

Vapor–Liquid Equilibria of Mixtures Containing Nitrogen, Oxygen, Carbon Dioxide, and Ethane

Jürgen Stoll, Jadran Vrabec, and Hans Hasse

Institut für Technische Thermodynamik und Thermische Verfahrenstechnik,
Universität Stuttgart, D-70550 Stuttgart, Germany

Vapor–liquid equilibria of binary and ternary mixtures containing nitrogen (N_2), oxygen (O_2), carbon dioxide (CO_2) and ethane (C_2H_6) are studied by molecular simulation using two-center Lennard-Jones plus point quadrupole models. Pure-component models are taken from recent work. Mixtures are described using the Lorentz-Berthelot combining rules. Predictions of vapor–liquid equilibria from pure-component data alone agree well with experimental data, for example, the azeotropic behavior of the carbon dioxide + ethane system is predicted correctly. Further improvements are achieved by adjusting one parameter in the energetic term of the combining rule to binary data. For this purpose, a simple and efficient procedure is proposed. Excellent agreement between the molecular models and experimental data for vapor–liquid equilibria, saturated densities, and enthalpies of vaporization is observed for the five binary systems studied in the present work ($N_2 + O_2$, $CO_2 + C_2H_6$, $O_2 + CO_2$, $N_2 + CO_2$, $N_2 + C_2H_6$). Vapor–liquid equilibria of two ternary mixtures ($N_2 + O_2 + CO_2$, $N_2 + CO_2 + C_2H_6$) are predicted well without any further adjustment of model parameters. Results from molecular simulation are compared to those from the Peng–Robinson equation of state, the PC-SAFT equation of state, and the BACKONE equation of state using the same data to determine model parameters. The quality of correlations with system-specific binary interaction parameters from molecular simulation and equations of state is similar, and the predictive power of molecular simulation is clearly superior.

Introduction

Reliable models for vapor–liquid equilibria of mixtures are important for many engineering tasks. Conventional approaches to modeling vapor–liquid equilibria, for example, semiempirical equations of state or lattice-based G^E -models, are well developed and hold little promise for further improvements. They are usually excellent correlation tools, but often lack in predictive power. An alternative and promising route to describe thermodynamic properties of mixtures is molecular modeling and simulation. In the present work, the application of molecular modeling and simulation to vapor–liquid equilibria of binary and ternary mixtures of the quadrupolar components nitrogen (N_2), oxygen (O_2), carbon dioxide (CO_2), and ethane (C_2H_6) is studied. The five binary mixtures, $N_2 + O_2$, $CO_2 + C_2H_6$, $O_2 + CO_2$, $N_2 + CO_2$, N_2

+ C_2H_6 , and the two ternary systems, $N_2 + O_2 + CO_2$, $N_2 + CO_2 + C_2H_6$, investigated here are of interest in various industries.

Various methods for simulating vapor–liquid equilibria with molecular models have been developed in recent years, for example, the Gibbs Ensemble Monte Carlo (Panagiotopoulos, 1987, 1989), the Gibbs–Duhem integration (Kofke, 1993a,b), the NpT + Test Particle Method (Möller and Fischer, 1990, 1992; Vrabec and Fischer, 1995), the bubble point pseudo-ensemble (Ungerer et al., 1999), the Grand Canonical Monte Carlo simulation (Boda et al., 2001), and the Grand Equilibrium (Vrabec and Hasse, 2002). The recently published Grand Equilibrium method for molecular simulation of vapor–liquid equilibria (Vrabec and Hasse, 2002) was applied in the present work.

For simulations, reliable molecular models for pure fluids and mixtures are needed. A large variety of molecular mod-

Correspondence concerning this article should be addressed to J. Vrabec.

els for pure fluids are available in the literature, many of which, however, describe vapor–liquid equilibria only qualitatively. Molecular models for the substances studied in the present work have been developed by Yang et al. (2000) (N_2 , O_2 , CO_2), Fischer et al. (1984) (N_2 , CO_2 , C_2H_6), Shukla (1994) (CO_2 , C_2H_6), Martin and Siepmann (1998) (C_2H_6), Chen and Siepmann (1999) (C_2H_6), Saager and Fischer (1991) (O_2), Lago et al. (1997) (N_2 , O_2 , C_2H_6), Rivera et al. (2000) (N_2), Möller and Fischer (1994) (CO_2), Garzón et al. (1994) (CO_2), Harris and Yung (1995) (CO_2), Nath et al. (1998a) (C_2H_6), Errington and Panagiotopoulos (1999) (C_2H_6), and Vrabec et al. (2001) (N_2 , O_2 , CO_2 , C_2H_6). Considerably less work has been devoted to molecular modeling of vapor–liquid equilibria of mixtures. For some recent examples, see Potoff and Siepmann (2001) ($\text{N}_2 + \text{CO}_2$, $\text{N}_2 + \text{CO}_2 + \text{propane}$), Rivera et al. (2000) ($\text{N}_2 + \text{butane}$), Kronome et al. (2000) ($\text{N}_2 + \text{C}_2\text{H}_6$), Nath et al. (1998b) (alkane mixtures), Potoff et al. (1999) ($\text{CO}_2 + \text{C}_2\text{H}_6$), Cui et al. (1999) ($\text{CO}_2 + \text{alkane}$), and Liu and Beck (1998) ($\text{CO}_2 + \text{C}_2\text{H}_6$). Mixtures studied in the present work have previously been investigated by Fincham et al. (1986) and Vrabec and Fischer (1996), who have presented vapor–liquid equilibria from molecular simulation for the system $\text{CO}_2 + \text{C}_2\text{H}_6$. To our knowledge, vapor–liquid equilibria of the system $\text{O}_2 + \text{CO}_2$ and the ternary mixtures studied here have not been investigated with molecular simulation in previous work.

In the present work, the two-center Lennard-Jones plus point quadrupole (2CLJQ) model is used to describe the properties of the pure components and their mixtures. Pure component models are taken from the recent work of our group (Stoll et al., 2001; Vrabec et al., 2001), which was devoted to the development of a set of compatible molecular models for 25 pure fluids based on the 2CLJQ model. Due to the physical relevance of the 2CLJQ model, that recent work has been restricted to low-molecular, symmetrical, quadrupolar pure substances. Dipolar or associating fluids like methanol or water have not been considered there, as the 2CLJQ model is not physically meaningful for such fluids. These 2CLJQ models allow accurate simulations of vapor–liquid equilibria and related thermodynamic properties of the modeled substances. The present work extends that study to mixtures.

Starting from defined pure-component models, the mixtures are described here on the basis of the Lorentz-Berthelot combining rules, which are known to give good results in many cases (Potoff and Siepmann, 2001). Predictions of vapor–liquid equilibria from pure-component data alone are studied, as well as the adjustment of one parameter in the energetic term of these combining rules to binary data. For that adjustment, a simple and efficient procedure is proposed. An alternative approach followed by some authors (for example, Potoff and Siepmann, 2001) is to determine parameters of pure fluids by including binary data in the model development. This route allows one to avoid the introduction of binary parameters for certain classes of mixtures, for example, alkanes, but is not generally applicable.

Simulation results from the molecular models for mixtures developed in this work are compared to simulation results from other authors, to experimental vapor–liquid equilibrium data, to results from the multiparameter equation of state from the program package DDMIX provided by the NIST

(Ely, 1989, 1990), and to results from the Peng-Robinson equation of state (Peng and Robinson, 1976). Additional results for vapor–liquid equilibria from the PC-SAFT (Gross and Sadowski, 2000) and the BACKONE (Müller et al., 1996; Weingerl et al., 2001) equations of state, which are based on theoretical principles accounting for molecular interactions, are discussed in the Appendix B. The parameter of all three equations of state are adjusted to the same data used for the determination of the parameters of the molecular models.

Molecular Models for Pure Substances

In the present work, quantitative effective state-independent 2CLJQ based molecular models are used, which have recently been developed by Vrabec et al. (2001) as a part of a study covering 25 pure components. The 2CLJQ model is a pairwise additive potential model consisting of two Lennard-Jones sites a distance L apart plus a point quadrupole of momentum Q placed in the geometric center of the molecule along the molecular axis connecting the two Lennard-Jones sites. The interaction energy of two molecules, i and j , is

$$u_{2CLJQ}(\mathbf{r}_{ij}, \boldsymbol{\omega}_i, \boldsymbol{\omega}_j, L, Q) = \sum_{a=1}^2 \sum_{b=1}^2 4\epsilon \left[\left(\frac{\sigma}{r_{ab}} \right)^{12} - \left(\frac{\sigma}{r_{ab}} \right)^6 \right] + \frac{3}{4} \frac{Q^2}{|r_{ij}|^5} f(\boldsymbol{\omega}_i, \boldsymbol{\omega}_j) \quad (1)$$

Herein, the vector \mathbf{r}_{ij} indicates the center–center distance of the two molecules; r_{ab} is one of the four LJ site–site distances; a counts the two sites of molecule i ; b counts those of molecule j . The LJ parameters σ and ϵ represent size and energy, respectively. The function $f(\boldsymbol{\omega}_i, \boldsymbol{\omega}_j)$ depends only on the orientations $\boldsymbol{\omega}_i$ and $\boldsymbol{\omega}_j$ of the molecules. It is given by Gray and Gubbins (1984). Cutoff corrections are described in the Appendix A.

