International Journal of Thermophysics, Vol. 9, No. 6, 1988

Equations of State for Hard-Sphere Fluids[1]

Y. Zhou[2] and G. Stell[2,3]

Equations of state and contact values of hard-sphere radial distribution functions (rdf's) which are given by a linear combination of the Percus–Yevick and scaled-particle virial expressions are considered. In the one-component case the mixing coefficient $\theta(\eta)$ is, in general, a function of the volume fraction η. In mixtures the coefficient $\theta(\eta_i, d_i)$, in general, depends upon the volume fraction η_i and diameter d_i of each species, i and j. For the contact values Y_{ij} of the rdf's, the mixing coefficients $\Theta_{ij}(\eta_k)$ also depend on species i and j. Density expansions for the exact θ for the one-component hard-sphere fluid are obtained and compared with several approximations made in earlier works and in our own work, as well as with simulations. For a mixture, it turns out that one cannot obtain the exact fourth virial coefficient by using a linear combination of the Percus–Yevick and scaled-particle virial expressions for Y_{ij} unless one allows Θ_{ij} to depend on mole fractions x_i even at the zeroth order of its density expansion. We also find that Θ_{ij} must depend on particle species i and j in order to satisfy the exact limits obtained earlier by Sung and Stell. A new equation of state for the binary hard-sphere mixture which satisfies all the exact limits we have considered is suggested.

KEY WORDS: contact value of radial distributions; equation of state; hard-sphere fluids; virial coefficients.

1. INTRODUCTION

Increasingly refined approximate equations of state for the hard-sphere fluid and hard-sphere mixture continue to be proposed [1–3] as a result of the availability of increasingly accurate simulation data [4] (for review, see Ref. 1).

---

[1] Paper presented at the Tenth Symposium on Thermophysical Properties, June 20–23, 1988, Gaithersburg, Maryland, U.S.A.

[2] Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794, U.S.A.

[3] Department of Mechanical Engineering, State University of New York at Stony Brook, Stony Brook, New York 11794, U.S.A.

From the solution of the Percus–Yevick (PY) equation, one obtains two equations of state; one is obtained from the virial equations, and the other from the compressibility equation [5]

$$\frac{\beta p_{\mathrm{v}}^{\mathrm{PY}}}{\rho}=\frac{1}{1-\eta}+\frac{3\xi_1\xi_2+3\xi_2^3}{\xi_0(1-\eta)^2} \tag{1}$$

$$\frac{\beta p_{\mathrm{c}}^{\mathrm{PY}}}{\rho}=\frac{1}{1-\eta}+\frac{3\xi_1\xi_2}{\xi_0(1-\eta)^2}+\frac{3\xi_2^3}{\xi_0(1-\eta)^3} \tag{2}$$

where

$$\xi_i=\frac{\pi}{6}\rho\sum_k^m x_k d_k^i, \qquad \eta=\xi_3 \tag{3}$$

ρ is the total number density, x_i and d_i are the molar fraction and diameter of species i, respectively, and subscripts v and c stand for virial and compressibility, respectively.

It turns out that a more accurate equation of state for hard-sphere systems is the combination of Eqs. (1) and (2) [7, 8]

$$p=(1-\theta)\,p_{\mathrm{c}}^{\mathrm{PY}}+\theta p_{\mathrm{v}}^{\mathrm{PY}} \tag{4}$$

where the θ should be a function of $\rho_i=x_i\rho$ and d_i in general.

Since the pressure obtained from the compressibility equation [Eq. (2)] in the PY approximation is the same as that obtained from the virial equation in scaled-particle theory (SPT) [6], we have

$$p_{\mathrm{c}}^{\mathrm{PY}}=p_{\mathrm{v}}^{\mathrm{SPT}} \tag{5}$$

A more accurate contact value of the pair distribution function corresponding to Eq. (4) has also been proposed [9]:

$$Y_{ij}=(1-\Theta_{ij})\,Y_{ij}^{\mathrm{SPT}}+\Theta_{ij}Y_{ij}^{\mathrm{PY}} \tag{6}$$

where Y_{ij} is the contact value of the pair distribution function for the pair i, j. Superscripts SPT and PY refer to the scaled-particle theory and PY approximation, respectively. Obviously, one must have $\Theta_{ij}=\Theta_{ji}$ if $i\neq j$. Putting Eq. (6) into the virial equation yields Eq. (4) if Θ_{ij} is independent of i and j $(\Theta_{ij}=\theta)$. For a one-component system, we have $\Theta_{ij}=\theta$.

