Computer Simulation of Molecular Fluid Mixtures: Results and Two New One-Fluid Models

Gary M. Sowers and Stanley I. Sandler
Dept. of Chemical Engineering, University of Delaware, Newark, DE 19716

Monte Carlo simulation results for binary mixtures of diatomic molecules with spheres, diatomic molecules of different bond lengths, and triatomic molecules with spheres, all interacting with the site-site Lennard-Jones potential, were obtained at three different volume ratios and a range of densities and compositions. We report the configurational internal energy of the mixture and of the 1-1, 1-2 and 2-2 pairs, and the compressibility factors at 195 state points. The site-site correlation functions also computed are available from the authors. Equations of state derived previously (Sowers and Sandler, 1991, 1992) for pure site-site Lennard-Jones fluids from a combination of perturbation theory and a three-parameter corresponding states principle are extended to mixtures using simple one-fluid mixing rules. These simple mixing rules allow us to make satisfactory predictions of the compressibilities computed from simulation without the use of binary interaction parameters. We also show that the effect of composition on the perturbation free energy $\beta A_p/N$ *not accounted for by one-fluid mixing rules is quite small, and therefore a more complicated mixing rule is not necessary in our equations of state for the mixtures studied.*

Introduction

In previous work (Sowers and Sandler, 1991, 1992), we presented new simulation results for pure fluids of nonspherical molecules, and two new analytic equations of state that correlate the simulation data with good accuracy. These equations are based on a three-parameter corresponding states principle similar to that used in perturbed-hard-chain theory. Here, we consider binary mixtures of nonspherical molecules that differ both in size and shape. Because only a limited quantity of simulation results for mixtures of molecular fluids has been published in the literature, we present new simulation data for mixtures of spheres with diatomics and linear triatomics, and for mixtures of diatomics with different bond lengths, all interacting with the site-site Lennard-Jones potential. In each mixture, the ratio of the molecular volumes of the two species varied from one to six, and results were obtained for the compressibility $Z=P/\rho kT$ and configurational internal energy $E-E^{\text{ideal gas}}$ of the mixture over a wide range of densities. Also, we use one-fluid mixing rules in our equations of state to make predictions for the model fluids and evaluate different mixing rules by comparing the predictions with simulation data. We find that the compressibility can be predicted with an average error of approximately 5% using one-fluid mixing rules with no binary interaction parameters. By dividing the configurational Helmholtz free energy into reference and perturbation parts and directly calculating the value of the perturbation contribution using the simulation results, we show that for the mixtures studied here the deviation of the perturbation free energy from that predicted using a one-fluid model is quite small.

Before proceeding further, we briefly review the available simulation and theoretical results for mixtures of nonspherical molecules. Binary mixtures of hard diatomics were studied using Monte Carlo simulation by Aviram and Tildesley (1978) and Wojcik and Gubbins (1983). Mixtures of hard spheres with hard diatomics and linear hard triatomics were simulated by Nezbeda et al. (1985). This study was extended to mixtures of nonlinear hard triatomics with several different types of molecules by Vortler et al. (1989). These simulations of mixtures of nonspherical hard molecules showed that the compressibility of the mixture is influenced substantially by the

---

Present address of G. M. Sowers: Dow Chemical Company, Plaquemine, LA 70765.

shape of the molecules. One of the earliest simulation studies of binary mixtures of nonspherical molecules interacting with site-site Lennard-Jones potentials was done by Tildesley et al. (1983), but only two state points for diatomic/diatomic mixtures were presented. A study of argon/nitrogen and argon/oxygen mixtures was published by Gupta and Coon (1986). In later work, Gupta (1986) presented results for the excess properties of equimolar mixtures of nitrogen and oxygen. Fincham et al. (1986, 1987) computed excess properties of model CO_2/C_2H_6 mixtures at 60 state points. Poor agreement with experimental data for real CO_2/C_2H_6 mixtures was found, presumably due to uncertainty in the intermolecular potentials and a relatively large statistical error in the simulation results. Massobrio et al. (1988) presented results for the configuration energy of diatomic/sphere and diatomic/tetratomic mixtures at 30 state points, and Mittag et al. (1989) have published simulation results for model CCl_4/CS_2 mixtures.

With the exception of the work by Massobrio et al., the goal of most of these simulations was to determine potential parameters that produce the best agreement between the simulation data and the experimental data for real mixtures. The simulation results were obtained at only a few state points in a limited range of composition and density. Since it is difficult to judge the accuracy of any theory of mixtures based on such limited simulation data, we present new simulation results over a wider range of density and composition. Our results provide a more comprehensive database for testing theories of molecular fluids mixtures than was previously available.

Perturbation theories have been successfully applied to mixtures of small, nonspherical molecules. The Lee-Levesque perturbation theory (Lee and Levesque, 1973) for mixtures of monatomic Lennard-Jones fluids was extended to mixtures of nonspherical molecules by Fischer and Lago (1983). The Leonard-Barker-Henderson theory (1970) was extended to mixtures of nonspherical molecules by Encisco and Lombardero (1981). The excess properties of binary mixtures of spheres and diatomics (Bohn et al., 1985), diatomics with different bond lengths (Bohn et al., 1986), and spherical and tetrahedral molecules (Bohn et al., 1988) have also been computed using perturbation theory. These theories give reasonably good agreement with simulation data and measured thermodynamic properties, but are difficult to implement and use, especially to compute phase diagrams. None of this work suggested improved mixing rules for equations of state.

A simpler alternative to perturbation theory is the conformal solution theory proposed by Longuet-Higgins (1951). Conformal solution theory is applicable to mixtures in which the interaction potential between a species i molecule and a species j molecule is of the form:

$$u_{ij}=\epsilon_{ij}\Gamma\left(\frac{r}{\sigma_{ij}}\right) \tag{1}$$

where ϵ_{ij} and σ_{ij} are characteristic energy and length parameters in the pair potential $\Gamma(r/\sigma_{ij})$. The most commonly used conformal solution mixing rules are the van der Waals one-fluid (vdW1) mixing rules, given by:

$$\epsilon_x\sigma_x^3=\sum_i\sum_j x_ix_j\epsilon_{ij}\sigma_{ij}^3 \tag{2}$$

and

$$\sigma_x^3=\sum_i\sum_j x_ix_j\sigma_{ij}^3 \tag{3}$$

discussed in detail by Leland et al. (1968). In this model, the mixture radial distribution functions $g_{ij}(r/\sigma_{ij})$ are assumed to be equal to the radial distribution function $g_0(r/\sigma_x)$ of a pure fluid with potential parameters ϵ_x and σ_x, evaluated at reduced temperature kT/ϵ_x and reduced density $\rho\sigma_x^3$. The compressibility of the mixture is equal to that of a hypothetical pure fluid whose potential parameters are given by Eqs. 2 and 3.

As written, the vdW1 mixing rules are strictly applicable only to mixtures of monatomic fluids. Waisman et al. (1984) proposed using Eqs. 2 and 3 for the size and energy parameters in mixtures of Lennard-Jones diatomic molecules, and a linear mole fraction average of the bond lengths ℓ_1 and ℓ_2 to obtain the bond length of a molecule in the reference fluid. Another one-fluid theory has been proposed by Deiters (1989) in which the exponent of σ_{ij} in Eqs. 2 and 3 is not an integer. When Deiters applied this model to real binary mixtures he also treated ϵ_{12} as an adjustable parameter, so it is difficult to judge whether his mixing rules offer any advantages over vdW1. Haile and Lee (1988) proposed a two-fluid theory based on the definition of a group-group distribution function that predicts their simulation data for the configurational energy of diatomic/sphere and tetratomic/sphere mixtures with reasonable accuracy.

Mixtures simulated in this work

Because simulation data for molecular fluid mixtures are relatively scarce, we have simulated three different mixtures at three volume ratios and a range of densities and compositions. The purpose of the simulations was to accumulate a database of results large enough to reach definite conclusions about mixing rules in our equations of state. We simulated binary mixtures of spheres and homonuclear diatomics, binary mixtures of homonuclear diatomics of different bond lengths, and binary mixtures of spheres and linear symmetric triatomics. The site-site Lennard-Jones potential

$$u_{ij}^{\alpha\gamma}=4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}^{\alpha\gamma}}\right)^{12}-\left(\frac{\sigma_{ij}}{r_{ij}^{\alpha\gamma}}\right)^{6}\right] \tag{4}$$

was used in all the simulations. In Eq. 4, we use $u_{ij}^{\alpha\gamma}$ to denote the interaction energy between an α-site on a molecule of species i and a γ-site on a molecule of species j. The potential parameters for interactions between two molecules of the same species are ϵ_{ii} and σ_{ii}, and the cross parameters for interactions between different species are given by:

$$\epsilon_{ij}=\sqrt{\epsilon_{ii}\epsilon_{jj}} \tag{5}$$

and

$$\sigma_{ij}=\frac{\sigma_{ii}+\sigma_{jj}}{2}. \tag{6}$$

All of the molecules in the mixtures we simulated were sym-

Table 1. Binary Mixtures Simulated in This Work Using the Monte Carlo Method*

Component 1—Diatomic, $\ell = 0.67\sigma_{11}$ Component 2—Sphere	σ_{11} Å
Case I, $V_1 = 6.25V_2$	5.1
Case II, $V_1 = V_2$	2.7673
Case III, $\sigma_{11} = \sigma_{22}$	3.4
Component 1—Diatomic, $\ell = 0.67\sigma_{11}$ Component 2—Diatomic, $\ell = 0.3292\sigma_{22}$	σ_{11} Å
Case I, $V_1 = 6.25V_2$	5.78
Case II, $V_1 = V_2$	3.1508
Case III, $\sigma_{11} = \sigma_{22}$	3.4
Component 1—Triatomic, $\ell = 0.67\sigma_{11}$ Component 2—Sphere	σ_{11} Å
Case I, $V_1 = 6.25V_2$	4.42
Case II, $V_1 = V_2$	2.4389
Case III, $\sigma_{11} = \sigma_{22}$	3.4

* In all cases, $\sigma_{22} = 3.4$ angstroms and $\epsilon_{11}/k = \epsilon_{22}/k = 120$ K. The molecular volumes of both species, V_1 and V_2, were computed using the formulas given by Sowers and Sandler (1992).

metric. The energy parameters ϵ_{11}/k and ϵ_{22}/k were both set equal to 120 K. The value of the size parameter of species 2, σ_{22}, was set equal to 3.4 Å, and in all cases a species 2 molecule was equal in size or smaller than a species 1 molecule.

Descriptions of the mixtures simulated are given in Table 1. Three different cases were studied for each mixture. For Case I mixtures, the ratio of molecular volumes V_1 and V_2 of the two species was fixed at $V_1/V_2 = 6.25$, and the size parameter of species 1, σ_{11}, was calculated from this ratio. For Case II mixtures, the molecular volumes of the two species were equal; for Case III mixtures, the size parameters σ_{11} and σ_{22} were equal. The critical properties of these mixtures were estimated using a linear mole fraction average of the critical properties of the pure species taken from reference 2. For all Case I mixtures, simulations were done at two different temperatures: $T/T_c = 1.1$ and 1.3, where T_c is the estimated critical temperature of the mixture. For Case II and III mixtures, simulations were done at one temperature, $T/T_c = 1.1$. For all three cases, simulation runs were done at four to eight densities in the range $0 < \rho \leq 3\rho_c$, where ρ_c is the estimated critical density of the mixture. The total number of molecules in the mixture was fixed at 112, and the three mole fractions were studied: $N_1/N = 32/112$, $56/112$, and $80/112$, or approximately $x_1 = 0.286$, 0.5, and 0.714. Results for the compressibility and configurational internal energy of the mixture and for each ij pair are tabulated in the Appendix. The site-site and center-of-mass distribution functions were also computed and stored in a database available from the authors.

