}^{k} \int_{r_{ji}^{**}}^{\infty} \frac{nN_{Av}}{V} x_j \epsilon_{ji}(r) 4\pi r^2 dr \tag{6}$$

$$\Delta S_{III.SR} = \frac{1}{2} nR \sum_{i=1}^{k} \sum_{j=1}^{k} x_i z_{(i)} x_{ji} \ell n \frac{x_{ji.hs}}{x_{ji}} \tag{7}$$

In these equations, k is Boltzmann's constant, n is the total number of moles and x_{ji} is the local mole fraction of j around a central molecule i ; if no other subscript appears, x_{ji} refers to the real mixture while subscript hs refers to the hard-sphere mixture.

The coordination number $z_{(i)}$ is the total number of neighbor molecules in the first shell around a central molecule of species i . The potential ϵ_{ji} is evaluated at distance r_{ji}^* . In our calculations, reported below, we use the Lennard-Jones potential but some other potential could be used.

One of our main problems is to obtain an expression for $z_{(i)}'$.
To do so, we set $z_{(i)}$ equal to the product of three quantities:

$$z_{(i)} = \sum_{j=1}^{k} \left(\begin{array}{l} \text{volume of first} \\ \text{coordination shell} \\ \text{formed by mole-} \\ \text{cules } j \end{array} \right) \left(\begin{array}{l} \text{number} \\ \text{density of} \\ \text{molecules} \\ j \end{array} \right) \left(\begin{array}{l} \text{density-dependent} \\ \text{Boltzmann factor} \\ \text{for i-j pair} \end{array} \right) \quad (8)$$

The purpose of the Boltzmann factor is to obtain consistency with the
theory of fluids at low densities where the radial distribution function $g_{ji}(r)$
is given by $\exp[-\varepsilon_{ji}(r)/kT]$. The purpose of the Boltzmann factor in
Eq. (8) is to correct the overall density to obtain a local density. Our
density-dependent Boltzmann factor takes the semiempirical form

$$\exp[-\alpha\varepsilon_{ij}(r_{ij}{}^*)/kT]$$

where α depends on density ρ such that

as $\rho \to 0$, $\alpha \to \alpha_0$, where α_0 is a constant near unity

and, as $\rho \to$ dense fluid, α becomes very small, i.e. $0 \leq \alpha \ll \alpha_0$

At high densities, the distribution of nearest neighbors depends primarily
on molecular geometry (packing effect) and only weakly on the ratio of
potential to kinetic energy. Therefore, α tends to zero as density increases.

For mixtures of spherical molecules, simple geometric considerations
give the first and second factors on the right side of Equation (8).
We obtain

$$Z_{(i)} = \sum_{j=1}^{k} \frac{4}{3}\pi \left(r_{ji}^{**3} - \sigma_{ji}^{3} \right) \frac{n_j N_{Av}}{V} \exp\left[-\alpha\varepsilon_{ji}(r_{ji}{}^*)/kT\right] \quad (9)$$

For the dimensions of the first shell, we write

$$r_{ij}^{*} = K^{*}\sigma_{ij} \tag{10}$$

$$r_{ij}^{**} = K^{**}\sigma_{ij} \tag{11}$$

where K^{*} and K^{**} are universal constants. Since r_{ij}^{*} is very close to the first peak of the g_{ij} radial distribution, we expect K^{*} to be near 1.15. To obtain a good approximation for K^{**}, we use computer-simulation data for local mole fractions, kindly sent to us by Professor K. Gubbins (1983); these data indicate that, for hard-sphere mixtures, the local composition varies somewhat in the region (1.0-1.5) σ_{ij} ; however for larger distances, the local composition does not change. This suggests to us that K^{**} should be close to 1.5; comparison of calculated and "observed" (computer-simulation) Henry's constants, as discussed later, indicates that the optimum values are $K^{*} = 1.150$ and $K^{**} = 1.575$.

Local Compositions

To find local composition x_{ij} , we minimize ΔA_{III} (Eq. 4) according to

$$d(\Delta A_{III})_{T,V,\ \text{bulk composition}} = 0 \tag{12}$$

subject to two restraints. The first of these follows from normalization (material balance) while the second follows from a balance of ij pairs: the number of ij pairs must equal the number of ji pairs. For a binary mixture, $(i=1, j=2)$ these restraints can be written

$$x_{11} + x_{21} = x_{12} + x_{22} = 1$$

$$z_{(1)}\ x_1\ x_{21} = z_{(2)}\ x_2\ x_{12}$$

For a binary mixture, there is only one independent variable which we here choose to be x_{21} . Eq. (12) becomes

$$\left(\frac{\partial \Delta A_{\text{III}}}{\partial x_{21}} \right)_{T,V,x_1} = 0 \tag{13}$$

Substituting Eqs. (5,6,7) into Eq. (13), we obtain

$$x_{21} = \frac{Z_{(1)} x_1 + Z_{(2)} x_2 - \sqrt{(Z_{(1)} x_1 + Z_{(2)} x_2)^2 - 4 x_1 x_2 Z_{(1)} Z_{(2)} \tau_{12}}}{2 Z_{(1)} x_1 \tau_{12}} \tag{14}$$

where $\tau_{12} = 1 - exp\{[\mathcal{E}_{21}(r_{21}^{*}) + \mathcal{E}_{12}(r_{12}^{*}) - \mathcal{E}_{11}(r_{11}^{*}) - \mathcal{E}_{22}(r_{22}^{*})]/kT\} x_{11,hs} x_{22,hs}/(x_{12,hs} x_{21,hs})$

Extension to ternary and higher mixtures is briefly discussed in Appendix II.

