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Equations of State for the Lennard-Jones Mixtures at High Temperatures

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The virial coefficients for binary mixtures at high temperatures were directly calculated up to the fifth term by use of a Monte-Carlo integration technique and the various empirical mixing rules that have been proposed for estimating mixture virial coefficients were tested. It was found that these empirical mixing rules tend to fail as the molecular size differences increased. Accurate compressibility of the Lennard–Jones binary mixtures were also calculated by adopting Metropolis Monte-Carlo simulations in order to examine validity of the fifth order virial equation of state. At high temperature ($T^*=20$), the compressibility factors calculated by the fifth order virial equation of state were in good agreement with the results of the simulations in the range of $V/b \geqslant 0.4$ ($b=2\pi\sigma^3 N_a/3$). It was also found that the van der Waals one fluid theory could provide accurate compressibility factors even for mixtures of molecules with large size differences at high temperatures.

Although detailed knowledge of the equation of state (EOS) for mixtures is required for the calculations of equilibrium properties of high density multi-component systems such as chemical equilibrium behind detonation waves, precise theoretical determination of the EOS for high density mixtures still remains very difficult. Because of this, various types of empirical or semi-empirical EOS have been widely used in many practical applications. Recent progress in Monte-Carlo and molecular dynamics simulations enables the direct calculations of properties of dense mixtures and the validity of empirical EOS has been examined against these simulation results.[1–4] However these examinations are often limited to relatively low temperature region. The accuracy of empirical EOS for dense mixtures at high temperatures still remains unclear. The primary purpose of the present study is to test the applicability of the virial EOS and the van der Waals one fluid theory to the prediction of properties of dense mixtures at high temperatures. Such examinations are especially important in exploring an adequate EOS for the calculations of detonation properties.

The virial EOS,

$$\frac{pV}{RT}=1+\frac{B(T)}{V}+\frac{C(T)}{V^2}+\frac{D(T)}{V^3}+\frac{E(T)}{V^4}+\cdots, \tag{1}$$

has several advantages for many practical applications. Its simple analytical form is well suitable to the determination of complex chemical equilibrium composition by minimizing the Gibbs free energy. In principle, the virial coefficients can be calculated theoretically on the basis of intermolecular potentials. However calculations of virial coefficients for mixtures are rather difficult; specially, exact calculation of the third and higher order virial coefficients for mixtures has not been performed. Although various empirical mixing rules for mixture virial coefficients[5–7] have been used in the past, these mixing rules have weak theoretical basis and therefore their validity has to be tested by comparing with exact mixture virial coefficients.

In the present study, the virial coefficients for binary mixtures of molecules interacting with Lennard–Jones (L–J) 12-6 potentials were calculated numerically up to fifth term. Calculations were performed with a hypothetical Lorentz–Berthelot rule for unlike L–J parameters. Although this rule is very simple, relathionship of mixing rule between the unlike L–J parameters and the virial coefficients is not straightforward. Resulting virial coefficients were compared with those derived from empirical mixing rules over wide ranges of interaction potential parameters. In addition, exact compressibility of binary L–J mixtures were directly calculated by the use of Metropolis Monte-Carlo simulation and results were compared with compressibility factors calculated by the fourth order virial EOS for the binary mixtures.

An effective one component treatment of dense mixtures is generally used in many practical EOS. Among these, the van der Waals one-fluid (vdW1) theory is the most popular and its validity at low temperatures has been investigated by comparing with the results of Monte-Carlo[8] or Molecular Dynamics[9] computer simulations. These investigations suggested that applicability of the vdW1 theory was questionable for systems that contain molecules having quite different intermolecular potential parameters. Although the vdW1 theory has been frequently applied to the calculations of detonation properties,[10] its validity has to be examined. Compressibility factors obtained from the vdW1 theory were also compared with the results of the Metropolis Monte-Carlo simulations in order to clarify the applicability of the vdw1 theory at high temperatures.

