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A general equation of state for supercritical fluid mixtures and molecular dynamics simulation of mixture *PVTX* properties

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Abstract—A general Equation of State (EOS), which we previously developed for pure nonpolar systems, is extended to polar systems such as water and to mixtures in this study. This EOS contains only two parameters for each pure component and two additional parameters for each binary mixture (no higher order parameters are needed for more complicated mixture systems). The two mixing parameters can be eliminated for nonaqueous mixtures with a slight loss of accuracy in both total mole volume and in excess volume (or nonideal mixing). Comparison with a large amount of experimental *PVTX* data in pure systems (including H_2O) and in the mixtures, H_2O–CO_2, CO_2–N_2, CH_4–CO_2, and N_2–CO_2–CH_4 results in an average error of 1.6% in density. Comparison with commonly used EOS for supercritical fluids shows that the EOS of this study covers far more *T-P-X* space with higher accuracy. We believe that it is accurate from supercritical temperature to 2000 K and from 0 to 25,000 bar or higher with an average error in density of less than 2% for both pure members and mixtures in the system H_2O–CO_2–CH_4–N_2–CO–H_2–O_2–H_2S–Ar and possibly with additional gases. Comparison with the published simulated data suggests that this EOS is approximately correct up to 300,000 bar and 2800 K.

We also simulated the *PVTX* properties of a number of supercritical fluid mixtures using molecular dynamics (MD) simulation. These results and those of other authors are well predicted by the EOS of this study.

1. INTRODUCTION

The pressure-volume-temperature-composition (*PVTX*) properties of natural fluids composed of pure members or mixtures of H_2O, CO_2, CH_4, N_2, H_2S, CO, Ar, He, H_2, and O_2 are very important in the study of various geochemical systems, since almost all thermodynamic properties can be derived from *PVTX* relations and these are among the most important fluids in nature. Although numerous experimental *PVTX* datasets have been published, all the experimental data together cover only a small *TPX* range. In order to bridge between the various *TPX* ranges of experiments, many Equations of State (EOS) have been proposed. However, even the well organized combination of many EOS, such as SUPERFLUID (Belonoshko et al., 1992a), which includes the EOS of Kerrik and Jacobs (1981), Jacobs and Kerrick (1981), Saul and Wagner (1989), Shi and Saxena (1992), and Belonoshko and Saxena (1992b), can only cover part of the *TPX* range in the supercritical range with an average error of about 4% in volume. Many EOS on Lennard-Jones (L-J) fluids have been published, but most of them are for pure systems, such as that by Johnson et al. (1993) and those reviewed by them. Ihm and Mason (1990) developed an analytical EOS for L-J hard sphere mixtures. However, this EOS deviates from the simulated results by 5–15% in pressures. The errors must be larger when applied to the real systems, such as H_2O–CO_2, because there is no adjustable parameters accounting for the mixing effect.

While experimental data are obviously preferred, in the last a few years, molecular dynamics (MD) and Monte Carlo (MC) simulations have been successfully used in the study of thermodynamical properties of fluids (Kubicki and Lasaga, 1990; Brodholt and Wood 1990, 1993a,b; Belonoshko and Saxena 1991a,b; Kalinichev and Heinzinger, 1992; Duan et al., 1992a, 1995). These studies indicate that simulations may produce data with an accuracy close to that of experiments.

In an earlier study (Duan et al., 1992a), we were able to simulate the *PVT* properties of CH_4 accurately over a very large *T*–*P* range. We proposed an EOS, the parameters of which were evaluated from the simulated *PVT* data together with some experimental data. By a simple scaling, this EOS may be used to accurately predict the *PVT* properties of many other pure components, such as CO_2, CO, N_2, and H_2 up to 2000 K and 22,000 bar with errors less than 1.5% in density. It is remarkable that the extension from CH_4 to other components requires a very limited number of experimental data points. Only two parameters are needed for each additional component.

The objective of this article is to introduce the extension of the general EOS of Duan et al. (1992a) to polar systems, such as H_2O, and to mixture systems composed of any of the components: H_2O, CO_2, CH_4, N_2, H_2S, CO, Ar, He, H_2, and O_2 from above the critical temperature of the least volatile component to 2000 K and from 0 bar to 25,000 bar or higher with errors less than 2%.

In order to compare the EOS with MD simulation, we simulated the *PVTX* properties of a number of mixture systems. These MD *PVTX* data of this study and of other authors are well predicted for a large *PVTX* range including regions where there is no experimental data.

In the next section (Section 2), the general EOS is dis-

Table 1. parameters for Eq. (1)

a_1	3.75504388D-02
a_2	-1.08730273D+04
a_3	1.10964861D+06
a_4	5.41589372D-04
a_5	1.12094559D+02
a_6	-5.92191393D+03
a_7	4.37200027D-06
a_8	4.95790731D-01
a_9	-1.64902948D+02
a_{10}	-7.07442825D-08
a_{11}	9.65727297D-03
a_{12}	4.87945175D-01
a_{13}	1.62257402D+04
a_{14}	8.99000000D-03

cussed. The remarkable simplicity and accuracy of the EOS over a large T-P-X range will be demonstrated by comparison with data and with the published EOS. In Section 3, the MD simulation method and results for mixtures are presented. Lastly, we give a brief summary.

