Molecular-Based Cubic Equations of State

M. Mohsen-Nia[1], H. Modarress[2] and G.A. Mansoori[1]

A new two-constant cubic equation of state is proposed. This model is based on the statistical mechanical information available for the repulsive thermodynamic functions and the phenomenological knowledge of the attractive potential tail contributions to the thermodynamic properties. A method for modification of cubic equations of state is presented based on the molecular theory of hard-sphere fluids. A simplified and accurate equation in the form of:

$$Z_{(rep)} = (1 + 2.48y_m)/(1 - 1.88y_m)$$

$$y_m = (1/4)(3\sum_i \sum_j x_i x_j y_{ij} + \sum_i x_i y_{ii});\ \ y_{ij} \equiv (\pi/6) N_0 d_{ij}^3/v;\ \ d_{ij} = (d_{ii} + d_{jj})/2$$

for pure and mixed hard-sphere (repulsive) molecular fluids with component diameters d_{ij} is proposed. This equation is then replaced as the repulsive term of the proposed model of cubic equations of state. A new two-constant-parameter cubic equation of state in the form of:

$$Z_m = (v + 1.3191\mathscr{b}_m)/(v - \mathscr{b}_m) - \\ (\sum \sum x_i x_j a_{ij})/RT)/\left[T^{1/2}(v + \sum x_i \mathscr{b}_i)\right]$$

$$\mathscr{b}_m = (1/4)(3\sum_i \sum_j x_i x_j \mathscr{b}_{ij} + \sum_i x_i \mathscr{b}_{ii});\ \ \mathscr{b}_{ij} = (\mathscr{b}_{ii}^{1/3} + \mathscr{b}_{jj}^{1/3})^3/8;$$

$$a_{ij} = (1 - k_{ij})(a_{ii}\ a_{jj})^{1/2}$$

is developed. It is shown that the proposed two-constant-parameter cubic equation of state is more accurate than the Redlich-Kwong equation, which has been considered to be the best two-constant-parameter cubic equation of state, for calculation of pure fluid and mixture properties.

INTRODUCTION

The success of industrial design and operation is related to the availability of accurate and simple equations of state for prediction of thermodynamic properties of fluids. Recent developments in thermodynamics of fluids and fluid mixtures indicate that more serious considerations must be given to fundamental approaches to produce simple and accurate analytical re-

---

1. Department of Chemical Engineering, University of Illinois, Chicago, IL 60680, USA.
2. Department of Chemical Engineering, Amir Kabir University, Tehran, I.R. Iran.

Scientia Iranica, Vol. 1, No. 3, © Sharif University of Technology, October 1994.

lationships for thermodynamic properties [1-3]. Although there has been considerable progress made in the development of equations of state based on the statistical mechanics, the cubic equations of state are still widely preferred in process design calculations. Equations such as the Redlich-Kwong [4], Peng-Robinson [5], Heyen [6] and their modifications, which are actually based on the van der Waals equation of state, are extensively used in engineering calculations.

In this report, we first present a simplified, but accurate, equation for pure and mixed hard-sphere fluids which can be replaced as the repulsive part of the cubic equations of state. Then we introduce a new version of cubic equations of state using the simplified hard-sphere model developed in part 1. A new cubic equation of state which contains two constant parameters is then introduced. The resulting equation of state is used for property prediction of a variety of fluids and fluid mixtures of practical interest. It has shown its simplicity and superior accuracy over the RK and other two-constant-parameter cubic equations of state.

THE NEW REPULSIVE TERM OF EQUATIONS OF STATE

The importance of short-range repulsive forces in an equation of state for determining the thermodynamic properties of fluids is well established by the works of numerous investigators [7-10]. This is because more accurate expression for the repulsive term of an equation of state results in much better agreement with the experimental data. However, the major weakness of the industrial equations of state is their inaccurate repulsive term:

$$Z_{(rep)} = v/(v-b) = 1/(1-4y), \qquad (1)$$

where

$$y \equiv b/4v = (\pi/6)N_0 d^3/v, \qquad (2)$$

y (dimensionless) is known as the packing-fraction, $b = (2\pi/3)N_0 d^3$, N_0 is the Avogadro number, d is the molecular hard-core diameter, v is the molar volume and the reduced density is $(\pi/6)N_0 \rho d_0^3$.

Table 1. Parameters of a generalized equation of state $Z = Z_{(rep)} - (av/RT)/\left[T^{\mathsf{E}}(v^2 + \ell v - d bc)\right]$ according to different cubic equations.

Equation of state	E	ℓ	d	y_{max}
van der Waals	0	0	0	0.43
Heyen	0	b+c	1	0.31
Peng-Robinson	0	2b	b/c	0.30
Redlich-Kwong	1/2	b	0	0.28

An accurate equation for representing the repulsive effect is the Carnahan-Starling (CS) hard-sphere equation of state [7]:

$$Z_{(rep)} = (1 + y + y^2 + y^3)/(1-y)^3, \qquad (3)$$

which can replace the repulsive term, $1/(1-4y)$, in the cubic equations. However, because after this modification, the resulting equation of state would no longer be cubic, Scott [11] introduced the following equation for the hard-sphere pure fluids:

$$Z_{(rep)} = (1+2y)/(1-2y) \; . \qquad (4)$$

Similarly, Kim, et al. [10] presented another equation for hard-spheres:

$$Z_{(rep)} = (1+3.08y)/(1-1.68y) \; . \qquad (5)$$

We consider a number of representative cubic equations of state in a generalized form as shown in Table 1. Parameter y_{max} appearing in Table 1 is the approximate maximum packing fraction for fluids (packing fraction at the triple-point) when the CS hard-sphere equation of state is used to modify the above equations (replacing $v/(v-b)$ term with Equation 3). Of course, the CS equation of state is valid up to the packing fraction of $y_{max} = 0.6$. Considering the fact that the packing fraction in the cubic equations of state (excluding the van der Waals equation which, because of its inaccuracy, is not used for practical calculations) do not reach $y = 0.35$, we propose the following hard-sphere equation of state:

$$Z_{rep} = (1 + 2.48y)/(1 - 1.88y) = (v + 0.62b)/(v - 0.47b) \ . \quad (6)$$

This equation reproduces the CS equation for the hard-sphere fluid with good accuracy for $0 < y < 0.35$ as is demonstrated in Figures 1 and 2. In Figure 1, the percentage deviation of calculating the hard-sphere compressibility factor from the exact CS equation, as calculated by Equation 6, is compared with the Scott and Kim, et al. models. According to this figure, Equation 6 is in better agreement with the CS equation than the other simplified hard-sphere equations for the packing fraction range of interest. The average absolute error for Equation 6 is actually in the range of the accuracy of the molecular dynamics simulation for the hard-sphere compressibility factor [12].

In Figure 2, the hard-sphere excess Helmholtz free energy (over the ideal gas):

$$(A - A_{ig})/RT = -2.319Ln(1 - 1.88y) = -2.319Ln(1 - 0.47b/v) \ , \quad (7)$$

as derived from Equation 6, is compared with the similar calculations using the Scott and Kim, et al. models. According to this figure, Equation 7 is in better agreement with the accurate CS equation of state than the other simplified hard-sphere models.

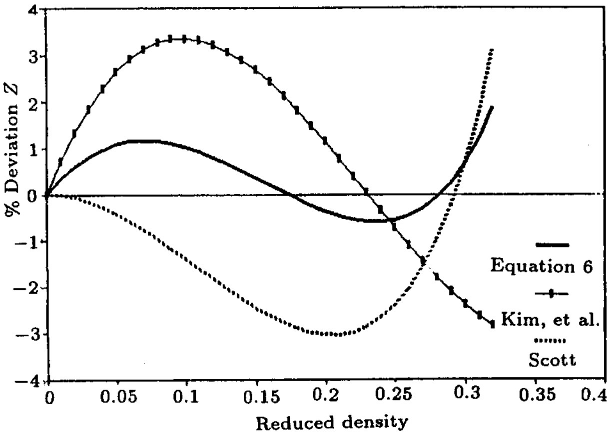

Figure 1. The compressibility factor.

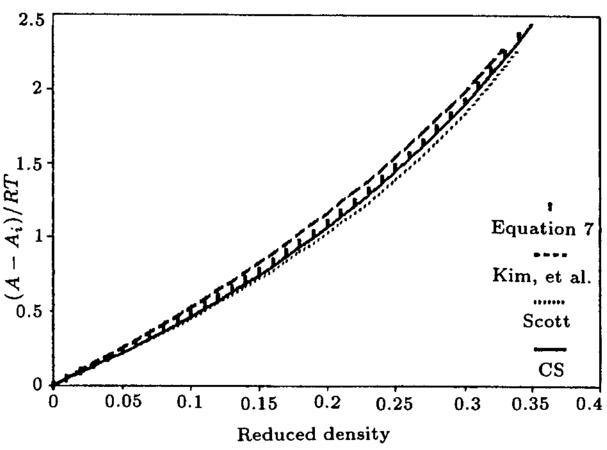

Figure 2. The hard-sphere excess Helmholtz free energy.

We have extended the applicability of Equations 6 and 7 to hard-sphere mixtures by writing them in the following forms:

$$Z_{m(rep)} = (1 + 2.52y_m)/(1 - 1.88y_m) = (v + 0.62b_m)/(v - 0.47b_m) \ , \quad (8)$$

$$(A_m - A_{mig})/RT = -2.319Ln(1 - 1.88y_m) = -2.319Ln(1 - 0.47b_m/v), \quad (9)$$

and using the following mixing and combining rules:

$$d^3_m = (1/4)(3\sum_i\sum_j x_i x_j d^3_{ij} + \sum_i x_i d^3_{ii})$$
$$\text{where } d_{ij} = (d_{ii} + d_{jj})/2, \quad (10)$$

where

$$y_m \equiv b_m/4v = (p/6)N_0 d^3_m/v \ , \quad (11)$$

is the mixture packing fraction. Then parameter b_m takes the following form:

$$b_m = (1/4)(3\sum_i\sum_j x_i x_j b_{ij} + \sum_i x_i b_{ii})$$
$$\text{where } b_{ij} = (b^{1/3}_{ii} + b^{1/3}_{jj})^3/8 \ . \quad (12)$$

Equation 7 joined with Equations 8 or 9 is tested extensively for discrete as well as

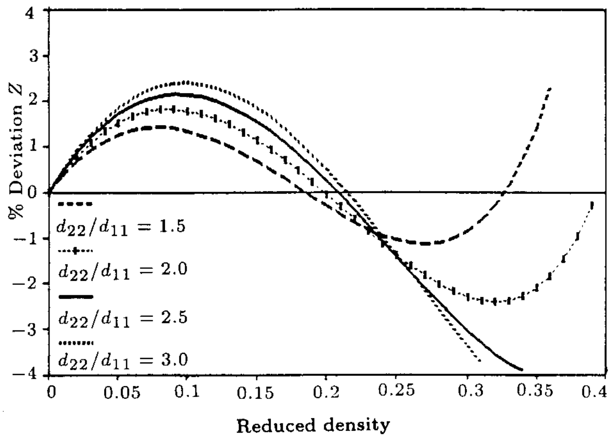

Figure 3. The percent deviation of the compressibility factor.

polydisperse hard-sphere mixtures and it is shown to be in very good agreement with the accurate, but complicated, MCSL hard-sphere mixture equation [13] for packing-fractions of up to 0.35. We have calculated the thermodynamic properties of equimolar binary mixtures ($x_1 = x_2 = 1/2$) with $d_{22}/d_{11} = 1.5, 2.0, 2.5$ and 3.0. The results of these calculations are compared with the accurate MCSL hard-sphere mixture equation of state as reported in Figures 3 and 4. The maximum percentage deviation of the binary hard-sphere mixture compressibility factor and excess Helmholtz free energy for diameter ratios of $d_{22}/d_{11} = 1.5$ to 3 is calculated to be 3% for the packing fraction range of interest in cubic equations of state. For d_{22}/d_{11} ratios of less than 3, the two theories would match even better than this reported case. The mixture reduced density is $(\pi/12)N_0\rho(d_{11}^3 + d_{22}^3)$.