1. Virial Coefficients for Binary L-J Mixtures

1-1 Calculation of Virial Coefficients. The virial coefficients for mixtures can be written as,

$$\begin{aligned} B_m &= \Sigma\Sigma\, X_iX_jB_{ij}, \\ C_m &= \Sigma\Sigma\Sigma\, X_iX_jX_kC_{ijk}, \\ D_m &= \Sigma\Sigma\Sigma\Sigma\, X_iX_jX_kX_lD_{ijkl}, \\ E_m &= \Sigma\Sigma\Sigma\Sigma\Sigma\, X_iX_jX_kX_lX_mE_{ijklm}, \end{aligned} \tag{2}$$

here X_i is the mole fraction of component i, and B_{ij}, C_{ijk},$\cdots$ are the virial coefficients which depend on intermolecular potentials for i, j, k,$\cdots\cdots$ molecules. For example, the coefficient D_{ijkl} depends on the potential energy functions between four molecules, i, j, k, and l, and can be expressed as a sum of the cluster integral. By using notations given by Rowlinson[11] for the irreducible cluster integral, the following expression for D_{ijkl} can be derived:

$$D_{ijkl} = -(D_4 + D_5 + D_6)/8. \tag{3}$$

Here, D_4, D_5, and D_6 are the integral of the product of Mayer F-functions. For an example, a term D_4 is expressed as follows,

$$D_4 = D_{4a} + D_{4b} + D_{4c}, \tag{4}$$

$$D_{4a} = \iiint f_{01}f_{12}f_{23}f_{30}\,dR_1dR_2dR_3, \tag{5a}$$

$$D_{4b} = \iiint f_{01}f_{13}f_{32}f_{20}\,dR_1dR_2dR_3, \tag{5b}$$

$$D_{4c} = \iiint f_{02}f_{21}f_{13}f_{30}\,dR_1dR_2dR_3, \tag{5c}$$

$$f_{ij} = \exp\left(-\frac{U_{ij}}{kT}\right) - 1. \tag{6}$$

Here, f_{ij} is a Mayer F-function, U_{ij} is the potential between molecules i and j, and R_i ($i \neq 0$) is the position vector between molecule i and molecule 0. It is noted that the values of D_{4a}, D_{4b}, and D_{4c} are all the same for a pure fluid, but they are different each other for the multi-component system. Similar expressions for other virial coefficients can also be derived by adopting the diagrams for the irreducible cluster integral given by Rowlinson.

Calculations of virial coefficients were performed for the Lennard–Jones (L–J) binary mixtures. Although the L–J potential is known to be inaccurate as a representation of the intermolecular interaction for high energy collisions, the L–J fluid provides a convenient model for testing various mixture theories. In the present calculations, the Lorentz–Berthelot mixing rule was used for unlike intermolecular interactions; i.e., the potential energy between unlike molecules i and j is given by the equation;

$$U_{12} = 4\varepsilon_{12}((\sigma_{12}/r)^{12} - (\varepsilon_{12}/r)^6). \tag{7}$$

The L–J parameters for unlike interaction, ε_{12} and σ_{12} are calculated from the L–J parameters for a pure fluid;

$$\varepsilon_{12} = (\varepsilon_{11}\varepsilon_{22})^{1/2} = \varepsilon_{11}\alpha^{1/2}, \tag{8}$$

$$\sigma_{12} = (\sigma_{11} + \sigma_{22})/2 = \sigma_{11}(1+\eta)/2, \tag{9}$$

here, $\alpha = \varepsilon_{22}/\varepsilon_{11}$ and $\eta = \sigma_{22}/\sigma_{11}$.