2. A GENERAL EOS FOR SUPERCRITICAL FLUIDS

In our earlier work (Duan et al., 1992a), we developed an accurate EOS for nonpolar pure systems, which has the following form:

$$Z = \frac{P_m V_m}{RT_m} = 1 + \frac{a_1 + a_2/T_m^2 + a_3/T_m^3}{V_m} + \frac{a_4 + a_5/T_m^2 + a_6/T_m^3}{V_m^2} + \frac{a_7 + a_8/T_m^2 + a_9/T_m^3}{V_m^4} + \frac{a_{10} + a_{11}/T_m^2 + a_{12}/T_m^3}{V_m^5} + \frac{a_{13}}{T_m^3 V_m^2}\left(1 + \frac{a_{14}}{V_m^2}\right)\exp\left(-\frac{a_{14}}{V_m^2}\right), \quad (1)$$

where P_m is in bar, T_m in K and V_m in dm^3, and R = 0.08314467. Here the subscript "m" means the reference fluid, i.e., methane. The parameters, a_1–a_{14}, are taken from Duan et al. (1992a) and are listed again in Table 1. For a fluid, such as CO_2, with L-J parameters σ and ϵ, the volume V (in cm^3) at a given T (K) and P (bar) is calculated as follows. First, V_m is calculated by substituting Eqns. 2 and 3 into Eqn. 1,

$$P_m = \frac{3.0626\sigma^3 P}{\epsilon}, \quad (2)$$

$$T_m = \frac{154T}{\epsilon}, \quad (3)$$

where L-J parameters, σ and ϵ, for a given species are given in Table 2. Most of the parameters can be found in the literature. We adjusted them slightly by fitting a few experimental PVT data points to Eqns. 1–3. Usually about twenty points in varying densities are sufficient. After V_m is calculated, V (in cm^3) is calculated by

$$V = 1000V_m\left(\frac{\sigma}{3.691}\right)^3. \quad (4)$$

The equations for calculating partial fugacity coefficients and enthalpy departure are listed in the Appendix.

2.1. Equation 1 for pure systems including H_2O

It was shown (Duan et al., 1992a) that the EOS (Eqn. 1) was able to predict PVT properties up to 2000 K and 22,000 bar with an average error of less than 1.5%. Here we use the two L-J parameters (Table 2) to extend Eqn. 1 to water. As shown in Table 3, the PVT data of H_2O are well predicted over a wide T-P range, which includes the experimental data of Brodholt and Wood (1994) up to 1873 K and 25,000 bar. This is remarkable because H_2O is regarded as a very polar molecule and difficult to treat thermodynamically. This may suggest that the angular part of water potential is averaged at high temperatures. It can also be seen from Table 3 that Eqn. 1 is more accurate than the program package "SUPERFLUID" (Belonoshko et al., 1992a), which includes a number of published EOS as listed below the table. Some of the included EOS in the package are much more complicated than Eqn. 1. The EOS of this study is also more accurate than SUPERFLUID for other components, such as N_2 and H_2.

2.2. Equation 1 for mixtures

The EOS for mixtures is based on the EOS for endmember (pure) species and a mixing rule which combines the parameters of endmembers. As stated above, each pure component has two parameters, ϵ and σ. They represent energy and size, respectively. Based on the conventional Bethelot-Lorentz rule, we proposed the following rule to combine the two parameters for mixtures:

$$\epsilon = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j k_{1,ij}\sqrt{\epsilon_i \epsilon_j} \quad (5)$$

$$\sigma = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j k_{2,ij}(\sigma_i + \sigma_j)/2, \quad (6)$$

where $k_{1,ij}$ and $k_{2,ij}$ are mixing parameters between particles

Table 2. L-J Potential Parameters

Species	ε (K)	σ (A)	Ref
H_2O	510	2.88	
CH_4	154.0 (147.8)	3.691 (3.73)	Jorgensen et al., 1984
CO_2	235.0 (247.0)	3.69 (3.69)	Ben-Amotz and Herschbach, 1990
CO	98.0 (98.0)	3.66 (3.69)	Ben-Amotz and Herschbach, 1990
O_2	115.7 (106.7)	3.365 (3.467)	Svehla, 1962
N_2	101.0(95.)	3.63(3.698)	Hirschfelder et al. 1964
H_2	34.6 (33.3)	2.91 (2.968)	Jones and Ingham, 1925
Cl_2	348.7	3.692	
H_2S	289.5	3.693	

The numbers in brackets are from the references.