When $\alpha = 1$, The local composition becomes

$$x_{21} = \frac{x_2 \sigma_{21}^3 exp[-\mathcal{E}_{21}(r_{21}^{*})/kT]}{x_1 \sigma_{11}^3 exp[-\mathcal{E}_{11}(r_{11}^{*})/kT] + x_2 \sigma_{21}^3 exp[-\mathcal{E}_{21}(r_{21}^{*})/kT]} \tag{15}$$

which is the same as that in Wilson's equation. Therefore, Wilson's local composition is, in a sense, "exact" at low densities, as previously pointed out by Chao and Leet (1983). However, at liquid-like densities, α is small compared to unity and therefore Wilson's equation overestimates nonrandomness, as pointed out previously (Nakanishi et al., 1982).

For hard-sphere mixtures $\varepsilon_{11} = \varepsilon_{22} = \varepsilon_{12} = 0$. In that case,

$$x_{21,hs} = x_2 \sigma_{21}^3 / (x_1 \sigma_{11}^3 + x_2 \sigma_{21}^3) \tag{16}$$

The equations given above provide an algebraic expression for Helmholtz energy A of a mixture containing spherical molecules that differ in size and potential energy. These equations were derived to provide a good

approximation to results obtained from computer simulation as shown in the next section.

Comparison of Results with Those from Monte Carlo and Perturbation-Theory Calculations

First, we consider dense binary mixtures whose molecules are of the same size. We use our algebraic equation to calculate local composition, residual chemical potential and Henry's constant over a wide range of ratio $\epsilon_{11}/\epsilon_{22}$. We compare our calculated results with those reported by Nakanishi (1982) and by Shing and Gubbins (1983), using Monte-Carlo computer simulation (MC) and perturbation theories (LHB = Leonard-Henderson Barker (1970); LL = Lee-Levesque (1973)). For characteristic energy ϵ_{12} , we use

$$\epsilon_{12} = (\epsilon_{11} \, \epsilon_{22})^{1/2}(1-k_{12}) \qquad (17)$$

For our present purposes we confine attention to dense liquid mixtures. For these we use $\alpha = 0$.

Figure 2 shows local compositions x_{11} or x_{22} for an equimolar mixture $(x_1 = x_2 = 1/2)$ where $\epsilon_{11} = \epsilon_{22}/2$; these local compositions are shown as a function of ϵ_{12} (lower abscissa) or k_{12} (upper abscissa). Our results agree well with those based on MC especially when we consider the probable uncertainty in the MC calculations.

The residual potential is shown in Figure 3 for the case $\epsilon_{11}/\epsilon_{22}=2$; $\epsilon_{22}/k = 100K$; $T = 120K$; $\rho\sigma_{22}^3 = 0.7$ and $\sigma_{11} = \sigma_{22} = 3.405\text{Å}$. Agreement is again good, probably within computational error.

The most sensitive test is provided by Henry's constant. Results are shown in Figure 4 for conditions similar to those in Figure 3 except that

$\epsilon_{12}/\epsilon_{22}$ is now the independent variable and $\epsilon_{12} = (\epsilon_{11} \epsilon_{22})^{1/2}$

with $k_{12} = 0$. Agreement with MC is excellent except for very small values

for $\epsilon_{12}/\epsilon_{22}$ which are almost never attained in real mixtures. However,

we are not convinced that the MC results are correct in the limit

$\epsilon_{12} \to 0$. This limit is for a mixture where $\epsilon_{11} = \epsilon_{12} = 0$; according

to MC, for this case, $H/\rho kT = 1$. But this corresponds to a zero residual

chemical potential for the solute. That, however, is not reasonable since

molecular diameters σ_1 and σ_2 are not zero: that is, we have a

hard-sphere solute dissolved in a real solvent. For such a solute, the residual

chemical potential should not vanish because the definition of residual refers

to an ideal gas, not a hard-sphere gas.

Figure 5 shows the variation of coordination numbers with the size ratio

$(\sigma_{12}/\sigma_{22})^3$. When the central molecule $i = 2$, the coordination

number z is about 12 when the size ratio goes to zero. For equal-sized molecules

z is near 10, and z is about 6 when the size ratio is somewhat larger than 2.

On the other hand, when central molecule $i = 1$ and the size ratio goes to

zero, the coordination number is very low because in that event the region

of local order is vanishingly small. But as the size ratio increases, the

coordination number rises to about 12.

Residual potentials are shown in Figures 6 and 7 for a variety of

conditions, as indicated. Figure 6 compares results obtained from this work

with those obtained for MC and from van der Waals n-fluid theories. For the

case shown, σ_{12} is only slightly larger than σ_{22}; for that case, one-fluid

van der Waals theory provides a fair approximation. Figure 7 provides

comparisons with MC and perturbation theories. It would be useful to make

comparisons for cases where $(\sigma_{12}/\sigma_{22})^3 > 1.5$ but, unfortunately, no MC

results are as yet available for such cases.

However, the effect of large differences in molecular size is shown dramatically in Figure 8 which shows Henry's constants calculated by MC, perturbation theories, and van der Waals theories. It is evident that the algebraic equation for Helmholtz energy A , described above, gives very good results. Figure 8 emphasizes that van der Waals n-fluid theories are very poor in the dilute region whenever there is a significant difference in molecular size.

Some calculations were also made for a few real mixtures of spherical (or nearly spherical) molecules. The results are shown in Table 1 ; pure-component parameters are shown in Appendix III. Results calculated with the method presented here are as good as those calculated from perturbation theory (Grundke et al.,1973).

Implications Toward a "Practical" Equation for Calculating Chemical Potentials in Mixtures

The results of this study lead to some useful suggestions toward a practical equation of the van der Waals form for the chemical potential of a component in a fluid mixture.