Theory

The goal of this work was to test equations of state for molecular fluid mixtures using simple one-fluid mixing rules. We have used the equations of state derived previously for pure fluids from a perturbation expansion of the configurational Helmholtz free energy. To extend these equations to mixtures we consider a mixture of ν species, in which the molecules interact with site-site potentials $u_{ij}^{\alpha\gamma}$. The site-site potential can be divided into reference and perturbation parts according to:

$$u_{ij}^{\alpha\gamma}(r_{ij}^{\alpha\gamma}) = u_{0_{ij}}^{\alpha\gamma}(r_{ij}^{\alpha\gamma}) + \lambda w_{ij}^{\alpha\gamma}(r_{ij}^{\alpha\gamma}) \tag{7}$$

where $u_{0_{ij}}^{\alpha\gamma}$ is the site-site pair potential of the reference system, $w_{ij}^{\alpha\gamma}$ is the site-site perturbation potential, and λ is a perturbation parameter between 0 and 1. There are m_i sites on a molecule of species i. Using this division of the potential, the configurational Helmholtz free energy of a mixture of ν components is (Encisco and Lombardero, 1981):

$$\frac{\beta A^{\text{CONF}}}{N} = \frac{\beta A_0^{\text{CONF}}}{N} + 2\pi\beta\rho \sum_{i=1}^{\nu}\sum_{j=1}^{\nu} x_i x_j \times \int_0^1 \int_0^\infty \sum_{\alpha=1}^{m_i}\sum_{\gamma=1}^{m_j} w_{ij}^{\alpha\gamma}(r_{ij}^{\alpha\gamma}) g_{ij}^{\alpha\gamma}(r_{ij}^{\alpha\gamma};\lambda) r_{ij}^{\alpha\gamma 2} dr_{ij}^{\alpha\gamma} d\lambda \tag{8}$$

$$= \frac{\beta A_0^{\text{CONF}}}{N} + \frac{\beta A_p}{N}. \tag{9}$$

The second term on the righthand side of Eq. 8, $\beta A_p/N$, is the perturbation free energy. The configurational Helmholtz free energy can be computed to first order from Eq. 8 by expanding the perturbation free energy about the point $\lambda = 0$ and retaining only the first term, and using an equation of state for the free energy of the reference system together with simulation data or the solution of an integral equation for $g_{ij}^{\alpha\gamma}(\lambda = 0)$, the site-site distribution functions of the reference system.

The numerical computation of the configurational Helmholtz free energy from the perturbation expansion, however, does not lead to a simple, analytic equation of state. In previous work, we computed the perturbation free energy of a monatomic Lennard-Jones fluid by integrating the relation:

$$\frac{\beta A_p}{N} = \int_0^\rho \frac{Z - Z_0}{\rho'} d\rho' \tag{10}$$

where Z_0 is the compressibility of the reference system computed from an equation of state, and Z is the compressibility of the Lennard-Jones fluid computed from simulation. We developed two models for the perturbation free energy based on a hard sphere and a square well reference system, respectively. These models were extended to molecular fluids using a three-parameter corresponding states principle similar to that used in perturbed-hard-chain theory (Beret and Prausnitz, 1975; Donohue and Prausnitz, 1978).

In perturbed-hard-chain theory, the configurational Helmholtz free energy $\beta A^{\text{CONF}}/N$ of a molecular fluid at temperature T and density ρ is:

$$\frac{\beta A^{\text{CONF}}(T,\rho)}{N} = c\frac{\beta A_m^{\text{CONF}}(T^*,\rho^*)}{N} \tag{11}$$

where $\beta A_m^{\text{CONF}}/N$ is the configurational Helmholtz free energy of a monatomic fluid with potential parameters $\epsilon q/c$ and $r\sigma^3$, evaluated at reduced temperature $T^* = ckT/\epsilon q$ and reduced density $\rho^* = \rho r\sigma^3$. There are three corresponding states parameters: c, q, and r. This corresponding states principle can also be applied to the reference and perturbation free energies separately:

$$\frac{\beta A_0^{\mathrm{CONF}}}{N} = c\frac{\beta A_{0_m}^{\mathrm{CONF}}}{N} \tag{12}$$

$$\frac{\beta A_p}{N} = c\frac{\beta A_{p_m}}{N} \tag{13}$$

where $\beta A_{0_m}^{\mathrm{CONF}}/N$ and $\beta A_{p_m}/N$ are the reference and perturbation free energies of a monatomic fluid evaluated at T^* and ρ^*. The most straightforward way to apply this corresponding states principle to mixtures is to use a one-fluid theory, in which the configurational Helmholtz free energy of a mixture of nonspherical molecules is given by:

$$\frac{\beta A^{\mathrm{CONF}}}{N}(T, \rho) = c_x\frac{\beta A_m^{\mathrm{CONF}}}{N}(T^*, \rho^*) \tag{14}$$

where $\beta A_m^{\mathrm{CONF}}/N$ is the configurational Helmholtz free energy of a mixture of monatomic fluids evaluated at the reduced temperature $T^* = (ckT/\epsilon q)_x$ and reduced density $\rho(r\sigma^3)_x$ of the mixture. As in perturbed-hard-chain theory, we will use a one-fluid mixing rule for c_x,

$$c_x = \sum_i x_i c_i \tag{15}$$

where c_i is the c parameter for pure species i. We will investigate two different mixing rules for $(ckT/\epsilon q)_x$ and $\rho(r\sigma^3)_x$: the mixing rule used originally in perturbed-hard-chain theory, and a new mixing rule based on vdW1 theory.

Equations of State for the Reference System

From Eq. 9 we see that the configurational Helmholtz free energy, and therefore the equation of state, can be divided into two parts: the reference system free energy and the perturbation free energy, given by Eqs. 12 and 13. Models for both are required to construct the complete equation of state. We will use a mixture of fused-hard-sphere molecules as the reference system. Equation 14 implies that the compressibility of a mixture of fused-hard-spheres, denoted by Z_0, is given by:

$$Z_0(\eta) - 1 = c_x[Z_m(\eta_m) - 1] \tag{16}$$

where $\eta = \rho\Sigma_i x_i V_i$ is packing fraction of the fused-hard-sphere mixture, and V_i is the volume of a molecule of species i. The compressibility Z_m of the hard sphere mixture is evaluated at a packing fraction η_m, where $\eta_m = \rho\Sigma_i x_i (rd^3)_{ii}$ and d_{ii} is the diameter of a constituent atom in a reference system molecule. If the Carnahan-Starling equation of state (Carnahan and Starling, 1969) with a one-fluid mixing rule for η_m is used to compute Z_m, the compressibility of the fused-hard-sphere reference system is:

$$Z_0 - 1 = c_x\left[\frac{1 + \eta_m + \eta_m^2 - \eta_m^3}{(1 - \eta_m)^3} - 1\right]. \tag{17}$$

Since this is a combination of the Carnahan-Starling equation of state with a one-fluid mixing rule, together with a three-parameter corresponding states principle, we will refer to this equation of state as the CS1/CSP equation. This equation is used as the reference term in most perturbed-hard-chain equations of state.

The Boublík-Mansoori (Boublík, 1970; Mansoori et al., 1971) equation is more accurate for hard-sphere mixtures than the Carnahan-Starling equation with a one-fluid mixing rule. Therefore, we propose an alternative to the CS1/CSP equation that has not been previously tested for mixtures of fused-hard-sphere molecules. We use the Boublík-Mansoori (BM) equation of state to compute Z_m, rather than the Carnahan-Starling equation. The resulting corresponding states equation for the compressibility of a fused-hard-sphere mixture is:

$$Z_0 - 1 = c_x\left[\frac{1 + A\eta_m + B\eta_m^2 - C\eta_m^3}{(1 - \eta_m)^3} - 1\right] \tag{18}$$

where

$$A = \frac{3ED}{F} - 2 \quad B = \frac{3E^3}{F^2} - \frac{3ED}{F} + 1 \tag{19}$$

$$C = \frac{E^3}{F^2} \quad D = \sum_i x_i r_i^{1/3} d_{ii} \tag{20}$$

$$E = \sum_i x_i r_i^{2/3} d_{ii}^2 \quad F = \sum_i x_i r_i d_{ii}^3 \tag{21}$$

$$\eta_m = \frac{\pi}{6}\rho F. \tag{22}$$

We will refer to this equation of state as the BM/CSP equation.

One-Fluid Models and Comparison with Simulation Results

The BM/CSP and the CS1/CSP reference system equations of state must be combined with a model for the perturbation free energy $\beta A_p/N$ to obtain complete equations for the configurational Helmholtz free energy. Two models for the perturbation free energy that were developed previously for pure molecular fluids will be considered here. These two models are discussed in detail in Sowers and Sandler (1991, 1992), including comparisons of the models with simulation data for pure fluids. We use one-fluid mixing rules exclusively to extend the models to mixtures, and then test the mixing rules by comparison with our simulation data for molecular fluid mixtures. There are three principal goals. First, we would like to know if one-fluid mixing rules allow us to predict the compressibilities obtained from simulation with good accuracy, or if there is evidence that more complicated density-dependent mixing rules are required. Second, we would like to know which of the two reference system equations, BM/CSP or CS1/CSP, performs best in a complete equation of state for mixtures of soft nonspherical molecules. Only the latter has been used in existing perturbed-hard-chain equations of state. Third, we will test both the one-fluid mixing rule that is used in most perturbed-hard-chain equations of state and a new one-fluid mixing rule that is similar to the vdW1 theory for monatomic fluids, as we would like to know which of these two is better. Our criterion will be the magnitude of the deviation of the equation of state and its mixing rule from the simulation data.

Table 2. Values of the Parameters a_1-a_3 and b_1-b_3 Used in Eqs. 26, 36 and 37

Eq. 26	Eqs. 36 and 37
$a_1 = 8.042$	$b_1 = -9.459$
$a_2 = 0.731$	$b_2 = -1.783$
$a_3 = -2.777 \times 10^{-2}$	$b_3 = 4.581$

The first model for the perturbation free energy that we consider is:

$$\frac{\beta A_p}{N} = -c_x \frac{a_1 \rho^*}{T^*} - c_x \left[\frac{a_2}{T^*} + a_3 \left\{ \frac{3}{T^{*2}} + \sqrt{\frac{1}{T^*}} \right\} \right] \{ \exp[-2\rho^*(\rho^* - 1)] - 1 \} \tag{23}$$

where

$$\rho^* = \rho (r\sigma^3)_x \tag{24}$$

and

$$T^* = (ckT/\epsilon q)_x. \tag{25}$$

This model has adjustable parameters a_1, a_2, and a_3 that were fit to simulation data for monatomic Lennard-Jones fluids (Sowers and Sandler, 1991), and three corresponding states parameters c, q, and r that were fit to simulation data for pure molecular fluids (Sowers and Sandler, 1992). These parameters are listed in Tables 2 and 3. A complete equation of state results from combining this model for the perturbation free energy with a model for the free energy of the reference mixture of fused hard spheres and using the relation $Z - 1 = \rho \partial (\beta A^{\mathrm{CONF}}/N)/\partial \rho$. From Eq. 23 we obtain:

$$Z = Z_0 - c_x \frac{a_1 \rho^*}{T^*} - 2c_x \left[\frac{a_2}{T^*} + a_3 \left\{ \frac{3}{T^{*2}} + \sqrt{\frac{1}{T^*}} \right\} \right] \times (2\rho^{*2} - \rho^*) \exp[-2\rho^*(\rho^* - 1)] \tag{26}$$

where Z_0 is the compressibility of the fused-hard-sphere reference mixture. For Z_0 we will use either the BM/CSP equation, Eq. 18, or the CS1/CSP equation, Eq. 17. The diameter of a constituent atom in a reference system molecule will be made temperature-dependent, as suggested by perturbation theories of molecular fluids. We will use the "hybrid" Barker-Henderson diameter (Aim and Nezbeda, 1984) given by:

$$d_{ij}(T) = \int_0^{2^{1/6}\sigma_{ij}} 1 - \exp[-\beta \{ u_{ij}^{\alpha\gamma}(r) + \epsilon_{ij} \}] dr. \tag{27}$$

For a discussion of this choice of the temperature-dependent diameter, see Sowers and Sandler (1991).