Table 3. Experimental PVT[1] Data *vs.* the EOS of This Study and Other EOS for H_2O

T(K)	P(bar)	$V^2_{Eq.(1)}$ (err%[3])	$V^4_{SUPERFL}$ (err%)	$V_{exp.}$	Ref
H_2O					
723.15	1	60089 (0.04)	60115 (0.09)	60062	D'ans et al., 1967
1073.15	5	17829 (0.01)	17826 (0.02)	17828	-
713.15	100	550.8 (5.11)	525.1 (0.21)	524	Burnham et al., 1969
1073.15	100	876.6 (0.21)	874 (-0.23)	876	-
713.15	1000	28.64 (0.23)	28.57 (0.00)	28.57	-
1073.15	1000	77.88 (-0.32)	78.15 (0.04)	78.12	-
813.15	5000	21.23 (-0.60)	21.32 (-0.20)	21.36	-
1273.15	5000	29.53 (0.06)	31.86 (8.00)	29.51	-
813.15	8900	18.74 (-0.20)	18.47 (-0.60)	18.7	-
1173.15	8900	22.57 (1.30)	21.76 (-2.30)	22.27	-
1203	9500	22.40 (0.70)	21.53 (-4.60)	22.56	Brodholt & Wood, 1994
1491	9500	25.00 (-3.30)	24.64 (-4.70)	25.86	-
1293	17500	19.29 (0.70)	18.07 (-5.60)	19.15	-
1393	17500	19.79 (1.30)	18.56 (-5.00)	19.54	-
1493	17500	20.29 (-1.00)	19.07 (-6.90)	20.49	-
1593	17500	20.78 (-3.20)	19.60 (-8.70)	21.47	-
1693	17500	21.28 (-2.30)	20.13 (-7.60)	21.79	-
1723	22000	19.86 (-1.40)	18.59 (-7.70)	20.15	-
1873	25000	19.61 (0.00)	18.32 (-6.60)	19.61	-
2614	349270	9.83 (3.80)	9.04 (-4.54)	(9.47)	Brodholt & Wood, 1993a[5]
2544	114980	13.43 (4.30)	12.19 (-5.28)	(12.87)	-
2344	38150	18.38 (2.00)	16.98 (-5.77)	(18.02)	-
2582	32960	19.97 (-0.25)	18.60 (-7.09)	(20.02)	-
H_2					
373.15	5000	19.98 (-1.16)	21.51 (6.43)	20.21	Tsiklis et al., 1975
373.15	6000	18.64 (-0.58)	20.48 (9.23)	18.75	-
373.15	7000	17.62 (0.00)	19.74 (12.03)	17.62	-
423.15	5000	20.99 (-0.10)	20.61 (-1.90)	21.01	-
423.15	6000	19.53 (-0.83)	18.97 (-3.71)	19.70	-
423.15	7000	18.43 (1.42)	17.75 (-2.31)	18.17	-
O_2					
473.15	5066	28.91 (-1.18)	29.76 (1.71)	29.26	Tsiklis and Koulikova, 1965
473.15	7092	26.10 (-2.53)	26.56 (-0.48)	26.78	-
573.15	5066	30.76 (-0.90)	31.63 (1.90)	31.04	-
573.15	9119	25.41 (2.10)	25.58 (2.77)	24.89	-
673.15	5066	32.61 (-0.08)	33.50 (2.63)	32.64	-
673.15	10132	25.68(-0.26)	25.65 (-0.39)	25.75	-
394.30	1802	38.60 (-0.35)	39.10 (0.93)	38.74	-
1295.90	6028	40.27 (0.67)	40.44 (1.10)	40.00	Belonoshko and Saxena, 1991b
407.10	4049	29.62 (-1.26)	29.53 (-1.57)	30.00	-
1193.80	17037	25.74 (2.95)	24.72 (-1.12)	25.00	-

1. All the volumes are in cm^3/mol
2. $V_{Eq.(1)}$ is the mole volume calculated by the EOS of this study. The comparison for CH_4, CO_2, N_2, COandCl_2 can be referred to Duan et al. (1992a).
3. err% = 100 . $(V_{EOS}-V_{exp})/V_{exp}$.
4. V_{SUPERF} is the mole volume calculated from the SUPREFLUID (Belonoshko et al., 1992a), which includes the EOS of Saul and Wagner (1989) for water at P <5000 bar), the EOS of Jacobs and Kerrick (1981) for methane, the EOS of Kerrick and Jacobs (1981) for carbon dioxide in the supercritical region, and the EOS of Belonoshko and Saxena (1992b) for all the components at P ≥ 5000 bar.
5. These are MD simulated data using TIP4P by Brodholt and Wood (1993a).

i and j and x_i and x_j are mole fractions for i and j. If i and j are the same kind of particle, $k_{1,ij} = 1$ and $k_{2,ij} = 1$. If not, they will be determined by experimental data. Theoretically, two data points are sufficient to evaluate $k_{1,ij}$ and $k_{2,ij}$ for a binary mixture. However, additional data points reduce experimental uncertainties. Mixing parameters for some systems are listed in Table 4. Once $k_{1,ij}$ and $k_{2,ij}$ are determined, the parameters σ and ϵ can be calculated by Eqns. 5 and 6.

Table 4 Mixing Parameters

System	$K_{1,ij}$	$K_{2,ij}$
H_2O–CO_2	0.840	1.03
CH_4–CO_2	0.8563	1.00
CH_4–N_2	0.9221	1.00
N_2–CO_2	1.00	1.00

The PVTX properties of mixtures can in turn be calculated through Eqns. 1–4. Now we illustrate the accuracy of Eqn. 1 with the mixing rule (Eqns. 5, 6) for mixtures by comparison with extensive experimental data in the systems H_2O–CO_2, CH_4–CO_2, CO_2–N_2, and CO_2–CH_4–N_2 and by comparison with a few of the most well-known EOS.