We find that, to an excellent approximation, the local mole fraction is

$$x_{ji} = \frac{x_j \sigma_{ji}^3 \exp[-\alpha \epsilon_{ji}(r_{ji}^*)/kT]}{\sum_{\ell=1}^{k} x_\ell \sigma_{\ell i}^3 \exp[-\alpha \epsilon_{\ell i}(r_{\ell i}^*)/kT]} \tag{18}$$

It can then be shown that

$$\Delta A_{III} = -n^2 a^H / V \tag{19}$$

where, for the mixture, van der Waals "constant" a^H is given by

$$a^H = \sum_{i=1}^{k} \sum_{j=1}^{k} x_i x_j a_{ij}^H \qquad (20)$$

and "constant" a_{ij}^H is related to reduced temperature kT/ϵ_{ij} by

$$a_{ij}^H = \epsilon_{ij} \sigma_{ij}^3 \left\{ 0.48 \left(\frac{\alpha \epsilon_{ij}}{kT} \right)^{-1} \left[exp\left(0.98 \frac{\alpha \epsilon_{ij}}{kT} \right) - 1 \right] + 0.18 \right\} \qquad (21)$$

where ϵ_{ij} is the Lennard-Jones energy parameter. It is important to emphasize that Equation (20) is not assumed but derived from our previously stated assumptions.

We use superscript H on "constant" a because we want to call attention to its definition which, as indicated by Eq. (19), is in terms of the Helmholtz energy. In the equation of state (EOS), "constant" a is somewhat different because it depends on density; the relation between a^H and a^{EOS} is found from $P=-(\partial A/\partial V)_{T,n_j}$; it is given by

$$a^{EOS} = a^H - V \left(\frac{\partial a^H}{\partial V} \right)_{T, n_j} \qquad (22)$$

If "constant" a depends only on temperature and composition, there is no difference between a^H and a^{EOS}. This is the case in popular semi-empirical equations (like Soave-Redlich-Kwong) but computer simulations clearly show that "constant" a depends on density in addition to temperature and composition.

The quadratic mixing rule indicated by Eq. (20) follows directly from our derivation, subject only to the use of approximate local mole fractions Eq. (18). However, since α depends on reduced density, "constant" a_{ij}^H (for i=j and for i ≠ j) also has a composition dependence; that dependence is not large (especially at high reduced density where $\alpha \ll 1$) but for highly

asymmetric mixtures $[\sigma_{ii} \gg \sigma_{jj}]$, it can be significant.

To illustrate, we fit the equations derived here to extensive experimental data for argon, we find that

$$\alpha = 0.60 - 0.58 \ (\rho\sigma^3)^{0.1865} \tag{23}$$

for the range $\rho\sigma^3 = 0$ to 0.8

We obtain an excellent fit of vapor pressures, liquid densities and second virial coefficients in the temperature range $85 < T < 1000$ K using the conventional Lennard-Jones parameters $\sigma = 3.27$ Å and $\epsilon/k = 109.4$ K.

Figure 9 shows reduced a^H as a function of reduced density $\rho\sigma^3$ and reduced temperature kT/ϵ .

For extension to mixtures, we <u>assume</u> that Eq. (23) can be generalized to

$$\alpha = 0.60 - 0.58 \ (\rho\bar{\sigma}^3)^{0.1865} \tag{24}$$

where

$$\bar{\sigma}^3 = \sum_{i=1}^{k} x_i \sigma_{ii}^3 \tag{25}$$

This definition of the reduced density for a mixture is based on the mean-density approximation discussed by Gonsalves and Leland (1978).

We can now illustrate the variation of a^H with composition. We consider a saturated, isothermal binary mixture at 150 K with $\epsilon_{11}/k = 100$ K ; $\sigma_{11} = 3.40$ Å ; $\epsilon_{22}/k = 200$ K and $\sigma_{22} = 4.40$ Å . For the mixture, we use $\sigma_{12} = (\sigma_{11} + \sigma_{22})/2$ and $\epsilon_{12} = (\epsilon_{11} \epsilon_{22})^{1/2}$. At saturation conditions, the change in reduced liquid density is small. As indicated on the right side of Figure 9, reduced a^H is not sensitive to reduced density in this region,

therefore we expect that, for the liquid mixture, a plot of a^H (for the mixture) versus x gives a curve very close to a parabola as given by "classical" van der Waals theory. Figure 10a shows the ratio of a^H to a^H(classical). We find that a^H (for the mixture), as calculated by the methods presented here, is closely approximated by the "classical" a^H when l_{12} is near -0.0375 .

However, the situation is qualitatively different for the saturated vapor. Here the reduced density changes appreciably with vapor composition. As indicated on the left side of Figure 9, reduced a^H varies significantly with reduced density in this region. In that case, we expect that a^H (for the mixture) is not a quadratic function of x for isothermal conditions at saturation. Figure 10b shows that there is no value of l_{12} which can make a^H(classical) agree with that calculated here.

To obtain the chemical potential, we combine Eq. (4) for ΔA_{III} with Eqs. (2,3) for the other contributions; for component i, chemical potential μ_i is found from

$$\mu_i = \left(\frac{\partial A}{\partial n_i} \right)_{T, V, n_j [i]} \tag{26}$$

When we perform this differentiation, we note that μ_i depends not only on a_{ii}^H and a_{jj}^H but also on the derivative of a_{ij}^H with composition (through the assumed dependence of α on reduced density). This dependence introduces an asymmetry in the chemical potential which one would not immediately expect from Eq. (20) which gives a^H (for the mixture) as a quadratic function of x .

From these considerations we conclude that the original van der Waals symmetric (quadratic) mixing rule for "constant" a^H gives a very good first approximation which, in any event, is exact at zero density. However, since coefficients $a_{ii}{}^H$, $a_{jj}{}^H$ and $a_{ij}{}^H$ are somewhat density-dependent, and since density depends on composition, we find that there are small deviations from van der Waals' symmetric mixing rule; at high densities, these are probably not significant unless there is a very large size difference. For liquid mixtures where the size difference is moderate, our study leads to a conclusion identical to that reached by Hoheisel and Kohler (1983): essentially all effects of size difference arise from the repulsive (Carnahan-Starling) contribution to the partition function. For such liquid mixtures, in the attractive contribution, it is proper to neglect effects of nonrandomness as suggested by the quadratic mixing rule for van der Waals "constant" a^H.