We will test two different sets of mixing rules for $(r\sigma^3)_x$ and $(\epsilon q/ckT)_x$. The first set was used in the original perturbed-hard-chain (PHC) theory (Donohue and Prausnitz, 1978):

$$(r\sigma^3)_x = \sum_i x_i r_i \sigma_{ii}^3 \tag{28}$$

$$(\epsilon q/ckT)_x = \sum_i \sum_j x_i x_j r_j q_i \epsilon_{ij} \sigma_{ij}^3 / (r\sigma^3)_x c_x kT. \tag{29}$$

The combining rules for ϵ_{ij} and σ_{ij} are given by Eqs. 5 and 6. We will refer to this set of mixing rules as the "original PHC" mixing rules. The second set of mixing rules is given by:

$$(r\sigma^3)_x = \sum_i x_i (r\sigma^3)_{ii} \tag{30}$$

$$(\epsilon q/ckT)_x = \sum_i \sum_j (\epsilon q/ckT)_{ij} (r\sigma^3)_{ij} / (r\sigma^3)_x \tag{31}$$

with combining rules

$$(r\sigma^3)_{ij} = \left[\frac{(r\sigma^3)_{ii}^{1/3} + (r\sigma^3)_{jj}^{1/3}}{2} \right]^3 \tag{32}$$

$$(\epsilon q/ckT)_{ij} = \sqrt{(\epsilon q/ckT)_{ii} (\epsilon q/ckT)_{jj}}. \tag{33}$$

This set of mixing rules is similar, but not identical to, the usual van der Waals one-fluid mixing rules for a monatomic fluid mixture with potential parameters $(\epsilon q/c)_{ii}$ and $(r\sigma^3)_{ii}$. The vdW1 mixing rules give good results for monatomic fluid mixtures in which the species are not too different in size. Therefore, for mixtures of small nonspherical molecules, Eqs. 30 and 31 seem more appropriate than the original PHC mixing rules, which are based in lattice theory. We will refer to Eqs. 30 and 31 as the "new PHC" mixing rules.

To test these mixing rules we computed the absolute average percent deviation between the equation of state and the simulation data, defined as:

Table 3. Value of Corresponding States Parameters c, q, and r Used in Eqs. 26, 36, and 37*

	Eq. 26			Eqs. 36 and 37		
Fluid	c	q	r	c	q	r
Sphere	1.000	1.000	1.000	1.000	1.000	1.000
Diatomic, $\ell = 0.3292\sigma$	1.056	2.714	1.311	1.056	2.674	1.298
Diatomic, $\ell = 0.67\sigma$	1.236	1.941	1.756	1.236	1.902	1.731
Linear triatomic, $\ell = 0.67\sigma$	1.538	3.048	2.532	1.538	3.011	2.501

*These parameters were fit to simulation data for pure molecular fluids (Sowers and Sandler, 1992).

Table 4. Comparison of Eq. 26 with Our Simulation Data for Diatomic/Sphere (*D/S*), Diatomic/Diatomic (*D/D*), and Triatomic/Sphere (*T/S*) Mixtures at Three Volume Ratios*

Z_0	Mixing Rule	D/S	D/D	T/S	$V_1/V_2=6.25$	$V_1=V_2$	$\sigma_{11}=\sigma_{22}$	All
BM/CSP	New PHC	5.55	2.58	5.94	3.04	7.90	4.37	4.65
BM/CSP	Original PHC	3.57	3.10	10.76	6.02	4.29	6.18	5.62
CS1/CSP	New PHC	8.71	5.03	10.14	10.15	7.90	3.94	7.89
CS1/CSP	Original PHC	16.31	10.50	9.21	20.58	4.29	4.87	12.12

* The entries in the first column denote the choice of reference system equation of state. The second column denotes the choice of mixing rule used in the equation of state. The entries in columns 3-9 of the table are absolute average percent deviations between the equation of state and the simulation data. The results for each type of mixture are given in columns 3, 4, and 5, while the results for the three volume ratios, independent of the type of mixture, are given in columns 6, 7, and 8. The results for all 195 state points are given in column 9.

$$\Delta Z\ \% = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{Z_i^{\mathrm{SIM}} - Z_i^{\mathrm{EOS}}}{Z_i^{\mathrm{SIM}}}\right| \times 100. \tag{34}$$

The results are shown in Table 4, where the equation of state for the reference fluid, Z_0, and the choice of mixing rule are given in columns 1 and 2. The performance of the equation of state/mixing rule pair is shown for each type of mixture simulated in columns 3-5. Results for each volume ratio, independent of the type of mixture, are shown in columns 6-8. Finally, the performance of the equation of state for all 195 state points is shown in the rightmost column.

We can make a few observations based on the results in Table 4. The BM/CSP reference term combined with the new PHC mixing rules for the perturbation term gives the best overall performance. The prediction of the simulation compressibilities is shown for diatomic/sphere and triatomic/sphere Case I mixtures at $T/T_c = 1.1$ in Figures 1 and 2. The percent deviations are quite low and, although higher than the deviations we computed for pure fluids, are acceptable given that we are using a one-fluid mixing rule with no adjustable parameters. The deviations would be smaller if a single binary interaction parameter is fit to the simulation data, but there is no justification for doing this because the cross parameters ϵ_{12} and σ_{12} are known exactly. For large volume ratios the use of the BM/CSP reference term gives substantially better performance than the CS1/CSP reference term, and for molecules of equal volume the two equations are identical. The new PHC mixing rules are superior to the original PHC mixing rules for large volume ratios and when the molecules in the mixture differ appreciably in shape, but are not as good for mixtures of molecules with equal volumes. In general, one-fluid mixing rules give reasonable predictions of the simulation data.

We also consider a model for the free energy that is based on an equation of state for the square well fluid, extended to Lennard-Jones monatomic fluids (Sowers and Sandler, 1991) and site-site Lennard-Jones molecular fluids (Sowers and Sandler, 1992). The model is:

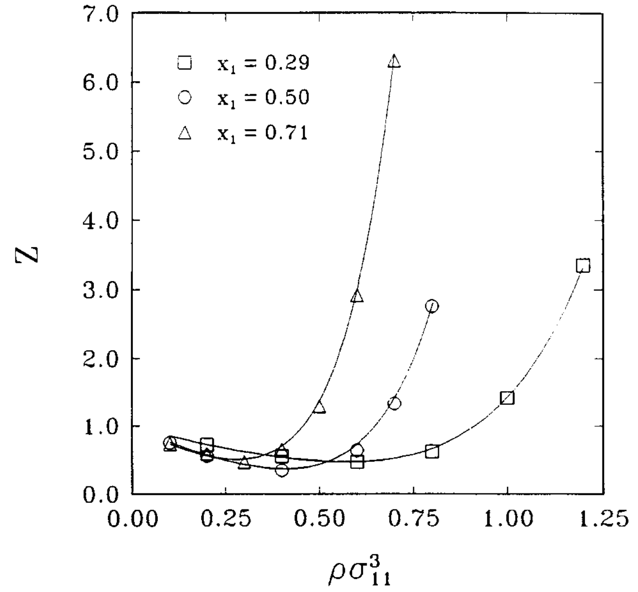

Figure 1. Prediction of the simulation compressibilities using Eq. 26 with the BM/CSP reference equation and the new PHC mixing rules.

The symbols are the compressibilities of a mixture of diatomics with bond length $\ell/\sigma = 0.67$ (component 1) and spheres (component 2). The ratio of molecular volumes is $V_1/V_2 = 6.25$.

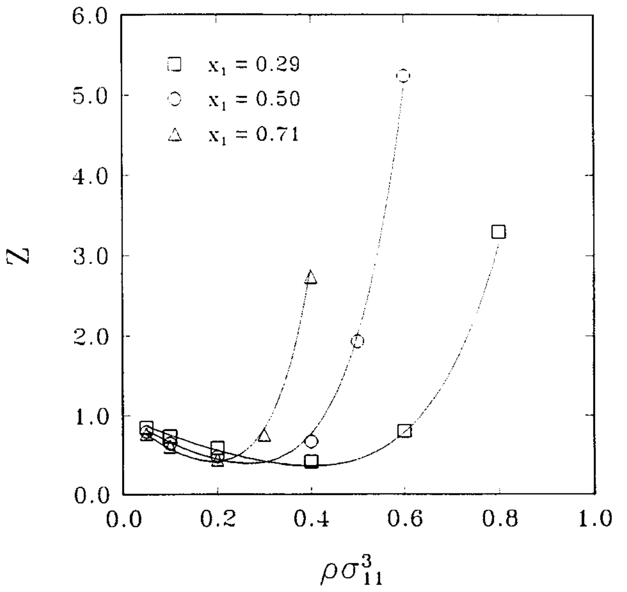

Figure 2. Prediction of the simulation compressibilities using Eq. 26 with the BM/CSP reference equation and the new PHC mixing rules.

The symbols are the compressibilities of a mixture of linear triatomics with bond length $\ell/\sigma = 0.67$ (component 1) and spheres (component 2). The ratio of molecular volumes is $V_1/V_2 = 6.25$.

Table 5. Comparison of Eqs. 36 and 37 with Our Simulation Data for Diatomic/Sphere (*D/S*), Diatomic/Diatomic (*D/D*), and Triatomic/Sphere (*T/S*) Mixtures at Three Volume Ratios*

Z_0	Mixing Rule	*D/S*	*D/D*	*T/S*	$V_1/V_2=6.25$	$V_1=V_2$	$\sigma_{11}=\sigma_{22}$	All
BM/CSP	New PHC, Eq. 36	5.52	3.33	6.84	4.18	7.51	4.68	5.17
BM/CSP	Original PHC, Eq. 36	5.31	4.66	12.58	8.58	4.63	7.69	7.32
BM/CSP	SPHC, Eq. 37	18.65	3.95	53.52	23.61	19.70	29.94	24.33
CS1/CSP	New PHC, Eq. 36	9.60	6.17	11.33	11.68	7.51	5.57	8.96
CS1/CSP	Original PHC, Eq. 36	13.61	10.29	7.36	16.91	4.63	5.08	10.55
CS1/CSP	SPHC, Eq. 37	13.32	10.14	37.91	17.06	19.70	24.62	19.79

*The meaning of each column heading is the same as in Table 4.

$$\frac{\beta A_p}{N} = -c_x Z_m \ln\left[1 + \{\exp(1/2T^*) - 1\}\frac{\eta}{(\pi\sqrt{2}/6)}\right] + c_x\frac{b_1}{T^*}\exp(-\sqrt{T^*})\rho^{*2} + c_x\left[\frac{b_2}{T^*} + \frac{b_3}{T^{*2}}\right]\rho^* \quad (35)$$

where ρ^* and T^* are defined in Eqs. 24 and 25. This model also has three parameters b_1, b_2 and b_3 that were fit to simulation data for the monatomic Lennard-Jones fluid, and three corresponding states parameters c, q, and r that were fit to simulation data for pure molecular fluids. The values of these parameters are given in Tables 2 and 3. The complete equation of state, obtained by combining this model with an equation for the free energy of a fused-hard-sphere reference system mixture, is:

$$Z = Z_0 - \frac{c_x Z_m[\exp(\epsilon q/2ckT)_x - 1]\eta}{\pi\sqrt{2}/6 + [\exp(\epsilon q/2ckT)_x - 1]\eta} + c_x\frac{2b_1}{T^*}\exp(-\sqrt{T^*})\rho^{*2} + c_x\left[\frac{b_2}{T^*} + \frac{b_3}{T^{*2}}\right]\rho^*. \quad (36)$$

For Z_0 we will again use both the BM/CSP and CS1/CSP equations. We will test the original PHC and the new PHC mixing rules in Eq. 36, as well as a third mixing rule used in the simplified perturbed-hard-chain (SPHC) equation (Kim et al., 1986). This mixing rule is applicable only to the second term on the righthand side of Eq. 36, which is derived from the Lee-Lombardo-Sandler (LLS) model for square well fluids (Lee et al., 1985). With the SPHC mixing rule, the equation of state is:

$$Z = Z_0 - \frac{Z_m\langle crd^3Y\rangle\rho}{\sqrt{2} + \frac{\langle crd^3Y\rangle\rho}{c_x}} + c_x\frac{2b_1}{T^*}\exp(-\sqrt{T^*})\rho^{*2} + c_x\left[\frac{b_2}{T^*} + \frac{b_3}{T^{*2}}\right]\rho^* \quad (37)$$

where

$$\langle crd^3Y\rangle = \sum_i\sum_j x_i x_j c_i r_j d_{ij}^3[\exp(\epsilon_{ij}q_i/2c_ikT) - 1]. \quad (38)$$

and T^* and ρ^* are defined in Eqs. 25 and 24.