The four model parameters σ , ϵ , Q , and L have been adjusted efficiently by Vrabec et al. (2001), to experimental pure fluid vapor–liquid equilibrium data using global correlations of the critical temperature, T_c , the saturated liquid density, ρ' , and the vapor pressure p_σ as functions of these four molecular parameters (Stoll et al., 2001). The 2CLJQ model parameters for the four pure fluids N_2 , O_2 , CO_2 , and C_2H_6 used in this work are given in Table 1.

The advantages of these quantitative molecular models are their simplicity, which reduces simulation time considerably compared to more sophisticated molecular models containing, for example, partial charges, and their accuracy: typical, relative deviations between simulation and experiment are

Table 1. Effective 2CLJQ Potential Model Parameters for the Fluids Used in This Work

Fluid	$\sigma/\text{\AA}$	$(\epsilon/k_B)/\text{K}$	$L/\text{\AA}$	$Q/\text{D}\text{\AA}$
N_2	3.3211	34.897	1.0464	1.4397
O_2	3.1062	43.183	0.9699	0.8081
CO_2	2.9847	133.22	2.4176	3.7938
C_2H_6	3.4896	136.99	2.3762	0.8277

Source: Values taken from Vrabec et al. (2001).

below 1% for the saturated liquid density, ρ' , below 3% for the vapor pressure, p_σ , and below 2% for the enthalpy of vaporization, Δh_v . This compares favorably, for example, to the Peng-Robinson equation of state, which yields typical relative deviations of about 12% for ρ' , 2% for p_σ , and 1% for Δh_v .

The compatibility of these models opens the route to the modeling of mixtures.

Molecular Models for Mixtures

Given the existing quantitative models for pure fluids, molecular modeling of binary mixtures reduces to modeling the interactions between unlike molecules, which requires less effort than the modeling of like interactions in pure fluids. For the description of the unlike Lennard-Jones interaction in binary mixtures of 2CLJQ fluids A and B , the unlike interaction parameters σ_{AB} and ϵ_{AB} have to be determined. For this purpose, the broadly used Lorentz-Berthelot combining rules are a good starting point (Maitland et al., 1981; Allen and Tildesley, 1987)

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} \quad (2)$$

$$\epsilon_{AB} = \sqrt{\epsilon_A \cdot \epsilon_B} \quad (3)$$

Applying σ_{AB} and ϵ_{AB} as given by Eqs. 2 and 3 in molecular simulations allows the prediction of mixture properties from pure-component data alone. Despite the simplicity of the 2CLJQ models, in many cases, predictions based on Eqs. 2 and 3 are already in reasonable agreement with experimental data. Further improvements can be achieved by introducing binary parameters η and ξ in the combining rules

$$\sigma_{AB} = \eta \cdot \frac{\sigma_A + \sigma_B}{2} \quad (4)$$

$$\epsilon_{AB} = \xi \cdot \sqrt{\epsilon_A \cdot \epsilon_B} \quad (5)$$

Fischer et al. (1989), and Vrabec and Fischer (1995, 1997), adjusted ξ and η successfully to molar excess enthalpies h^E and molar excess volumes v^E . It is important to point out that in all cases investigated by these authors (argon + methane, methane + carbon dioxide, methane + ethane, ethane + carbon dioxide), the value of η was very close to unity. Kronome et al. (2000) published vapor-liquid equilibria of the mixture $N_2 + C_2H_6$ from molecular simulation with $\eta = 1$ in their binary model that agree well with experimental

data. According to these findings, the value

$$\eta = 1 \quad (6)$$

was assumed for all binary mixtures considered here.

Numbers for ξ were determined in the present work by an adjustment to experimental vapor-liquid equilibrium data of binary mixtures. To develop an efficient method for this purpose, first a case study was carried out. For several isotherms and mixtures at given liquid-phase composition x , the sensitivities of the vapor pressure, p , and of the vapor-phase composition, y , to variations of ξ around unity were investigated. It was found in all cases that the vapor pressure p decreases almost linearly with increasing ξ , whereas the vapor phase composition y shows very little sensitivity to variations of ξ . This behavior was exploited to determine the value of ξ . For this purpose, at a selected vapor-liquid equilibrium state point (p, T, x, y) for each binary mixture, the vapor pressures for three different values of ξ close to unity, that is, ξ_1, ξ_2, ξ_3 , were calculated: p_1, p_2, p_3 . A linear fit $p(\xi) = a \cdot \xi + b$ proved to be sufficient to describe the results. The value of ξ is obtained from equating that fit to the experimental value of the vapor pressure, p_{exp} . This procedure is simple and efficient and gives good results for modeling all binary mixtures studied in the present work. Work on 40 additional binary mixtures, which is in progress in our group, supports this finding.

Values for ξ of the five binary mixtures studied here are given in Table 2. The adjustment of ξ was done on the basis of the state points given in Table 3. Criteria for choosing these state points were preferably equimolar liquid mixture and medium temperature.

No additional parameters are introduced in the models for ternary mixtures, nor were any pure-substance parameters altered.

Results for Binary Mixtures

Mixtures of nitrogen (N_2), oxygen (O_2), carbon dioxide (CO_2), and ethane (C_2H_6) were studied in the present work.

Table 2. Binary Interaction Parameters ξ for the Mixtures Modeled in This Work

Mixture	2CLJQ ξ
$N_2 + O_2$	1.007
$CO_2 + C_2H_6$	0.954
$O_2 + CO_2$	0.979
$N_2 + CO_2$	1.041
$N_2 + C_2H_6$	0.974

Table 3. State Points Used for Adjusting the Binary Interaction Parameters ξ and the Binary Parameters k_{ij} in the Peng-Robinson, PC-SAFT, and BACKONE Equations of State

Mixture	T/K	p/MPa	Liquid-Phase Mole Fraction	Vapor-Phase Mole Fraction	Reference
$N_2 + O_2$	105	0.7432	$x_{N_2} = 0.5$	$y_{N_2} = 0.7020$	Knapp et al. (1982)
$CO_2 + C_2H_6$	263.15	2.8958	$x_{CO_2} = 0.4250$	$y_{CO_2} = 0.5140$	Knapp et al. (1982)
$O_2 + CO_2$	253.15	8.106	$x_{O_2} = 0.141$	$y_{O_2} = 0.574$	Fredenslund and Sather (1970)
$N_2 + CO_2$	270	9.2914	$x_{N_2} = 0.1319$	$y_{N_2} = 0.4173$	Knapp et al. (1982)
$N_2 + C_2H_6$	260	7.1059	$x_{N_2} = 0.1647$	$y_{N_2} = 0.5576$	Grausø et al. (1977)

Table 4. Binary Equation of State Parameters k_{ij} for the Mixtures Modeled in this Work

Mixture	Peng-Robinson k_{ij}	PC-SAFT (cf. Appendix B) k_{ij}	BACKONE (cf. Appendix B) k_{ij}
N ₂ + O ₂	-0.00978	-0.00160	-0.003
CO ₂ + C ₂ H ₆	0.13008	0.10289	0.0914
O ₂ + CO ₂	-0.04838	0.05929	-0.01
N ₂ + CO ₂	-0.01493	-0.01793	-0.04
N ₂ + C ₂ H ₆	0.05233	0.04313	-0.025

Results for five out of the six possible binary mixtures from this set of components are discussed below. The remaining system, O₂ + C₂H₆, is not included in the study, as no vapor–liquid equilibrium data were found in the literature for that system.

Results from molecular simulations with the models presented in this work are compared to simulation results from other authors and to results from the Peng-Robinson equation of state (Peng and Robinson, 1976). The parameterization of the Peng-Robinson equation of state requires the acentric factor, ω , the critical temperature, T_c , and the critical pressure, p_c , of the pure fluids. These data were taken from Reid et al. (1987).

In Appendix B, additional results for vapor–liquid equilibria from the PC-SAFT equation of state (Gross and Sadowski, 2000) and the BACKONE equation of state (Müller et al., 1996; Weingerl et al., 2001) are discussed.

The binary parameters, k_{ij} , of these three equations of state were adjusted to the same experimental data used for the development of the binary molecular models, cf. Tables 3 and 4.

