A NEW MIXING RULE BASED ON A STATISTICAL MECHANICAL PERTURBATION THEORY APPLICABLE TO NONPOLAR ASYMMETRIC MIXTURES

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A new mixing rule based on a statistical mechanical perturbation theory is proposed. It gives similar results to the van der Waals one-fluid model for mixtures of equisized molecules. A generalized equation of state utilizing the new mixing rule is applied to the calculation of high-pressure vapor-liquid equilibria for nonpolar asymmetric mixtures.

Comparisons are made with experimental data for binary systems containing hydrogen. The agreement of calculated and experimental high pressure vapor-liquid equilibria is rather good.

Introduction

Recently, much attention has been given to extending an equation of state (EOS) for pure fluids to mixtures. The general procedure for such extensions is to use the van der Waals one-fluid model⁽²⁸⁾ (vdW1). The vdW1 gives good results for symmetric systems.

For extension to asymmetric systems, a local composition, two-fluid model (LC) was studied by many authors.^{9,17,29,30} It seems important how rigorously characteristics of the attractive interaction between molecules are evaluated. Usually the LC is empirically treated to obtain good results in industrial calculations.

A statistical mechanical perturbation theory gives reasonable results for mixtures of molecules that differ in size. In this paper, a new mixing rule based on a statistical mechanical perturbation theory is proposed to extend an EOS for pure fluids to mixtures of asymmetric molecules that differ extremely in size. The generalized EOS proposed previously⁽⁶⁾ is used in the calculation of high-pressure vapor-liquid equilibria.

1. A New Mixing Rule

The Barker-Henderson perturbation theory⁽¹⁾ gives reasonable results for Lennard-Jones potential fluids. The first-order Helmholtz free energy for mixtures is expressed as follows:

$$\frac{A_1^M}{NkT} = \frac{2\pi\rho}{kT} \sum_i \sum_j x_i x_j \left[\int_{d_{ij}}^{\infty} u_{ij} g_{ij}^{hs} r^2 dr - \int_{d_{ij}}^{\sigma_{ij}} u_{ij} g_{ij}^{hs} r^2 dr \right] \quad (1)$$

where u_{ij} is the Lennard-Jones potential and g_{ij}^{hs} is the radial distribution function of hard-sphere mixtures. The first term of Eq. (1) is rewritten as follows:

$$\int_{d_{ij}}^{\infty} u_{ij} g_{ij}^{hs} r^2 dr = 4\epsilon_{ij} d_{ij}^3 S_{ij} \quad (2)$$

$$S_{ij} = I_{ij}^{(12)}/c_{ij}^{12} - I_{ij}^{(6)}/c_{ij}^6 \quad (3)$$

$$I_{ij}^{(n)} = \int_1^{\infty} \frac{1}{t_{ij}^{n-2}} g_{ij}^{hs} dt_{ij} \quad (4)$$

$$c_{ij} = \frac{d_{ij}}{\sigma_{ij}} = \int_0^1 \left[1 - \exp\left(-\frac{u_{ij}^*}{T_{ij}^*}\right) \right] d\left(\frac{r}{\sigma_{ij}}\right) = f(T_{ij}^*) \quad (5)$$

where $t_{ij} = r/d_{ij}$, $T_{ij}^* = kT/\epsilon_{ij}$, $u_{ij}^* = u_{ij}/\epsilon_{ij}$ and d_{ij} is the hard-sphere diameter. Since numerical calculation of Eq. (4) is time-consuming, it may not be applicable to industrial calculations as suggested by Rogers and Prausnitz.⁽²³⁾

In this work, I_{ij} defined in Eq. (4) was empirically approximated from the analogy of the radial distribution function at $r = d_{ij}$ for hard-sphere mixtures⁽¹¹⁾ as follows (see **Appendix**):

$$I_{ij}^{(n)} = I_{\text{pure}}^{(n)} + \delta_{ij} \left[I_{\text{pure}}^{(n)} - \frac{1}{(1-y)(n-3)} \right] \quad (6)$$

$$\delta_{ij} = (1-\alpha y) \ln(\sqrt{d_i d_j} \eta_2 / \eta_3) \quad (7)$$

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$$I_{\text{pure}}^{(n)} = \int_1^\infty \frac{1}{t^{n-2}} g_{\text{pure}}^{hs} dt = \sum_i a_{ni} y^{i-1} \quad (8)$$