As summarized by Duan et al. (1992b), there are more than one thousand *PVTX* data points published for the H_2O–CO_2 system covering the supercritical range up to 6000 bar and 1073 K. All the data are well predicted with accuracy very close to experiment. The data of Greenwood (1969) and Sterner and Bodnar (1991) cover the most extensive *T-P* range. Some of the representative points are listed in Table 5, which shows that the EOS of this study can predict the densities with average errors less than 2%. The largest errors occur for the water-rich mixtures when the temperatures approach critical temperature of water and pressure is around 500 bar, which can be over 10%. We also compared the experimental data with the computer program "SUPER-

Table 5. Comparison of Experimental PVTX Data in the System H_2O–CO_2 with the EOS of This Study and with the EOS of Kerrick and Jacobs (1981) and of Belonoshko and Saxena (1992b)

T(K)	P(bar)	x_{CO2}	$V_{Eq.(1)}$ (err%)	$V_{KJ\ or\ BS}$ (err%)	$V_{exp.}$	Ref
673.15	2000	.747	46.98 (0.08)	46.02 (-1.24)	46.6	Sterner & Bodnar,1991
673.15	2000	.372	35.56 (1.30)	34.34 (-2.17)	35.1	-
673.15	3000	.747	40.85 (0.61)	39.85 (-1.85)	40.6	-
673.15	3000	.372	31.52 (1.34)	30.46 (-2.06)	31.1	-
673.15	4000	.747	37.45 (0.40)	36.47 (-2.23)	37.3	-
673.15	4000	.372	29.25 (0.85)	28.24 (2.62)	29.0	-
673.15	5000	.372	27.71 (-0.33)	26.74 (-3.81)	27.8	-
773.15	2000	.747	51.40 (-1.14)	50.72 (-2.46)	52.0	-
773.15	2000	.372	40.07 (2.22)	38.36 (-2.14)	39.2	-
773.15	3000	.747	43.71 (-0.21)	42.97 (-1.89)	43.8	-
773.15	3000	.372	34.46 (0.76)	33.13 (-3.13)	34.2	-
773.15	4000	.747	39.61 (-0.49)	38.85 (-2.39)	39.8	-
773.15	4000	.372	31.50 (1.29)	30.28 (-2.64)	31.1	-
773.15	5000	.747	36.93 (-0.72)	36.73 (-1.26)	37.2	-
773.15	5000	.372	29.57 (0.93)	28.65 (-2.22)	29.3	-
773.15	6000	.372	28.17 (0.97)	27.04 (-3.08)	27.9	-
973.15	3000	.747	49.53 (-2.11)	49.66 (-1.86)	50.6	-
973.15	3000	.372	40.36 (2.96)	39.43 (0.59)	39.2	-
973.15	4000	.372	35.83 (1.22)	34.93 (-1.33)	35.4	-
973.15	5000	.747	40.40 (-2.40)	41.43 (-0.30)	41.4	-
973.15	5000	.372	33.04 (0.41)	33.00 (-0.51)	32.9	-
973.15	6000	.747	37.91 (-1.27)	38.17 (-0.60)	38.4	-
973.15	6000	.372	31.12 (0.06)	30.45 (-2.09)	31.1	-
723.15	100	.200	566.0 (0.64)	549.5 (-2.29)	562.4	Greenwood, 1969
723.15	500	.200	87.36 (8.30)	195.5 (-22.26)	80.7	-
923.15	100	.200	750.1 (0.66)	744.9 (0.04)	745.2	-
923.15	500	.200	138.8 (0.32)	135.4 (-2.17)	138.4	-
1023.15	100	.200	839.3 (0.57)	835.2 (0.08)	834.5	-
1023.15	500	.200	161.1 (-0.83)	160.3 (-1.37)	162.5	-
723.15	100	.500	580.5 (0.17)	568.9 (-1.81)	579.4	-
723.15	500	.500	107.1 (-3.00)	85.6 (-22.53)	110.5	-
923.15	100	.500	762.9 (0.97)	753.4 (-0.28)	755.5	-
923.15	500	.500	152.9 (-0.77)	150.2 (-2.53)	154.1	-
1073.15	100	.500	894.9 (1.87)	884.3 (0.66)	878.5	-
1073.15	500	.500	183.7 (-0.45)	183.6 (0.54)	184.6	-
723.15	100	.800	595.2 (-0.69)	588.3 (-1.84)	599.3	-
723.15	500	.800	122.6 (-2.49)	116.4 (-7.40)	125.7	-
923.15	100	.800	775.0 (0.80)	761.9 (0.89)	768.8	-
923.15	500	.800	164.7 (-1.15)	165.0 (0.96)	166.6	-
1073.15	100	.800	905.7 (1.62)	889.1 (-0.22)	891.3	-
1073.15	500	.800	190.0 (-0.23)	195.5 (0.51)	194.5	-