Two types of calculations were carried out for both the molecular simulation and the equations of state. One calculation was performed without using the adjusted binary interaction parameter ξ or k_{ij} , that is, a prediction of the properties of the mixture from pure-component data alone, and the other using the binary parameters. Because the prediction from pure-component data alone is used only as reference, it was not carried out for all isotherms. The vapor–liquid equilibrium calculation was done at given temperature, T , and liquid-phase composition, x . Data on the vapor pressure, p , vapor-phase composition, y , saturated liquid density, ρ' , and enthalpy of vaporization, Δh_v , are reported.

Supplementary material containing all numerical results and further figures not presented here is available at <http://www.itt.uni-stuttgart.de/review.html>.

Vapor–liquid equilibria

Nitrogen + Oxygen. Knowledge of vapor–liquid equilibria of this binary system is fundamental in various industrial applications such as air liquefaction and air separation. Figure 1 shows results from the present work for the vapor pressure and the vapor-phase mole fraction for three isotherms. The results for the 105 K isotherm show that predictions from pure-component data alone are in very good agreement with the experimental data for that system, both for the molecular simulation and for the Peng-Robinson equation of state. Simulations with adjusted ξ excellently describe the experimen-

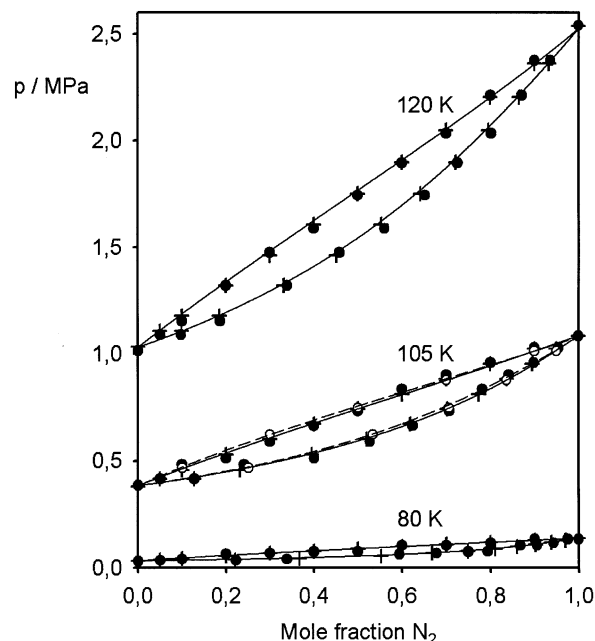


Figure 1. Vapor–liquid equilibria of the mixture N₂ + O₂.

Simulation results, this work (●: ξ adjusted, ○: $\xi = 1$), Peng-Robinson equation of state (—: k_{ij} adjusted, ---: $k_{ij} = 0$), experimental data from Knapp et al. (1982) (+).

tal data. As can be expected, the Peng-Robinson equation of state also yields excellent results.

Carbon Dioxide + Ethane. This mixture is important in the petrochemical industry. Due to its low boiling azeotrope, this system has a more complex phase behavior than the nitrogen + oxygen system. For this system results for vapor–liquid equilibria from molecular simulation are available from Liu and Beck (1998) and from Potoff et al. (1999).

Results from Gibbs Ensemble Monte Carlo simulations of Liu and Beck (1998) and results from the present work are very similar. This could be expected, as Liu and Beck (1998) used 2CLJQ type pure-component models determined by Vrabec and Fischer (1996) and Möller et al. (1992) and Lorentz-Berthelot combining rules with two adjusted binary parameters η and ξ taken from Vrabec and Fischer (1996). Therefore, a direct comparison to results from Liu and Beck (1998) is omitted here for brevity.

Potoff et al. (1999) performed Grand Canonical Histogram-Reweight Monte Carlo simulations with computationally expensive exponential-6-type models with fixed partial charges and, in the case of ethane, intramolecular degrees of freedom, taken from Errington and Panagiotopoulos (1999). The models used by Potoff et al. (1999) were obtained from experimental pure-substance vapor–liquid equilibrium data. Potoff et al. (1999) performed simulations with the Lorentz-Berthelot and the Kong combining rules (Kong, 1973), without adjusting binary parameters.

In Figure 2, simulation results from the present work are compared to results from the Peng-Robinson equation of state and to simulation data from Potoff et al. (1999) obtained with the Kong combining rules. Figure 2 shows that even without a binary parameter the present molecular simulations predict

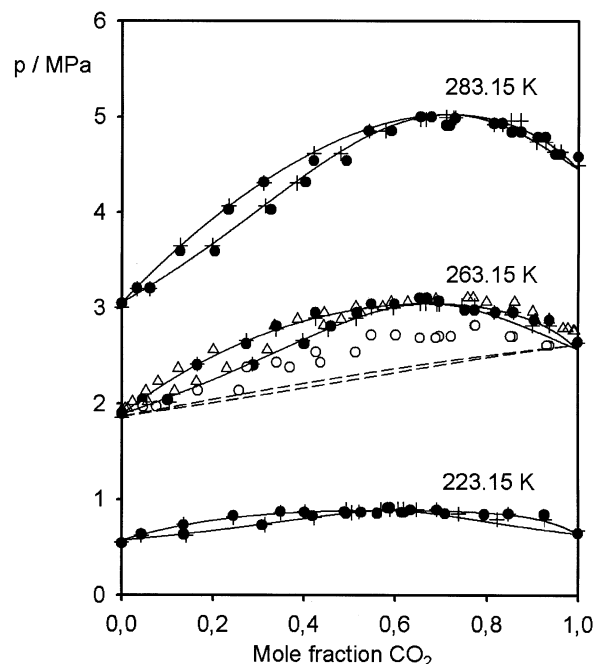


Figure 2. Vapor-liquid equilibria of the mixture $\text{CO}_2 + \text{C}_2\text{H}_6$.

Simulation results, this work (●: ξ adjusted, ○: $\xi = 1$), Potoff et al. (1999) (Δ : Kong combining rules), Peng-Robinson equation of state (—: k_{ij} adjusted, ---: $k_{ij} = 0$), experimental data from Knapp et al. (1982) (+).

the azeotropic behavior. This is a clear advantage of molecular simulation over the Peng-Robinson equation of state, which predicts no azeotrope. The results of the sophisticated model of Potoff et al. (1999) are in very good agreement with experimental data. A somewhat better accuracy is obtained using the model presented here with adjusted binary interaction parameter ξ .

Oxygen + Carbon Dioxide. Vapor-liquid equilibria of mixtures of oxygen and carbon dioxide are encountered in the petrochemical and food processing industries. Fluid-phase equilibria in that system only exist at temperatures and pressures for which pure oxygen is supercritical. This becomes evident from a comparison to the locations of the critical point of pure oxygen and the triple point of pure carbon dioxide in the pressure vs. temperature diagram. To our knowledge, no vapor-liquid equilibrium data of this mixture from molecular simulation have been published previously.

A typical result for a phase diagram of that mixture is shown in Figure 3. Again, the prediction from molecular simulation without using ξ is already in very good agreement with experimental data. In contrast, the prediction from the Peng-Robinson equation of state without using k_{ij} is poor for the bubble line. As long as the pressure is not too close to the critical pressure of the mixture, both methods with adjusted binary parameter are in fair agreement with experimental data. For this mixture, the average statistical uncertainties of the simulation data are quite large; they are about ± 0.35 MPa for the pressure and about ± 0.02 for the vapor composition. Similar results were obtained for the 223.15 K and the 283.15 K isotherm (not shown in Figure 3).

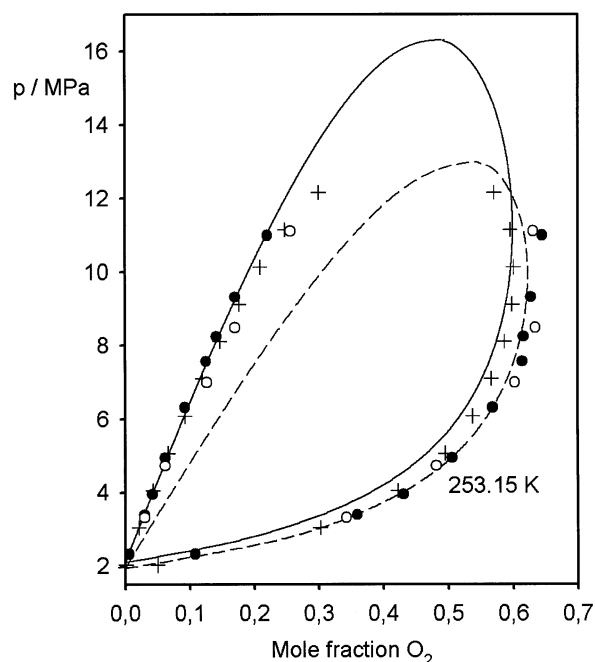


Figure 3. Vapor-liquid equilibria of the mixture $\text{O}_2 + \text{CO}_2$ at 253.15 K.