Equation 36 separately with either the BM/CSP or CS1/CSP reference term and the original PHC or new PHC mixing rules, as well as Eq. 37 with either the BM/CSP or CS1/CSP reference term and the SPHC mixing rule, were compared to our simulation data for molecular fluid mixtures. The results are given in Table 5, which has the same format at Table 4. Once again, we find that one-fluid mixing rules give satisfactory results for the mixtures studied. Equation 36 with the BM/CSP reference term and the new PHC mixing rules performs the best overall. Clearly, the CS1/CSP reference term is a poor choice for mixtures in which the molecular volume or the shapes of the components are much different. With the BM/CSP reference term, the original PHC mixing rules are superior only for mixtures where the molecular volumes of each species are the same. Equation 37 performs poorly for these mixtures and gives reasonable results only for diatomic/diatomic mixtures, where the shapes, and thus the corresponding states parameters c_i, q_i, and r_i, are similar. The predictions of the simulation compressibilities computed from Eq. 36 for diatomic/sphere and diatomic/diatomic Case I mixtures at $T/T_c = 1.1$ are shown in Figures 3 and 4.

Alternatives to One-Fluid Mixing Rules

One-fluid mixing rules are commonly used in engineering equations of state because of their simplicity. However, it has

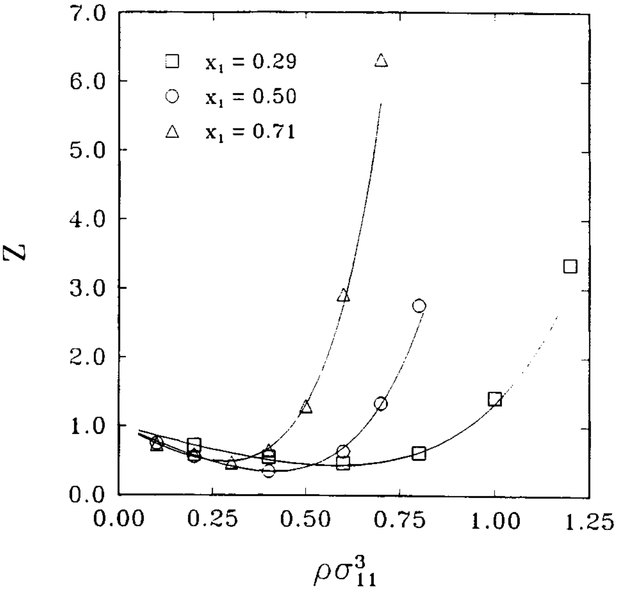

Figure 3. Prediction of the simulation compressibilities using Eq. 36 with the BM/CSP reference equation and the new PHC mixing rules.

The symbols are the compressibilities of a mixture of diatomics with bond length $\ell/\sigma = 0.67$ (component 1) and spheres (component 2). The ratio of molecular volumes is $V_1/V_2 = 6.25$.

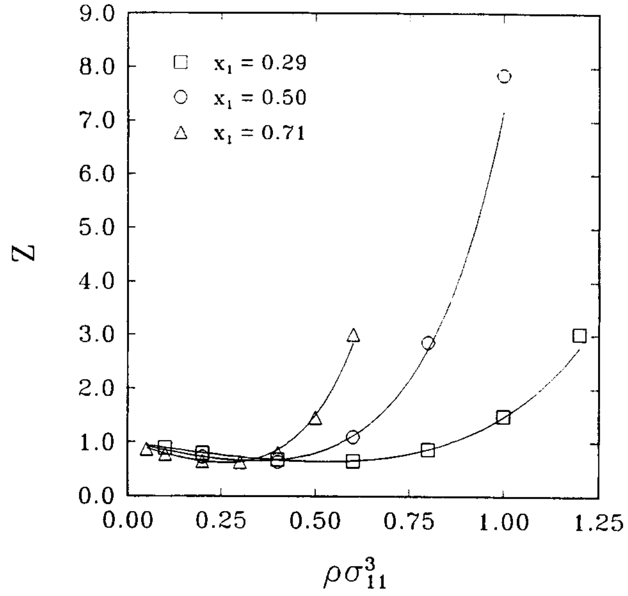

Figure 4. Prediction of the simulation compressibilities using Eq. 36 with the BM/CSP reference equation and the new PHC mixing rules.

The symbols are the compressibilities of a mixture of diatomics with bond length $\ell/\sigma = 0.67$ (component 1) and diatomics with bond length $\ell/\sigma = 0.3292$ (component 2). The ratio of molecular volumes is $V_1/V_2 = 6.25$.

been shown (Huber and Ely, 1987) that the performance of one-fluid mixing rules deteriorates as the size ratio of the species in the mixture increases. In comparison with the available simulation data for monatomic fluids, vdW1 mixing rules are usually adequate as long as the ratio of atomic diameters σ_{22}/σ_{11} is less than about 1.3 (Henderson and Leonard, 1971). When equations of state with one-fluid mixing rules are used to compute phase diagrams of real fluid mixtures, however, the agreement with experiment is sometimes poor, especially for highly asymmetric mixtures.

One approach that leads to improvement in some cases is to allow the mixing rule to depend on both composition and density. Density-dependent mixing rules have been proposed which have the theoretically required quadratic dependence on composition at low density, and a different, nonquadratic composition dependence at higher densities. Since these mixing rules often contain adjustable parameters that are fit to experimental data, they sometimes improve the correlative ability of the equation of state. Density-dependent mixing rules have been reviewed by Copeman and Mathias (1986).

The accuracy of our one-fluid models can be evaluated by considering the effect of composition on the perturbation free energy $\beta A_p/N$, given by:

$$\frac{\beta A_p}{N} = 2\pi\beta\rho \sum_{i=1}^{\nu}\sum_{j=1}^{\nu} x_i x_j \times \int_0^1\int_0^\infty \sum_{\alpha=1}^{m_i}\sum_{\gamma=1}^{m_j} w_{ij}^{\alpha\gamma}(r_{ij}^{\alpha\gamma}) g_{ij}^{\alpha\gamma}(r_{ij}^{\alpha\gamma};\lambda) r_{ij}^{\alpha\gamma 2} dr_{ij}^{\alpha\gamma} d\lambda. \quad (39)$$

The species compositions appear explicitly and implicitly in the double summation over mole fractions, since the site-site distribution functions $g_{ij}^{\alpha\gamma}$ depend on composition, density, and temperature. Our mixture equations of state are derived by making two assumptions. First, we assume that the three-parameter corresponding states principle given by Eq. 14 relates the free energy of a molecular fluid mixture to the free energy of a monatomic fluid mixture. Second, we assume that a one-fluid theory with mixing rules given by Eqs. 30 and 31 is exact. The perturbation free energy can then be written:

$$\frac{\beta A_p}{N} = c_x 2\pi(\epsilon q/ckT)_x \rho(r\sigma^3)_x \int_0^1\int_0^\infty w_0(r^*) g_0(r^*) r^{*2} dr^* = c_x F[(\epsilon q/ckT)_x, (r\sigma^3)_x]. \quad (40)$$

If the composition is varied while c_x, $(\epsilon q/ckT)_x$, and $\rho(r\sigma^3)_x$ are held constant and our assumptions are valid, then the perturbation free energy will also remain constant. (Note that the integrand does not depend on composition, because g_0 is the radial distribution function of a hypothetical pure monatomic fluid.)

We now wish to determine if the perturbation free energy has a more complicated composition dependence that is not accounted for by one-fluid mixing rules. To do this we define a quantity A_x by rearranging Eq. 40:

$$A_x = \frac{\beta A_p/N}{c_x(\epsilon q/ckT)_x} = 2\pi\rho(r\sigma^3)_x \int_0^1\int_0^\infty w_0(r^*) g_0(r^*) r^{*2} dr^*. \quad (41)$$

If our one-fluid theory was exact, there would be no observable composition dependence in A_x when $(r\sigma^3)_x$ is held constant. If A_x were plotted against the reduced density $\rho(r\sigma^3)_x$ at constant $(\epsilon q/ckT)_x$ at a series of compositions, the results would lie on a single curve. Composition dependence in the perturbation free energy that is not accounted for by a one-fluid theory would lead to separate curves for each composition.

We computed $\beta A_p/N$ numerically for the mixtures we simulated using the relation:

$$\frac{\beta A_p}{N} = \int_0^\rho \frac{Z - Z_0}{\rho'} d\rho' \quad (42)$$

the BM/CSP equation for the reference system compressibility Z_0, and the data in Table 6 for Z. We then computed A_x at a constant value of $(\epsilon q/ckT)_x$ and plotted the results against reduced density $\rho(r\sigma^3)_x$ at three different compositions. The results for Case I diatomic/sphere mixtures at $(\epsilon q/ckT)_x = 0.588$ are shown in Figure 5, where the symbols representing each of the three compositions lie on essentially the same curve. The results for the other mixtures we studied are similar. Since we obtained reasonably good agreement with our simulation data using one-fluid mixing rules and the results for A_x at different compositions lie on a single curve, we conclude that a more complicated mixing rule with density dependence and/or additional adjustable parameters is not justified for the mixtures we have simulated.

Conclusions

We have presented new simulation results for mixtures of

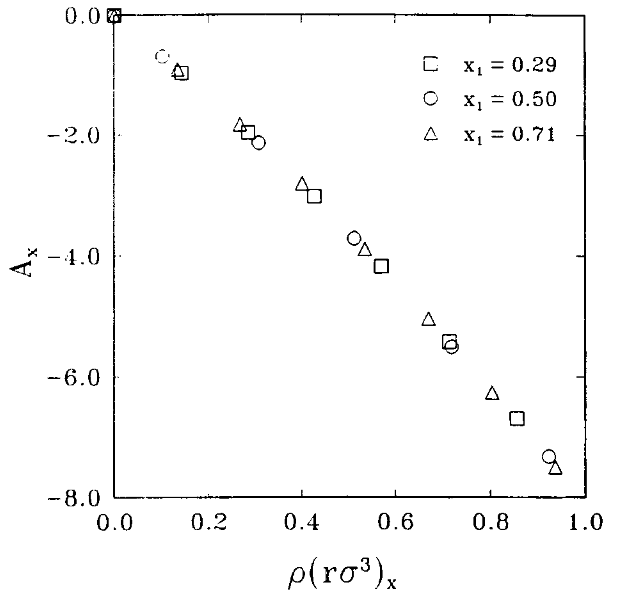

Figure 5. Quantity $A_x = (\beta A_p/N)/c_x(\epsilon q/ckT)_x$ computed for Case I diatomic/sphere mixtures with $(\epsilon q/ckT)_x = 0.588$.

The reduced density is defined as $\rho(r\sigma^3)_x = \Sigma_i x_i \rho r_i \sigma_i^3$.

site-site Lennard-Jones diatomics and spheres, mixtures of diatomics with different bond lengths, and mixtures of linear triatomics and spheres. Three volume ratios, three compositions, and four to eight densities at at least one temperature were studied, and results for 195 state points were reported. These results were used to test two one-fluid models based on perturbed-hard-chain theory. We proposed an equation for the reference mixture of fused-hard-spheres, the BM/CSP equation, that has not been previously used in perturbed-hard-chain equations of state. We also proposed one-fluid mixing rules that are more similar to the usual vdW1 mixing rules than the mixing rules used in the original perturbed-hard-chain theories. Based on comparisons of the predictions of the equations of state with the compressibilities from simulation, we found that the use of the BM/CSP reference term improves the overall performance of each equation of state, especially for mixtures in which the volume or shape difference is large. For mixtures of species with identical molecular volumes, there is no difference between the BM/CSP and the currently used CS1/CSP reference equations. For a given reference system equation, the new PHC mixing rules are superior to the original PHC mixing rules in most cases studied. They are slightly worse only when used in Eq. 26 with BM/CSP reference term for diatomic/sphere mixtures and for Case II mixtures. We also found that the effect of composition on the perturbation free energy $\beta A_p/N$ that is not accounted for by one-fluid mixing rules is quite small, and therefore a more complicated density-dependent mixing rule is not necessary in our equations of state for the mixtures we simulated. Both of our equations of state predict the compressibilities of the mixture with an average error of approximately 5% without the use of binary interaction parameters.