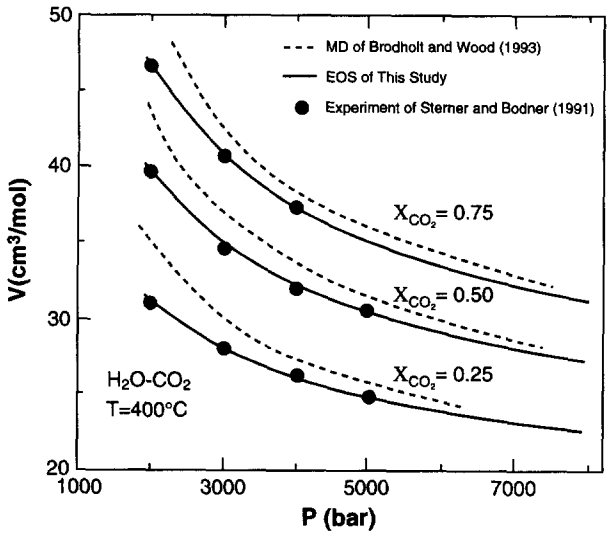

FIG. 1. Comparison of experimental data in the system H_2O–CO_2 with the EOS of this study and with the MD results (Brodholt and Wood, 1993).

FLUID" (Belonoshko, 1992a), which includes a number of EOS popular with geochemists, as listed below Table 3. It can be seen that Eqn. 1 yields better predictions than the combination of the two commonly used EOS, the EOS of Kerrick and Jacobs (1981) for low pressures and the EOS of Belonoshko and Saxena (1992b) for high pressures. Both of these EOS are more complicated than Eqn. 1 of this study.

Table 6. MD Results (Brodholt and Wood, 1993b) *vs.* the EOS of this Study and the EOS of Belonoshko and Saxena (1992b) in the System H_2O–CO_2

T(K)	P(bar)	x_{CO2}	$V_{Eq.(1)}$ (err%)	V_{BS} (err%)	V_{MD}
667	26670	.75	23.66 (-1.41)	23.82 (-0.79)	24
666	13250	.75	27.61 (-1.39)	27.20 (-2.86)	28
1426	17180	.75	30.47 (-4.78)	29.53 (-7.72)	32
1539	12940	.75	34.25 (-4.86)	33.78 (-6.17)	36
682	32030	.50	20.30 (1.50)	20.16 (0.80)	20
694	13820	.50	24.29 (1.20)	23.66 (-1.42)	24
1429	29170	.50	23.37 (-2.60)	21.94 (-8.58)	24
1580	19700	.50	26.97 (-3.68)	25.72 (-8.14)	28
638	38590	.25	16.41 (2.56)	16.47 (2.94)	16
683	14590	.25	20.06 (0.30)	19.69 (-1.55)	20
1538	38590	.25	23.55 (-1.88)	22.20 (-7.50)	24
1500	12340	.25	27.05 (-3.39)	26.17 (-6.54)	28

Table 7. The Accuracy of Eq. (1) in predicting Mixture PVTX Properties

System	T(K)	P(bar)	avr.err*	maximum err	err if **	# of exp. data
CO_2–N_2	298-398	30-600	0.48%	1.4%	0.48%	154
CH_4–CO_2	310-598	1-1000	0.90%	4.3%	2.35%	624
CH_4–CO_2–N_2	473	1000	0.50%	1.30%	0.53%	12

* $\text{avr.err} = \frac{1}{N}\sum_{1}^{N} 100(V_{Eq.(1)} - V_{exp})/V_{exp}$

** average error if all the interaction parameters equal unity ($k_{1,ij}=1$, $k_{2,ij}=1$).

For example, the EOS of Belonoshko and Saxena (1992b) has thirty-three parameters, but Eqn. 1 has only fourteen.

Brodholt and Wood (1993b) simulated the *PVTX* properties of this binary up to high pressures and temperatures using the potential TIP4P for H_2O and MSM for CO_2. Both of the potentials are much more complicated than LJ potential. However, as shown in Fig. 1, their simulated results are much less accurate than the EOS of this study, which will be shown in the next section to be consistent with our MD results using LJ potential. Under very high pressure conditions, where there is no experimental data for comparison, the EOS of this study yields similar volumes to the MD results of Brodholt and Wood (1993b) (see Table 6).

Equations 1–6 were also used to study the binary mixtures CO_2–N_2 and CO_2–CH_4 and the ternary system CO_2–CH_4–N_2. We compared hundreds of data points with the EOS (Table 7). It is found that all the experimental data are well predicted with an average deviation less than 1.5%. The high accuracy of the EOS for the ternary system, with no ternary interaction parameter involved, suggests that at least for this system the ternary interaction is negligible. There is no data at pressures higher than 1000 bar for these systems. However, the accuracy of the EOS for the H_2O–CO_2 system up to high pressures demonstrated above and for the pure systems (Duan et al., 1992a) leaves little doubt that this EOS is accurate at least up to 2000 K and 25000 bar (see Table 3) for these systems. Table 8 shows that this EOS is much more accurate than the EOS in "SUPERFLUID" (Belonoshlo et al., 1992a), where experimental data are from Seitz et al. (1994).