$$y = \frac{\pi}{6} \rho \sum_i x_i d_i^3 \quad (9)$$

$$\eta_m = \sum_i x_i d_i^m \quad (10)$$

In this paper, Eq. (6) is called a new mixing rule. α in Eq. (7) is 1.1, which was determined from fitting to the exact S_{ij} calculated with the Percus-Yevic equation¹¹⁾ for the radial distribution function of hard-sphere mixtures. x_i is the mole fraction of component i and a_{ni} in Eq. (8) was given in the previous paper.³¹⁾ As S_{22} is more sensitive to the vapor-liquid equilibria for mixtures than S_{11} , where $d_1 < d_2$, α was determined to fit the exact S_{22} .

Figure 1 shows comparisons of equimolar S_{ij} for a binary mixture, $d_2/d_1 = 2$. In these calculations, c_{ij} is set at 0.95. The dashed lines express the mean-density approximation¹⁵⁾ results, where the integrals for mixtures are approximated with the corresponding pure-fluid integrals, and $I_{11} = I_{22} = I_{12} = I_{\text{pure}}$. **Figure 2** shows comparisons of S_{ij} at $y = 0.3$ for $d_2/d_1 = 2$. As shown in these figures, Eq. (6) gives relatively good results with average deviations of 1.7, 0.8 and 0.7% for S_{11} , S_{12} and S_{22} , respectively, in the regions of $0.1 < y < 0.4$, $1.2 < d_2/d_1 < 3$ and $0.1 < x_1 < 0.9$. Equation (6) will be also valid for variable c_{ij} and for other potentials like the 6-18 potential.

2. Equation of State for Mixtures

The Helmholtz free energy for pure fluids is expressed by using the generalized EOS proposed previously¹⁶⁾ as follows:

$$\frac{A}{NkT} = \frac{A_{hs}}{NkT} + \frac{A_1}{NkT} + \frac{A_2}{NkT} \quad (11)$$

$$\frac{A_1}{NkT} = 6 \times 3^{3/2} y \left(\frac{\gamma}{T^*} \right) [Z(y, c)_{\text{pure}}^{(18)}/c^{18} - Z(y, c)_{\text{pure}}^{(6)}/c^6] \quad (12)$$

$$Z(y, c)_{\text{pure}}^{(n)} = I_{\text{pure}}^{(n)} - \left[\frac{G_1 - G_2}{n-3} (1 - c^{n-3}) + \frac{G_2}{n-4} (1 - c^{n-4}) \right] \quad (13)$$

$$G_1 = (1 - y/2)/(1 - y)^3 \quad (14)$$

$$G_2 = \sum_{i=1}^4 b_i y^i \quad (15)$$

$$\frac{A_2}{NkT} = -40.5 \left(\frac{\gamma}{T^*} \right)^2 y F(T^*, y)_{\text{pure}} \quad (16)$$

$$F(T^*, y)_{\text{pure}} = \sum_{i=1}^6 E_i(T^*) y^{i-1} \quad (17)$$

$$E_i(T^*) = E_{i1} + E_{i2} T^* + E_{i3}/T^* + E_{i4}/T^{*2} + E_{i5}/T^{*5} \quad (18)$$

Fig. 1. Comparisons of calculated and exact S_{ij} for equimolar model mixtures.

Fig. 2. Comparisons of calculated and exact S_{ij} at $y = 0.3$.

The values of b_i and E_{ij} were given in the previous paper.¹⁶⁾

The Helmholtz free energy for mixtures is generally expressed as follows:

$$\frac{A^M}{NkT} = \frac{A_{hs}^M}{NkT} + \frac{A_1^M}{NkT} + \frac{A_2^M}{NkT} \quad (19)$$

where A_{hs}^M is the Helmholtz free energy of hard-sphere fluids, the property of which was rigorously given by Mansoori *et al.*¹⁴⁾ for the Carnahan-Starling EOS.³⁾ The Helmholtz free energy for perturbation terms is generally expressed as follows:

$$\frac{A_1^M}{NkT} = 3^{3/2} \pi \rho \sum_i \sum_j x_i x_j \left(\frac{\gamma_{ij}}{T_{ij}^*} \right) d_{ij}^3 \times (Z_{ij}^{(18)}/c_{ij}^{18} - Z_{ij}^{(6)}/c_{ij}^6) \quad (20)$$

$$\frac{A_2^M}{NkT} = -\frac{27}{4} \pi \rho \sum_i \sum_j x_i x_j \left(\frac{\gamma_{ij}}{T_{ij}^*} \right)^2 d_{ij}^3 F_{ij} \quad (21)$$