When $\theta=\frac{1}{3}$, Eq. (4) reduces to the Carnahan–Starling (CS) equation of state [7] for a pure hard-sphere fluid and the Mansoori–Carnahan–Starling–Leland (MCSL) equation of state for mixtures [8]. However, it turns out that the pressure predicted by the CS equation of state is systematically lower than recent accurate simulation data [4]. A new simple equation has been suggested by Kolafa [3], which yields a better fit to simulation data, and it has been extended to mixtures and hard convex bodies by Boublík [2]. We find that their equations correspond to $\theta = \frac{2}{9}(1+\eta)$ in Eq. (4) (although neither Kolafa [3] nor Boublík [2] expressed their results in terms of θ).

In Section 2 we analyze the optimized $\theta(\eta)$ which can fit simulation data [4] for a single-component hard-sphere fluid . Then in Section 3, we analyze the optimized Θ_{ij} for the hard-sphere mixtures. It turns out that Eq. (6) is not able to predict the exact fourth virial coefficient for the binary hard-sphere mixtures unless the Θ_{ij} are allowed to depend upon the mole fraction x_i of the components. Requirements of the exact point-solvent limit [1] together with another exact equation [10] in the combined low solute-concentration continuum-solvent limit provide a crucial test for the equations of the contact values and equations of state for mixtures. We show that Θ_{ij} must depend on i and j in order to satisfy these exact relations.

2. EQUATIONS OF STATE FOR ONE-COMPONENT HARD-SPHERE FLUIDS

The equation of state obtained from Eq. (4) is

$$\frac{\beta p}{\rho} = \frac{1}{1-\eta} + \frac{3\xi_1\xi_2}{\xi_0(1-\eta)^2} + \frac{3\xi_2^3(1-\eta\theta)}{\xi_0(1-\eta)^3} \tag{7}$$

For a one-component hard-sphere system, this reduces to

$$\frac{\beta p}{\rho} = \frac{1+\eta+\eta^2-3\eta^3\theta}{(1-\eta)^3} \tag{8}$$

Here the exact θ must depend on η. If we use the pressure which is obtained from simulation data [4] in Eq. (8), then we can obtain simulation results of θ as a function of the packing fraction. Results are shown in Fig. 1. $\theta = \frac{1}{3}$ and $\theta = 2(1+\eta)/9$ are also plotted for comparison. It shows that $\theta = 2(1+\eta)/9$ is much more accurate than $\theta = \frac{1}{3}$.

However, some other linear expressions of θ are also worth considering. We find that when we choose $\theta(\eta) = 5/23 + (3/13)\eta$, the equation of state is even closer to simulation data (Figs. 2 and 3). Comparison among some other recently suggested equations of state is also made in Figs. 2 and 3. It shows that linear combinations of the PY virial and compressibility equations (8) yield highly accurate equations of state for extremely simple θ.

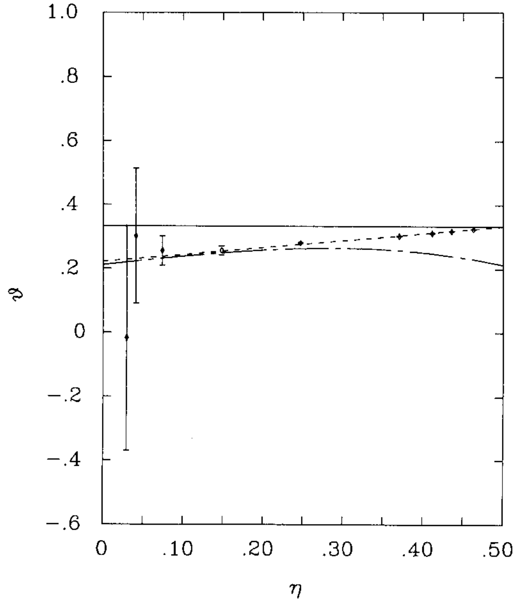

Fig. 1. The mixing coefficient θ as a function of the packing fraction (η). CS result (——); Kolafa result (– – –); simulation [4] (◇); results from Eq. (13) (---). The result from Eq. (14) is indistinguishable from the Kolafa result at high density and from the result of Eq. (13) at low density.