Acknowledgment

This work was supported by grant number FG-85ER13436 from the U.S. Department of Energy to the University of Delaware. We also thank the Pittsburgh Supercomputer Center, the University of Delaware Computing Center, and the National Science Foundation for generous grants of computing time and equipment.

Literature Cited

Aim, K., and I. Nezbeda, "Perturbed Hard Sphere Equations of State of Real Fluids: II. Effective Hard Sphere Diameters and Residual Properties," *Fluid Phase Eq.*, **17**, 1 (1984).

Aviram, I., and D. J. Tildesley, "A Monte Carlo Study of Mixtures of Hard Diatomic Molecules," *Mol. Phys.*, **35**, 365 (1978).

Beret, S., and J. M. Prausnitz, "Perturbed Hard-Chain Theory: an Equation of State for Fluids Containing Small or Large Molecules," *AIChE J.*, **21**, 1123 (1975).

Bohn, M., S. Lago, J. Fischer, and F. Kohler, "Excess Properties of Liquid Mixtures from Perturbation Theory: Results for Model Systems and Predictions for Real Systems," *Fluid Phase Eq.*, **23**, 137 (1985).

Bohn, M., J. Fischer, and F. Kohler, "Prediction of Excess Properties for Liquid Mixtures: Results from Perturbation Theory for Mixtures with Linear Molecules," *Fluid Phase Eq.*, **31**, 233 (1986).

Bohn, M., R. Lustig, J. Fischer, and F. Kohler, "Thermodynamic Perturbation Theory for Mixtures of Spherical and Tetrahedral Molecules," *Mol. Phys.*, **64**, 595 (1988).

Boublík, T., "Hard Sphere Equation of State," *J. Chem. Phys.*, **53**, 471 (1970).

Carnahan, N. F., and K. E. Starling, "Equation of State for Nonattracting Rigid Spheres," *J. Chem. Phys.*, **51**, 635 (1969).

Copeman, T. W., and P. M. Mathias, "Recent Mixing Rules for Equations of State: An Industrial Perspective," *Equations of State: Theories and Applications*, p. 352, Amer. Chem. Soc. (1986).

Deiters, U. K., "Extended 1-fluid Theory for Mixtures Containing Non-spherical Molecules," *Fluid Phase Eq.*, **48**, 185 (1989).

Donohue, M. D., and J. M. Prausnitz, "Perturbed Hard-Chain Theory for Fluid Mixtures: Thermodynamic Properties for Mixtures in Natural Gas and Petroleum Technology," *AIChE J.*, **24**, 849 (1978).

Encisco, E., and M. Lombardero, "Perturbation Theory for Multicomponent Molecular Fluid," *Mol. Phys.*, **44**, 725 (1981).

Fincham, D., N. Quirke, and D. J. Tildesley, "Computer Modelling of Molecular Liquid Mixtures: I. A Diatomic Lennard-Jones Model Mixture," *J. Chem. Phys.*, **84**, 4535 (1986).

Fincham, D., N. Quirke, and D. J. Tildesley, "Computer Modelling of Molecular Liquid Mixtures: II. The Excess Properties of a Diatomic Lennard-Jones Mixture for CO_2/C_2H_6," *J. Chem. Phys.*, **87**, 6117 (1987).

Fischer, J., and S. Lago, "Thermodynamic Perturbation Theory for Molecular Liquid Mixtures," *J. Chem. Phys.*, **78**, 5750 (1983).

Gupta, S., "Computer Simulation of Condensed Gas Mixtures," *Fluid Phase Eq.*, 31, 221 (1986).

Gupta, S., and J. E. Coon, "Structure and Thermodynamics of Molecular Liquid Mixtures," *Mol. Phys.*, **57**, 1049 (1986).

Haile, J. M., and L. L. Lee, "Group Contribution Methods for Molecular Mixtures: III. Solution of Groups Tested via Computer Simulation," *Fluid Phase Eq.*, **44**, 175 (1988).

Henderson, D., and P. J. Leonard, "Liquid Mixtures," *Physical Chemistry—An Advanced Treatise*, Vol. VIIIB, Chap. 7, H. Eyring, D. Henderson, and W. Jost, eds., Academic Press, New York (1971).

Huber, M. L., and J. F. Ely, "Improved Conformal Solution Theory for Mixtures with Large Size Ratios," *Fluid Phase Eq.*, **37**, 105 (1987).

Kim, C. H., P. Vimalchand, M. D. Donohue, and S. I. Sandler, "Local Composition Model for Chainlike Molecules: A New Simplified Version of the Perturbed Hard-Chain Theory," *AIChE J.*, **32**, 1726 (1986).

Lee, K.-H., M. Lombardo, and S. I. Sandler, "The Generalized van der Waals Partition Function: II. Application to the Square-Well Fluid," *Fluid Phase Eq.*, **21**, 177 (1985).

Lee, L. L., and D. Levesque, "Perturbation Theory for Mixtures of Simple Liquids," *Mol. Phys.*, **26**, 1351 (1973).

Leland, T. W., J. S. Rowlinson, and G. A. Sather, "Statistical Thermodynamics of Mixtures of Molecules of Different Sizes," *Trans. Farad. Soc.*, **64**, 1447 (1968).

Leonard, P. J., D. Henderson, and J. A. Barker, "Perturbation Theory and Liquid Mixtures," *Trans. Farad. Soc.*, **64**, 2439 (1970).

Longuet-Higgins, H. C., "The Statistical Thermodynamics of Multicomponent Mixtures," *Proc. Roy. Soc.* (*London*), **A205**, 247 (1951).

Mansoori, G. A., N. F. Carnahan, K. E. Starling, and T. W. Leland, "Equilibrium Thermodynamic Properties of the Mixture of Hard Spheres," *J. Chem. Phys.*, **54**, 1523 (1971).

Massobrio, C., J. M. Haile, and L. L. Lee, "Group Contribution Methods for Molecular Mixtures: II. Computer Simulation Results," *Fluid Phase Eq.*, **44**, 145 (1988).

Mittag, U., J. Samiss, and T. H. Dorfmüller, "Molecular Dynamics Simulation of the Liquid Mixture CCl_4/CS_2: I. Thermodynamic and Structural Properties," *Mol. Phys.*, **66**, 51 (1989).

Nezbeda, I., M. R. Reddy, and W. R. Smith, "Computer Simulation Studies of Molecular Fluid Mixtures: I. Hard Spheres, Heteronuclear Dumbells, and Linear Triatomics," *Mol. Phys.*, **55**, 447 (1985).

Sowers, G. M., and S. I. Sandler, "Equations of State from Generalized Perturbation Theory: II. The Lennard-Jones Fluid," *Fluid Phase Eq.*, **67**, 127 (1991).

Sowers, G. M., and S. I. Sandler, "Simulation Results and Corresponding States Correlations for Pure Rigid Molecular Fluids," *Mol. Phys.*, accepted (1992).

Tildesley, D. J., E. Encisco, and P. Sevilla, "Monte Carlo Simulation and Thermodynamic Perturbation Theory for Mixtures of Diatomic Molecules," *Chem. Phys. Lett.*, **100**, 508 (1983).

Vortler, H. L., J. Kolafa, and I. Nezbeda, "Computer Simulation Studies of Hard Body Fluid Mixtures," *Mol. Phys.*, **68**, 547 (1989).

Waisman, E. M., J. L. Lebowitz, and D. MacGowan, "A One Molecular Fluid Approximation for Diatomic Fluid Mixtures," *J. Chem. Phys.*, **81**, 6096 (1984).

Wojcik, M., and K. E. Gubbins, "Thermodynamics of Hard Dumbbell Mixtures," *Mol. Phys.*, **49**, 1401 (1983).

Appendix: Simulation Results

Table 6. Compressibilities of Diatomic/Sphere Mixtures for Case I, Where $\sigma_{11} = 1.5\sigma_{22}$*

N_1	kT/ϵ_{11}	$\rho\sigma_{11}^3$	Z	Z_{11}^{CONF}	Z_{12}^{CONF}	Z_{22}^{CONF}
32	1.90	0.20	0.7185	-0.1183	-0.1269	-0.0363
32	1.90	0.40	0.5515	-0.1950	-0.2034	-0.0500
32	1.90	0.60	0.4644	-0.2758	-0.2137	-0.0461
32	1.90	0.80	0.6181	-0.2752	-0.1177	0.0110
32	1.90	1.00	1.4169	-0.0552	0.2961	0.1759
32	1.90	1.20	3.3508	0.5629	1.2998	0.4881
32	2.67	0.20	0.8921	-0.0554	-0.0461	-0.0064
32	2.67	0.60	0.9472	-0.0998	0.0106	0.0364
32	2.67	0.80	1.3235	-0.0341	0.2411	0.1165
32	2.67	1.20	4.0448	0.8141	1.6415	0.5891
56	2.00	0.10	0.7475	-0.1708	-0.0736	-0.0081
56	2.00	0.20	0.5582	-0.3029	-0.1252	-0.0137
56	2.00	0.40	0.3420	-0.4895	-0.1579	-0.0106
56	2.00	0.60	0.6366	-0.3847	0.0033	0.0181
56	2.00	0.70	1.3308	-0.0442	0.3144	0.0607
56	2.00	0.80	2.7553	0.8061	0.8182	0.1311
56	2.00	1.00	8.9833	4.5174	3.0670	0.3989
56	2.75	0.20	0.8252	-0.1361	-0.0378	-0.0009
56	2.75	0.40	0.8528	-0.1742	0.0145	0.0125
56	2.75	0.60	1.4397	0.0975	0.2902	0.0521
56	2.75	0.80	3.5039	1.2872	1.0535	0.1640
80	2.35	0.10	0.7311	-0.2315	-0.0356	-0.0017
80	2.35	0.20	0.5906	-0.3604	-0.0472	-0.0018
80	2.35	0.30	0.4701	-0.4867	-0.0429	-0.0002
80	2.35	0.40	0.6488	-0.3838	0.0269	0.0057
80	2.35	0.50	1.2904	0.0827	0.1934	0.0143
80	2.35	0.60	2.9132	1.3330	0.5546	0.0256
80	2.35	0.70	6.3149	4.0522	1.2006	0.0621
80	3.25	0.05	0.9375	-0.0584	-0.0045	0.0004
80	3.25	0.20	0.8816	-0.1298	0.0099	0.0015
80	3.25	0.40	1.2874	0.1280	0.1496	0.0097
80	3.25	0.60	3.7310	2.0217	0.6720	0.0377

* The quantity $Z_{ij}^{CONF} = P_{ij}^{CONF}/\rho kT$, where P^{CONF} is the configurational pressure.

Table 7. Compressibilities of Diatomic/Sphere Mixtures for Case II, Where $V_{11} = V_{22}$*

N_1	kT/ϵ_{11}	$\rho\sigma_{11}^3$	Z	Z_{11}^{CONF}	Z_{12}^{CONF}	Z_{22}^{CONF}
32	1.79	0.05	0.7838	-0.0359	-0.1106	-0.0696
32	1.79	0.10	0.6193	-0.0618	-0.1920	-0.1269
32	1.79	0.20	0.4434	-0.0969	-0.2997	-0.1600
32	1.79	0.30	0.6265	-0.1096	-0.2545	-0.0094
32	1.79	0.40	1.7725	-0.0261	0.1673	0.6313
32	1.79	0.50	5.0778	0.1681	1.6582	2.2515
56	2.00	0.05	0.7827	-0.0855	-0.1076	-0.0242
56	2.00	0.10	0.6146	-0.1484	-0.1940	-0.0429
56	2.00	0.20	0.4461	-0.2340	-0.2765	-0.0434
56	2.00	0.30	0.5735	-0.2623	-0.2049	0.0406
56	2.00	0.40	1.6839	0.0076	0.3174	0.3591
56	2.00	0.50	4.9568	0.7802	1.9827	1.1941
80	2.25	0.05	0.7896	-0.1370	-0.0664	-0.0070
80	2.25	0.10	0.6394	-0.2397	-0.1111	-0.0097
80	2.25	0.20	0.4516	-0.3757	-0.1661	-0.0067
80	2.25	0.30	0.6520	-0.3210	-0.0613	0.0342
80	2.25	0.40	1.7231	0.1877	0.4012	0.1343
80	2.25	0.50	5.4588	1.6359	2.1545	0.6681

* The quantity $Z_{ij}^{CONF} = P_{ij}^{CONF}/\rho kT$, where P^{CONF} is the configurational pressure.