From the new mixing rule (Eq. (6)), $Z_{ij}^{(n)}$ and F_{ij} are expressed as follows:

$$Z_{ij}^{(n)} = Z(y, c_M)_{\text{pure}}^{(n)} + \delta_{ij} \left[Z(y, c_M)_{\text{pure}}^{(n)} - \frac{c_M^{n-3}}{(1-y)(n-3)} \right] \quad (22)$$

$$F_{ij} = F(y, T_M^*)_{\text{pure}} + \delta_{ij} \left[F(y, T_M^*)_{\text{pure}} - \frac{E_1(T_M^*)}{(1-y)} \right] \quad (23)$$

and

$$\left. \begin{aligned} \varepsilon_{ij} &= (1 - k_{ij})\sqrt{\varepsilon_i \varepsilon_j}; \quad \sigma_{ij} = (\sigma_i + \sigma_j)/2 \\ \gamma_{ij} &= \sqrt{\gamma_i \gamma_j}; \quad \gamma_i = \gamma_{0i} + \gamma_{1i}/T_i^* + \gamma_{2i}/T_i^{*2} \end{aligned} \right\} \quad (24)$$

$$T_M^* = kT/\varepsilon_M; \quad c_M = f(T_M^*) \quad (25)$$

The potential parameters for mixtures, which will be derived from the conformal-solution theory using the mean-density approximation,¹⁵⁾ were assumed to evaluate ε_M in Eq. (25).

$$\left. \begin{aligned} \varepsilon_M d_M^3 &= \sum \sum x_i x_j \varepsilon_{ij} d_{ij}^3 \\ \gamma_M \varepsilon_M d_M^3 &= \sum \sum x_i x_j \gamma_{ij} \varepsilon_{ij} d_{ij}^3 \\ \gamma_M^2 \varepsilon_M^2 d_M^3 &= \sum \sum x_i x_j \gamma_{ij}^2 \varepsilon_{ij}^2 d_{ij}^3 \end{aligned} \right\} \quad (26)$$

In this paper, these types of equations are called parameter-mixing rules.

From thermodynamic considerations, the pressure is derived as follows:

$$\begin{aligned} P &= \rho^2 kT [\partial(A/NkT)/\partial\rho]_{T,N} \\ &= P_{hs} + 3^{3/2} \pi \rho^2 kT \sum \sum x_i x_j \left(\frac{\gamma_{ij}}{T_{ij}^*} \right) d_{ij}^3 \\ &\quad \times (Z_{ij}^{(18)}/c_{ij}^{18} - Z_{ij}^{(6)}/c_{ij}^6) \\ &\quad - \frac{27}{4} \pi \rho^2 kT \sum \sum x_i x_j \left(\frac{\gamma_{ij}}{T_{ij}^*} \right)^2 d_{ij}^3 F'_{ij} \end{aligned} \quad (27)$$

where

$$\left. \begin{aligned} Z_{ij}^{(n)'} &= \partial \rho Z_{ij}^{(n)}/\partial \rho \\ F'_{ij} &= \partial \rho F_{ij}/\partial \rho \end{aligned} \right\} \quad (28)$$

As pointed out by Mollerup,¹⁸⁾ mixing rules should reduce to a random-mixture model when fitted to random-mixture data. For mixtures of equisized molecules, $d_i = d_j$, δ_{ij} becomes zero and the free energy for the attractive part becomes as follows:

$$\begin{aligned} \frac{A_1^M}{NkT} &= 3^{3/2} \frac{\pi \rho}{kT} \sum \sum x_i x_j \gamma_{ij} \varepsilon_{ij} d_{ij}^3 (Z(y, c_M)_{\text{pure}}^{(18)}/c_{ij}^{18} \\ &\quad - Z(y, c_M)_{\text{pure}}^{(6)}/c_{ij}^6) \end{aligned} \quad (29)$$

$$\frac{A_2^M}{NkT} = -\frac{27}{4} \frac{\pi \rho}{(kT)^2} F(y, T_M^*)_{\text{pure}} \sum \sum x_i x_j (\gamma_{ij} \varepsilon_{ij})^2 d_{ij}^3 \quad (30)$$