The virial expansion of the equations of state for different θ is as follows: $\theta = \frac{1}{3}$ (CS equation),

$$\frac{\beta p}{\rho} = 1 + 4\eta + 10\eta^2 + 18\eta^3 + 28\eta^4 + 40\eta^5 + 54\eta^6 + \cdots \tag{9}$$

$\theta = 2(1+\eta)/9$ (Kolafa equation),

$$\frac{\beta p}{\rho} = 1 + 4\eta + 10\eta^2 + 18\frac{1}{3}\eta^3 + 28\frac{1}{3}\eta^4 + 40\eta^5 + 53\frac{1}{3}\eta^6 + \cdots \tag{10}$$

$\theta = 5/23 + (3/13)\eta$,

$$\frac{\beta p}{\rho} = 1 + 4\eta + 10\eta^2 + 18.348\eta^3 + 28.3511\eta^4 + 40.01\eta^5 + 53.32\eta^6 + \cdots \tag{11}$$

For comparison, the exact results [1] are

$$\frac{\beta p}{\rho} = 1 + 4\eta + 10\eta^2 + 18.3648\eta^3 + 28.2245\eta^4 + 39.83\eta^5 + 56.1\eta^6 + \cdots \tag{12}$$

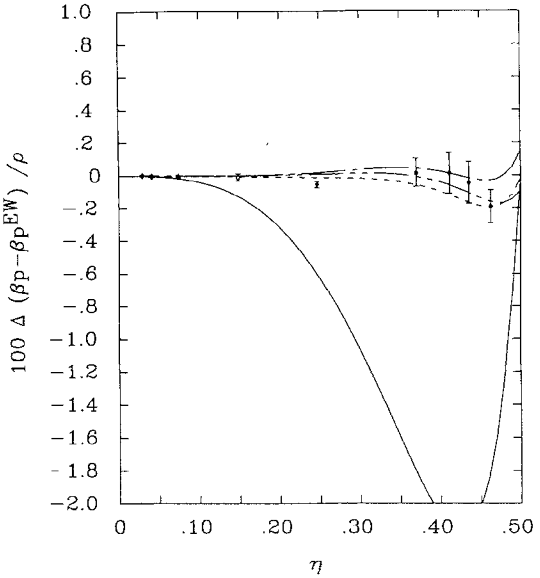

Fig. 2. $100\Delta(\beta p-\beta p^{\mathrm{EW}})/\rho$ as a function of the packing fraction, where p^{EW} is the Padé approximation result obtained in Ref. 4. CS equation (——); Kolafa equation (– – –); $\theta=5/23+3/13\eta$ (—–—); equation obtained by adjusting B_6 and B_7 [Eq. (14)] (----); simulation [4] (◇).

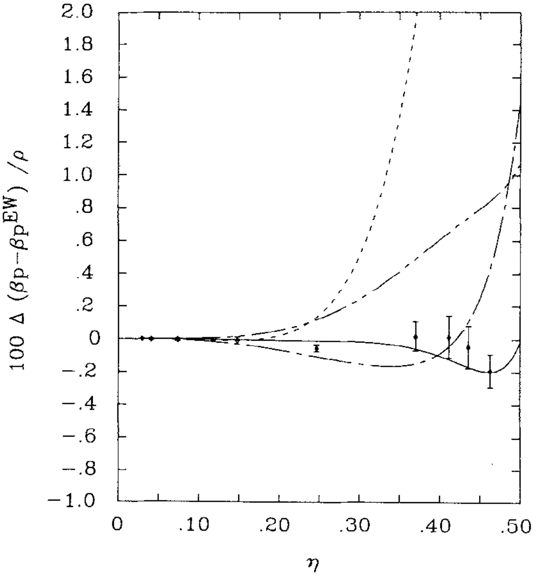

Fig. 3. $100\Delta(\beta p-\beta p^{\mathrm{EW}})/\rho$ as a function of the packing fraction, where p^{EW} is the Padé approximation result obtained in Ref. 4. $\theta=2(1+\eta)/9$ compared with other equations recently suggested in Ref. 2. Kolafa equation (——); Eq. (27) in Ref. 2 (– – –); Eq. (28) in Ref. 2 (—–—); Eq. (29) in Ref. 2 (----); simulation [4] (◇).