Simulation results, this work (●: ξ adjusted, ○: $\xi = 1$), Peng-Robinson equation of state (—: k_{ij} adjusted, ---: $k_{ij} = 0$), experimental data from Fredenslund and Sather (1970) (+).

Nitrogen + Carbon Dioxide. Vapor-liquid equilibria of this mixture are important in natural gas processing. Similar to the system $\text{O}_2 + \text{CO}_2$, vapor-liquid equilibria of $\text{N}_2 + \text{CO}_2$ only exist at temperatures and pressures for which pure N_2 is supercritical.

At 253.15 K vapor-liquid equilibrium data from Predictive Configurational-Bias Histogram-Reweight Monte Carlo simulations are available from Potoff and Siepmann (2001). These authors applied newly parameterized rigid Lennard-Jones-based molecular models with partial charges. In the parameterization of their CO_2 model, Potoff and Siepmann (2001) included vapor-liquid equilibrium data of the binary system $\text{CO}_2 + \text{propane}$, whereas their N_2 model is parameterized on the basis of pure-component vapor-liquid equilibrium data alone. Results from Potoff and Siepmann (2001) are based on the Lorentz-Berthelot combining rules.

Figures 4 and 5 show phase diagrams of the system $\text{N}_2 + \text{CO}_2$ at 218.15 K and 253.15 K, where simulation results from the present work and from Potoff and Siepmann (2001) are compared to experimental data and to results from the Peng-Robinson equation of state. In this work, the binary parameters of the molecular and the Peng-Robinson equation of state were adjusted to experimental data at 270 K, so that the present results shown in Figures 4 and 5 represent an extrapolation in temperature.

At 218.15 K both the present molecular simulation data and the Peng-Robinson equation of state agree very well with the experiment. Results of a similar quality were obtained for 232.15 K and 270 K, and are not shown here. Predictive simulations ($\xi = 1$) from this work at 218.15 K are, despite some

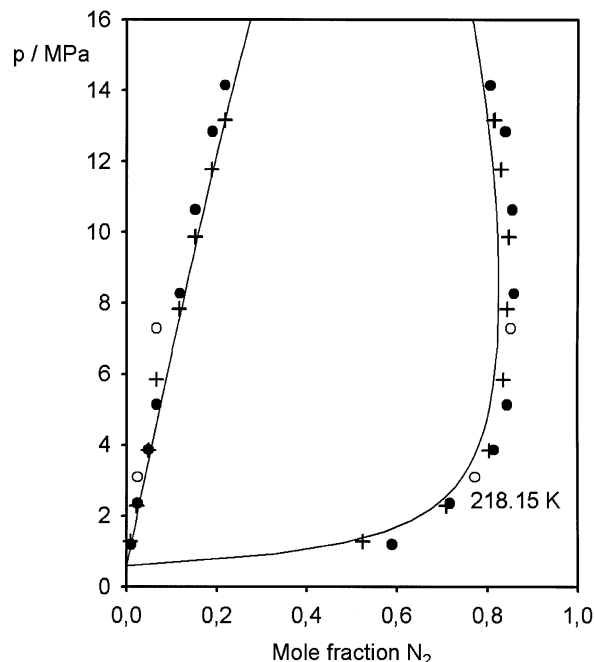


Figure 4. Vapor-liquid equilibria of the mixture $N_2 + CO_2$ at 218.15 K.

Simulation results, this work (●: ξ adjusted, ○: $\xi = 1$), Peng-Robinson equation of state (—: k_{ij} adjusted), experimental data from Knapp et al., 1982 (+).

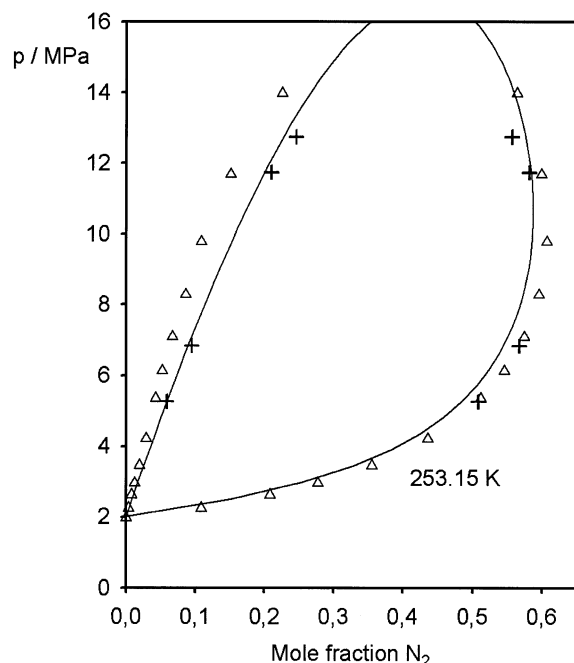


Figure 5. Vapor-liquid equilibria of the mixture $N_2 + CO_2$ at 253.15 K.

Potoff and Siepmann (2001) (Δ : pure-component parameters of CO_2 have been adjusted to the mixture $CO_2 +$ propane, Lorentz-Berthelot combining rules), Peng-Robinson equation of state (—: k_{ij} adjusted), experimental data from Knapp et al. (1982) (+).

deviations in the pressure, generally in fair agreement with the experimental results. The quality of these predictions is similar to the quality of the correlation of Potoff and Siepmann (2001) (cf. Figure 5). Overall, this demonstrates the higher accuracy of the present molecular model. The Peng-Robinson equation of state with adjusted binary parameter shows reasonable agreement with experimental data.

Nitrogen + Ethane. Knowledge of phase equilibria of this mixture is needed in the petrochemical industry. Similar to the systems discussed earlier, at temperatures and pressures where fluid phase equilibria exist in that mixture, pure N_2 is always supercritical. At 200 K and 260 K vapor-liquid equilibria from the extended NpT + test particle method have been published by Kronome et al. (2000). These authors applied unpolar 2CLJ models from Vrabec and Fischer (1996) and Kriebel et al. (1996), in which unlike interactions were modeled with Lorentz-Berthelot combining rules with an adjusted binary interaction parameter ξ . This mixture model is very similar to the present model.

Figure 6 shows a comparison of simulation results from the present work and from Kronome et al. (2000) to experimental data at 200 K and to the Peng-Robinson equation of state. Excellent agreement between both molecular models and experiment is found. The results from the present work are predictions in the sense that the binary parameter was adjusted to data at 260 K (not shown here). The Peng-Robinson equation of state shows considerable deviations on the bubble line and overestimates the critical region.

Saturated liquid densities and enthalpies of vaporization

Saturated Liquid Densities. In Figures 7 and 8 saturated liquid densities of the binary mixtures from molecular simulation are compared to data from the multiparameter equation of state available in the program package DDMIX provided by the NIST (Ely, 1989, 1990) and to results from the Peng-Robinson equation of state. As DDMIX has been designed for accurate descriptions of saturated densities of mixtures, these values are used here as reference data. It can be seen from Figures 7 and 8 that the results from molecular simulation describe the saturated liquid densities of the studied binary mixtures reliably in very good agreement with DDMIX data. As expected, the Peng-Robinson equation of state does not yield satisfactory results in most cases. The results for the mixture $O_2 + CO_2$ are not shown here, as they are very similar to those for the system $N_2 + CO_2$.

Enthalpies of Vaporization. Methods for predicting enthalpies of vaporization of mixtures are important as experimental data are often scarce. In Figures 9 and 10 residual enthalpies of vaporization from molecular simulation are, due to a lack of experimental data, compared to data from DDMIX (Ely, 1989, 1990) and to results from the Peng-Robinson equation of state. Residual enthalpies of vaporization were calculated as

$$\Delta h_v^{res}(T, p, \mathbf{x}, \mathbf{y}) = [h''(T, p, \mathbf{y}) - h^{id}(T, \mathbf{y})] - [h'(T, P, \mathbf{x}) - h^{id}(T, \mathbf{x})] \quad (7)$$

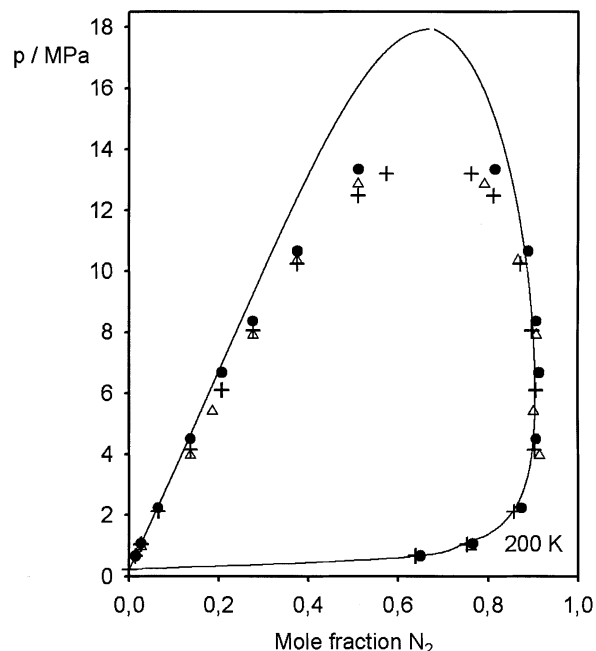


Figure 6. Vapor-liquid equilibria of the mixture $N_2 + C_2H_6$ at 200 K.