At low temperature limit, c_{ij} approaches unity. Then Eq. (29) becomes:

$$\begin{aligned} \frac{A_1^M}{NkT} &= 3^{3/2} \frac{\pi \rho}{kT} (Z(y, c_M)_{\text{pure}}^{(18)} - Z(y, c_M)_{\text{pure}}^{(6)}) \\ &\quad \times \sum \sum x_i x_j \gamma_{ij} \varepsilon_{ij} \sigma_{ij}^3 \end{aligned} \quad (31)$$

Equations (30) and (31) indicate that the new mixing rule gives similar expressions to the vdW1 model for mixtures of equisized molecules at low temperature limit.

$$\gamma_M \varepsilon_M \sigma_M^3 = \sum \sum x_i x_j \gamma_{ij} \varepsilon_{ij} \sigma_{ij}^3 \quad (32)$$

$$(\gamma_M \varepsilon_M)^2 \sigma_M^3 = \sum \sum x_i x_j (\gamma_{ij} \varepsilon_{ij})^2 \sigma_{ij}^3 \quad (33)$$

and from the approximation in Eq. (26) and the definition of y , Eq. (9), the remaining parameter-mixing rules are:

$$\left. \begin{aligned} \sigma_M^3 &= \sum x_i \sigma_i^3 (= \sum \sum x_i x_j \sigma_{ij}^3 \text{ at } \sigma_i = \sigma_j) \\ \varepsilon_M \sigma_M^3 &= \sum \sum x_i x_j \varepsilon_{ij} \sigma_{ij}^3 \end{aligned} \right\} \quad (34)$$

On the other hand, at high temperature limit, where $g_{ij}^{hs} \rightarrow 1$, the new mixing rule gives similar expressions to the vdW1 model for all kinds of nonpolar mixtures. It is expected at any temperature that the new mixing rule gives results for vapor-liquid equilibria for equisized mixtures similar to the results utilizing the vdW1 type parameter-mixing rules.

At low densities, the EOS utilizing the proposed mixing rule gives the second virial coefficient as follows:

$$\begin{aligned} B_M/N_{av} &= \frac{2}{3} \pi \sum \sum x_i x_j d_{ij}^3 + 3^{3/2} \pi \sum \sum x_i x_j \frac{\gamma_{ij}}{T_{ij}^*} d_{ij}^3 \\ &\quad \times (c_M^{15}/15c_{ij}^{18} - c_M^3/3c_{ij}^6) \\ &\quad - \frac{27}{4} \pi \sum \sum x_i x_j \left(\frac{\gamma_{ij}}{T_{ij}^*} \right)^2 d_{ij}^3 E_1(T_M^*) \end{aligned} \quad (35)$$

Since c_M and T_M^* depend on mole fractions, Eq. (35) does not have a quadratic mole-fraction dependence. But it approximately equals the second virial coefficient having such dependence. The second virial coefficients calculated from Eq. (35) agreed well with those calculated from a quadratic mole-fraction dependent expression with an absolute average error of 1.9 cm³/mol for the N_2 - n -heptane mixture, where the second virial coefficient for the mixture varies from -1300 to 25 cm³/mol.

3. Potential Parameters for Pure Substances

The potential parameters for hydrogen, which is a quantum gas, were assumed as follows as suggested by Gunn *et al.*⁸⁾

$$\left. \begin{aligned} \varepsilon_{ij} &= \varepsilon_{ij}^c / (1 + 21.8/M_{ij}T) \\ \sigma_{ij}^3 &= (\sigma_{ij}^c)^3 / (1 - 9.91/M_{ij}T) \\ 1/M_{ij} &= (1/M_i + 1/M_j)/2 \end{aligned} \right\} \quad (36)$$

where ε^c and σ^c are the classical potential parameters. The parameters for hydrogen were determined from the vapor pressures²¹⁾ and PVT data²²⁾ by a method similar to that described previously.¹⁶⁾ The average deviations for vapor pressures (21 to 31.5 K), PVT data (44 to 589 K, 0.1 to 69 MPa) and saturated liquid densities⁶⁾ (15 to 27 K) are 0.1, 0.5 and 4.2%, respectively. The absolute error for the second virial coefficients⁴⁾ is 7.7 cm³/mol at temperatures from 14 to 400 K. The potential parameters for other sub-