which give us an exact $\theta(\eta)$ by expanding Eq. (8):

$$\theta(\eta) = 0.2117333 + 0.2899666\eta - 0.0836333\eta^2 - 0.9729\eta^3 \tag{13}$$

Thus, the exact θ for the one-component hard-sphere fluid depends on the density if one goes beyond the third virial coefficient. As in Ref. 4, we also can adjust the virial coefficients B_6 and B_7 to fit simulation data. The results of $\theta(\eta)$ are

$$\theta(\eta) = 0.2117333 + 0.2899666\eta - 0.17\eta^2 + 0.155\eta^3 \tag{14}$$

with reduced virial coefficients

$$B_6 = 40.1, \qquad B_7 = 53.5 \tag{15}$$

3. EQUATIONS OF STATE FOR BINARY HARD-SPHERE MIXTURES

For hard-sphere mixtures, the virial expansion of pressure yields [11]

$$\frac{\beta p}{\rho} = 1 + B\rho + C\rho^2 + D\rho^3 + \cdots \tag{16}$$

with

$$B = \sum_{ij} x_i x_j B_{ij} \tag{17a}$$

$$C = \sum_{ijk} x_i x_j x_k C_{ijk} \tag{17b}$$

$$D = \sum_{ijkl} x_i x_j x_k x_l D_{ijkl} \tag{17c}$$

where B_{ij}, C_{ijk}, and D_{ijkl} are the second, the third, and the fourth virial coefficients for hard-sphere mixtures, respectively.

It is well known that both the PY approximation and the SPT give the exact first three virial coefficients for hard-sphere mixtures [5, 6] and the good fourth virial coefficient (Table I). If one assumes that the contact values of cavity function satisfy Eq. (6), then one can obtain the pressure via the virial equation:

$$\beta p = \rho + \frac{2\pi}{3} \sum_{ij} x_i x_j d_{ij}^3 Y_{ij} \rho^2 \tag{18}$$

where $d_{ij} = (d_i + d_j)/2$.

Table I. The fourth virial coefficients of binary hard-sphere mixtures, which are reduced by $(d_{12})^9$, in different approximations [$\Theta_{ij}=2(1+\eta)/9$ gives results between that of $\Theta_{ij}=0$ and that of $\Theta_{ij}=\frac{1}{3}$, very close to the latter]

$d_1/d_2=0.6$	$\Theta_{ij}=0$	$\Theta_{ij}=\frac{1}{3}$	$\Theta_{ij}=1$	This work[a]	Exact [11][a]
D_{1111}	0.20478	0.19400	0.1724516	0.1979	0.19789
D_{1112}	0.68681	0.65188	0.5820241	0.6654	0.66367
D_{1122}	2.22513	2.1142	1.892473	2.1576	2.0900
D_{1222}	6.90905	6.5625	5.869485	6.6950	6.7957
D_{2222}	20.3207	19.251	17.11220	19.641	19.637

[a] $\Theta_{ii}=0.2117$ and Θ_{12} from Eq. (32). The "exact" results are numerical, nonanalytic assessments. The D_{1111} and D_{2222} of this work are exact and analytically expressible.