Simulation results, this work (●: ξ adjusted), Kronome et al. (2000) (Δ : Lorentz-Berthelot combining rules, ξ adjusted), Peng-Robinson equation of state (—: k_{ij} adjusted), experimental data from Grausø et al. (1977) (+).

The data from DDMIX are considered here as a reasonable estimate for values of the enthalpy of vaporization. It can be seen that results from molecular simulation are close

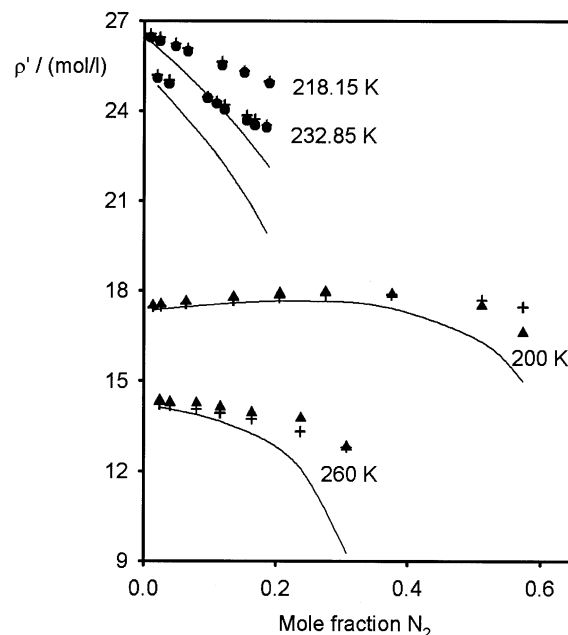


Figure 8. Saturated liquid density of the mixtures $N_2 + CO_2$ (●) and $N_2 + C_2H_6$ (▲).

Simulation results, this work (●, ▲), Peng-Robinson equation of state (—), DDMIX (Ely, 1990) (+).

to the data from DDMIX on all isotherms, whereas, in some cases, the Peng-Robinson equation of state produces larger deviations from DDMIX data. Similar results were obtained for the other systems studied here.

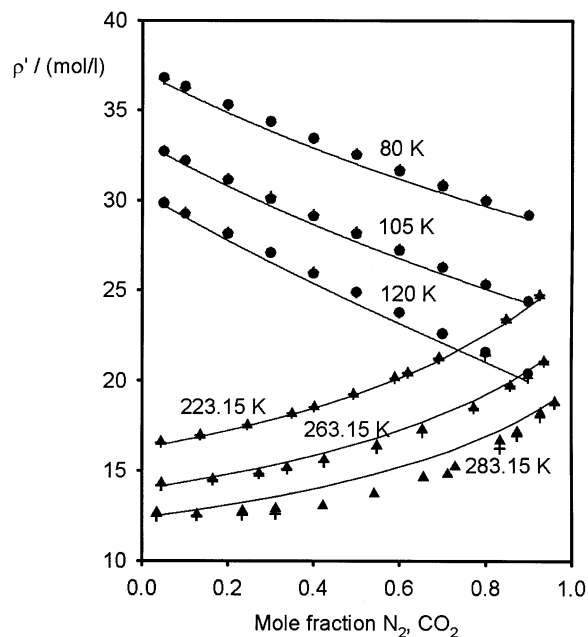


Figure 7. Saturated liquid density of the mixtures $N_2 + O_2$ (●) and $CO_2 + C_2H_6$ (▲).

Simulation results, this work (●, ▲), Peng-Robinson equation of state (—), DDMIX (Ely, 1990) (+).

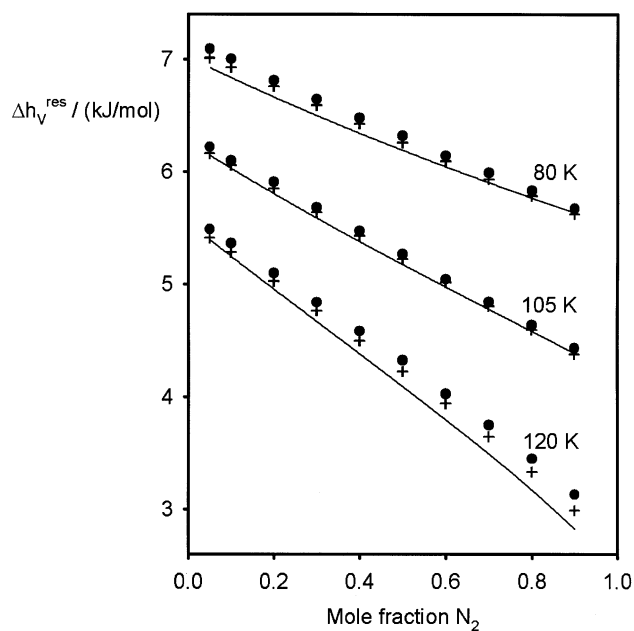


Figure 9. Enthalpy of vaporization of the mixture $N_2 + O_2$.

Simulation results, this work (●), Peng-Robinson equation of state (—), DDMIX (Ely, 1990) (+).

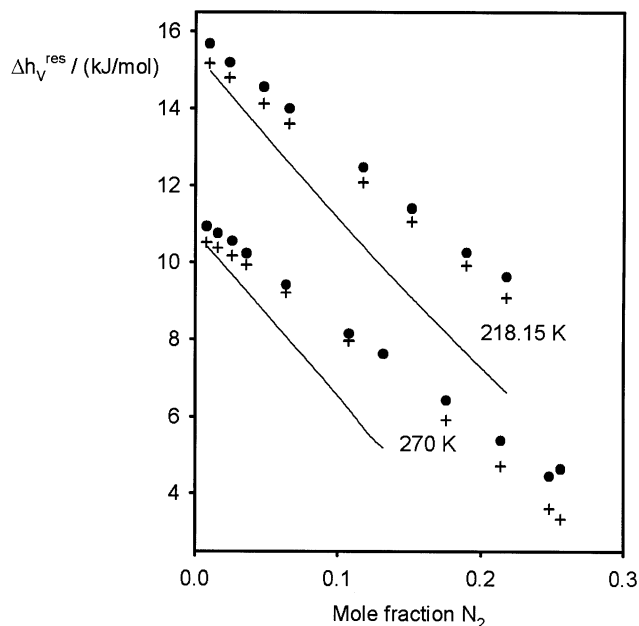


Figure 10. Enthalpy of vaporization of the mixture $N_2 + CO_2$.

Simulation results, this work (●), Peng-Robinson equation of state (—), DDMIX (Ely, 1990) (+).

Vapor-Liquid Equilibria of Ternary Mixtures

In the present work, pairwise additive interaction potentials are used for modeling of molecular interactions, and so no ternary interaction parameters are introduced. Therefore, the molecular models developed using binary data can straightforwardly be applied without any alterations to predict vapor-liquid equilibria of ternary and multicomponent mixtures. The ternary systems $N_2 + O_2 + CO_2$ and $N_2 + CO_2 + C_2H_6$ were studied in the present work. Results from

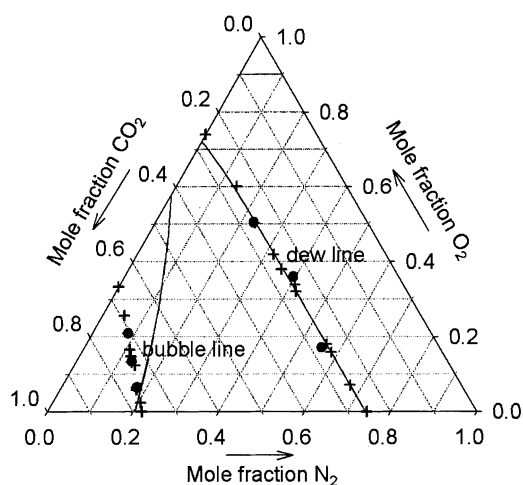


Figure 11. Phase diagram for the mixture $N_2 + O_2 + CO_2$ at $T = 232.85$ K, $p = 12.4$ MPa.