As discussed above, binary experimental data are used for the evaluation of the mixing parameters. In order to achieve the goal to calculate the *PVTX* properties of any mixtures composed of members in the H_2O–CO_2–CH_4–N_2–CO–H_2–O_2–H_2S–Ar system, many more data for binaries are needed. Unfortunately, they are not available and measuring all the binaries in these mixtures involves a tremendous amount of experimental work. Therefore, we would like to estimate errors of this EOS without the mixing parameter. As shown in Table 7, when all the binary interaction parameters are set to 1.0, the deviations of the calculated volumes from the data only increase slightly. This can be true for all nonpolar or weakly polar mixtures. For aqueous mixtures such as the H_2O–CO_2 system, the loss of accuracy is greater. The deviations of the calculated volumes using Eqns. 1–6 from the data of Sterner and Bodnar (1991) and Greenwood (1969) increase from an average 1.5% when using the interaction parameters in Table 2 to 3.6% when $k_{1,H_2O-CO_2} = 1$ and $k_{2,H_2O-CO_2} = 1$.

Setting the interaction parameters to 1 does not imply ideal mixing. This can be easily proven by calculating the excess volume defined as

$$V^{\text{exc.}} = V^{\text{mixture}} - \sum_{i}^{N} x_i V_i^{\text{pure}}. \tag{7}$$

Nonzero excess volume means nonideal mixing. Large excess volume means very nonideal mixing. As an example, we calculate the excess volumes of the CO_2–N_2 system, assuming $k_{1,N_2-CO_2} = 1$ and $k_{2,N_2-CO_2} = 1$ (Table 9). It can be seen that the excess volume can be very large (over 16% of the total volume under some T-P conditions) and this

Table 8. Comparison of Eq. (1) with experimental data in the system CH_4–CO_2–N_2

T(k)	P(bar)	x_{CH_4}	x_{CO_2}	x_{N_2}	$V_{Eq.(1)}$	$V^*_{SUPERFL}$	V(exp.)
473.15	1000	.100	.800	.100	56.25	54.48	56.64
473.15	1000	.200	.600	.200	58.49	53.55	58.92
473.15	1000	.300	.400	.300	60.72	52.62	61.08
473.15	1000	.400	.200	.400	62.34	51.69	62.90
473.15	1000	.800	.100	.100	62.02	59.22	62.21
473.15	1000	.600	.200	.200	61.85	56.25	62.22
473.15	1000	.400	.300	.300	61.48	53.29	61.80
473.15	1000	.200	.400	.400	60.91	50.23	61.27
473.15	1000	.100	.100	.800	63.81	43.23	64.71
473.15	1000	.200	.200	.600	62.79	47.12	63.43
473.15	1000	.300	.300	.400	61.69	51.01	62.07
473.15	1000	.400	.400	.200	60.53	54.90	60.70

* The calculated molar volume (cm^3/mol) using SUPERFLUID (Belonoshko et al., 1992a), which includes a number of EOS.

Table 9. The Volume and Excess Volume of the Mixture System CO_2–N_2

T(K)	P(bar)	x_{CO2}	$V_{Eq.(1)}$	$V_{exp.}$	$V^{exc.}$
298	76	0.5048	275.89	274.12	14.01
298	152	0.5048	122.17	120.91	18.38
323	76	0.5048	314.26	314.20	14.20
323	152	0.5048	144.61	144.98	24.3
348	76	0.5048	350.49	350.83	12.73
348	152	0.5048	165.8	166.8	16.8
398	76	0.5048	418.8	418.85	10.6
398	152	0.5048	204.8	205.7	12.5
398	202	0.5048	175.3	176.3	12.1
398	227	0.5048	137.2	138.5	9.78

All the volumes are in cm^3/mol, the experimental data are from Haney and Bliss (1944).

excess volume can be correctly calculated without adjusting any interaction parameters.

3. MOLECULAR DYNAMICS SIMULATION OF GAS MIXTURES

It is desirable to develop some analytical equation which can calculate thermodynamic properties directly from the interaction potential (IP). However, this cannot be done even for simple IP such as LJ potential. That is why we have to use the relatively expensive molecular dynamics (MD) and Monte Carlo (MC) methods to simulate thermodynamic properties. In our previous studies (Duan et al., 1992a, 1995), we used a scaling method to derive *PVT* properties from the MD results for methane. Because of the scaling properties of the LJ potential, it is only necessary to simulate the properties of the assigned species, methane. The properties of other pure fluids can be calculated directly from these simulated results without further simulation. Here we report our similar achievements for mixtures. In the following we first describe our MD simulation for mixtures and then show that the MD simulated *PVTX* properties for mixtures can be accurately represented by Eqns. 1–6.