The second virial coefficient for the binary mixture, B_{12}, is directly obtained form the reduced second virial coefficient, $B^*(T^*)$, for the pure fluid;

$$B_{12}(T^*_{12}) = b_{12}B^*(T^*_{12}), \tag{10}$$

here $T^*_{12} = kT/\varepsilon_{12}$ and $b_{12} = 2\pi\sigma_{12}^3N_a/3$ (N_a is the Avogadro number). In order to obtain higher-order virial coefficients for mixtures, various types of irreducible cluster integrals such as given in Eq. 5 have to be calculated. Although Barker et al.[12] have used the Simpson's formula to integrate these cluster integrals for a pure fluid, it is quite difficult to apply their method to a multi-component system. A numerical integration technique proposed by Conroy[13] was employed in the present calculation. Points are selected at random in space of the integration variables and the integrands are evaluated at these points. It was found that the mean value of the integrands did not converge well to the integral unless large number of points were used. However, the calculations were speeded up by employing a stratified sampling technique. For the calculation of the third virial coefficients, the intermolecular distance in the range of 0.001σ to 10σ was divided into 4 regions. These segments of intermolecular distance construct 4^2 sub-spaces of the integration variables (*strata*). Sampling points in each strata were selected by using quasi-random numbers.[13] In case of fourth and fifth virial coefficients, intermolecular distances were divided into 9 and 10 regions so that 9^3 and 10^4 strata were composed for fourth and fifth virial coefficients, respectively. It was found that total numbers of 1.6×10^6, 7.29×10^6, and 1×10^8 sampling points were required for the calculation of the third, forth, and fifth virial coefficients in order to achieve the relative accuracy within 1%.

The fifth virial coefficient for a pure fluid at $T^*=20$ were also calculated to test the integration scheme. A value of 0.0207 for the normalized fifth virial coefficient, $E_{11111}^* = E_{11111}/b_{11}^4$, is in good agreement with a value of 0.0209 calculated by Barker et al.[12] The normalized virial coefficients for unlike interactions, C^*_{ijk}, D^*_{ijkl}, and E^*_{ijklm}, were calculated at $T^*_{11}=20$ for 'σ-equal' fluid ($\eta=1$) and 'ε-equal' fluid ($\alpha=1$); results are summarized in Tables 1 and 2, respectively. Calculations of the fifth virial coefficient were only performed for parameter sets of $\alpha=1$, $\eta=2$ and $\alpha=3$, $\eta=1$, since these calculations needed very long CPU time (120 min on Cray X-MP/416).

1-2 Comparisons with Empirical Virial Coefficients for Mixtures. Although several empirical virial coefficients for unlike interactions have been proposed in

Table 1. Normalized Virial Coefficients for the ε-Equal Fluid ($\varepsilon_{11}=\varepsilon_{22}$) at $T^*_{11}=20$
(Values for a pure fluid are taken from Ref. 12.)

$\eta=\sigma_{11}/\sigma_{22}$	1	1.25	1.5	1.75	2.0
B^*_{11}	0.5254	0.5254	0.5254	0.5254	0.5254
B^*_{12}	0.5254	0.7480	1.0260	1.3650	1.7728
B^*_{22}	0.5254	1.0260	1.7732	2.8158	4.2032
C^*_{111}	0.2464	0.2464	0.2464	0.2464	0.2464
C^*_{112}	0.2464	0.3895	0.5764	0.8100	1.1008
C^*_{122}	0.2464	0.6088	1.3019	2.5133	4.4992
C^*_{222}	0.2464	0.9399	2.8067	7.0773	15.770
D^*_{1111}	0.0832	0.0832	0.0832	0.0832	0.0832
D^*_{1112}	0.0832	0.1386	0.2157	0.3186	0.4413
D^*_{1122}	0.0832	0.2295	0.5382	1.1053	2.1504
D^*_{1222}	0.0832	0.3777	1.3301	3.9000	10.086
D^*_{2222}	0.0832	0.6199	3.1985	12.808	42.598
E^*_{11111}	0.0209	0.0209	0.0209	0.0209	0.0209
E^*_{11112}	0.0209				0.1282
E^*_{11122}	0.0209				0.7578
E^*_{11222}	0.0209				4.6694
E^*_{12222}	0.0209				18.268
E^*_{22222}	0.0209				85.606

Table 2. Normalized Virial Coefficients for the σ-Equal Fluid ($\sigma_{11}=\sigma_{22}$) at $T^*_{11}=20$
(Values for a pure fluid are taken from Ref. 12.)