Simulation results, this work (●), Peng-Robinson equation of state (—), k_{ij} adjusted, experimental data from Zenner and Dana (1963) (+).

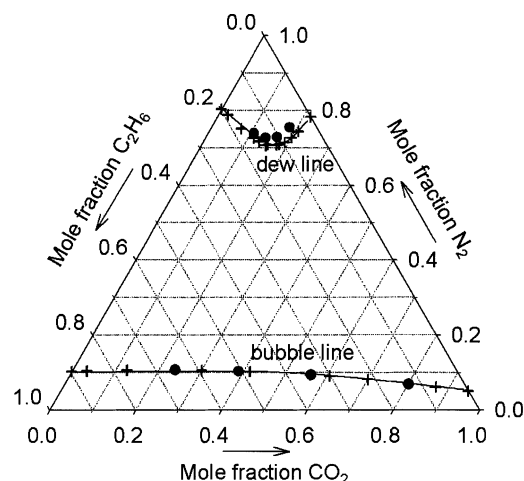


Figure 12. Phase diagram for the mixture $N_2 + CO_2 + C_2H_6$ at $T = 220$ K, $p = 4$ MPa.

Simulation results, this work (●), Peng-Robinson equation of state (—), k_{ij} adjusted, experimental data from Brown et al. (1989) (+).

molecular simulation are compared to experimental data and to results from the Peng-Robinson equation of state.

Nitrogen + Oxygen + Carbon Dioxide. Knowledge of vapor-liquid equilibria of this ternary mixture is needed in the food processing and brewing industry. In Figure 11 the mole fractions on the bubble and on the dew lines are given at 232.85 K and 12.4 MPa. Predictions from molecular simulation are in excellent agreement with the experimental vapor-liquid equilibrium data. The Peng-Robinson equation of state yields good results for the dew line, but shows clear deviations on the bubble line, which are due to shortcomings of the models for the binary systems. Similar results were obtained for 232.85 K and 5.2 MPa (not shown here).

Nitrogen + Carbon Dioxide + Ethane. Results for the $N_2 + CO_2 + C_2H_6$ system are shown in Figure 12. This system shows a strong curvature of the dew line, which is predicted quantitatively both by the molecular simulation and the Peng-Robinson equation of state. Slight deviations in the molecular simulation results for the dew line are due to similar deviations in the binary systems $N_2 + CO_2$ and $N_2 + C_2H_6$, respectively.

Conclusions

Recently, Vrabec et al. (2001) developed compatible molecular models of the 2CLJQ type for 25 pure fluids for accurate simulations of phase equilibria for low-molecular, symmetrical, quadrupolar substances. Four of these models—for nitrogen, oxygen, carbon dioxide, and ethane—are applied here for studies of binary and ternary mixtures. A consistent strategy was used to model all studied mixtures.

Using Lorentz-Berthelot combining rules, predictions from molecular simulation without adjustment of binary parameters already yield results that agree very well in many cases with experimental data for the mixtures. These predictions are more reliable than those of the Peng-Robinson equation

of state. The examples presented in Appendix B show that the same holds for the PC-SAFT and the BACKONE equations of state.

Compared to these predictions, further improvements of the molecular models are achieved using a single binary interaction parameter. An efficient procedure for the adjustment of this binary parameter to experimental binary vapor–liquid equilibrium data is presented. In this way, an excellent agreement of results from molecular simulation and experimental data is achieved, which is similar to the results from equations of state with adjusted binary parameters.

Finally, it is shown that the binary molecular models developed here can be directly applied for the successful predictions of vapor–liquid equilibria of ternary mixtures.

This work will be extended to other mixtures of the 25 pure components modeled by Vrabec et al. (2001).

Acknowledgments

The authors gratefully acknowledge financial support by Deutsche Forschungsgemeinschaft, Sonderforschungsbereich 412, University of Stuttgart. We also thank Dr. M. Wendland, Vienna, for making available the program code of the BACKONE equation of state.

Notation

- a = interaction site index
- a = coefficient in linear function
- b = interaction site index
- b = coefficient in linear function
- f = function
- G^E = excess Gibbs energy, J
- h^E = molar excess enthalpy, J/mol
- Δh_V = molar enthalpy of vaporization, kJ/mol
- i = particle index
- j = particle index
- k_B = Boltzmann constant, 1.38065×10^{-23} J/K
- k_{ij} = binary parameter in equation of state
- L = distance of Lennard-Jones sites in a molecule, Å
- m^{PC} = segment number (PC-SAFT parameter)
- p = pressure, MPa
- p_c = critical pressure, MPa
- p_σ = vapor pressure of pure substance, MPa
- Q = quadrupole momentum, DÅ
- Q^{*2} = reduced quadrupole momentum (BACKONE parameter)
- r_{ab} = site–site distance, Å
- r_{ij} = distance vector of centers of mass of molecules i and j , Å
- T = temperature, K
- T_c = critical temperature, K
- T_0 = characteristic temperature (BACKONE parameter), K
- u = pair potential, J
- v^E = molar excess volume, m³/kmol
- x = liquid-phase composition
- x = liquid-phase mole fraction
- y = vapor-phase composition
- y = vapor-phase mole fraction

Greek letters

- α = anisotropy parameter (BACKONE parameter)
- σ = size parameter, Å
- σ^{PC} = segment diameter (PC-SAFT parameter), Å
- ϵ = energy parameter, J
- ϵ^{PC} = attraction parameter (PC-SAFT parameter), J
- ρ = density, kmol/m³
- ρ_0 = characteristic density (BACKONE parameter), kmol/m³
- ξ = binary interaction parameter
- η = binary interaction parameter
- ω = acentric factor
- ω = orientation vector

Subscripts and superscripts

- A = interaction between molecules A – A
- B = interaction between molecules B – B
- AB = interaction between molecules A – B
- 2CLJQ = two-center Lennard-Jones plus point quadrupole
- exp = experimental
- i = particle index
- j = particle index
- id = ideal gas state
- res = residual property
- r = saturated property on bubble line
- w = saturated property on dew line

Literature Cited

- Allen, M. P., and D. J. Tildesley, *Computer Simulation of Liquids*, Clarendon Press, Oxford (1987).
- Andersen, H. C., “Molecular Dynamics Simulations at Constant Pressure and/or Temperature,” *J. Chem. Phys.*, **72**, 2384 (1980).
- Boda, D., T. Kristóf, J. Liszi, and I. Szalai, “A New Simulation Method for the Determination of Phase Equilibria in Mixtures in the Grand Canonical Ensemble,” *Mol. Phys.*, **99**, 2011 (2001).
- Brown, T. S., E. D. Sloan, and A. J. Kidnay, “Vapor-Liquid Equilibria in the Nitrogen + Carbon Dioxide + Ethane System,” *Fluid Phase Equilibria*, **51**, 299 (1989).
- Chapman, W. G., G. Jackson, and K. E. Gubbins, “Phase Equilibria of Associating Fluids. Chain Molecules with Multiple Bonding Sites,” *Mol. Phys.*, **65**, 1057 (1988).
- Chapman, W. G., K. E. Gubbins, G. Jackson, and M. Radosz, “New Reference Equation of State for Associating Liquids,” *Ind. Eng. Chem. Res.*, **29**, 1709 (1990).
- Chen, B., and J. I. Siepmann, “Transferable Potentials for Phase Equilibria. 3. Explicit-Hydrogen Description of Normal Alkanes,” *J. Phys. Chem. B*, **103**, 5370 (1999).
- Cui, S. T., H. D. Cochran, and P. T. Cummings, “Vapor-Liquid Phase Coexistence of Alkane-Carbon Dioxide and Perfluoroalkane-Carbon Dioxide Mixtures,” *J. Phys. Chem. B*, **103**, 4485 (1999).
- Ely, J. F., J. W. Magee, and W. M. Haynes, *NBS Standard Reference Database 14, DDMIX, Version 9.06*, NIST, Boulder, CO (1989).
- Ely, J. F., “A Predictive, Exact Shape Factor Extended Corresponding States Model for Mixtures,” *Adv. Cryog. Eng.*, **35**, 1511 (1990).
- Errington, J. R., and A. Z. Panagiotopoulos, “A New Intermolecular Potential Model for the n-Alkane Homologous Series,” *J. Phys. Chem. B*, **103**, 6314 (1999).
- Fincham, D., N. Quirke, and D. J. Tildesley, “Computer Simulation of Molecular Liquid Mixtures. I. A Diatomic Lennard-Jones Model Mixture for CO₂/C₂H₆,” *J. Chem. Phys.*, **84**, 4535 (1986).
- Fischer, J., R. Lustig, H. Breitenfelder-Manske, and W. Lemming, “Influence of Intermolecular Potential Parameters on Orthobaric Properties of Fluids Consisting of Spherical and Linear Molecules,” *Mol. Phys.*, **52**, 485 (1984).
- Fischer, J., D. Möller, A. Chialvo, and J. M. Haile, “The Influence of Unlike Molecule Interaction Parameters on Liquid Mixture Excess Properties,” *Fluid Phase Equilibria*, **48**, 161 (1989).
- Fredenslund, A., and G. A. Sather, “Gas-Liquid Equilibrium of the Oxygen-Carbon Dioxide System,” *J. Chem. Eng. Data*, **15**, 17 (1970).
- Frenkel, D., and B. Smit, *Understanding Molecular Simulation, From Algorithms to Applications*, Academic Press, San Diego, p. 140 (2002).
- Garzón, B., S. Lago, C. Vega, E. de Miguel, and L. F. Rull, “Computer Simulation of Vapor-Liquid Equilibria of Linear Quadrupolar Fluids. Departures from the Principle of Corresponding States,” *J. Chem. Phys.*, **101**, 4166 (1994).
- Graus, L., A. Fredenslund, and J. Møllerup, “Vapor-Liquid Equilibrium Data for the Systems C₂H₆ + N₂, C₂H₄ + N₂, C₃H₈ + N₂, and C₃H₆ + N₂,” *Fluid Phase Equilibria*, **1**, 13 (1977).
- Gray, C. G., and K. E. Gubbins, *Theory of Molecular Fluids*, Vol. 1, *Fundamentals*, Clarendon Press, Oxford, p. 76 (1984).
- Gross, J., and G. Sadowski, “Application of Perturbation Theory to a Hard-Chain Reference Fluid: An Equation of State for Square-Well Chains,” *Fluid Phase Equilibria*, **168**, 183 (2000).
- Harris, J. G., and K. H. Yung, “Carbon Dioxide’s Liquid-Vapor Coexistence Curve and Critical Properties As Predicted by a Simple Molecular Model,” *J. Phys. Chem.*, **99**, 12021 (1995).