In order to test further the accuracy of the proposed hard-sphere mixture equation for multi-component mixtures, we use it to calculate thermodynamic properties of polydisperse hard-sphere systems through different distribution functions $f(r)$. Following the method of Salacuse and Stell [14] we can express Equation 10 for the polydisperse systems as the following:

$$d_m^3 = (1/16)(7m_3 + 9m_2m_1) \ , \tag{13}$$

where, m_1, m_2 and m_3 are the first, second and third moments of distribution function, respectively, defined as:

$$m_i = \int_0^\infty r^i f(r) dr \ . \tag{14}$$

For the normal distribution:

$$f_N(r) = (1/2ph)^{1/2} \exp\left[-(r-\bar{r})^2/2h\right] , \tag{15}$$

the moments are given by:

$$m_1 = \bar{r} + (2\eta/\pi)^{1/2}, \tag{16}$$

$$m_2 = \bar{r}^2 + \eta + 2(2\eta/\pi)^{1/2}, \tag{17}$$

$$\begin{aligned} m_3 = {} & \bar{r}^3 + 2(2/\pi)^{1/2}\eta^{3/2} + 3\eta\bar{r} \\ & + 3\bar{r}^2(2\eta/\pi)^{1/2}, \end{aligned} \tag{18}$$

where η and $\bar{r}$ are the variance and mean, respectively. Therefore, the mixture packing fraction, Equation 11, for the normal distribution is as the following:

$$\begin{aligned} y_m = \left(\frac{\pi N_0 \bar{r}^3}{6v}\right) & \left[1 + \left(\frac{3}{r}\right)\left(\frac{2\eta}{\pi}\right)^{\frac{1}{2}} + \right. \\ & \left. \left(\frac{1.875\pi + 2.25}{\pi\bar{r}^2}\right)\eta + \left(\frac{1.4375\eta}{\bar{r}^3}\right)\left(\frac{2\eta}{\pi}\right)^{\frac{1}{2}}\right] \end{aligned} \tag{19}$$

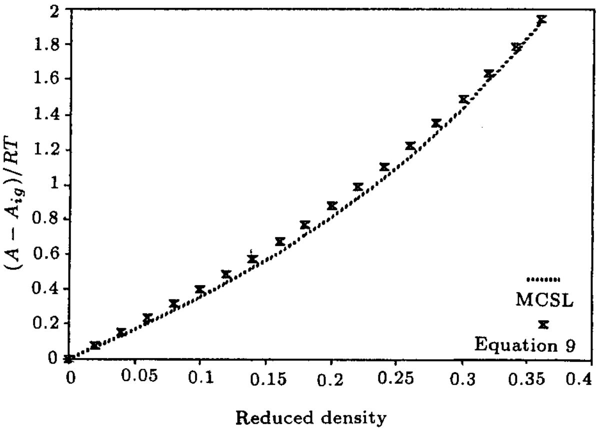

Figure 4. The excess Helmholtz free energy according to Equation 9.

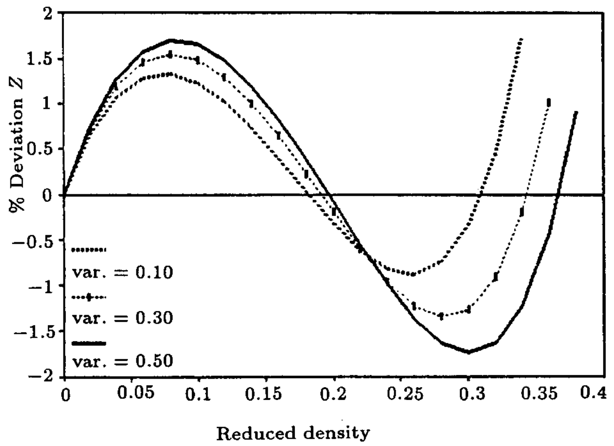

Figure 5. The percent deviation of the compressibility factor for the polydisperse hard-sphere mixture with normal distribution.

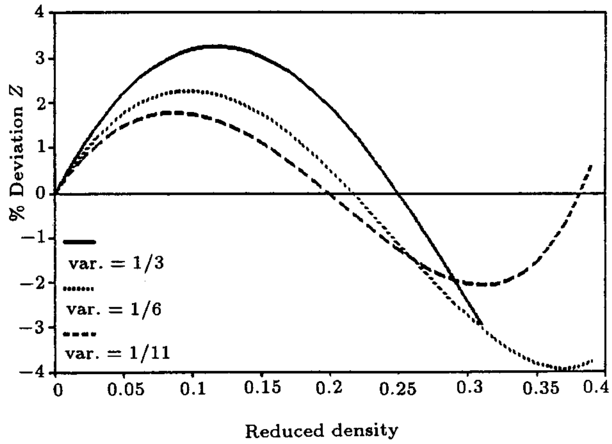

Figure 7. The percent deviation of hard-sphere mixture compressibility factor for the polydisperse hard-sphere mixture with Shultz distribution.