$\alpha=\varepsilon_{11}/\varepsilon_{22}$	1	2	3	4
B^*_{11}	0.5254	0.5254	0.5254	0.6254
B^*_{12}	0.5254	0.5058	0.4833	0.4609
B^*_{22}	0.5254	0.4609	0.3608	0.2433
C^*_{111}	0.2464	0.2464	0.2464	0.2464
C^*_{112}	0.2464	0.2601	0.2672	0.2716
C^*_{122}	0.2464	0.2734	0.2857	0.2924
C^*_{222}	0.2464	0.2861	0.3038	0.3151
D^*_{1111}	0.0832	0.0832	0.0832	0.0832
D^*_{1112}	0.0832	0.0910	0.0956	0.0989
D^*_{1122}	0.0832	0.0992	0.1087	0.1151
D^*_{1222}	0.0832	0.1075	0.1210	0.1291
D^*_{2222}	0.0832	0.1156	0.1327	0.1341
E^*_{11111}	0.0209	0.0209	0.0209	0.0209
E^*_{11112}	0.0209		0.0257	
E^*_{11122}	0.0209		0.0315	
E^*_{11222}	0.0209		0.0385	
E^*_{12222}	0.0209		0.0458	
E^*_{22222}	0.0209		0.0546	

the past, these have weak theoretical basis and the validity of empirical formulae for the fourth and fifth coefficients has never been tested against results of strict numerical calculations. Among these, following three approximations for mixture virial coefficients were tested.

(i) Based on the statistical mechanical expression of the third virial coefficient, Orentlincher et al.[5] proposed the following expression,

$$C_{ijk}=(C_{ij}C_{jk}C_{ki})^{1/2}. \tag{11}$$

The coefficient C_{ij} is defined by a similar relation to Eq. 10:

$$C_{ij}=b_{ij}{}^2C^*(T^*{}_{ij}). \tag{12}$$

Here C^* is the reduced virial coefficient for a pure fluid.

(ii) Rowlinson et al.[6] have examined several scaling approximations for mixture virial coefficients by comparing with exact values of C_{112}. They recommended to use the following expressions:

$$C_{ijk}=(b_{ij}b_{jk}b_{ki})^{2/3}C^*(kT/\varepsilon_{ijk}), \tag{13}$$

$$\varepsilon_{ijk}=(\varepsilon_{ij}\varepsilon_{jk}\varepsilon_{ki})^{1/3}. \tag{14}$$

(iii) McHenry[7] proposed an empirical formula given below:

$$C_{ijk}=b_{ijk}{}^2C^*(kT/\varepsilon_{ijk}), \tag{15}$$

$$b_{ijk}=2\pi[(\sigma_{ij}+\sigma_{jk}+\sigma_{ki})/3]^3N_a/3. \tag{16}$$

Extension of these mixing rules (i)—(iii) to higher order virial coefficients is straightforward. In the above equations, the reduced virial coefficients for a pure fluid, $B^*(T^*)$, $C^*(T^*)$,···, are required to calculate mixture virial coefficients. These values were obtained by a spline interpolation of the pure-component virial coefficients given by Barker et al.[12] Resulting third and fourth virial coefficients based on the approximations (i) and (ii) are compared with the values calculated by the direct numerical integration in Fig. 1 for 'σ-equal' fluid as a function of α. It is noted that the approximations (ii) and (iii) give the same results for σ-equal fluid. As can be seen in the figure, the approximation (ii) generally gives better agreement with the results of direct numerical calculations than the approximation (i). However, errors in approximations (i) and (ii) are within 5% in the range of $\varepsilon \leqslant 4$. Figure 2 shows comparisons of mixture virial coefficients based on the approximations (ii) and (iii) with those obtained by the numerical calculations for 'ε-equal' fluid as a function of the size parameter ratio, η. In this case, the approximation (ii) is also better than (iii), but its error is more than 10% at $\eta=2$ and is rapidly increasing with increasing the difference in molecular size.