The contact value obtained from Eq. (6) after plugging in the PY [5] and SPT [6] results can be written as

$$Y_{ij}=\frac{1}{(1-\eta)}+\frac{3\xi_2 d_i d_j}{(1-\eta)^2(d_i+d_j)}+(1-\Theta_{ij})\frac{3\xi_2^2 d_i^2 d_j^2}{(1-\eta)^3(d_i+d_j)^2} \qquad (19)$$

where $\Theta_{ij}=0$, $\frac{1}{3}$, $2(1+\eta)/9$, and 1 give the pressure obtained from the PY virial equation, MCSL equation, Boublík equation, and equation from the SPT, respectively, if one combines Eqs. (18) and (19). The predictions of the fourth virial coefficients by these equations are compared with exact results [11] in Table I. It can be seen that the MCSL results are better than the SPT and the PY predictions. If we take $\Theta_{ij}=0.2117$, the first nonzero term of the density expansion of the exact Θ for one-component hard spheres [Eq. (13)], we recover the exact D_{1111} and D_{2222} (within the accuracy of "exact" results in Ref. 10) and obtain better results for D_{1112} and D_{1222} than results obtained from either $\Theta_{ij}=\frac{1}{3}$ or $\Theta_{ij}=2(1+\eta)/9$. However, the prediction for D_{1122} is the worst among these three approximations. It turns out that we are not able to fit the exact fourth virial coefficients by adjusting Θ_{12} (D_{1111} and D_{2222} depend only on Θ_{11} and Θ_{22}, respectively) if we assume that Θ_{ij} is independent of the mole fraction x_i at the zeroth order of its density expansion $\Theta_{ij}^{(0)}$ (the higher-order terms do not contribute to the fourth virial coefficients). From Eq. (6), we have

$$1-\Theta_{ij}=\frac{Y_{ij}^{\text{exact}}-Y_{ij}^{\text{PY}}}{Y_{ij}^{\text{SPT}}-Y_{ij}^{\text{PY}}} \qquad (20)$$

which leads to

$$1-\Theta_{ij}=\frac{Y_{ij}^{\text{exact}}-Y_{ij}^{\text{PY}}}{\rho^2(\sum_i x_i d_i^2)^2}\left(\frac{12}{\pi^2}\right)(1-\eta)^3\left(\frac{d_i+d_j}{d_i d_j}\right)^2 \qquad (21)$$

Expanding out in powers of ρ we have, to the zeroth order, the equation

$$1 - \Theta_{ij}^{(0)} = \left(\frac{12}{\pi^2}\right)\left(\frac{d_i + d_j}{d_i d_j}\right)^2 \frac{\sum_{kl} x_k x_l I_{ijkl}}{(\sum_i x_i d_i^2)^2} \tag{22}$$

where

$$I_{ijkl} = \left(\frac{1}{2}\right)^{\delta_{kl}} \int f_{ik}(r_{13})\, f_{jl}(r_{24})\, e_{kl}(r_{34})\, f_{il}(r_{14})\, f_{jk}(r_{23})\, d\mathbf{r}_k\, d\mathbf{r}_l \tag{23}$$

with $r_{12} = d_{ij}$. Here $f_{ij}(r_{12})$ is the Mayer f function and $e_{ij} = f_{ij} + 1$. Therefore, $\Theta_{ij}^{(0)}$ must, in general, depend on x_i. From Eq. (23) it is easy to see that $I_{ijkl} = I_{jikl}$ and $I_{ijkl} = I_{ijlk}$.

For a binary mixture, if $x_1 = 0$ or 1, one must obtain the zeroth-order density expansion $\theta^{(0)} = 0.2117333$ for a one-component hard-sphere system from Eq. (22). Therefore, one has

$$I_{1111} = \frac{\pi^2 d_1^6}{48}\,[1 - \theta^{(0)}] \tag{24a}$$

$$I_{2222} = \frac{\pi^2 d_2^6}{48}\,[1 - \theta^{(0)}] \tag{24b}$$

One can also expand Y_{ij} in terms of the number density:

$$Y_{ij} = Y_{ij}^{(0)} + \sum_k x_k Y_{ijk}^{(1)} \rho + \sum_{kl} x_k x_l Y_{ijkl}^{(2)} \rho^2 + \cdots \tag{25}$$