Table 8. Compressibilities of Diatomic/Sphere Mixtures for Case III, Where $\sigma_{11} = \sigma_{22}$*

N_1	kT/ϵ_{11}	$\rho\sigma_{11}^3$	Z	Z_{11}^{CONF}	Z_{12}^{CONF}	Z_{22}^{CONF}
32	1.79	0.10	0.7234	-0.0650	-0.1421	-0.0695
32	1.79	0.20	0.5206	-0.1208	-0.2417	-0.1169
32	1.79	0.30	0.4096	-0.1545	-0.3059	-0.1300
32	1.79	0.40	0.4743	-0.1709	-0.2781	-0.0767
32	1.79	0.50	0.8279	-0.1295	-0.1465	0.1038
32	1.79	0.60	1.7209	-0.0373	0.2835	0.4748
56	2.00	0.10	0.6895	-0.1604	-0.1269	-0.0233
56	2.00	0.20	0.4937	-0.2735	-0.2008	-0.0320
56	2.00	0.30	0.4137	-0.3237	-0.2407	-0.0218
56	2.00	0.40	0.5525	-0.3274	-0.1438	0.0237
56	2.00	0.50	1.3585	-0.1048	0.2963	0.1670
56	2.00	0.60	3.1856	0.5176	1.2082	0.4597
80	2.25	0.10	0.6635	-0.2483	-0.0824	-0.0058
80	2.25	0.20	0.4824	-0.4033	-0.1100	-0.0043
80	2.25	0.30	0.4417	-0.4714	-0.0897	0.0028
80	2.25	0.40	0.9126	-0.2124	0.0941	0.0310
80	2.25	0.50	2.4353	0.6847	0.6539	0.0967
80	2.25	0.60	6.0998	3.0307	1.8043	0.2649

* The quantity $Z_{ij}^{CONF} = P_{ij}^{CONF}/\rho kT$, where P^{CONF} is the configurational pressure.

Table 9. Configurational Internal Energies of Diatomic/Sphere Mixtures for Case I, Where $\sigma_{11}=1.5\sigma_{22}$

N_1	kT/ϵ_{11}	$\rho\sigma_{11}^3$	$\frac{E^{CONF}}{N\epsilon_{11}}$	$\frac{E_{11}^{CONF}}{N\epsilon_{11}}$	$\frac{E_{12}^{CONF}}{N\epsilon_{11}}$	$\frac{E_{22}^{CONF}}{N\epsilon_{11}}$
32	1.90	0.20	−1.3028	−0.4497	−0.6458	−0.2074
32	1.90	0.40	−2.4649	−0.8210	−1.2322	−0.4117
32	1.90	0.60	−3.5239	−1.1107	−1.7972	−0.6160
32	1.90	0.80	−4.6665	−1.4706	−2.3559	−0.8399
32	1.90	1.00	−5.8585	−1.8234	−2.9910	−1.0441
32	1.90	1.20	−6.9056	−2.1397	−3.5529	−1.2130
32	2.67	0.20	−1.1313	−0.3850	−0.5610	−0.1853
32	2.67	0.60	−3.2840	−1.0462	−1.6620	−0.5758
32	2.67	0.80	−4.3963	−1.3845	−2.2510	−0.7607
32	2.67	1.20	−6.2923	−1.9977	−3.1938	−1.1008
56	2.00	0.10	−1.2030	−0.7586	−0.3945	−0.0499
56	2.00	0.20	−2.2257	−1.3620	−0.7634	−0.1003
56	2.00	0.40	−4.0289	−2.3619	−1.4661	−0.2009
56	2.00	0.60	−5.9785	−3.4579	−2.2131	−0.3075
56	2.00	0.70	−7.0001	−4.0420	−2.6056	−0.3525
56	2.00	0.80	−7.9333	−4.5763	−2.9566	−0.4005
56	2.00	1.00	−9.0295	−5.2001	−3.3725	−0.4569
56	2.75	0.20	−1.9302	−1.1542	−0.6858	−0.0904
56	2.75	0.40	−3.7555	−2.1976	−1.3726	−0.1852
56	2.75	0.60	−5.6486	−3.2860	−2.0810	−0.2813
56	2.75	0.80	−7.3848	−4.2988	−2.7155	−0.3727
80	2.35	0.10	−1.6597	−1.3451	−0.2992	−0.0153
80	2.35	0.20	−3.1471	−2.5236	−0.5926	−0.0309
80	2.35	0.30	−4.4716	−3.5445	−0.8806	−0.0464
80	2.35	0.40	−5.9116	−4.6756	−1.1714	−0.0646
80	2.35	0.50	−7.4052	−5.8479	−1.4750	−0.0823
80	2.35	0.60	−8.8326	−6.9614	−1.7827	−0.0885
80	2.35	0.70	−9.8299	−7.7572	−1.9683	−0.1043
80	3.25	0.05	−0.7296	−0.5891	−0.1341	−0.0068
80	3.25	0.20	−2.8101	−2.2432	−0.5386	−0.0285
80	3.25	0.40	−5.5475	−4.3985	−1.0883	−0.0604
80	3.25	0.60	−8.1403	−6.4550	−1.6018	−0.0842

Table 10. Configurational Internal Energies of Diatomic/Sphere Mixtures for Case II, Where $V_{11}=V_{22}$

N_1	kT/ϵ_{11}	$\rho\sigma_{11}^3$	$\frac{E^{CONF}}{N\epsilon_{11}}$	$\frac{E_{11}^{CONF}}{N\epsilon_{11}}$	$\frac{E_{12}^{CONF}}{N\epsilon_{11}}$	$\frac{E_{22}^{CONF}}{N\epsilon_{11}}$
32	1.79	0.05	−0.8738	−0.1334	−0.4176	−0.3228
32	1.79	0.10	−1.7079	−0.2641	−0.8126	−0.6312
32	1.79	0.20	−3.1536	−0.4622	−1.4833	−1.2080
32	1.79	0.30	−4.5773	−0.6425	−2.1445	−1.7903
32	1.79	0.40	−6.0244	−0.8327	−2.8387	−2.3530
32	1.79	0.50	−7.0907	−0.9095	−3.5259	−2.6554
56	2.00	0.05	−1.0130	−0.3755	−0.4860	−0.1519
56	2.00	0.10	−1.9670	−0.7375	−0.9329	−0.2966
56	2.00	0.20	−3.6539	−1.3108	−1.7772	−0.5654
56	2.00	0.30	−5.2586	−1.8234	−2.5858	−0.8498
56	2.00	0.40	−6.9415	−2.4398	−3.3821	−1.1220
56	2.00	0.50	−8.2750	−2.9944	−4.0263	−1.2586
80	2.25	0.05	−1.1349	−0.7115	−0.3758	−0.0477
80	2.25	0.10	−2.1939	−1.3804	−0.7222	−0.0913
80	2.25	0.20	−4.0504	−2.5156	−1.3511	−0.1833
80	2.25	0.30	−5.9435	−3.6406	−2.0370	−0.2667
80	2.25	0.40	−7.8661	−4.8295	−2.6877	−0.3519
80	2.25	0.50	−9.2174	−5.6747	−3.4470	−0.1006

Table 11. Configurational Internal Energies of Diatomic/Sphere Mixtures for Case III, Where $\sigma_{11}=\sigma_{22}$

N_1	kT/ϵ_{11}	$\rho\sigma_{11}^3$	$\frac{E^{CONF}}{N\epsilon_{11}}$	$\frac{E_{11}^{CONF}}{N\epsilon_{11}}$	$\frac{E_{12}^{CONF}}{N\epsilon_{11}}$	$\frac{E_{22}^{CONF}}{N\epsilon_{11}}$
32	1.79	0.10	−1.1931	−0.2608	−0.5836	−0.3488
32	1.79	0.20	−2.2595	−0.4701	−1.1112	−0.6783
32	1.79	0.30	−3.1922	−0.6385	−1.5658	−0.9879
32	1.79	0.40	−4.1376	−0.7824	−2.0384	−1.3168
32	1.79	0.50	−5.1500	−1.0106	−2.4809	−1.6585
32	1.79	0.60	−6.1414	−1.1409	−3.0586	−1.9420
56	2.00	0.10	−1.5697	−0.7307	−0.6753	−0.1636
56	2.00	0.20	−2.9537	−1.3406	−1.2993	−0.3139
56	2.00	0.30	−4.1775	−1.8476	−1.8609	−0.4690
56	2.00	0.40	−5.4381	−2.3349	−2.4786	−0.6247
56	2.00	0.50	−6.7831	−2.8771	−3.1406	−0.7653
56	2.00	0.60	−8.0311	−3.4455	−3.7102	−0.8753
80	2.25	0.10	−1.9491	−1.3740	−0.5238	−0.0514
80	2.25	0.20	−3.5810	−2.4810	−1.0005	−0.0994
80	2.25	0.30	−5.1867	−3.5476	−1.4913	−0.1478
80	2.25	0.40	−6.9113	−4.7337	−1.9772	−0.2005
80	2.25	0.50	−8.5915	−5.8842	−2.4693	−0.2379
80	2.25	0.60	−9.8391	−6.8037	−2.7807	−0.2548

Table 12. Compressibilities of Diatomic/Diatomic Mixtures for Case I, Where $\ell_{11}=0.67\sigma_{11}$, $\ell_{22}=0.3292\sigma_{22}$, and $\sigma_{11}=1.7\sigma_{22}$[*]

N_1	kT/ϵ_{11}	$\rho\sigma_{11}^3$	Z	Z_{11}^{CONF}	Z_{12}^{CONF}	Z_{22}^{CONF}
32	3.60	0.10	0.8905	−0.0126	−0.0568	−0.0400
32	3.60	0.20	0.7969	−0.0215	−0.1067	−0.0749
32	3.60	0.40	0.6787	−0.0264	−0.1705	−0.1243
32	3.60	0.60	0.6563	−0.0051	−0.1904	−0.1482
32	3.60	0.80	0.8708	0.1170	−0.1190	−0.1272
32	3.60	1.00	1.4870	0.3412	0.1777	−0.0319
32	3.60	1.20	3.0264	0.9385	0.8975	0.1904
32	4.92	0.20	0.9338	0.0016	−0.0321	−0.0356
32	4.92	0.60	1.0560	0.0812	0.0302	−0.0554
32	4.92	0.80	1.4107	0.2189	0.1979	−0.0059
32	4.92	1.20	3.5433	0.9752	1.2110	0.3582
56	3.30	0.20	0.7302	−0.0830	−0.1476	−0.0392
56	3.30	0.40	0.6346	−0.0869	−0.2159	−0.0626
56	3.30	0.60	1.1007	0.2376	−0.0918	−0.0451
56	3.30	0.80	2.8633	1.3630	0.4766	0.0238
56	3.30	1.00	7.8558	4.4797	2.1170	0.2590
56	4.50	0.20	0.9321	0.0073	−0.0542	−0.0210
56	4.50	0.40	1.0601	0.1098	−0.0210	−0.0287
56	4.50	0.60	1.7015	0.5003	0.2020	−0.0005
56	4.50	0.80	3.5645	1.6781	0.8038	0.0834
80	3.00	0.05	0.8752	−0.0771	−0.0431	−0.0045
80	3.00	0.10	0.7768	−0.1350	−0.0798	−0.0084
80	3.00	0.20	0.6474	−0.2024	−0.1361	−0.0141
80	3.00	0.30	0.6332	−0.1862	−0.1627	−0.0179
80	3.00	0.40	0.8025	−0.0217	−0.1598	−0.0160
80	3.00	0.50	1.4534	0.5338	−0.0634	−0.0170
80	3.00	0.60	3.0074	1.8290	0.1805	−0.0021
80	4.08	0.05	0.9500	−0.0270	−0.0203	−0.0027
80	4.08	0.20	0.9386	−0.0027	−0.0522	−0.0065
80	4.08	0.40	1.4101	0.4130	0.0057	−0.0085
80	4.08	0.60	3.6407	2.2242	0.4032	0.0139

[*] The quantity $Z_{ij}^{CONF}=P_{ij}^{CONF}/\rho kT$, where P^{CONF} is the configurational pressure.