However, it appears that, for mixtures where σ_{11} and σ_{22} differ appreciably, a^H (for the mixture) is not a quadratic function of x at moderate densities, e.g. in the vapor phase along the saturation line, whenever that phase is well removed from the ideal-gas limit.

This conclusion follows from our assumption that, for a mixture, α is a function of reduced density with the mixing rule given by Eq. (25). This assumption requires more detailed study. We cannot now come to any definite conclusion because, unfortunately, computer simulations are currently available only at high reduced densities, not at intermediate reduced densities.

Conclusion

Our results indicate once more that the original van der Waals theory (which separates repulsive and attractive contributions to the Helmholtz energy) provides a remarkably good approximation, for pure fluids and for mixtures, provided that the reduced density is high. Our present position is that, for

relatively simple mixtures, we know what to do at the two ends of the density spectrum: small densities (where the second virial coefficient is sufficient) and high densities where the mean-field approximation is good. Our ignorance is in the intermediate-density region. Hopefully, computer-simulation workers will supply intermediate-density results in the not-too-distant future. Such results are necessary for further progress toward a reliable equation of state for fluid mixtures.

Our study shows that computer simulations are extremely useful for providing guidance in the development of algebraic equations for the Helmholtz-energy as a function of temperature, density and composition. While it is likely that, in some future generation, all desired thermodynamic properties will be generated by computer simulations alone, it is also likely that limitations in molecular theory and in computing capacity will make it necessary for many years to depend on algebraic expressions for practical calculations as required for chemical process design.

Appendix IV gives a convenient summary of our proposed "practical" equation of state at its present state of development.

Table 1

COMPARISON OF EXCESS PROPERTIES
AT $P = 0$ and $x_1 = 0.5$
G^E and H^E in $J \cdot mol^{-1}$ and V^E in $cm^3 \cdot mol^{-1}$

SYSTEM	PROPERTY	EXPERIMENTAL	PERTURBATION THEORY	THIS WORK
Ar + Kr (116 K)	k_{ij}	0.004	0.017	0.008
	G^E	84	84	84
	H^E	–	45	38
	V^E	−0.52	−0.47	−0.55
Kr + Xe (161 K)	k_{ij}		0.022	0.012
	G^E	115	115	115
	H^H	–	69	61
	V^E	−0.70	−0.50	−0.57
Ar + N$_2$ (84 K)	k_{ij}	0.001	−0.001	−0.006
	G^E	34	34	34
	H^E	51	35	39
	V^E	−0.18	−0.27	−0.32
Ar + CO (84 K)	k_{ij}	0.014	0.014	0.007
	G^E	57	57	57
	H^E	–	79	86
	V^E	0.10	−0.07	−0.09
Ar + CH$_4$ (91 K)	k_{ij}	0.012	0.028	0.020
	G^E	74	74	74
	H^E	103	89	90
	V^E	0.17	0.03	0.03
O$_2$ + Ar (84 K)	k_{ij}	0.018	0.013	0.010
	G^E	37	37	37
	H^E	60	52	56
	V^E	0.14	−.06	0.07
O$_2$ + N$_2$ (78 K)	k_{ij}		−0.002	−0.008
	G^E	42	42	42
	H^E	44	43	48
	V^E	−0.21	−0.26	−0.32
N$_2$ + CO (84 K)	k_{ij}	0.014	0.010	0.008
	G^E	23	23	23
	H^E	–	34	36
	V^E	0.13	0.07	0.07
CO + CH$_4$ (91 K)	k_{ij}	0.002	0.017	0.005
	G^E	115	115	115
	H^E	105	96	91
	V^E	−0.32	−0.48	−0.62

FIGURE CAPTIONS

Fig. 1 Short-range order and long-range randomness

Fig. 2 Variation of local compositions with $\epsilon_{12}/\epsilon_{11}$ and k_{12}.

$\epsilon_{22}=2\epsilon_{11}$, $\epsilon_{12}=\sqrt{\epsilon_{11}\epsilon_{22}}(1-k_{12})$, $\sqrt{\epsilon_{11}\epsilon_{22}}/k=119.8$ K,

$\sigma_{22}=3.405$ Å , $\rho\sigma^3=0.75$, T=120 K , $x_1=0.5$

MC: Monte Carlo results by Nakanishi et al. (1982)

Fig. 3 Reduced residual chemical potential for mixtures with energy ratio

$\epsilon_{11}/\epsilon_{22}= 2$, $\epsilon_{22}/k = 100$ K, T = 120 K , $\rho\sigma_{22}^3 = 0.7$,

$\sigma_{22} = 3.405$ Å .

MC: Monte Carlo method, LHB: Leonard-Henderson-Barker theory,

LL: Lee-Levesque method (Shing and Gubbins, 1983)

Fig. 4 Henry's constant (or residual chemical potential in infinite dilution,

$\mu_1^r(x_1=0)/kT = \ln(H_{1,2}/\rho kT)$) for mixtures with different energy

ratio $\epsilon_{12}/\epsilon_{22}$.

$\epsilon_{22}/K = 100$ K , T = 120 K , $\rho\sigma_{22}^3 = 0.7$, $\sigma_{22} = 3.405$ Å.

MC, LHB, LL: See caption of Fig. 3

Fig. 5 Variation of coordination numbers with size ratio for $x_1 = 0.5$.