- Knapp, H., R. Döring, L. Oellrich, U. Plöcker, and J. M. Prausnitz, *Vapor-Liquid Equilibria of Mixtures of Low-Boiling Substances*, DECHEMA Chemistry Data Series, Vol. VI, Frankfurt/Main (1982).
- Kofke, D. A., "Gibbs-Duhem Integration: A New Method for Direct Evaluation of Phase Coexistence by Molecular Simulation," *Mol. Phys.*, **78**, 1331 (1993a).
- Kofke, D. A., "Direct Evaluation of Phase Coexistence by Molecular Simulation via Integration Along the Saturation Line," *J. Chem. Phys.*, **98**, 4149 (1993b).
- Kong, C. L., "Combining Rules for Intermolecular Potential Parameters: II. Rules for the Lennard-Jones (12-6) Potential and the Morse Potential," *J. Chem. Phys.*, **59**, 2464 (1973).
- Kriebel, C., A. Müller, M. Mecke, J. Winkelmann, and J. Fischer, "Prediction of Thermodynamic Properties for Fluid Nitrogen with Molecular Dynamics Simulations," *Int. J. Thermophys.*, **17**, 1349 (1996).
- Kronome, G., I. Szalai, M. Wendland, and J. Fischer, "Extension of the NpT + Test Particle Method for the Calculation of Phase Equilibria of Nitrogen + Ethane," *J. Mol. Liq.*, **85**, 237 (2000).
- Lago, S., B. Garzón, S. Calero, and C. Vega, "Accurate Simulations of the Vapor-Liquid Equilibrium of Important Organic Solvents and Other Diatomics," *J. Phys. Chem. B*, **101**, 6763 (1997).
- Liu, A., and T. L. Beck, "Vapor-Liquid Equilibria of Binary and Ternary Mixtures Containing Methane, Ethane, and Carbon Dioxide from Gibbs Ensemble Simulations," *J. Phys. Chem. B*, **102**, 7627 (1998).
- Lustig, R., "Angle-Average for the Powers of the Distance Between Two Separated Vectors," *Mol. Phys.*, **65**, 175 (1988).
- Maitland, G. C., M. Rigby, E. B. Smith, and W. A. Wakeham, *Intermolecular Forces*, Clarendon Press, Oxford, p. 519 (1981).
- Martin, M. G., and J. I. Siepmann, "Transferable Potentials for Phase Equilibria: 1. United-Atom Description of n-Alkanes," *J. Phys. Chem. B*, **102**, 2569 (1998).
- Möller, D., and J. Fischer, "Vapour Liquid Equilibrium of a Pure Fluid From Test Particle Method in Combination with NpT Molecular Dynamics Simulations," *Mol. Phys.*, **69**, 463 (1990).
- Möller, D., and J. Fischer, "Erratum, Vapour Liquid Equilibrium of a Pure Fluid from Test Particle Method in Combination with NpT Molecular Dynamics Simulations," *Mol. Phys.*, **75**, 1461 (1992).
- Möller, D., J. Oprzynski, A. Müller, and J. Fischer, "Prediction of Thermodynamic Properties of Fluid Mixtures by Molecular Dynamics Simulations: Methane-Ethane," *Mol. Phys.*, **75**, 363 (1992).
- Möller, D., and J. Fischer, "Determination of an Effective Intermolecular Potential for Carbon Dioxide Using Vapour-Liquid Phase Equilibria from NpT + Test Particle Simulations," *Fluid Phase Equilibria*, **100**, 35 (1994).
- Müller, A., J. Winkelmann, and J. Fischer, "BACKONE Family of Equations of State: 1. Nonpolar and Polar Pure Fluids," *AIChE J.*, **42**, 1116 (1996).
- Nath, S. K., F. A. Escobedo, and J. J. de Pablo, "On the Simulation of Vapor-Liquid Equilibria for Alkanes," *J. Chem. Phys.*, **108**, 9905 (1998a).
- Nath, S. K., F. A. Escobedo, J. J. de Pablo, and I. Patramai, "Simulation of Vapor-Liquid Equilibria for Alkane Mixtures," *Ind. Eng. Chem. Res.*, **37**, 3195 (1998b).
- Panagiotopoulos, A. Z., "Direct Determination of Phase Coexistence Properties of Fluids by Monte Carlo Simulation in a New Ensemble," *Mol. Phys.*, **61**, 813 (1987).
- Panagiotopoulos, A. Z., "Exact Calculations of Fluid-Phase Equilibria by Monte Carlo Simulation in a New Statistical Ensemble," *Int. J. Thermophys.*, **10**, 447 (1989).
- Peng, D.-Y., and D. B. Robinson, "A New Two-Constant Equation of State," *Ind. Eng. Chem. Fundam.*, **15**, 59 (1976).
- Potoff, J. J., J. R. Errington, and A. Z. Panagiotopoulos, "Molecular Physics Lecture, Molecular Simulation of Phase Equilibria for Mixtures of Polar and Non-Polar Components," *Mol. Phys.*, **97**, 1073 (1999).
- Potoff, J. J., and J. I. Siepmann, "Vapor-Liquid Equilibria of Mixtures Containing Alkanes, Carbon Dioxide, and Nitrogen," *AIChE J.*, **47**, 1676 (2001).
- Reid, R. C., J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th ed., McGraw-Hill, New York (1987).
- Rivera, J. L., J. Alejandre, S. K. Nath, and J. J. de Pablo, "Thermodynamic and Transport Properties of Nitrogen and Butane Mixtures," *Mol. Phys.*, **98**, 43 (2000).
- Saager, B., and J. Fischer, "Prediction of Thermodynamic Properties for Fluid Oxygen with MD Simulations," *Fluid Phase Equilibria*, **66**, 103 (1991).
- Saager, B., and J. Fischer, "Construction and Application of Physically Based Equations of State: II. The Dipolar and Quadrupolar Contributions to the Helmholtz Energy," *Fluid Phase Equilibria*, **72**, 67 (1992).
- Saager, B., J. Fischer, and M. Neumann, "Reaction Field Simulations of Monatomic and Diatomic Dipolar Fluids," *Mol. Sim.*, **6**, 27 (1991).
- Shukla, K., "Phase Equilibria and Thermodynamic Properties of Molecular Fluids from Perturbation Theory I. Pure Fluids," *Fluid Phase Equilibria*, **94**, 19 (1994).
- Stoll, J., J. Vrabec, H. Hasse, and J. Fischer, "Comprehensive Study of the Vapour-Liquid Equilibria of the Pure Two-Centre Lennard-Jones plus Pointquadrupole Fluid," *Fluid Phase Equilibria*, **179**, 339 (2001).
- Ungerer, P., A. Boutin, and A. H. Fuchs, "Direct Calculation of Bubble Points by Monte Carlo Simulation," *Mol. Phys.*, **97**, 523 (1999).
- Vrabec, J., and J. Fischer, "Vapour Liquid Equilibria of Mixtures from the NpT plus Test Particle Method," *Mol. Phys.*, **85**, 781 (1995).
- Vrabec, J., and J. Fischer, "Vapour-Liquid Equilibria of Binary Mixtures Containing Methane, Ethane and Carbon Dioxide from Molecular Simulation," *Int. J. Thermophys.*, **17**, 889 (1996).
- Vrabec, J., and J. Fischer, "Vapor-Liquid Equilibria of the Ternary Mixture CH₄ + C₂H₆ + CO₂ from Molecular Simulation," *AIChE J.*, **43**, 212 (1997).
- Vrabec, J., J. Stoll, and H. Hasse, "A Set of Molecular Models for Symmetric Quadrupolar Fluids," *J. Phys. Chem. B*, **105**, 12126 (2001).
- Vrabec, J., and H. Hasse, "Grand Equilibrium: Vapor-Liquid Equilibria by a New Molecular Simulation Method," *Mol. Phys.*, **100**, 3375 (2002).
- Weingerl, U., M. Wendland, J. Fischer, A. Müller, and J. Winkelmann, "Backbone Family of Equations of State: 2. Nonpolar and Polar Fluid Mixtures," *AIChE J.*, **47**, 705 (2001).
- Yang, J., Y. Ren, A.-M. Tian, and H. Sun, "COMPASS Force Field for 14 Inorganic Molecules, He, Ne, Ar, Kr, Xe, H₂, O₂, N₂, NO, CO, CO₂, NO₂, CS₂, and SO₂, in Liquid Phases," *J. Phys. Chem. B*, **104**, 4951 (2000).
- Zenner, G. H., and L. I. Dana, "Liquid-Vapor Equilibrium Compositions of Carbon Dioxide-Oxygen-Nitrogen Mixtures," *Chem. Eng. Prog. Symp. Ser.*, **59**, 36 (1963).