At high temperature ($T^*{}_{11}=20$), it can be concluded that these empirical mixing rules (i)—(iii) for binary L–J mixtures give relatively small errors ($\leqslant$5%) for the mixture which contains molecules of similar size even if the L–J energy parameters of these molecules are quite different. However none of these approximations can

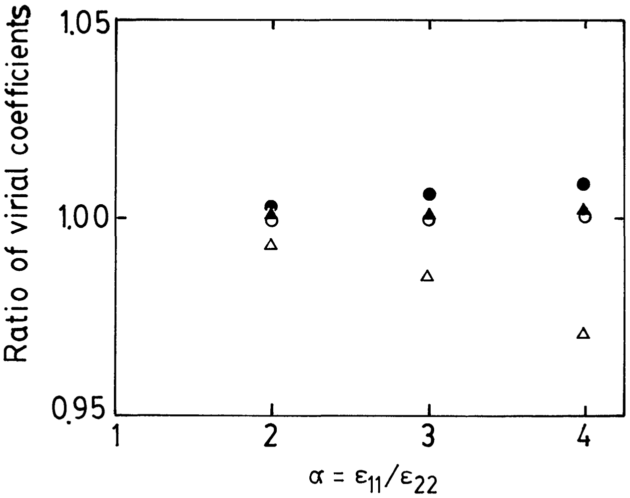

Fig. 1. Comparison of the unlike virial coefficients, C_{122}(closed points) and D_{1122}(open points), at $T^*_{11}=20$ for the σ-equal fluid calculated by the empirical mixing rules with Monte-Carlo calculations. Vertical axis is the ratio of [empirical virial coefficient]/[exact Monte-Carlo virial coefficient]. Triangles: mixing rule (i), Circles: mixing rule (ii).

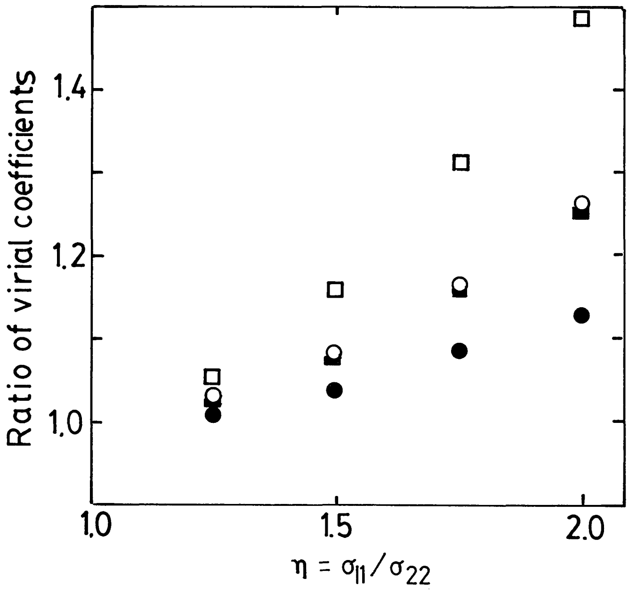

Fig. 2. Comparison of the unlike virial coefficients, C_{122}(closed points) and D_{1122}(open points), at $T^*_{11}=20$ for the ε-equal fluid calculated by the emprical mixing rules with Monte-Carlo calculations. Vertical axis is the ratio of [empirical virial coefficient]/[exact Monte Carlo virial coefficient]. Circles: mixing rule (ii), Squares: mixing rule (iii).

provide the precise third and fourth virial coefficients for mixtures containing molecules which have large difference in size.

2. Compressibility Factors at High Temperatures

2-1 Metropolis Monte-Carlo Calculation of Compressibility Factors. The compressibility factors for the L–J fluid of a single component has been widely studied by using Monte-Carlo[14–17] or molecular dynamics[18–22] simulations. Nicolas, Gubbins, Street, and Tildesley (NGST) proposed the EOS for L–J pure fluid which had 33 parameters.[14] These parameters were determined by fitting the compressibility factors to the results of their own molecular dynamics simulations together with many other results of Monte-Carlo and molecular dynamics calculations at $T^*\leqslant6$ and $V/b\geqslant0.4$ (V is the specific volume). Although the applicability of these simulations with limited number of molecules to much higher density range is not clear, Wood and Parker[1] showed that the Metropolis Monte-Carlo simulation[23] could be useful for the region of $V/b\geqslant0.2$ at the temperature of $2T_c$ (T_c=the critical temperature). Since this density region is high enough for the application to many detonation problem, it might be interesting to calculate the high temperature compressibility factors by the Metropolis Monte-Carlo simulation.