We can calculate the compressibility factor and Helmholtz free energy of this polydisperse hard-sphere mixture by joining Equation 19 with Equations 8 and 9. For the Schultz distribution:

$$f_s(r) = \frac{1}{s!}\left(\frac{s+1^{s+1}}{\bar{r}}\right)r^s\left[-\left(\frac{s+1}{\bar{r}}\right)r\right], \tag{20}$$

where $\bar{r}$ is the first moment of the distribution and s is related to variance of $f_s(r)$ by:

$$\eta(r) = \mathrm{var}(r) = \frac{\bar{r}^2}{s+1'}, \tag{21}$$

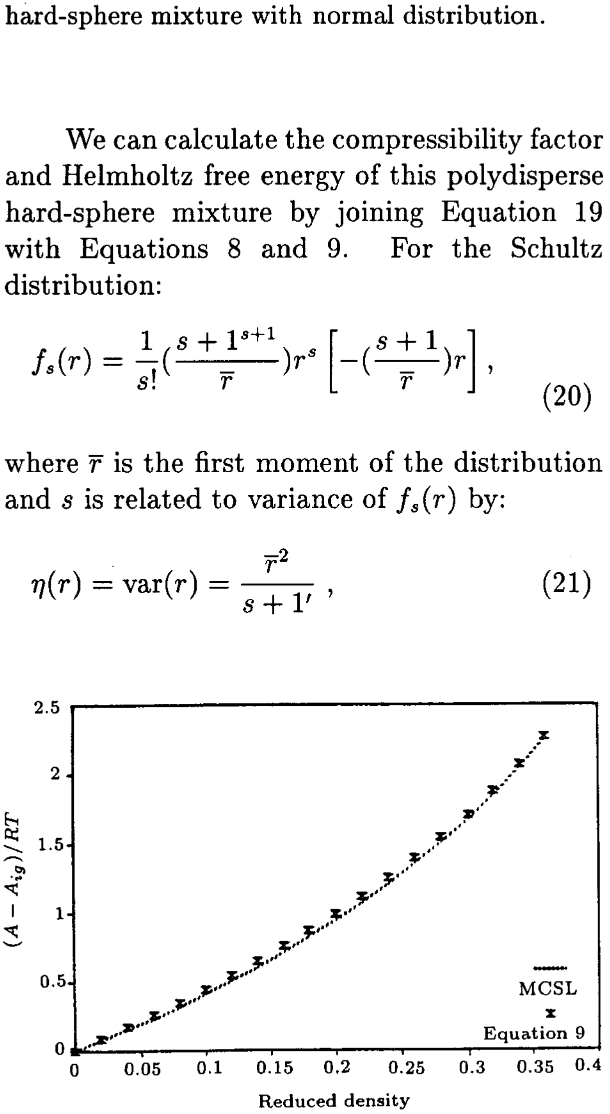

Figure 6. The excess Helmholtz free energy for the polydisperse hard-sphere mixture with normal distribution.

we can derive the following expressions for the packing fraction of the Schultz polydisperse hard-sphere mixture:

$$y_m = \left(\frac{\pi N_0 \bar{r}^3}{6v}\right)\left(\frac{(s+2)(8s+15)}{8(s+1)^2}\right). \tag{22}$$

Then, by replacing this equation in Equations 8 and 9, we can calculate the compressibility factor and Helmholtz free energy of the Schultz polydisperse hard-sphere mixture.

We have calculated the thermodynamic properties of polydisperse mixtures of hard-spheres obeying the normal and Schultz distributions. The results of these calculations are compared with the accurate polydisperse MCSL hard-sphere equation of state [13,14] in Figures 5 to 8. According to these figures, the deviations of the multi-component hard-sphere mixture compressibility factor and Helmholtz free energy for Shultz (with $\bar{r} = 1$ & $\eta = 1/3, 1/6, 1/11$) and normal (with $\bar{r} = 1$ & h=0.1, 0.3, 0.5) distributions are quite low and acceptable for the packing fraction range of interest in industrial equation of state. The mixture reduced density for Figures 5 and 6 is $(\pi/6)N_0\rho m_3$ and for Figures 7 and 8 is $(\pi/6)N_0\rho(s+3)(s+2)/(s+1)^2$.

We have made other calculations for values of $\bar{r}$ other than unity with similar results as in Figures 5-8 which will not be reported here.

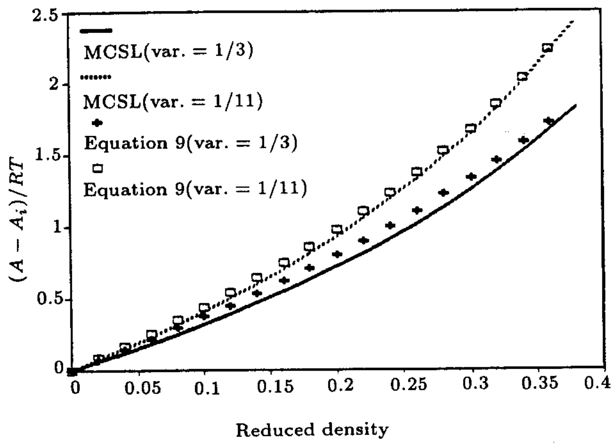

Figure 8. The excess hard-sphere mixture Helmholtz free energy for the polydisperse hard-sphere mixture with Shultz distribution.

THE NEW VERSIONS OF CUBIC EQUATIONS OF STATE

Since Table 1 indicates that the packing fraction range ($0 < y < 0.35$) is sufficient for these equations (except for van der Waals equation, which is not generally used for industrial calculations) we are proposing the following new version for these equations of state:

$$Z =(v + 0.62b)/(v - 0.47b) - (av/RT)/ \\ [T^{\mathsf{E}}(v^2 + \ell v - dbc)] \ . \qquad (23)$$

The difference between this equation and the generalized equation reported in Table 1 is the replacement of the new repulsive compressibility factor given by Equation 6. Provided the proper numerical values of E, ℓ, and d are replaced in this equation, one can reproduce the new versions of the equations of state reported in Table 1. It should be pointed out that this change of the repulsive term will no longer keep the Peng-Robinson and Heyen equations in cubic form.