$\epsilon_{22}/k = 100$ K , $\sigma_{22} = 3.405$ Å , T = 120 K , $\rho\sigma^3 = 0.7$

Fig. 6 Reduced residual chemical potential for mixtures with

($\sigma_{12}/ \sigma_{22})^3=1.5$, $\epsilon_{22}/k=100$ K, T=120 K, $\sigma_{22}=3.405$ Å,

$\rho\sigma^3=0.7$.

Comparison with Monte Carlo results (Shing and Gubbins, 1983) and

van der Waals n-fluid models

(a) for component 1   (b) for component 2

Fig. 7   Reduced residual chemical potential for mixtures with
$(\sigma_{12}/\sigma_{22})^3 = 1.5$, $\epsilon_{22}/k = 100$ K, $T = 120$ K, $\sigma_{22} = 3.405$ Å,
$\rho\sigma^3 = 0.7$ .Comparison with Monte Carlo results and Perturbation
theory. MC, LHB, LL: see caption of Fig. 3.

(a) for component 1   (b) for component 2

Fig. 8   Henry's constant (or residual chemical potential at infinite
dilution) for mixtures with different size ratio $(\sigma_{12}/\sigma_{22})^3$,
$\epsilon_{22}/k = 100$ K, $\sigma_{22} = 3.405$ Å, $T = 120$ K, $\rho\sigma^3 = 0.7$.
Comparison with (a) Monte Carlo results and van der Waals
n-fluid models (b) Perturbation theory.
MC, LHB, LL: see caption of Fig. 3

Fig. 9   Variation of reduced van der Waals constant $a_{ij}^{H}/(\epsilon_{ij}/k)/(N_{Av}\sigma_{ij}^3)$
with reduced density $\rho\sigma^3$ and reduced temperature kT/ϵ_{ij} .

Fig.10   Variation of reduced van der Waals constant $a_{ij}^{H}/(\epsilon_{ij}/k)/(N_{Av}\sigma_{ij}^3)$
with composition.