Table 13. Compressibilities of Diatomic/Diatomic Mixtures for Case II, Where $\ell_{11}=0.67\sigma_{11}$, $\ell_{22}=0.3292\sigma_{22}$, and $V_{11}=V_{22}$*

N_1	kT/ϵ_{11}	$\rho\sigma_{11}^3$	Z	Z_{11}^{CONF}	Z_{12}^{CONF}	Z_{22}^{CONF}
32	3.50	0.05	0.7944	−0.0060	−0.0702	−0.1293
32	3.50	0.10	0.6482	−0.0103	−0.1143	−0.2272
32	3.50	0.20	0.5049	−0.0116	−0.1478	−0.3357
32	3.50	0.30	0.5855	0.0141	−0.0942	−0.3343
32	3.50	0.40	1.3066	0.0958	0.2391	−0.0283
32	3.50	0.50	3.7267	0.3282	1.2943	1.1042
56	3.21	0.05	0.7910	−0.0313	−0.1033	−0.0745
56	3.21	0.10	0.6611	−0.0429	−0.1698	−0.1262
56	3.21	0.20	0.5064	−0.0413	−0.2435	−0.2087
56	3.21	0.30	0.5976	0.0163	−0.2026	−0.2160
56	3.21	0.40	1.4302	0.3011	0.2280	−0.0988
56	3.21	0.50	4.0690	0.9407	1.6716	0.4573
80	2.88	0.05	0.7834	−0.0799	−0.1056	−0.0311
80	2.88	0.10	0.6321	−0.1319	−0.1796	−0.0564
80	2.88	0.20	0.4618	−0.1774	−0.2790	−0.0818
80	2.88	0.30	0.5602	−0.0736	−0.2617	−0.1045
80	2.88	0.40	1.4904	0.4559	0.0987	−0.0641
80	2.88	0.50	4.4436	2.0427	1.3163	0.0846

* The quantity $Z_{ij}^{CONF}=P_{ij}^{CONF}/\rho kT$, where P^{CONF} is the configurational pressure.

Table 14. Compressibilities of Diatomic/Diatomic Mixtures for Case III, Where $\ell_{11}=0.67\sigma_{11}$, $\ell_{22}=0.3292\sigma_{22}$, and $\sigma_{11}=\sigma_{22}$*

N_1	kT/ϵ_{11}	$\rho\sigma_{11}^3$	Z	Z_{11}^{CONF}	Z_{12}^{CONF}	Z_{22}^{CONF}
32	3.54	0.10	0.6946	−0.0096	−0.1083	−0.1875
32	3.54	0.20	0.5492	−0.0124	−0.1466	−0.2918
32	3.54	0.30	0.5474	0.0042	−0.1438	−0.3129
32	3.54	0.40	0.8087	0.0572	−0.0070	−0.2415
32	3.54	0.50	1.8012	0.1770	0.4907	0.1339
32	3.54	0.60	4.2573	0.4422	1.6639	1.1514
56	3.25	0.10	0.7014	−0.0440	−0.1496	−0.1050
56	3.25	0.20	0.5521	−0.0592	−0.2311	−0.1577
56	3.25	0.30	0.5856	−0.0131	−0.2280	−0.1733
56	3.25	0.40	1.0361	0.1624	0.0040	−0.1303
56	3.25	0.50	2.5258	0.6493	0.7496	0.1269
56	3.25	0.60	6.0081	1.7123	2.5699	0.7259
80	2.92	0.05	0.8060	−0.0809	−0.0904	−0.0227
80	2.92	0.10	0.6784	−0.1271	−0.1520	−0.0426
80	2.92	0.20	0.5224	−0.1695	−0.2450	−0.0631
80	2.92	0.30	0.5886	−0.1029	−0.2325	−0.0760
80	2.92	0.40	1.2485	0.3316	−0.0222	−0.0609
80	2.92	0.50	3.4024	1.6200	0.7560	0.0264

* The quantity $Z_{ij}^{CONF}=P_{ij}^{CONF}/\rho kT$, where P^{CONF} is the configurational pressure.

Table 15. Configurational Internal Energies of Diatomic/Diatomic Mixtures for Case III, Where $\ell_{11}=0.67\sigma_{11}$, $\ell_{22}=0.3293\sigma_{22}$, and $\sigma_{11}=1.7\sigma_{22}$

N_1	kT/ϵ_{11}	$\rho\sigma_{11}^3$	$\frac{E^{CONF}}{N\epsilon_{11}}$	$\frac{E_{11}^{CONF}}{N\epsilon_{11}}$	$\frac{E_{12}^{CONF}}{N\epsilon_{11}}$	$\frac{E_{22}^{CONF}}{N\epsilon_{11}}$
32	3.60	0.10	−1.0050	−0.1747	−0.5274	−0.3028
32	3.60	0.20	−1.9806	−0.3412	−1.0361	−0.6033
32	3.60	0.40	−3.8585	−0.6594	−2.0062	−1.1929
32	3.60	0.60	−5.7031	−0.9808	−2.9151	−1.8072
32	3.60	0.80	−7.5819	−1.3175	−3.8335	−2.4310
32	3.60	1.00	−9.5070	−1.6268	−4.8396	−3.0406
32	3.60	1.20	−11.1663	−1.8030	−5.8467	−3.5166
32	4.92	0.20	−1.7590	−0.3072	−0.9277	−0.5252
32	4.92	0.60	−5.2779	−0.9296	−2.7277	−1.6205
32	4.92	0.80	−7.0631	−1.2141	−3.6664	−2.1820
32	4.92	1.20	−10.2810	−1.6052	−5.3231	−3.3516
56	3.30	0.20	−2.7094	−1.0833	−1.3120	−0.3141
56	3.30	0.40	−5.2450	−2.0873	−2.5356	−0.6221
56	3.30	0.60	−7.8751	−3.1650	−3.7733	−0.9369
56	3.30	0.80	−10.3891	−4.1143	−5.0572	−1.2176
56	3.30	1.00	−11.7561	−4.2528	−5.9754	−1.5279
56	4.50	0.20	−2.4411	−0.9915	−1.1787	−0.2717
56	4.50	0.40	−4.8644	−1.9673	−2.3510	−0.5459
56	4.50	0.60	−7.3348	−2.9402	−3.5658	−0.8283
56	4.50	0.80	−9.4813	−3.6638	−4.6932	−1.1234
80	3.00	0.05	−0.9280	−0.6107	−0.2913	−0.0260
80	3.00	0.10	−1.8163	−1.1882	−0.5745	−0.0536
80	3.00	0.20	−3.4849	−2.2769	−1.1028	−0.1053
80	3.00	0.30	−5.1618	−3.3518	−1.6439	−0.1661
80	3.00	0.40	−6.7919	−4.4487	−2.1402	−0.2030
80	3.00	0.50	−8.5205	−5.5929	−2.6635	−0.2641
80	3.00	0.60	−10.1036	−6.5924	−3.1776	−0.3335
80	4.08	0.05	−0.8176	−0.5442	−0.2511	−0.0225
80	4.08	0.20	−3.1775	−2.1008	−0.9872	−0.0897
80	4.08	0.40	−6.3563	−4.1774	−1.9971	−0.1814
80	4.08	0.60	−9.3337	−6.0423	−3.0016	−0.2891

Table 16. Configurational Internal Energies of Diatomic/Diatomic Mixtures for Case II, Where $\ell_{11}=0.67\sigma_{11}$, $\ell_{22}=0.3292\sigma_{22}$, and $V_{11}=V_{22}$

N_1	kT/ϵ_{11}	$\rho\sigma_{11}^3$	$\frac{E^{CONF}}{N\epsilon_{11}}$	$\frac{E_{11}^{CONF}}{N\epsilon_{11}}$	$\frac{E_{12}^{CONF}}{N\epsilon_{11}}$	$\frac{E_{22}^{CONF}}{N\epsilon_{11}}$
32	3.50	0.05	−1.5987	−0.0887	−0.5854	−0.9246
32	3.50	0.10	−3.1091	−0.1701	−1.1434	−1.7956
32	3.50	0.20	−5.8222	−0.3334	−2.1433	−3.3455
32	3.50	0.30	−8.4587	−0.5116	−3.1528	−4.7944
32	3.50	0.40	−11.2467	−0.6759	−4.2610	−6.3098
32	3.50	0.50	−13.7074	−0.8323	−5.1559	−7.7192
56	3.21	0.05	−1.5152	−0.2894	−0.7526	−0.4738
56	3.21	0.10	−2.9245	−0.5584	−1.4487	−0.9175
56	3.21	0.20	−5.4743	−1.0748	−2.7159	−1.6828
56	3.21	0.30	−7.9527	−1.6101	−3.9338	−2.4081
56	3.21	0.40	−10.5865	−2.1585	−5.2872	−3.1424
56	3.21	0.50	−12.9080	−2.5622	−6.6435	−3.7076
80	2.88	0.05	−1.4354	−0.6226	−0.6528	−0.1600
80	2.88	0.10	−2.7630	−1.2002	−1.2530	−0.3099
80	2.88	0.20	−5.1466	−2.2843	−2.2940	−0.5683
80	2.88	0.30	−7.4785	−3.3474	−3.3556	−0.7756
80	2.88	0.40	−9.9837	−4.4959	−4.5322	−0.9586
80	2.88	0.50	−12.1509	−5.4370	−5.5667	−1.1534

Table 17. Configurational Internal Energies of Diatomic/Diatomic Mixtures for Case III, Where $\ell_{11}=0.67\sigma_{11}$, $\ell_{22}=0.3292\sigma_{22}$, and $\sigma_{11}=\sigma_{22}$

N_1	kT/ϵ_{11}	$\rho\sigma_{11}^3$	$\frac{E^{CONF}}{N\epsilon_{11}}$	$\frac{E_{11}^{CONF}}{N\epsilon_{11}}$	$\frac{E_{12}^{CONF}}{N\epsilon_{11}}$	$\frac{E_{22}^{CONF}}{N\epsilon_{11}}$
32	3.54	0.10	−2.6125	−0.1726	−1.0164	−1.4237
32	3.54	0.20	−4.9737	−0.3345	−1.9226	−2.7161
32	3.54	0.30	−7.1924	−0.5062	−2.7633	−3.9224
32	3.54	0.40	−9.4880	−0.6838	−3.6776	−5.1274
32	3.54	0.50	−11.8466	−0.8287	−4.7165	−6.3042
32	3.54	0.60	−13.7663	−0.9082	−5.5550	−7.3089
56	3.25	0.10	−2.5812	−0.5588	−1.2864	−0.7360
56	3.25	0.20	−4.8827	−1.0641	−2.4622	−1.3565
56	3.25	0.30	−7.0621	−1.5710	−3.5600	−1.9312
56	3.25	0.40	−9.3976	−2.1303	−4.7076	−2.5596
56	3.25	0.50	−11.6460	−2.6233	−5.8976	−3.1252
56	3.25	0.60	−13.2884	−2.9112	−6.8272	−3.5499
80	2.92	0.05	−1.3164	−0.6152	−0.5727	−0.1285
80	2.92	0.10	−2.5511	−1.1861	−1.1124	−0.2526
80	2.92	0.20	−4.8289	−2.2919	−2.0809	−0.4561
80	2.92	0.30	−6.9493	−3.3321	−3.0003	−0.6169
80	2.92	0.40	−9.3190	−4.4986	−3.9855	−0.8249
80	2.92	0.50	−11.4599	−5.5104	−4.9902	−0.9593

Table 18. Compressibilities of Triatomic/Sphere Mixtures for Case I, Where $\ell_{11}=0.67\sigma_{11}$ and $\sigma_{11}=1.3\sigma_{22}$*