By applying the critical point constraints $(\partial P/\partial v)_{T_c} = (\partial^2 P/\partial v^2)_{T_c} = 0$ (for all the cubic equations) and $Z = Z_c$ (for the three-parameter equations, like Heyen) we can derive expressions for parameters of the new version of equations of state with respect to the critical properties as reported in Table 2.

A NEW TWO-CONSTANT-PARAMETER CUBIC EQUATION OF STATE

By replacing $\theta_3 = 0$ in Equation 23, it will become a cubic equation in the following form:

$$Z =(v + 0.62b)/(v - 0.47b) - (a/RT)/ \\ [T^{\mathsf{E}}(v + \ell)] \, . \qquad (24)$$

The choices of E and ℓ are still at our disposal. For the sake of simplicity, we choose $\mathsf{E} = 1/2$, as proposed by Redlich and Kwong (RK) [4], and $\ell = 0.47b$ as it appears in the denominator of the repulsive term of Equation 23. As a result, we introduce a new cubic equation of state as the following:

$$Z =(v + 1.3191\ell)/(v - \ell) - (a/RT)/ \\ \left[T^{1/2}(v + \ell)\right] . \qquad (25)$$

Equation 25 is a cubic equation of state in terms of volume and contains only two constant parameters. By applying the critical point constraints, we determine parameters a and ℓ as the following:

$$a = 0.48748R^2T_c^{5/2}/P_c \quad \text{and} \\ \ell = 0.064662RT_c/P_c \ . \qquad (26)$$

The critical compressibility factor $Z_c = 0.333$ will remain the same as the RK equation of state. In order to demonstrate the accuracy of repulsive term of this equation of state, we have calculated the maximum packing fractions as reported in Table 3 for different fluids. According to this table, for all the fluids studied, the maximum packing fractions are in the allowable range of $0 < y < 0.35$ where the repulsive part of Equation 25 accurately represents the CS hard-sphere equation of state.

Extension of Equation 25 to mixtures will take the following form:

$$Z_m = (v + 1.3191\ell_m)/(v - \ell_m) - \\ (\sum\sum x_i x_j a_{ij})/RT)/\left[T^{1/2}(v + \sum x_i \ell_i)\right] , \qquad (27)$$

Table 2. Parameters of the new version of cubic equations of state $Z = (v + 0.62b)/(v - 0.47b) - (av/RT)/\left[T^{\mathsf{E}}(v^2 + \ell v - dbc)\right]$ with respect to the critical properties.

Equation of state	a/RT_cv_c	b/v_c	c/v_c	Z_c	
				New	Original
van der Waals	1.429	0.542	0	0.364	0.375
Heyen	1.945*	0.371*	0.997*	0.27	0.27
Peng-Robinson	1.951	0.370	0	0.272	0.307
Redlich-Kwong	1.513	0.341	0	0.314	0.333

* These values are based on $Z_c = 0.27$.

where

$$\ell_m = (1/4)(3\sum_i\sum_j x_i x_j \ell_{ij} + \sum_i x_i \ell_{ii}),$$

$$\ell_{ij} = (\ell_{ii}^{1/3} + \ell_{jj}^{1/3})^3/8 \,,$$

$$a_{ij} = (1 - k_{ij})(a_{ii}\ a_{jj})^{1/2}$$

In Equation 27 we have applied the new mixing rule for repulsive term (Equation 12). For the attractive term, we have used the usual cubic equation mixing rules in order to be able to observe the corrections in the repulsive term of this equation for mixture calculations. It should be pointed out that there are other possibilities for the mixing rules of the attractive term of this equation of state [15,16]. This new equation of state is used to predict properties of pure fluids and mixtures as is reported below.

Table 3. Calculation of the maximum packing fraction for different fluids according to Equation 25.

Fluid	y_{max}
Ethane	0.33
n-Butane	0.33
n-Propane	0.34
Oxygen	0.31
Isobutane	0.34
Ethylene	0.31
N_2O_4	0.28
H_2S	0.29
NF_3	0.34

RESULTS AND DISCUSSION

Cubic equations of state can be classified into two categories: (1) Those with two constant parameters like the van der Waals, Berthelot, Dieterici and Redlich-Kwong equations. (2) Those with more than two parameters or two or more temperature-dependent parameters, including the Peng-Robinson, Heyen and Soave equations [3]. Among the first category of cubic equations of state, the RK equation is still considered to be the most accurate equation of all. As a result, in order to test the accuracy of Equation 25, which is also of the first category, for prediction of the properties of pure fluids and mixtures, it is compared here with the RK equation. Table 4 shows the comparisons of the result of density calculations using Equation 25 with the RK equation and the experimental data [17-32]. According to this table, the results of Equation 25 are generally superior to the RK equation except for methane and hydrogen sulfide.

In order to test the applicability of Equation 27 for mixtures, we have used it for calculation of the properties of a number of mixtures. In all the calculations reported here for Equation 27, and for the RK equation, we

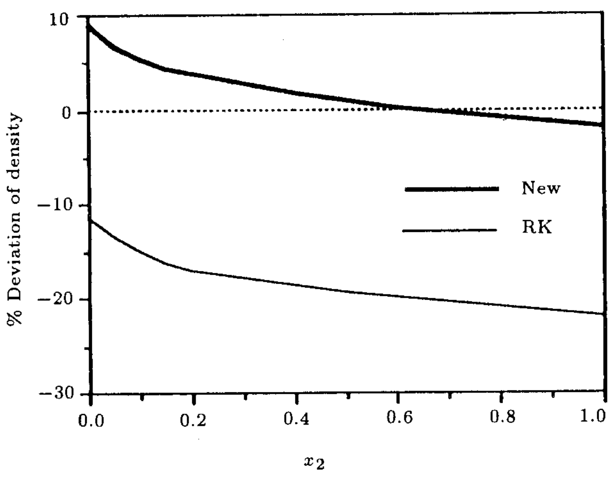

Figure 9. The calculated percent deviation of (n-octane + n-dodecane) liquid mixture density from the experimental data [33], versus n-dodecane mole fraction.