3.1. The choice of effective interaction potential

The crucial step in the MD simulation is the specification of the interaction potential (IP) between species in the system. At present, a theoretically derived IP is not available which can account for all the effects, such as dipole moments, induced dipole moments, mass, angle, etc. Therefore, all IP currently used contain some parameters which must be evaluated from experiment. Our choice of the LJ potential is based on our demonstration of its ability to predict the properties with accuracy to experimental data. The LJ potential is defined by the equation

$$V_{ij} = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]. \quad (8)$$

In a pure system consisting of particles represented by i, there are only i-i interactions. The values of ϵ and σ can be found from the literature or can be easily determined from Eqn. 1. Same parameters as the EOS are used here for simulation (Table 2). In a mixture system of particles i and j, there are i-j interactions in addition to i-i and j-j interactions. In the simulations reported here, we use the rule corresponding to Eqns. 5 and 6 to calculate the two L-J parameters of the unlike molecules, ϵ_{ij} and σ_{ij}.

$$\epsilon_{ij} = k_{1,ij}\sqrt{\epsilon_i \epsilon_j}. \quad (9)$$

$$\sigma_{ij} = k_{2,ij}(\sigma_i + \sigma_j)/2. \quad (10)$$

The mixing parameters are also taken from the EOS above (Table 4) because we want to compare the EOS and the simulated results.

Table 10. EOS vs. MD simulated PVTX properties of the system H_2O–CO_2

x_{CO_2}	V_{MD}	$V_{Eq.1}$	T(simu., K)	P(simu.,bar)
0.371	34.52	35.35	670.1±2.9	1977±51
0.371	27.7	27.59	673.5±3.8	5011±154
0.371	31.51	30.77	869.7±2.9	5200±101
0.875	43.20	43.10	673.5±5.2	3095±66
0.875	41.50	41.22	876.3±3.5	5198±149
0.875	40.80	40.85	973.3±4.8	5898±149
0.50	35.0	34.70	1399.4±5.7	8367±82
0.50	35.0	34.95	1000.7±6.1	5544±55
0.50	35.0	35.06	728.2±4.2	3391±31
0.50	25.0	25.00	865.8±7.0	15262±231
0.50	25.0	24.96	1100.7±10.1	19001±222
0.50	25.0	24.625	1788.5±12.4	29340±307
0.50	15.0	14.67	1790.4±17.3	187686±4560
0.50	15.0	14.91	1007.7±13.3	154544±4022

V_{MD} (cm^3/mol) is the simulated volume of this study.

3.2. The simulation method

Our simulations were performed at constant energy, constant volume and constant number of particles. In most cases 256 particles were included in the simulation cube. For systems with mole volumes larger than 600 cm^3/mole, 500 particles were used. The coordinates of molecules were initiated either with a face-centered cubic lattice (fcc) or a previous configuration. The molecules were randomly designated as different molecules. For example, for a mixture of 50% N_2 + 50% CH_4, we randomly choose 50% particles as N_2 and another 50% as CH_4. The fcc lattice was heated to about 8000 K and 10,000 steps were taken to insure equilibration. The system was then brought approximately to the desired temperature by scaling the velocity of molecules. At the approximately desired temperature, the system run for 2000

Table 11 EOS *vs.* MD Simulated Results of the System CH_4–CO_2–N_2

x_{CH_4}	x_{CO_2}	x_{N_2}	V_{MD}	$V_{Eq.1}$	T(K)	P(bar)
.3906	.3906	.2188	50.0	49.60	291.0±3	673.2±28
.3906	.3906	.2188	50.0	49.50	383.1±4	1201.4±54
.3906	.3906	.2188	50.0	49.39	484.0±6	1711.2±66
.3906	.3906	.2188	50.0	49.96	562.9±5	2019.4±65
.3906	.3906	.2188	50.0	49.24	722.8±9	2816.3±102
.3906	.3906	.2188	50.0	49.22	973.4±8	3905.1±120
.3906	.3906	.2188	25.0	24.84	973.0±11	29859.1±333
.3906	.3906	.2188	25.0	24.81	470.4±5	21263.1±297
.3750	.3125	.3125	50.0	49.71	302.2±7	794.3±25
.3750	.3125	.3125	50.0	49.61	362.5±3	1128.2±41
.3750	.3125	.3125	50.0	49.40	461.6±5	1628.0±55
.3750	.3125	.3125	50.0	49.38	602±7	2272.7±88
.3750	.3125	.3125	50.0	49.31	1201±12	4840.8±125

V_{MD}(cm^3/mol) is the simulated volume of this study

steps for equilibrium followed by 3000 steps of data collection. The trajectories of particles were calculated using the Verlet algorithm (Allen and Tildesley, 1989). The minimum image criterion and periodic boundary conditions were used. All interactions between molecules in the box and their minimum image neighbors are included in the calculation of energy and pressure. The timestep was $2.4*10^{-15}$ s. At each Verlet timestep, the instantaneous temperature is calculated as

$$T = \frac{2\,\mathrm{E}}{3\,\mathrm{N}k_\mathrm{B}}, \tag{11}$$

and the pressure as

$$P = \frac{\mathrm{N}k_\mathrm{B}T}{V} - \frac{1}{3V}\sum_i \sum_{j>i} r_{ij}\frac{\partial V_{ij}}{\partial r_{ij}} + P_{\mathrm{LRC}}, \tag{12}$$

where E is total kinetic energy, k_B is Boltzman constant, V_{ij} is the potential energy between particles i and j, r_{ij} is the distance between i and j, and P_{LRC} is a long-range correction pressure calculated from

$$P_{\mathrm{LRC}} = \frac{\pi\epsilon\sigma^3}{V^2}\left[\frac{32}{9}\left(\frac{\sigma}{r_c}\right)^9 - \frac{16}{3}\left(\frac{\sigma}{r_c}\right)^3\right], \tag{13}$$

where r_c is the cutoff radius.