Substituting Eq. (25) into Eq. (18) and comparing with Eqs. (16) and (17), we have

$$D_{1111} = \frac{2\pi}{3}\, d_{11}^3\, Y_{1111}^{(2)} \tag{26a}$$

$$D_{1112} = \frac{\pi}{6}\, d_{11}^3 [Y_{1112}^{(2)} + Y_{1121}^{(2)} + Y_{1211}^{(2)} + Y_{2111}^{(2)}] \tag{26b}$$

$$D_{1122} = \frac{\pi}{9}\, d_{11}^3 [Y_{1122}^{(2)} + Y_{2211}^{(2)} + Y_{1212}^{(2)} + Y_{1221}^{(2)} + Y_{2112}^{(2)} + Y_{2121}^{(2)}] \tag{26c}$$

$$D_{1222} = \frac{\pi}{6}\, d_{12}^3 [Y_{1222}^{(2)} + Y_{2122}^{(2)} + Y_{2212}^{(2)} + Y_{2221}^{(2)}] \tag{26d}$$

$$D_{2222} = \frac{2\pi}{3}\, d_{22}^3\, Y_{2222}^{(2)} \tag{26e}$$

This equation is true for both exact and approximate $Y^{(2)}_{ijkl}$. Since

$$I_{ijkl}=[Y^{(2)}_{ijkl}]^{\text{exact}}-[Y^{(2)}_{ijkl}]^{\text{PY}} \tag{27}$$

we have

$$I_{1211}=\frac{3}{\pi d_{11}^3}[D^{\text{exact}}_{1112}-D^{\text{PY}}_{1112}]-I_{1112} \tag{28a}$$

$$I_{1212}=\frac{9}{4\pi d_{11}^3}[D^{\text{exact}}_{1122}-D^{\text{PY}}_{1122}]-\frac{1}{4}(I_{1122}+I_{2211}) \tag{28b}$$

$$I_{2212}=\frac{3}{\pi d_{12}^3}[D^{\text{exact}}_{1222}-D^{\text{PY}}_{1222}]-I_{1222} \tag{28c}$$

where

$$[Y^{(2)}_{ijkl}]^{\text{PY}}=\frac{\pi^2}{36}\frac{d_k^2d_l^2}{(d_i+d_j)}[3(d_k+d_l)\,d_id_j+d_kd_l(d_i+d_j)] \tag{29}$$

and D^{PY}_{ijkl} is obtained from Eqs. (29) and (26). It is worth noting that D_{1111} and D_{2222} are the fourth virial coefficients for pure component 1 and pure component 2, respectively. This is easy to see if one lets $x_1=0$ or 1 in Eq. (16).

For binary hard-sphere mixtures, when we take the point-solvent limit $(d_2\to 0)$, we have an exact result [1],[4]

$$\beta p=\beta p_1^{\text{pure}}+\frac{\rho_2}{(1-\eta_1)} \tag{30a}$$

$$Y_{12}=1/(1-\eta_1) \tag{30b}$$

where $\eta=\eta_1+\eta_2$, $\eta_i=(\pi/6)\rho_id_i^3$, and $\rho_i=x_i\rho$. It is easy to show that the pressure obtained from Eqs. (18) and (19) does satisfy this exact relation if $\Theta_{ii}(d_j=0)=\theta$.

When we take the infinite-dilution limit of the solute and the continuum limit of solvent $[\eta_1\to 0,\ (d_2/d_1)\to 0]$, another exact result can be obtained [10]. It is

$$Y_{12}=1+4\eta_2Y_{22},\qquad \eta_1\to 0,\ (d_2/d_1)\to 0 \tag{31}$$

It turns out [10] that the contact value of the PY pair distribution function $(\Theta_{ij}=1)$ is far from this exact result. In contrast, the contact value

---

[4] The result is stated in Ref. 1 without proof. The result was also independently obtained by Zhou and Stell.

predicted by SPT($\Theta_{ij}=0$) is exactly satisfied. The MCSL ($\Theta_{ij}=\frac{1}{3}$) and Boublík [$\Theta_{ij}=2(1+\eta)/9$] equations are intermediate in this regard (see Table II).