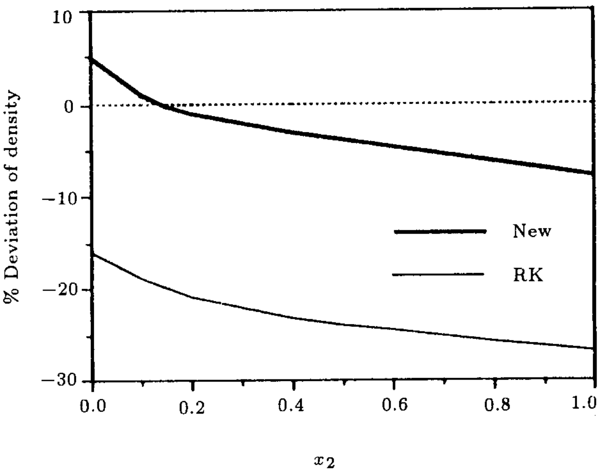

Figure 10. The percent deviation of (n-decane + n-tetradecane) liquid mixture density from the experimental data [33], versus n-tetradecane mole fraction.

have chosen the value of the unlike-interaction parameters as $K_{ij} = 0$. This choice of $k_{ij} = 0$ is made in order not to complicate the comparisons of different equations of state with the fitting of k_{ij}. However, for more accurate calculations of mixture properties, this parameter may be also fitted to some mixture data.

In Figures 9 and 10, the density calculations for two different binary high-pressure (500 bar) liquid mixtures (n-octane + n-dodecane and n-decane + n-tetradecane) are reported and are compared with the results of the RK equation. For these equations $T = 298.15$ K. According to these figures, predictions by Equation 27 are better than the RK equation.

We also have done solubility and VLE calculations for mixtures. In Figure 11, the solubility of methane in n-hexane is reported versus temperature at two different pressures of 40.5 and 81.1 bars. According to this

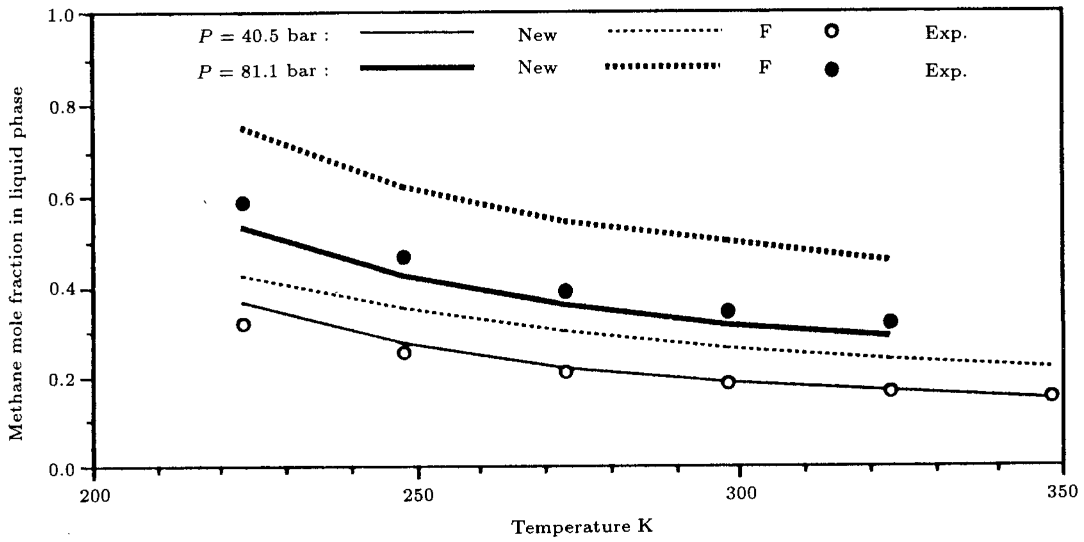

Figure 11. Predictions of the solubility of methane in n-hexane [34].

Table 4. Comparsion of this work and RK equations of state for density prediction of different compounds.

Compound	Temperature Range, (k)	Pressure Range, (atm)	No. of Date [Ref. No.]	AAD%	
				RK	This Work
CO2	250-1000	40-400	143 [18]	3.9	2.4
H2S	300-700	5-400	101 [28]	1.8	2.2
SO2	285-500	1-315	115 [31]	5.0	2.6
N2	200-1000	10-700	183 [19]	3.4	2.8
02	200-1000	5-500	120 [31,32]	1.9	1.7
Methane	91-500	10-700	170 [25]	3.0	3.4
Propane	200-700	5-700	140 [26]	3.1	2.6
i-Butane	200-700	10-600	130 [27]	3.3	3.1
n-Pentane	300-650	10-600	160 [24,32]	4.6	3.9
Neopentane	300-600	5-400	60 [22]	3.1	2.8
n-Hexane	298-1000	1-500	100 [29]	5.7	3.3
n-Heptane	300-1000	1-500	130 [23,29]	5.8	2.8
n-Octane	320-1000	1-500	80 [29]	6.3	2.2
n-Nonane	300-600	15-1000	90 [21,23]	7.9	2.6
n-Decane	300-500	15-500	130 [30]	8.8	2.5
n-Undecane	300-570	50-1000	40 [20,23]	10.3	3.2
n-Dodecane	300-570	1-600	20 [17]	11.3	3.7
n-Tridecane	300-570	50-1050	50 [20,23]	13.3	4.7
n-c15	310-410	1-600	30 [17]	15.6	6.4
Overall			**1992**	**6.2**	**3.1**