N_1	kT/ϵ_{11}	$\rho\sigma_{11}^3$	Z	Z_{11}^{CONF}	Z_{12}^{CONF}	Z_{22}^{CONF}
32	2.08	0.05	0.8466	−0.0826	−0.0576	−0.0132
32	2.08	0.10	0.7354	−0.1465	−0.0987	−0.0194
32	2.08	0.20	0.5853	−0.2182	−0.1644	−0.0321
32	2.08	0.40	0.4111	−0.3420	−0.2261	−0.0209
32	2.08	0.60	0.8014	−0.3187	0.0067	0.1134
32	2.08	0.80	3.2951	0.3686	1.4061	0.5211
32	2.88	0.10	0.8745	−0.0720	−0.0490	−0.0046
32	2.88	0.40	0.8978	−0.1682	0.0156	0.0503
32	2.88	0.60	1.6338	0.0104	0.4089	0.2147
32	2.88	0.80	4.0492	0.7832	1.6261	0.6408
56	2.50	0.05	0.7941	−0.1585	−0.0436	−0.0039
56	2.50	0.10	0.6448	−0.2743	−0.0764	−0.0045
56	2.50	0.20	0.4734	−0.4450	−0.0790	−0.0028
56	2.50	0.40	0.6687	−0.4851	0.1098	0.0440
56	2.50	0.50	1.9324	0.1574	0.6562	0.1188
56	2.50	0.60	5.2403	2.1454	1.8340	0.2608
56	3.46	0.05	0.9185	−0.0711	−0.0105	0.0001
56	3.46	0.20	0.8467	−0.1886	0.0234	0.0120
56	3.46	0.40	1.5602	0.1203	0.3690	0.0711
56	3.46	0.50	2.9565	0.8930	0.9184	0.1463
80	2.88	0.05	0.7636	−0.2128	−0.0230	−0.0006
80	2.88	0.10	0.6051	−0.3680	−0.0264	−0.0005
80	2.88	0.20	0.4337	−0.5688	−0.0010	0.0033
80	2.88	0.30	0.7499	−0.3733	0.1102	0.0129
80	2.88	0.40	2.7375	1.1296	0.5644	0.0442
80	3.96	0.05	0.9112	−0.0897	0.0004	0.0004
80	3.96	0.20	0.9621	−0.1200	0.0747	0.0073
80	3.96	0.30	1.6317	0.3530	0.2612	0.0176
80	3.96	0.40	3.7927	2.0485	0.7056	0.0391

* The quantity $Z_{ij}^{CONF}=P_{ij}^{CONF}/\rho kT$, where P^{CONF} is the configurational pressure.

Table 19. Compressibilities of Triatomic/Sphere Mixtures for Case II, Where $\ell_{11}=0.67\sigma_{11}$ and $V_{11}=V_{22}$*

N_1	kT/ϵ_{11}	$\rho\sigma_{11}^3$	Z	Z_{11}^{CONF}	Z_{12}^{CONF}	Z_{22}^{CONF}
32	2.08	0.025	0.8302	−0.0426	−0.0906	−0.0367
32	2.08	0.075	0.6077	−0.0873	−0.2207	−0.0844
32	2.08	0.100	0.5210	−0.1187	−0.2754	−0.0850
32	2.08	0.200	0.6569	−0.1295	−0.2934	0.0797
32	2.08	0.300	2.7530	0.0089	0.4948	1.2498
56	2.50	0.025	0.8348	−0.0807	−0.0748	−0.0098
56	2.50	0.075	0.6057	−0.1958	−0.1795	−0.0191
56	2.50	0.100	0.5413	−0.2304	−0.2152	−0.0131
56	2.50	0.200	0.6519	−0.2722	−0.1753	0.0994
56	2.50	0.300	2.8007	0.2394	0.8628	0.6985
80	2.88	0.075	0.6127	−0.2865	−0.0997	−0.0011
80	2.88	0.100	0.5337	−0.3433	−0.1235	0.0005
80	2.88	0.200	0.6322	−0.3691	−0.0406	0.0419
80	2.88	0.300	2.8155	0.7124	0.9010	0.2021

* The quantity $Z_{ij}^{CONF}=P_{ij}^{CONF}/\rho kT$, where P^{CONF} is the configurational pressure.

Table 20. Compressibilities of Triatomic/Sphere Mixtures for Case III, Where $\ell_{11}=0.67\sigma_{11}$ and $\sigma_{11}=\sigma_{22}$*

N_1	kT/ϵ_{11}	$\rho\sigma_{11}^3$	Z	Z_{11}^{CONF}	Z_{12}^{CONF}	Z_{22}^{CONF}
32	2.08	0.10	0.6594	−0.1377	−0.1586	−0.0442
32	2.08	0.20	0.4850	−0.2110	−0.2494	−0.0545
32	2.08	0.30	0.4318	−0.2653	−0.2870	−0.0159
32	2.08	0.40	0.7300	−0.2332	−0.1538	0.1170
32	2.08	0.50	1.7629	−0.1156	0.3973	0.4812
32	2.08	0.60	4.3287	0.3103	1.8460	1.1725
56	2.50	0.05	0.7737	−0.1531	−0.0676	−0.0056
56	2.50	0.10	0.6104	−0.2679	−0.1150	−0.0068
56	2.50	0.20	0.4758	−0.3777	−0.1486	0.0021
56	2.50	0.30	0.5904	−0.4213	−0.0403	0.0520
56	2.50	0.40	2.5348	1.7788	0.3751	0.1311
56	2.50	0.50	5.1925	1.4478	2.1785	0.5661
80	2.88	0.05	0.7401	−0.2198	−0.0391	−0.0011
80	2.88	0.10	0.5778	−0.3753	−0.0465	−0.0005
80	2.88	0.20	0.4748	−0.5090	−0.0233	0.0070
80	2.88	0.30	1.1504	−0.1152	0.2305	0.0352
80	2.88	0.40	4.3241	1.9981	1.2114	0.1149

* The quantity $Z_{ij}^{CONF}=P_{ij}^{CONF}/\rho kT$, where P^{CONF} is the configurational pressure.

Table 21. Configurational Internal Energies of Triatomic/Sphere Mixtures for Case I, Where $\ell_{11}=0.67\sigma_{11}$ and $\sigma_{11}=1.3\sigma_{22}$

N_1	kT/ϵ_{11}	$\rho\sigma_{11}^3$	$\frac{E^{CONF}}{N\epsilon_{11}}$	$\frac{E_{11}^{CONF}}{N\epsilon_{11}}$	$\frac{E_{12}^{CONF}}{N\epsilon_{11}}$	$\frac{E_{22}^{CONF}}{N\epsilon_{11}}$
32	2.08	0.05	−0.7706	−0.3949	−0.2980	−0.0778
32	2.08	0.10	−1.5163	−0.7787	−0.5852	−0.1524
32	2.08	0.20	−2.6192	−1.1994	−1.1119	−0.3079
32	2.08	0.40	−4.4392	−1.7942	−2.0320	−0.6126
32	2.08	0.60	−6.4211	−2.3963	−3.0908	−0.9372
32	2.08	0.80	−8.4927	−3.1518	−4.1704	−1.1763
56	2.50	0.05	−1.3097	−0.9420	−0.3320	−0.0357
56	2.50	0.10	−2.3952	−1.6787	−0.6453	−0.0712
56	2.50	0.20	−4.1827	−2.8150	−1.2245	−0.1430
56	2.50	0.40	−7.6697	−4.8971	−2.4751	−0.3013
56	2.50	0.50	−9.6766	−6.1709	−3.1465	−0.3591
56	2.50	0.60	−11.3066	−7.2729	−3.6188	−0.4230
56	3.46	0.05	−0.9948	−0.6728	−0.2894	−0.0327
56	3.46	0.20	−3.6748	−2.3987	−1.1422	−0.1339
56	3.46	0.40	−7.2459	−4.6707	−2.3063	−0.2686
56	3.46	0.50	−9.0247	−5.8345	−2.8572	−0.3361
80	2.88	0.05	−1.8944	−1.6298	−0.2535	−0.0113
80	2.88	0.10	−3.4369	−2.9184	−0.4963	−0.0224
80	2.88	0.20	−6.1603	−5.1366	−0.9793	−0.0442
80	2.88	0.30	−9.0283	−7.4819	−1.4808	−0.0690
80	2.88	0.40	−12.0886	−10.0155	−1.9845	−0.0946
80	3.96	0.05	−1.5098	−1.2714	−0.2284	−0.0104
80	3.96	0.20	−5.6391	−4.6835	−0.9139	−0.0418
80	3.96	0.30	−8.4810	−7.0240	−1.3981	−0.0586
80	3.96	0.40	−11.2383	−9.3603	−1.8053	−0.0766

Table 22. Configurational Internal Energies of Triatomic/Sphere Mixtures for Case II, Where $\ell_{11}=0.67\sigma_{11}$ and $V_{11}=V_{22}$

N_1	kT/ϵ_{11}	$\rho\sigma_{11}^3$	$\frac{E^{CONF}}{N\epsilon_{11}}$	$\frac{E_{11}^{CONF}}{N\epsilon_{11}}$	$\frac{E_{12}^{CONF}}{N\epsilon_{11}}$	$\frac{E_{22}^{CONF}}{N\epsilon_{11}}$
32	2.08	0.025	−0.8135	−0.1944	−0.3930	−0.2266
32	2.08	0.075	−2.2166	−0.4734	−1.0874	−0.6557
32	2.08	0.100	−2.9472	−0.6714	−1.4094	−0.8660
32	2.08	0.200	−5.2980	−1.0572	−2.5504	−1.6905
32	2.08	0.300	−7.6258	−1.3801	−3.8523	−2.3972
56	2.50	0.025	−0.9955	−0.4562	−0.4353	−0.1040
56	2.50	0.075	−2.7867	−1.2473	−1.2345	−0.3049
56	2.50	0.100	−3.6033	−1.6086	−1.5932	−0.4014
56	2.50	0.200	−6.5427	−2.7164	−3.0443	−0.7820
56	2.50	0.300	−9.5660	−4.0366	−4.4181	−1.1113
80	2.88	0.075	−3.2996	−2.2545	−0.9517	−0.0933
80	2.88	0.100	−4.2100	−2.8630	−1.2233	−0.1237
80	2.88	0.200	−7.8534	−5.2374	−2.3676	−0.2484
80	2.88	0.300	−11.6100	−7.6326	−3.6659	−0.3115

Table 23. Configurational Internal Energies of Triatomic/Sphere Mixtures for Case III, Where $\ell_{11}=0.67\sigma_{11}$ and $\sigma_{11}=\sigma_{22}$

N_1	kT/ϵ_{11}	$\rho\sigma_{11}^3$	$\frac{E^{CONF}}{N\epsilon_{11}}$	$\frac{E_{11}^{CONF}}{N\epsilon_{11}}$	$\frac{E_{12}^{CONF}}{N\epsilon_{11}}$	$\frac{E_{22}^{CONF}}{N\epsilon_{11}}$
32	2.08	0.10	−1.8954	−0.7157	−0.8489	−0.3308
32	2.08	0.20	−3.2660	−1.0338	−1.5858	−0.6464
32	2.08	0.30	−4.5328	−1.3435	−2.2290	−0.9603
32	2.08	0.40	−5.8863	−1.6536	−2.9524	−1.2802
32	2.08	0.50	−7.3043	−2.0528	−3.6650	−1.5865
32	2.08	0.60	−8.4775	−2.3071	−4.4193	−1.7510
56	2.50	0.05	−1.5008	−0.9371	−0.4869	−0.0768
56	2.50	0.10	−2.7524	−1.6705	−0.9287	−0.1532
56	2.50	0.20	−4.8704	−2.7964	−1.7696	−0.3044
56	2.50	0.30	−6.8376	−3.7325	−2.6516	−0.4535
56	2.50	0.40	−8.8880	−4.5153	−3.7832	−0.5894
56	2.50	0.50	−11.0227	−6.0783	−4.2914	−0.6530
80	2.88	0.05	−1.9983	−1.6068	−0.3673	−0.0244
80	2.88	0.10	−3.7618	−2.9993	−0.7147	−0.0478
80	2.88	0.20	−6.5972	−5.1005	−1.4035	−0.0930
80	2.88	0.30	−9.7705	−7.5109	−2.1238	−0.1400
80	2.88	0.40	−12.8551	−9.9236	−2.7783	−0.1600

Manuscript received Dec. 9, 1991, and revision received Sept. 21, 1992.