In the present study, compressibility factors at high temperatures both for pure and multi-component systems were calculated by using Metropolis Monte-Carlo technique and the results were compared with the compressibility factors calculated by the virial EOS. The results presented here employed 256 particles in a cubic cell with periodic boundary conditions. A chain length of 10^5 was generated to achieve the convergence of the calculated pressures after first 6×10^4 chains were discard in order to ensure the complete relaxation of the system from the fcc initial configuration. A new configuration in the chains was constructed by moving a particle in the cell. A particle to be moved and its displacement were determined by random numbers. The rate of convergence with chain length was governed by a value of the maximum displacement of a particle to construct a new configuration in the chains. Optimum value for this maximum displacement was found to be 0.075σ.

Results of the Metropolis Monte-Carlo simulations for pure L–J fluid at $T^*=2.5$ and 20 are compared with compressibility factors calculated by the fifth order virial EOS in Fig. 3. As can be seen in the figure, the fifth order virial EOS is only valid in very low density region at $T^*=2.5$, whereas the virial series is readily converged at $T^*=20$ in the range of $V/b\leqslant0.2$. At high temperatures, less terms seem to be needed to achieve the convergence of the virial series. In Fig. 3 compressibility factors calculated by the NGST EOS are also shown for comparison. Although the NGST EOS were derived from simulation data in the range of $0.5\leqslant T^*\leqslant6$ and $0.4\leqslant V/b\leqslant1.4$, results of the present Metropolis Monte-Carlo simulations are in good agreement with the NGST EOS in the range of $V/b\geqslant0.2$ even at $T^*=20$. This indicates that the NGST EOS can be applicable at high temperatures for the calculation of detonation properties.

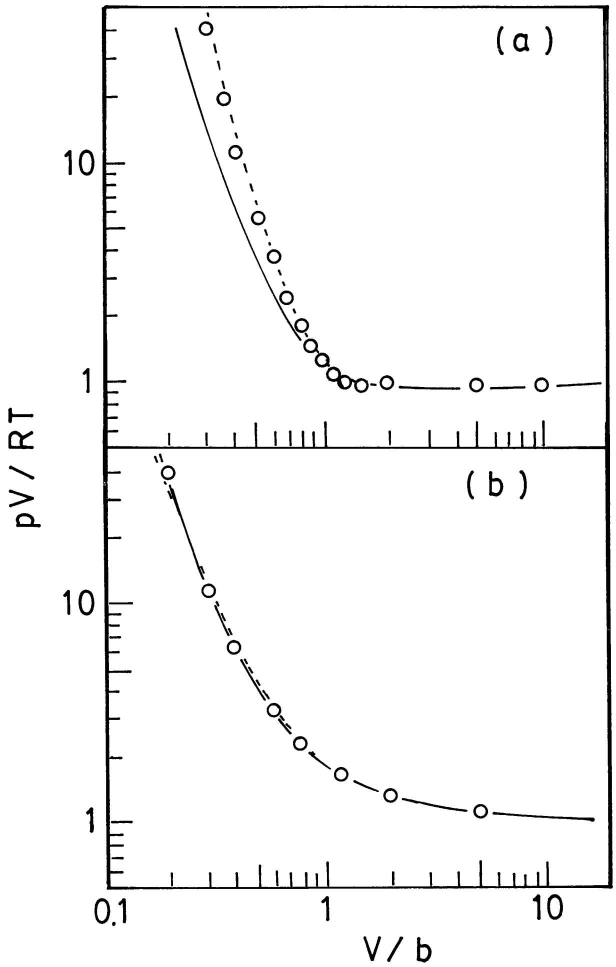

Fig. 3. Compressibility factor of the L–J pure fluid at $T^*=2.5$ (a) and $T^*=20$ (b). Circles: Metropolis Monte-Carlo simulation, solid line: the fifth order virial equation of state, broken line: the NGST equation of state (Ref. 14).