Table 1. Potential parameters for pure substances

Substance	ε/k [K]	$\sigma \times 10^{10}$ [m]	γ_0	γ_1	γ_2
H ₂ ^a	39.492	2.8447	1.2009	-0.0570	0.0699
N ₂	145.13	3.4801	0.8996	0.0099	0.0042
CO ₂	409.45	3.5561	0.6628	0.0939	-0.0007
Methane	210.04	3.6128	0.9590	-0.0068	0.0044
<i>n</i> -Hexane	710.36	5.6809	0.5929	0.1237	-0.0031
<i>n</i> -Heptane	767.35	5.9311	0.5461	0.1525	-0.0057
<i>n</i> -Decane	897.06	6.7001	0.4358	0.2269	-0.0124
Benzene	750.40	5.0089	0.6765	0.0883	-0.0002
Toluene	810.63	5.3788	0.6308	0.1081	-0.0018
<i>m</i> -Xylene	869.97	5.6944	0.5635	0.1436	-0.0050

Values of ε and σ for hydrogen are ε^e and σ^e , respectively.

stances were obtained from the generalized correlations¹⁶⁾ and are listed in **Table 1**.

4. Calculation of High-Pressure Vapor-Liquid Equilibria

The generalized EOS for mixtures utilizing the proposed mixing rule, Eq. (6), is applied to the calculation of high-pressure vapor-liquid equilibria. In these calculations, the binary interaction parameters, k_{ij} , which are introduced in Eq. (24), were fitted to experimental liquid-phase compositions at experimental temperatures and pressures, and are listed in **Table 2** for several systems. In phase equilibrium calculations, the chemical potential for component i was obtained by numerical differentiations of free energy with respect to N_i .

$$\mu_i = (\partial A / \partial N_i)_{T, N_{j \neq i}} \quad (37)$$

Although an analytical expression for chemical potentials can be obtained from Eq. (37), it will be more troublesome. **Figures 3 to 6** show typical results for calculated vapor-liquid equilibria. In Figs. 3 and 4, the calculated results for nonpolar mixtures which differ in size are compared with experimental data.^{5,13)} The solid lines express the calculated results using the new mixing rule, and one-point dashed lines express the calculated results with optimum interaction parameter using the vdW1 type parameter-mixing rules for whole perturbed terms in Eqs. (11) to (18), which are expressed as follows:

$$\left. \begin{aligned} \sigma_M^3 &= \sum \sum x_i x_j \sigma_{ij}^3 \\ \varepsilon_M \sigma_M^3 &= \sum \sum x_i x_j \varepsilon_{ij} \sigma_{ij}^3 \\ \gamma_M \varepsilon_M \sigma_M^3 &= \sum \sum x_i x_j \gamma_{ij} \varepsilon_{ij} \sigma_{ij}^3 \end{aligned} \right\} \quad (38)$$

Agreement between experimental data and calculated results utilizing the new mixing rule is rather good.

In Figs. 5 and 6, the results for mixtures containing hydrogen are compared with experimental data. For the hydrogen (1)-methane (2) system,²⁷⁾ the molecular size is appreciably different. At low tempera-

Fig. 3. Vapor-liquid equilibria for the N₂-*n*-heptane system.⁵⁾ Solid line, proposed mixing rule with optimum k_{12} ; one-point dashed line, vdW1 model with optimum k_{12} .

Fig. 4. Vapor-liquid equilibria for methane-benzene system.¹³⁾ Solid and one-point dashed lines as in Fig. 3.

Fig. 5. Vapor-liquid equilibria for H₂-methane system.²⁷⁾ Solid and one-point dashed lines as in Fig. 3.

tures, quantum effects may not be negligible. For the hydrogen (1)-*n*-heptane (2) system,²²⁾ the ratios