Since Eq. (6) does not satisfy exact equations in the limit of zero concentration of solute and continuum of solvent if one uses $\Theta_{ij}=\Theta$, one must go further to get good results in this regard. Sung and Stell, in Ref. 10, have suggested one appropriate modification. However, their equation does not satisfy the exact point-solvent limit result [Eq. (30)]. We find that if one lets

$$\Theta_{12}=(x_1\Theta_{11}+x_2\Theta_{22})\left[1-(1-\eta)\left(\frac{d_1-d_2}{d_1+d_2}\right)^2\right] \tag{32}$$

then we will have a pressure expression that satisfies all the exact limits we have discussed. If $d_1=d_2$ or $x_1=0, 1$, with $\Theta_{11}=\Theta_{22}$, we have

$$\Theta_{12}=\Theta_{11}=\Theta_{22}=\Theta \tag{33}$$

which reduces to the exact equation of state for one-component hard-sphere fluids [Eq. (8)]. An approximation that suggests itself is therefore Eq. (32) with Θ_{11} and Θ_{22} given by $1.05\Theta_{ii}^{(0)}(1+\eta)$, where the exact $\Theta_{ii}^{(0)}$ is used, because this becomes the Kalafa approximation in the one-component limit. Here, $\Theta_{11}=\Theta_{22}=2(1+\eta)/9$ when $d_1=d_2$ and 1.05 is the ratio of $\frac{2}{9}$ and 0.211733.... A somewhat simpler alternative approximation is given, for all i and j, by

$$\Theta_{ij}=1.05\Theta_{ij}^{(0)}(1+\eta) \tag{34}$$

Table II. The Ratio $(1+4\eta_2 Y_{22})/Y_{12}$ at the Limit of $\eta_1=0$ and $d_2=0$[a]

η_2	$\Theta_{ij}=0$ (SPT)	$\Theta_{ij}=\frac{1}{3}$ (MCSL)	$\Theta_{ij}=1$ (PY)
0	1	1	1
0.1	1	1.0082	1.0250
0.2	1	1.0267	1.0857
0.3	1	1.0485	1.1687
0.4	1	1.0686	1.2667
0.5	1	1.0833	1.3750
1	1	1	2

[a] The result for $\Theta=2(1+\eta)/9$ is similar to $\Theta=\frac{1}{3}$ and is omitted here. A similar table can be found in Ref. 10.

again with the exact $\Theta_{ij}^{(0)}$, but this will no longer exactly satisfy Eq. (30). Once Θ_{ij} is known, the mixing coefficient $\theta(\eta_i, d_i)$ defined in Eq. (4) is given by

$$\theta = \frac{\sum_{ij} x_i x_j \Theta_{ij} [Y_{ij}^{\mathrm{SPT}} - Y_{ij}^{\mathrm{PY}}] d_{ij}^3}{\sum_{ij} x_i x_j [Y_{ij}^{\mathrm{SPT}} - Y_{ij}^{\mathrm{PY}}] d_{ij}^3} \tag{35}$$

ACKNOWLEDGMENTS

Y.Z. gratefully acknowledges the financial support of the National Science Foundation and G.S. gratefully acknowledges the financial support of the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy. We are also indebted to Professor Harold L. Friedman, Dr. J. Blawzdziewicz, and Dr. Enci Zhong for many fruitful discussions.

REFERENCES

1. T. Boublík and I. Nezbeda, *Coll. Czech. Chem. Commun.* **51**:2301 (1986).
2. T. Boublík, *Mol. Phys.* **59**:371 (1986).
3. J. Kolafa, Unpublished (see Refs. 1 and 2 for details).
4. J. J. Erpenbeck and W. W. Wood, *J. Stat. Phys.* **35**:321 (1984).
5. J. L. Lebowitz, *Phys. Rev.* **133**:A895 (1964).
6. J. L. Lebowitz, E. Helfand, and E. Praestgaard, *J. Chem. Phys.* **43**:774 (1965).
7. N. F. Carnahan and K. E. Starling, *J. Chem. Phys.* **51**:639 (1969).
8. G. A. Mansoori, N. F. Carnahan, K. E. Starling, and T. W. Leland, *J. Chem. Phys.* **54**:1523 (1971).
9. E. W. Grundke and D. Henderson, *Mol. Phys.* **24**:269 (1972).
10. W. Sung and G. Stell, *J. Chem. Phys.* **80**:3350 (1984).
11. M. Rigby and E. B. Smith, *Trans. Faraday Soc.* **59**:2469 (1963).