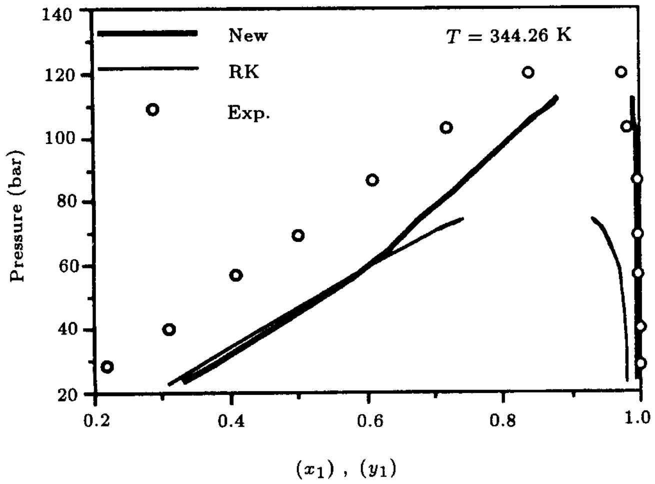

Figure 12. The equilibrium pressure-composition diagram for (methane + n-decane) system [35].

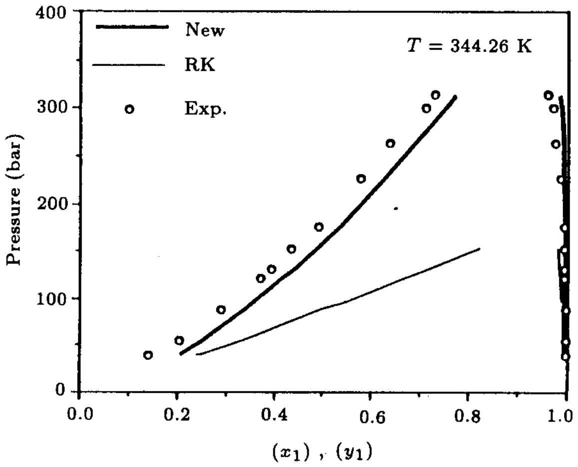

Figure 13. The equilibrium pressure-composition diagram for (carbon dioxide + n-decane) system [36].

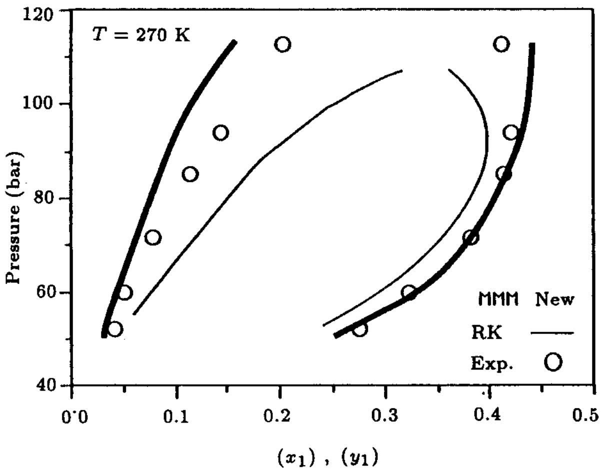

Figure 14. Prediction of the equilibrium pressure-composition diagram for (nitrogen + carbon dioxide) system [37].

figure also, the predictions by Equation 27 are closer to the experimental data than the RK equation.

In Figures 12 to 14, equilibrium pressure-composition diagrams for methane + n-decane (at 344.26 K), carbon dioxide + n-decane (at 344.26 K) and for nitrogen + carbon dioxide system (at 270.0 K) are reported. According to these three figures, the predictions by Equation 27 are far better than the predictions by the RK equation.

The proposed equation may be made even more accurate by choosing its parameters a & ℓ to be dependent on temperature, as is usually done in other industrial equations of state. In all the comparisons between the calculations and experimental data made here, the results of calculations are compared with the properties of non-associating fluids. This is due to the fact that equations of state, which are based on the classical statistical mechanical theories, are valid for non-associating fluids only.

ACKNOWLEDGEMENTS

This research is supported in part by the National Science Foundation, USA, Grant No. CTS-9108595 and in part by the Ministry of Science and Higher Education, IRR.

NOMENCLATURE

A	Helmholtz free energy
a	attractive constant in equation of state
b	repulsive constant in equation of state
c	third parameter in equation of state
d	molecular hard-core diameter
$f_z(R)$	distribution function
k_{ij}	binary interaction parameter
N_0	Avogadro number
P	Pressure
R	gas constant
r	random variable
$\bar{r}$	the mean value and first moment in normal and Schultz distribution function respectively
T	temperature
X	mole fraction
y	packing fraction
Z	compressibility factor
s	a parameter in Schultz distribution function, is defined in Equation 21

Greek letters

$\theta_1, \theta_2, \theta_3$	constants in equation of state
ρ	density
π	3.1415927
η	variance of normal distribution function

Subscripts

c	critical property
i, j	component indices
ij	property of i-j interaction
ig	ideal gas property
m	mixture property
N	normal distribution
s	Schultz distribution

REFERENCES

1. Sengers, J.V., Jin, Gx., and Tang, S. "Thermodynamic behavior of fluid mix-

22. Das, T.R., Reed, C.O., Jr. and Eubank, P.T. "PVT surface and thermodynamic properties of neo-pentane", *J. of Chem. Eng. Data*, **22**(1), pp 16-21 (1977).

23. Doolittle, A.K. *J. Chem. Eng. Data*, **9**, p 275 (1964).

24. Gehrig, M. and Lentz, S. "Values of P(V,T) for n-pentane in the range of 5 to 250 MPa and 313 to 643 K", *J. Chem. Thermodynamics*, **11**, pp 291-300 (1979).