The compressibility factors for the equimolar L–J binary mixture obtained by the present Metropolis Monte-Carlo simulations at $T^*{}_{11}=20$ are shown in Fig. 4 for the ε-equal mixture with $\eta=2$ and in Fig. 5 for the σ-equal mixture with $\alpha=3$. In both cases the fifth order virial EOS gives excellent agreement with the present simulation results. These results suggest that the virial EOS converges much faster at high temperatures than at low temperatures in the range of $V/b \geqslant 0.2$.

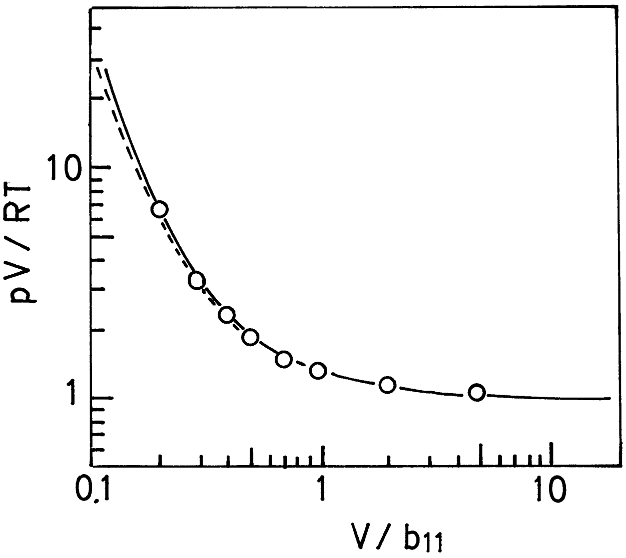

Fig. 4. Compressibility factor of the L–J binary mixture at $T^*_{11}=20$. $\alpha=\varepsilon_{11}/\varepsilon_{22}=1$ and $\eta=\sigma_{11}/\sigma_{22}=2$. Circles: Metropolis Monte-Carlo simulation, solid line: the fifth order virial equation of state, broken line: the vdW1 theory with the NGST equation of state (Ref. 14).

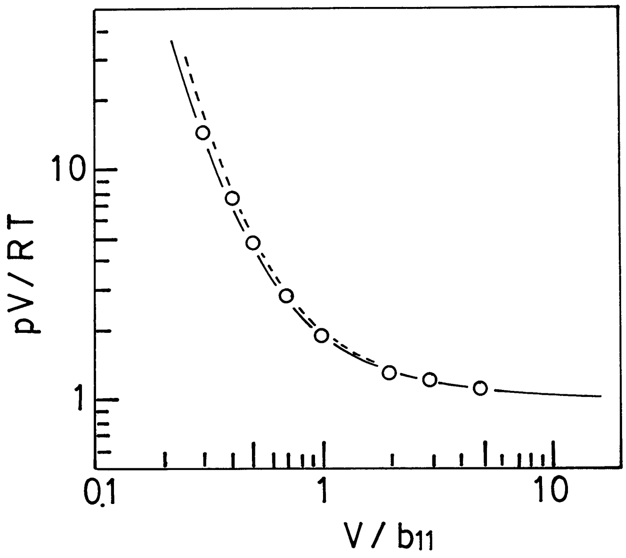

Fig. 5. Compressibility factor of the L–J binary mixture at $T^*_{11}=20$. $\alpha=\varepsilon_{11}/\varepsilon_{22}=3$ and $\eta=\sigma_{11}/\sigma_{22}=1$. Circles: Metropolis Monte-Carlo simulation, solid line: the fifth order virial equation of state, broken line: the vdW1 theory with the NGST equation of state (Ref. 14).