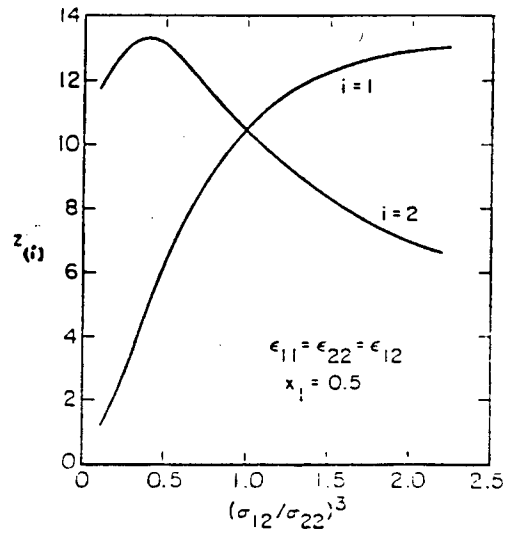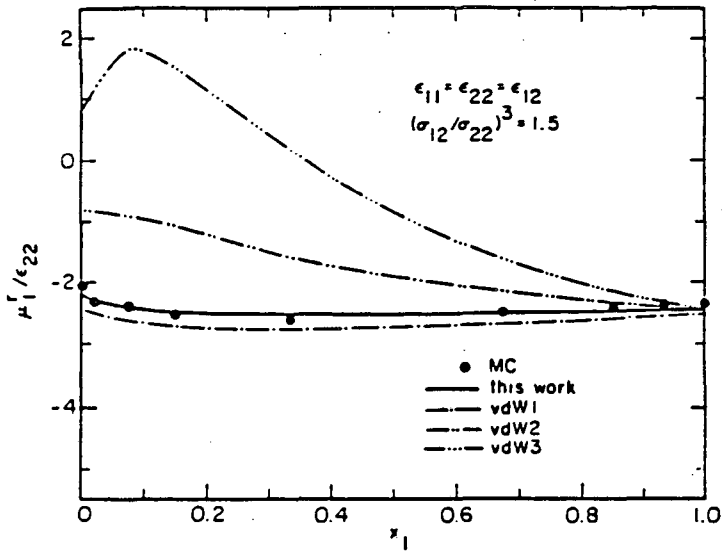(a) for saturated liquid   (b) for saturated vapor
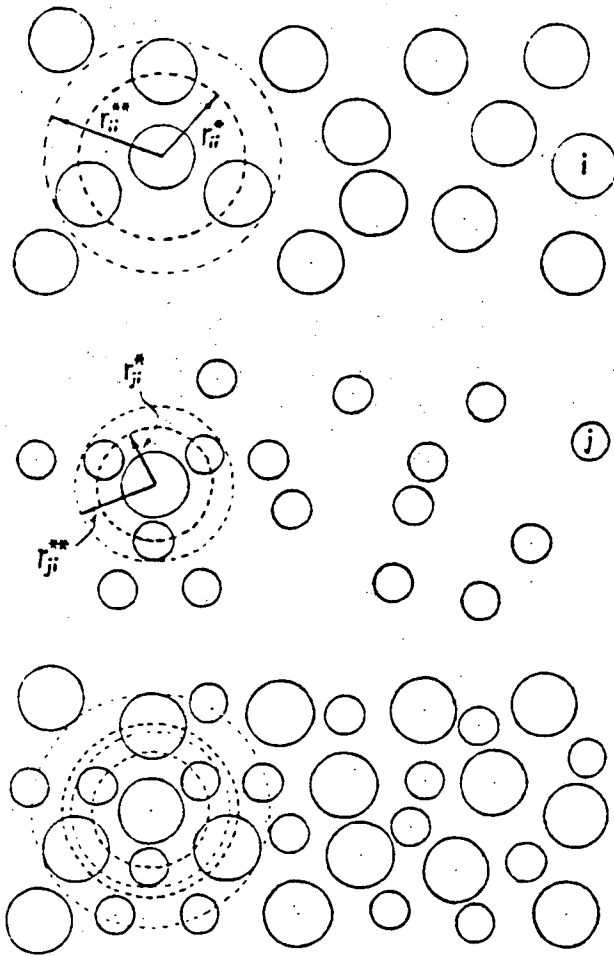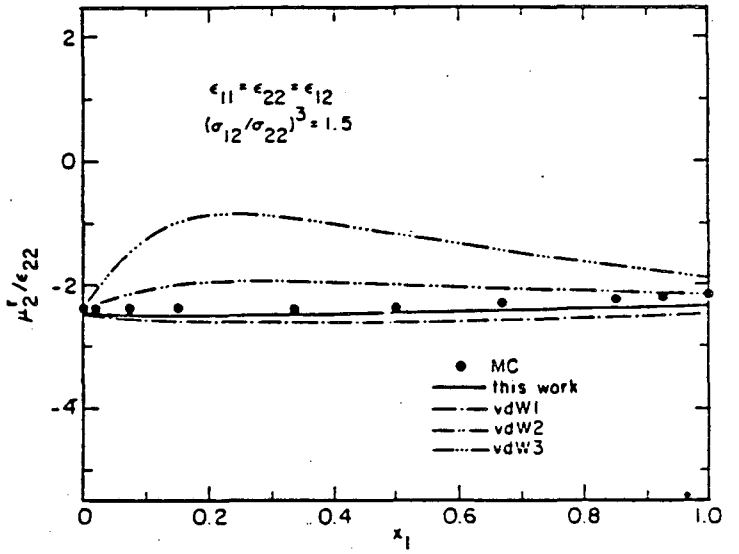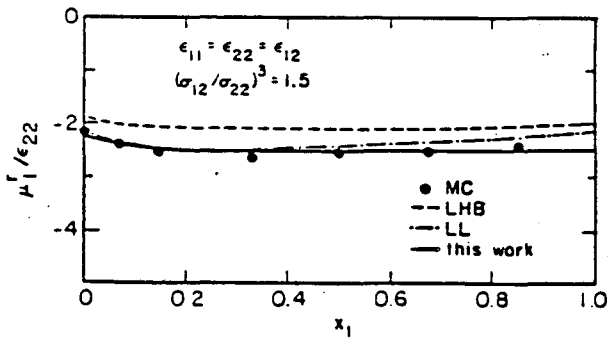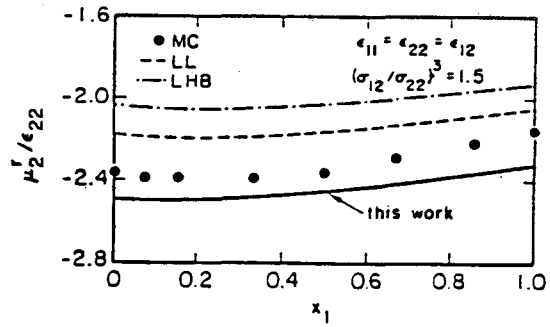
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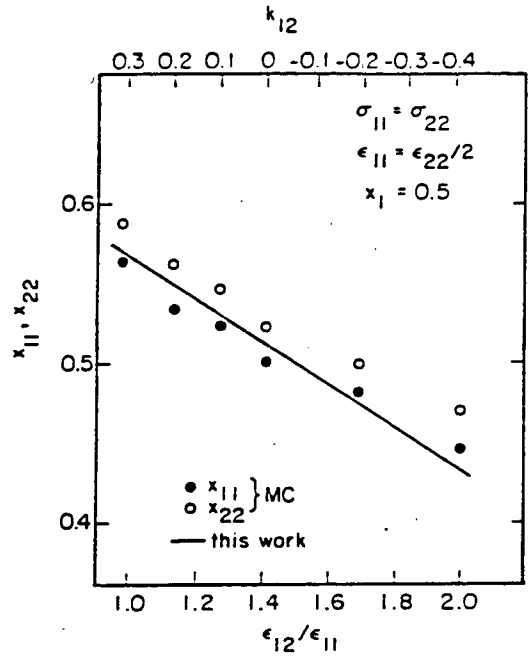
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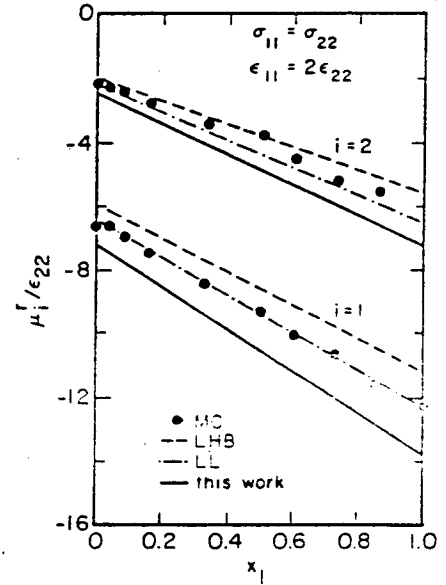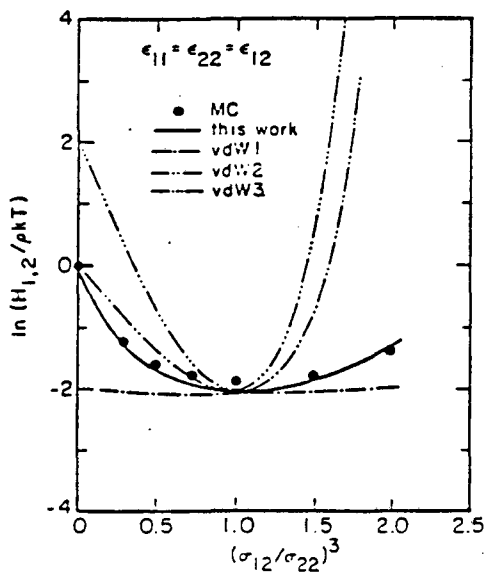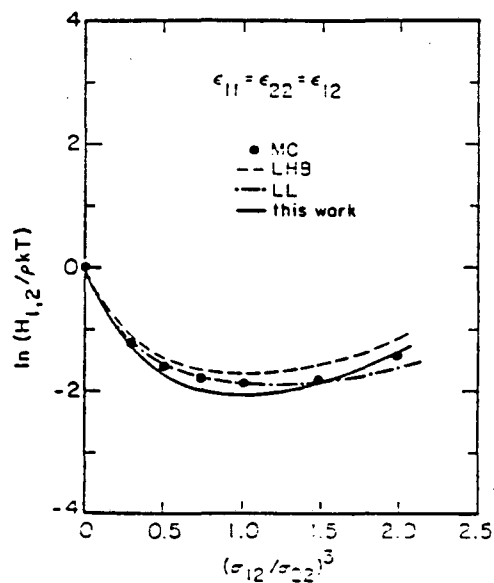
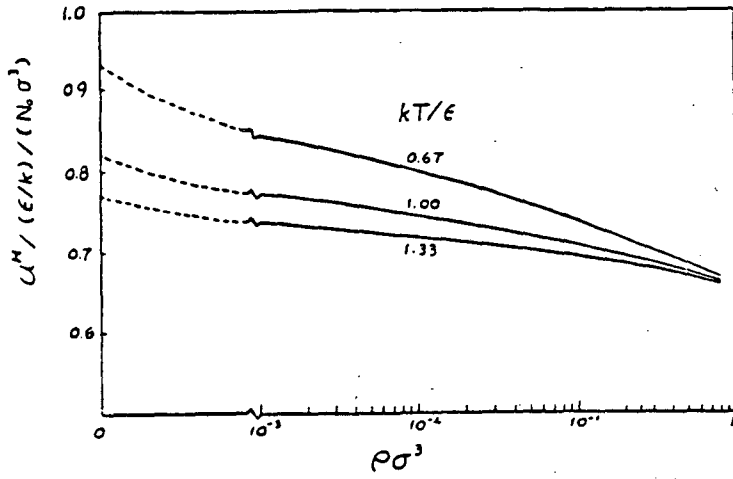