Table 2. Interaction parameters for several nonpolar mixtures

System	Temperature [K]	Maximum pressure [MPa]	k_{12} [—]	$\Delta x^* \times 100$	$\Delta y^{**} \times 100$	ND***
H ₂ -Methane ²⁷⁾	92.3	130.	-0.005	0.78	1.94	10
	100.0	90.	-0.009	1.41	1.98	9
	110.0	62.	-0.014	1.72	2.17	8
	130.0	34.	-0.021	0.88	0.75	9
	150.0	22.	-0.03	1.08	2.82	7
	170.0	12.	-0.04	0.52	3.02	5
H ₂ - <i>n</i> -Heptane ²²⁾	424.15	80.	0.185	0.36	0.40	8
	471.65	70.	0.12	0.75	1.83	10
	498.85	35.	0.08	0.56	3.29	8
H ₂ - <i>n</i> -Decane ²⁴⁾	462.45	25.	0.28	0.17	0.36	7
	503.35	25.	0.26	0.24	0.73	7
	542.95	25.	0.24	0.26	2.03	7
	583.45	25.	0.20	1.94	1.76	5
	542.15	32.	0.08	0.36	1.49	6
H ₂ -Toluene ¹⁰⁾	568.15	28.	0.05	0.60	2.82	4
N ₂ - <i>n</i> -Heptane ⁵⁾	453.15-497.15	27.	0.14	1.47	2.10	18
CO ₂ - <i>n</i> -Hexane ¹²⁾	313.15-353.15	11.	0.19	0.79	0.29	19
CO ₂ - <i>n</i> -Decane ²⁵⁾	393.15	12.	0.18	0.33	0.61	8
	462.55	5.	0.245	0.14	0.16	4
	542.95	5.	0.23	0.07	1.07	4
CO ₂ -Toluene ²⁶⁾	583.65	5.	0.215	0.23	1.50	4
	393.25-542.85	5.	0.145	0.28	2.55	12
CO ₂ - <i>m</i> -Xylene ¹⁹⁾	394.3-477.6	17.	0.155	1.15	0.63	16
Methane- <i>n</i> -Decane ¹³⁾	542.75	13.	0.14	0.30	1.35	4
	583.05	9.	0.12	1.13	2.87	5
Methane-Benzene ¹³⁾	421.05-501.15	24.	0.07	1.10	3.81	18
Methane-Toluene ¹³⁾	422.45-543.15	25.	0.085	1.10	2.08	25
Methane- <i>m</i> -Xylene ¹⁹⁾	394.3-477.6	14.	0.09	1.09	0.71	21

* $\Delta x = \left[\sum_{i=1}^{ND} (x_{cal} - x_{exp})^2 / ND \right]^{1/2}$; x is mole fraction of solute in liquid phase

** $\Delta y = \left[\sum_{i=1}^{ND} (y_{cal} - y_{exp})^2 / ND \right]^{1/2}$; y is mole fraction of solute in vapor phase

*** ND: Number of data points

Fig. 6. Vapor-liquid equilibria for H₂-*n*-heptane system.²²⁾ Solid and one-point dashed lines as in Fig. 3. Dashed lines express results using GT method.

σ_2/σ_1 and ϵ_2/ϵ_1 are 2.1 and 19.4, respectively. Although quantum effects may be negligible at high temperatures, the molecules differ extremely in size and well depth of potential function for this system.

The generalized EOS utilizing the vdW1 type parameter-mixing rules using temperature-dependent parameters for quantum gases gives poor results for such asymmetric systems. On the other hand, same EOS utilizing the new mixing rule was successfully applied to correlate high pressure vapor-liquid equilibria.

The interaction parameters for nonpolar asymmetric mixtures, especially for systems containing hydrogen, depended on temperature as listed in Table 2, and smooth relations between interaction parameters and temperatures were obtained as suggested by Nishiumi.²⁰⁾ This is probably due to empirical treatment of quantum effects, inaccuracy of EOS and uncertainties in mixing rules.

For other nonpolar asymmetric systems listed in Table 2, the calculated vapor-liquid equilibria utiliz-

Fig. 7. Vapor-liquid equilibria for equisized model mixtures; $d_2/d_1 = 1$ ($\sigma_1 = 3.6 \times 10^{-10}$ m), $\epsilon_2/\epsilon_1 = 4$ ($\epsilon_1/k = 200$ K), $\gamma_2 = \gamma_1 = 1$. Lines as in Fig. 3.

ing the new mixing rule agreed with experimental data, as well as for the systems discussed above. In this table, comparisons of calculated and experimental vapor and liquid compositions at experimental temperatures and pressures except near the critical points for mixture are made. The third column in Table 2 shows the maximum pressures for which comparisons were made.