2-2 Effective One Component Treatment of Dense Mixtures. The fifth order virial EOS gives accurate compressibility factors both for a single and multi-component systems at high temperatures, if the density is not too high. However, in many practical applications of the virial EOS such as calculations of chemical equilibrium in Chapman–Jouguet detonation, temperature derivatives of the virial coefficients are required. Since calculation of derivatives of virial coefficients by the Monte-Carlo or other numerical integration method is quite difficult, the analytical expression of the EOS is desirable for dense mixtures. The van der Waals one fluid theory is the one of the most widely used analytical expression of the equation of state in which a hypothetical effective one component potential is used for all of the intermolecular interactions. The parameters of this effective one component L–J potential, σ_m and ε_m, is given by following equations:

$$\sigma_m{}^3=\sum\sum X_iX_j\sigma_{ij}{}^3, \tag{17}$$

$$\varepsilon_m=\sum\sum X_iX_j\varepsilon_{ij}\sigma_{ij}{}^3/\sigma_m{}^3. \tag{18}$$

By adopting the NGST EOS to define the EOS for this effective one component fluid, the compressibility factors were calculated and results are compared in Figs. 4 and 5. The van der Waals theory gives good agreement with the simulation results for ε-equal fluid and slightly higher values than the simulations for the mixtures of $\alpha=3$ and $\eta=1$. However the disagreement in this case is less than 10% in the range of $V/b\geqslant 0.4$.

It has been shown that the prediction of van der Waals mixture theory deteriorates as the molecular size difference between the species of the mixture increases at low temperatures.[2,4,24] Our results in Figs. 4 and 5 indicate that the accuracy of the van der Waals one fluid theory is considerably improved at high temperatures.

Recently Hamad and Mansoori[24] proposed a new dense fluid theory of mixtures which can be applicable for mixtures of molecules with large size and energy differences. Their theory is based on the effective one component treatment and the L–J parameters for mixtures are obtained by solving the following set of equations:

$$\frac{C^*(kT/\varepsilon_m)}{B^{*2}(kT/\varepsilon_m)}=\frac{\Sigma\Sigma\Sigma X_iX_jX_kC_{ijk}}{(\Sigma\Sigma X_iX_jB_{ij})^2}, \tag{19}$$

$$\sigma_m{}^3=\frac{\Sigma\Sigma X_iX_j\sigma_{ij}{}^3B^*(kT/\varepsilon_{ij})}{B^*(kT/\varepsilon_m)}. \tag{20}$$

The use of Eqs. 19 and 20 in calculating the mixture L–J parameters requires knowledge of the unlike interaction third virial coefficients. They used empirical mixing rules (i)—(iii) for C_{ijk} to solve Eqs. 19 and 20 and found their theory gave accurate values of Henry's constant, pressure, and internal energy of dense mixtures at low temperatures. At high temperatures, empirical mixing rules (i)—(iii) are not accurate, as shown in the previous section. We tried to solve Eqs. 19 and 20 with the exact unlike interaction third virial coefficients calculated by the Monte-Carlo integrations at $T^*_{11}=20$. However the attempt was failed because of the numerical instability. It is also noted that a value of σ_m in Eq. 20 is different from $\sigma_{11}=\sigma_{22}$ for the σ-equal mixtures if $\alpha\neq 1$. The applicability of Eqs. 19 and 20 at high temperatures seems to be limited unless the precise analytical expressions for C_{ijk} are available.

3. Conclusions

The virial coefficients for unlike intermolecular interactions were calculated up to the fifth order term by the direct numerical integration of cluster integral. Several empirical mixing rules for the unlike interaction virial coefficients were tested at high temperature against the results of the numerical integration. The accuracy of these approximate virial coefficients were found to be not enough for the mixtures which contained species having different molecular size.

Although the fifth order virial equation of state understimates the compressibility factors at low temperatures, it gives accurate compressibility factors of dense fluid mixtures in the range of $V/b\geqslant 0.4$ at $T^*=20$. It is also found that the van der Waals one fluid theory can provide good approximation for compressibility of mixtures regardless the difference in molecular size at high temperatures. The van der Waals one fluid theory with accurate analytical equation of state for a pure fluid such as the NGST equation of state is promising for predicting properties of high temperature dense mixtures.

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