Fig. 3
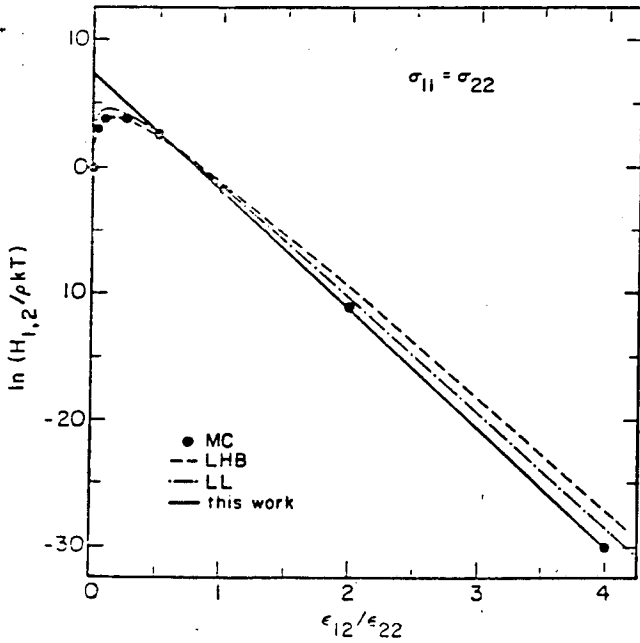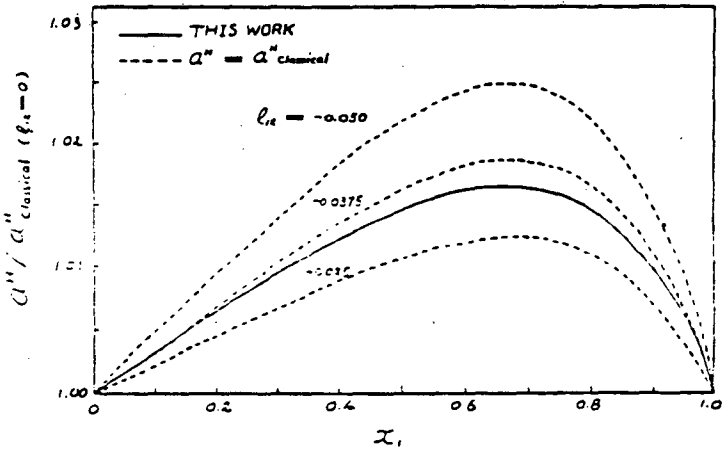

Fig. 4

Fig. 6 (a)
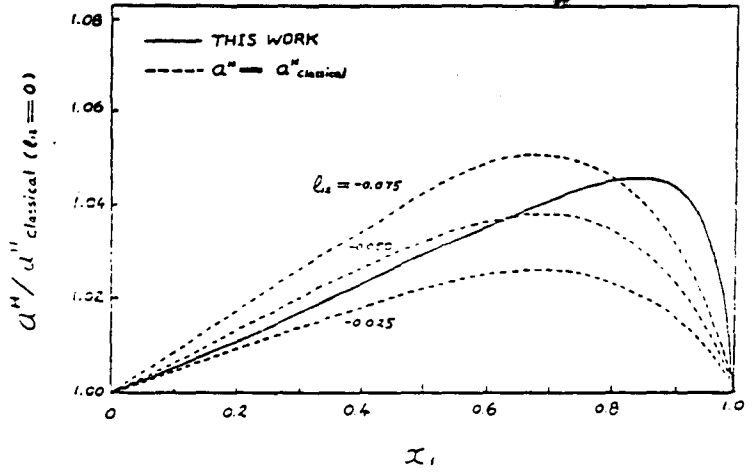
Fig. 6 (b)