Another method to extend an EOS for pure fluids to mixtures, proposed by Gubbins and Twu⁷⁾ (GT), is also tested, where the mean-density approximation was used. Utilizing this approximation, Z_{ij} and F_{ij} are expressed as follows:

$$\left. \begin{aligned} Z_{ij}^{(n)} &= Z(y_M, c_{ij})_{\text{pure}}^{(n)} \\ F_{ij} &= F(y_M, T_{ij}^*)_{\text{pure}} \end{aligned} \right\} \quad (39)$$

$$y_M = \frac{\pi}{6} \rho d_M^3; \quad d_M^3 = \sum_i \sum_j x_i x_j d_{ij}^3 \quad (40)$$

Equation (39) was applied to calculations of vapor-liquid equilibria for the H_2 - n -heptane system at 498.9 K. As shown by dashed lines in Fig. 6, this method gives poor results for mixtures which differ extremely in size, and fails to converge at high pressures.

In Fig. 7, the calculated results utilizing the new mixing rule are compared with the results utilizing parameter-mixing rules, Eq. (38), for equisized model mixtures. The results utilizing the new mixing rule deviate slightly from the results utilizing parameter-mixing rules, Eq. (38). Although Eqs. (32), (33) and (34) should all be used in the determination of potential parameters for mixtures, it is impossible to satisfy all equations with the three parameters ϵ_M , σ_M and γ_M . This is probably the reason why the two results deviate slightly from each other.

Conclusion

The generalized equation of state proposed previously has been applied successfully to the calculation of high-pressure vapor-liquid equilibria for nonpolar asymmetric mixtures containing hydrogen, utilizing a new mixing rule (Eq. (6)) based on statistical mechanical perturbation theory. For mixtures of equisized molecules, this mixing rule gives results similar to those of the vdW1 model.

This mixing rule may be empirically applicable to other perturbed type equations like the van der Waals equation of state.

Appendix

The rigorous expression of the radial distribution function at $r = d_{ij}$ for hard-sphere mixtures¹¹⁾ is:

$$g_{ij}^{hs}(d_{ij}) = g_{\text{pure}}^{hs}(d) + \left(\frac{2d_j}{d_i + d_j} \frac{\eta_2}{\eta_3} - 1 \right) \left[g_{\text{pure}}^{hs}(d) - \frac{1}{1-y} \right] \quad (\text{A-1})$$

We assume $g_{ij}^{hs}(r)$ as follows:

$$g_{ij}^{hs}(r) = g_{\text{pure}}^{hs}(r) + \delta_{ij} \left[g_{\text{pure}}^{hs}(r) - \frac{1}{1-y} \right] \quad (\text{A-2})$$

Eq. (A-2) may be a good approximation in the range of $r \approx d$. By inserting Eq. (A-2) into Eq. (4), Eq. (6) is obtained, where the form of δ_{ij} is empirically determined from fitting to the exact S_{ij} , which is expressed by Eq. (7).

Nomenclature

A	= Helmholtz free energy	[J]
a_{ni}	= constant, Eq. (8)	[-]
B	= second virial coefficient	[m ³ /mol]
b_i	= constant, Eq. (15)	[-]
c	= cut-off parameter	[-]
d	= effective hard-sphere diameter	[m]
E	= constant, Eq. (18)	[-]
g	= radial distribution function	[-]
k	= Boltzmann constant	[J/K]
M	= relative molecular mass	[-]
N	= number of molecules	[-]
N_{av}	= Avogadro constant	[1/mol]
P	= pressure	[Pa]
r	= intermolecular distance	[m]
T	= temperature	[K]
t	= r/d	[-]
u	= intermolecular potential	[J]
x	= mole fraction	[-]
y	= reduced density	[-]
y	= mole fraction in vapor phase, Fig. 7	[-]
α	= parameter defined in Eq. (7)	[-]
γ	= third parameter	[-]
δ	= parameter defined in Eq. (7)	[-]
ϵ	= well depth in potential function	[J]
η	= parameter defined in Eq. (10)	[-]
μ	= chemical potential	[J]
ρ	= number density	[1/m ³]
σ	= collision diameter	[m]

<Superscripts and Subscripts>

<i>c</i>	= classical value
cal	= calculated value
exp	= experimental value
<i>M</i>	= property of mixture
*	= reduced property
<i>i, j</i>	= component <i>i, j</i>
<i>hs</i>	= property of hard-sphere system
pure	= property of pure component

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