3.3. The simulated results and discussion

Some of the simulated results of the binary system H_2O–CO_2, and the ternary CH_4–CO_2–N_2 are listed in Tables 10 and 11, respectively. The statistical uncertainty in temperature and pressure were obtained by dividing each simulation run into thirty blocks (after discarding the equilibration period). Some of the initial compositions and mole volumes for the H_2O–CO_2 system were specified according to experiment in order to compare the simulated results and experimental data. It can be found from the two tables that the calculated volumes from Eqn. 1 are very close to the simulated results. Therefore, we have numerically proven that the EOS of this study can very accurately predict the simulated properties of mixtures. This is significant because what used to be obtained from the complicated simulation or from experiment now can be obtained from the EOS within a small tolerance of error.

4. SUMMARY

We have presented an EOS (Eqns. 1–6) for supercritical pure and mixture systems of H_2O, CO_2, CH_4, N_2, H_2S, O_2, H_2, CO, and other possible gases. By comparison with thousands of experimental data points, we have demonstrated that this EOS is accurate from above critical points and 0 bar to at least 2000 K and 2,5000 bar with average deviations from experimental data of less than 2% in volume. For pressures above 25,000, there is no experimental data available. However, the MD simulated data (using TIP4P and MSM potentials) for water up to 350,000 bar and 2800 K and for H_2O–CO_2 mixture system up to 40,000 bar and 1600 K are predicted by this EOS with deviations less than 5%.

Compared with other popular general EOS (e.g., Belonoshko and Saxena, 1992b) or corresponding state EOS (e.g., Lee and Kesler, 1975) or specific EOS for supercritical fluids (e.g., Kerrick and Jacobs, 1981; Jacobs and Kerrick, 1981), the EOS of this study covers far more *T-P-X* space, with better accuracy and simplicity.

The MD simulated results of this study using the LJ potential and those of other authors using more complicated potentials are well predicted by this EOS. This is significant because what used to be obtained from the complicated simulation now can be approximately obtained from the EOS.

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APPENDIX: PARTIAL FUGACITY COEFFICIENT AND ENTHALPY DEPARTURE

The partial fugacity coefficient of species i in a mixture can be derived from Eqn. 1 as

$$\ln \phi_i = Z - 1 - \ln(Z) + \frac{a_1 + a_2/T_m^2 + a_3/T_m^3}{v_m} + \frac{a_4 + a_5/T_m^2 + a_6/T_m^3}{2v_m^2} + \frac{a_7 + a_8/T_m^2 + a_9/T_m^3}{4v_m^4} + \frac{a_{10} + a_{11}/T_m^2 + a_{12}/T_m^3}{5v_m^4} + \frac{a_{13}}{2a_4T_m^3} \times \left[2 - \left(2 + \frac{a_{14}}{v_m^2}\right)\exp\left(-\frac{a_{14}}{v_m^2}\right)\right] - \left\{\frac{2a_2/T_m^3 + 3a_3/T_m^4}{v_m} + \frac{2a_5/T_m^3 + 3a_6/T_m^4}{2v_m^2} + \frac{2a_8/T_m^3 + 3a_9/T_m^4}{4v_m^4} + \frac{2a_{11}/T_m^3 + 3a_{12}/T_m^4}{5v_m^5} + \frac{3a_{13}}{2a_{14}T_m^4}\left[2 - \left(2 + \frac{a_{14}}{v_m^2}\right) exp\left(-\frac{a_{14}}{v_m^2}\right)\right]\right\}\left[\frac{2T_m}{\epsilon}\left(\epsilon - \sum_j k_{1,ij}x_j\sqrt{\epsilon_i\epsilon_j}\right)\right] + \frac{6}{\sigma}\left(1 - Z\right)\left(\sigma - \sum_j k_{2,ij}x_j(\sigma_i + \sigma_j)/2\right)$$

and the enthalpy departure from ideal gas [$\Delta H = H(T, P) - H(T, 0\ \text{bar})$] as

$$\Delta H = \frac{\epsilon}{154}RT(Z-1) + \frac{\epsilon}{154}RT^2\left\{\frac{2a_2/T_m^3 + 3a_3/T_m^4}{v_m} + \frac{2a_5/T_m^3 + 3a_6/T_m^4}{2v_m^2} + \frac{2a_8/T_m^3 + 3a_9/T_m^4}{4v_m^4} + \frac{2a_{11}/T_m^3 + 3a_{12}/T_m^4}{5v_m^5} + \frac{3a_{13}}{2a_{14}T_m^4}\left[2 - \left(2 + \frac{a_{14}}{v_m^2}\right)\exp\left(-\frac{a_{14}}{v_m^2}\right)\right]\right\}.$$