25. Goodwin, R.D. "The thermophysical properties of methane, from 90 to 500 K at pressures to 700 bar", NBS Technical Note 653, National Bureau of Standards, USA (1974).

26. Goodwin, R.D. and Haynes, W.M. "Thermophysical properties of propane from 85 to 700 K at pressures to 70 MPa", NBS Monograph 170, National Bureau of Standards, USA (1982).

27. Goodwin, R.D. and Haynes, W.M. "Thermophysical properties of isobutane from 114 to 700 K at pressures to 70 MPa", NBS Technical Note 1051, National Bureau of Standards, USA (1982).

28. Goodwin, R.D. "Hydrogen sulfide provisional thermophysical properties from 188 to 700 K at pressures to 75 MPa", NBSIR 83-1694, National Bureau of Standards, U.S. Department of Commerce, Boulder, Colorado, USA (1983).

29. Hall, K.R., Ed. *TRC Thermodynamic Table - Hydrocarbons*, Thermodynamic Research Center, Texas A & M University System, USA (1986).

30. Lee, A.L. "Viscosity of light hydrocarbons", Monograph of API Research Project No. 65, Am. Petrol. Inst., Washington, D.C. (1965).

31. Vargaftik. *Tables of the Thermodynamical Properties of Liquids and Gases*, John Wiley and Sons, New York (1975).

32. Wagner, W. and DeReuck, K.M. *Oxygen - International Thermodynamic Tables of the Fluid State-9*, IUPAC Project Centre, Imperial College, London, Blackwell Scientific Publications (1987).

33. Takagi, T. and Teranishi, H. "Ultrasonic speed and thermodynamics for binary solutions of n-alkanes under high pressures" *Fluid Phase Equilibria*, **20**, p 315 (1985).

34. Shim, J. and Kohn, J.P. "Multiphase and volumetric equilibria of methane-n-hexane binary system at temperatures between 110° and 150° C", *J. Chem. Eng. Data*, **7**, pp 3-8 (1962).

35. Reamer, H.H., Fiskin, J.M. and Sage, B.H. "Phase equilibria in hydrocarbon systems, phase behavior in the methane-n-butane-n-decane system", *Ind. Eng. Chem.*, **41**, pp 2871-2875 (1949).

36. Reamer, H.H. and Sage, B.H. "Phase equilibrium in hydrocarbon systems, volumetric and phase behavior of the n-decane+carbon dioxide system", *J. Chem. Eng. Data*, **8**, pp 508-513 (1963).

37. Somait, F.A. and Kidnay, A., "Liquid vapor equilibria at 270 K for systems containing nitrogen, methane and carbon dioxide", *J. Chem. Eng. Data*, **23**, pp 301-305 (1978).

22. Das, T.R., Reed, C.O., Jr. and Eubank, P.T. "PVT surface and thermodynamic properties of neo-pentane", *J. of Chem. Eng. Data*, **22**(1), pp 16-21 (1977).

23. Doolittle, A.K. *J. Chem. Eng. Data*, **9**, p 275 (1964).

24. Gehrig, M. and Lentz, S. "Values of P(V,T) for n-pentane in the range of 5 to 250 MPa and 313 to 643 K", *J. Chem. Thermodynamics*, **11**, pp 291-300 (1979).

25. Goodwin, R.D. "The thermophysical properties of methane, from 90 to 500 K at pressures to 700 bar", NBS Technical Note 653, National Bureau of Standards, USA (1974).

26. Goodwin, R.D. and Haynes, W.M. "Thermophysical properties of propane from 85 to 700 K at pressures to 70 MPa", NBS Monograph 170, National Bureau of Standards, USA (1982).

27. Goodwin, R.D. and Haynes, W.M. "Thermophysical properties of isobutane from 114 to 700 K at pressures to 70 MPa", NBS Technical Note 1051, National Bureau of Standards, USA (1982).

28. Goodwin, R.D. "Hydrogen sulfide provisional thermophysical properties from 188 to 700 K at pressures to 75 MPa", NBSIR 83-1694, National Bureau of Standards, U.S. Department of Commerce, Boulder, Colorado, USA (1983).

29. Hall, K.R., Ed. *TRC Thermodynamic Table - Hydrocarbons*, Thermodynamic Research Center, Texas A & M University System, USA (1986).

30. Lee, A.L. "Viscosity of light hydrocarbons", Monograph of API Research Project No. 65, Am. Petrol. Inst., Washington, D.C. (1965).

31. Vargaftik. *Tables of the Thermodynamical Properties of Liquids and Gases*, John Wiley and Sons, New York (1975).

32. Wagner, W. and DeReuck, K.M. *Oxygen - International Thermodynamic Tables of the Fluid State-9*, IUPAC Project Centre, Imperial College, London, Blackwell Scientific Publications (1987).

33. Takagi, T. and Teranishi, H. "Ultrasonic speed and thermodynamics for binary solutions of n-alkanes under high pressures" *Fluid Phase Equilibria*, **20**, p 315 (1985).

34. Shim, J. and Kohn, J.P. "Multiphase and volumetric equilibria of methane-n-hexane binary system at temperatures between 110° and 150° C", *J. Chem. Eng. Data*, **7**, pp 3-8 (1962).

35. Reamer, H.H., Fiskin, J.M. and Sage, B.H. "Phase equilibria in hydrocarbon systems, phase behavior in the methane-n-butane-n-decane system", *Ind. Eng. Chem.*, **41**, pp 2871-2875 (1949).

36. Reamer, H.H. and Sage, B.H. "Phase equilibrium in hydrocarbon systems, volumetric and phase behavior of the n-decane+carbon dioxide system", *J. Chem. Eng. Data*, **8**, pp 508-513 (1963).

37. Somait, F.A. and Kidnay, A., "Liquid vapor equilibria at 270 K for systems containing nitrogen, methane and carbon dioxide", *J. Chem. Eng. Data*, **23**, pp 301-305 (1978).