Fig. 7 (a)

Fig. 7 (b)

Fig. 8 (a)

Fig. 8 (b)

Fig. 9

Fig. 10   (a)

Fig. 10   (b)

APPENDIX I ΔA_{II} from van der Waals n-fluid model:

(1) One-fluid

$$\Delta A_{II} = nRT\,(4\xi - 3\xi^2)/(1-\xi)^2 \qquad (I\text{-}1)$$

where

$$\xi = \frac{\pi}{6}\,\frac{nN_{Av}}{V}\,\bar{\sigma}^3$$

$$\bar{\sigma}^3 = \sum_{i=1}^{k}\sum_{j=1}^{k} x_i x_j \sigma_{ij}^3 \quad , \quad \sigma_{ij} = (\sigma_i + \sigma_j)/2$$

(2) Two-fluid

$$\Delta A_{II} = nRT \sum_{i=1}^{k} x_i\,(4\xi_i - 3\xi_i^2)/(1-\xi_i)^2 \qquad (I\text{-}2)$$

where

$$\xi_i = \frac{\pi}{6}\,\frac{nN_{Av}}{V}\,\bar{\sigma}_i^3$$

$$\bar{\sigma}_i^3 = \sum_{j=1}^{k} x_j \sigma_{ij}^3 \quad , \quad \sigma_{ij} = (\sigma_i + \sigma_j)/2$$

(3) Three-fluid

$$\Delta A_{II} = nRT \sum_{i=1}^{k}\sum_{j=1}^{k} x_i x_j\,(4\xi_{ij} - 3\xi_{ij}^2)/(1-\xi_{ij})^2 \quad (I\text{-}3)$$

where

$$\xi_{ij} = \frac{\pi}{6}\,\frac{nN_{Av}}{V}\,\sigma_{ij}^3 \quad , \quad \sigma_{ij} = (\sigma_i + \sigma_j)/2$$

APPENDIX II Calculation of local compositions for a multicomponent mixture

For a k-component system, the total number of local mole fractions

is k^2 . However, these are subject to two kinds of restraints. The

first follows from normalization represented by k equations of the form

$$\sum_{j=1}^{k} x_{ji} = 1 \qquad\qquad i = 1,\ldots,k \qquad\qquad \text{(II-1)}$$

The second follows from a balance of ij pairs, represented by k(k-1)/2

equations of the form

$$z_{(i)} \; x_i \; x_{ji} = z_{(j)} \; x_i \; x_{ij} \qquad i = 1, \ldots, k \; ; \; j = i + 1, \ldots, k \qquad \text{(II-2)}$$

The total number of independent variables is equal to $k^2-k-k(k-1)/2$

= k(k-1)/2.

Differentiating Helmholtz energy change ΔA_{III} with respect to

these k(k-1)/2 independent local mole fractions, we obtain k(k-1)/2 equations

$$\left(\frac{\partial \Delta A_{III}}{\partial x_{ji}} \right) = 0 \qquad\qquad \text{(II-3)}$$

When we solve these equations, we obtain k(k-1)/2 local mole fractions.

For a binary, an analytical expression for local mole fractions can be

easily obtained as is shown by Equation (14). For a multicomponent system,

especially when k>3, the situation becomes more difficult. In this case,

it is better to use simplified local mole fractions as shown in Equation

(18).

APPENDIX III Potential parameters for pure fluids

Fluid	$\epsilon/k/K$	$\sigma/\text{Å}$
Argon	119.8	3.405
Krypton	167.0	3.633
Methane	152.0	3.74
Nitrogen	101.3	3.612
Oxygen	119.8	3.36
Carbon monoxide	104.2	3.62

APPENDIX IV Summary of "practical" equation of state at its present

stage of development

The equation of state is found from

$$P = -\left(\frac{\partial A}{\partial V}\right)_{T,\text{all } n}$$

where A is given by Equation (1); ΔA_I is given by Equation (2) and ΔA_{II}

is given by Equation (3).

For ΔA_{III} use Equations (19), (20), (21), (24) and (25).

The chemical potential μ is given by Equation (26). An expression for

the contribution of ΔA_{II} to μ is found in "Applied Statistical Mechanics"

by T. M. Reed and K. E. Gubbins, page 258. However, the equation given there

is in a form significantly different from that used here. Interested readers

can obtain a copy of our expression by writing to one of the authors.

List of symbols

A	Helmholtz energy
a	van der Waals "constant"
G	Gibbs energy
H	Enthalpy
$H_{1,2}$	Henry's constant of 1 in 2
K^*, K^{**}	constants
k	Boltzmann's constant
k_{12}	binary parameter
l_{12}	binary parameter
LHB	Leonard-Henderson-Barker
LL	Lee-Levesque
MC	Monte Carlo
N_{Av}	Avogadro's number
n	number of moles
P	pressure
r	intermolecular distance
r^*	location of molecules in first coordination shell
r^{**}	outer radius of first coordination shell
R	gas constant
S	Entropy
T	temperature
V	volume
x	mole fraction
$x_{12}, x_{21}, \ldots$	local mole fraction
$z_{(i)}$	coordination number for molecule i

α	density dependent constant
ε	potential energy
ϵ	energy parameter
μ	chemical potential
σ	size parameter
ρ	number density

Superscripts

E	excess properties
EOS	derived from equation of state
H	derived from Helmholtz energy expression
r	residual
°	standard state

Subscripts

hs	hard sphere
LR	long range
SR	short range
$1,2,\ldots,i,j,k$	component index
I,II,III	step in model construction

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