Appendix A: Technical Details of Molecular Simulations

The evaluation of the molecular interaction, cf. Eq. 1, was truncated at the center-center cutoff radius indicated below. Assuming no preferential orientations in the fluid beyond the cutoff radius, the Lennard-Jones tail corrections for the internal energy, the pressure, and the chemical potential were calculated with the method proposed by Lustig (1988). Under these conditions of isotropy, tail corrections related to the quadrupolar term in Eq. 1 vanish beyond the cutoff radius.

For the adjustment of the binary interaction parameter, ξ , 864 particles were used for liquid simulations and about 300 particles for vapor simulations. For these simulations, the cutoff radius was set to 5σ . Liquid simulation runs were carried out with 100,000 time steps (one time step ≈ 3 fs) in the NpT ensemble using rigid-body molecular dynamics with the quaternion algorithm (Allen and Tildesley, 1987) for molecular rotation. For barostating, Andersen's algorithm (Andersen, 1980) was applied. Thermostating in all molecular dynamics simulations was obtained from velocity scaling after each integration time step (Allen and Tildesley, 1987). Al-

though this simple and, therefore, attractive method of thermostating should not be applied to calculations of properties that are sensitive to fluctuations of the kinetic energy, cf. Saager et al. (1991) and Frenkel and Smit (2002), reliable results are obtained for vapor–liquid equilibria, as has been shown by Stoll et al. (2001) in a comparison of vapor–liquid equilibria of pure 2CLJQ model fluids from molecular dynamics simulations with velocity scaling to Monte Carlo simulations, where thermostating is no issue.

Vapor simulation runs were performed using the Monte Carlo technique with 100,000 loops. Within one loop, attempts to translate, rotate, insert, or delete particles were performed at random using predefined probabilities. Particle rotation was described with random vectors on unit spheres. For the simulations on most of the isotherms for binary systems shown in Figures 1, 2, 3, 4, 6, the number of particles in the liquid phase was reduced to 500, in the vapor phase the average particle number was 200, and the cutoff radii were 4σ in both phases. Ternary simulations, cf. Figures 11 and 12, were carried out with 864 particles in the liquid phase and about 300 particles in the vapor phase, and the cutoff radii were 5σ in both phases.

Appendix B: Results from PC-SAFT and BACKONE Equations of State

As the Peng-Robinson equation of state does not yield very satisfactory results as a predictive tool, additional calculations were performed with more sophisticated equations of state: the PC-SAFT (Gross and Sadowski, 2000) and the BACKONE (Müller et al., 1996; Weingerl et al., 2001) equations of state. In contrast to the Peng-Robinson equation of state, which is a representative of the class of empirical cubic equations of state, the PC-SAFT and the BACKONE equations of state represent another approach for designing equations of state, as they are based on theoretical principles that account for molecular interactions.

The PC-SAFT equation of state applies particularly well to associating fluids or fluids with chainlike molecules, but it does not model explicitly any polar contributions. In this work, where nonassociating but quadrupolar components are investigated, the PC-SAFT equation of state was applied without the term accounting for association. In contrast, the BACKONE equation of state contains terms that explicitly account for polar contributions. Both equations of state feature a single binary interaction parameter, k_{ij} , in their mixing or combining rules.

More detailed explanations on the structure of these equations of state and on the parameters employed are skipped here; they are available in the original papers, cf. Chapman et al. (1988, 1990), and Gross and Sadowski (2000) for PC-SAFT, and Saager and Fischer (1992), Müller et al. (1996), and Weingerl et al. (2001) for BACKONE.

In the present work, PC-SAFT parameters for the four fluids N_2 , O_2 , CO_2 , C_2H_6 were adjusted to the vapor–liquid equilibrium data, that was also used for the development of the 2CLJQ models (Vrabec et al., 2001). The PC-SAFT parameters are given Table B1, while the BACKONE parameters, cf. Table B2, are taken from Müller et al. (1996). The PC-SAFT and BACKONE parameters are named in the notation list.

Table B1. Parameters for the PC-SAFT Equation of State for the Fluids Used in This Work

Fluid	$\sigma^{PC}/\text{\AA}$	$(\epsilon^{PC}/k_B)/K$	m^{PC}
N_2	3.2975	89.492	1.2365
O_2	3.1711	113.98	1.1457
CO_2	2.5731	152.85	2.5461
C_2H_6	3.5186	191.15	1.6105

Table B2. Parameters for the BACKONE Equation of State for the Fluids Used in This Work

Fluid	α	$\rho_0/(\text{kmol}/\text{m}^3)$	T_0/K	Q^{*2}
N_2	1.0471	11.133	125.74	0.487
O_2	1.0244	13.629	154.58	0.0
CO_2	1.3919	10.549	291.28	2.181
C_2H_6	1.2127	6.800	305.32	0.0

Source: Values taken from Müller et al. (1996) (SIMBACK1 values for O_2 and QUABACK1 values for N_2 , CO_2 , C_2H_6).

Figure B1 compares the vapor–liquid equilibria of the binary mixture carbon dioxide + ethane from the PC-SAFT and from the BACKONE equations of state to experimental data. It can be seen that these equations of state show the same poor predictive qualities as the Peng-Robinson equation of state (cf. Figure 2), as they do not predict the azeotrope. In the case of adjusted binary parameter, k_{ij} , both equations of state are in excellent agreement with experimental data.

Vapor–liquid equilibria of the binary mixture oxygen + carbon dioxide from the PC-SAFT and from the BACKONE

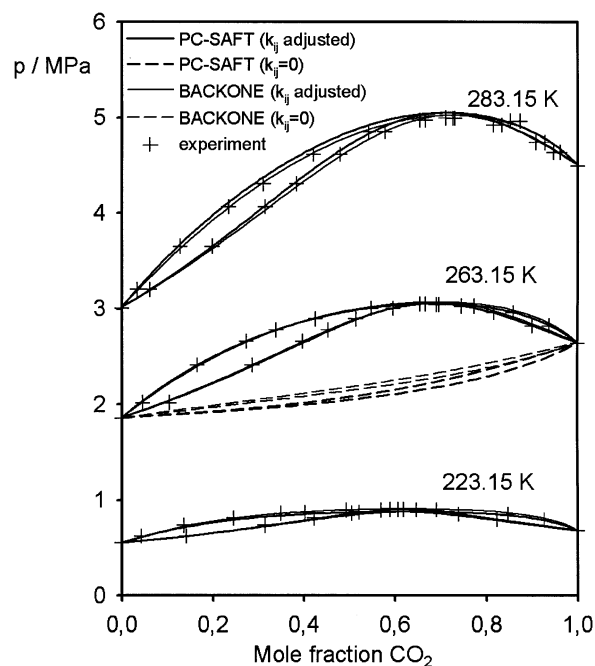


Figure B1. Vapor–liquid equilibria of the mixture CO_2 + C_2H_6 .

PC-SAFT equation of state and BACKONE equation of state compared to experimental data from Knapp et al. (1982).

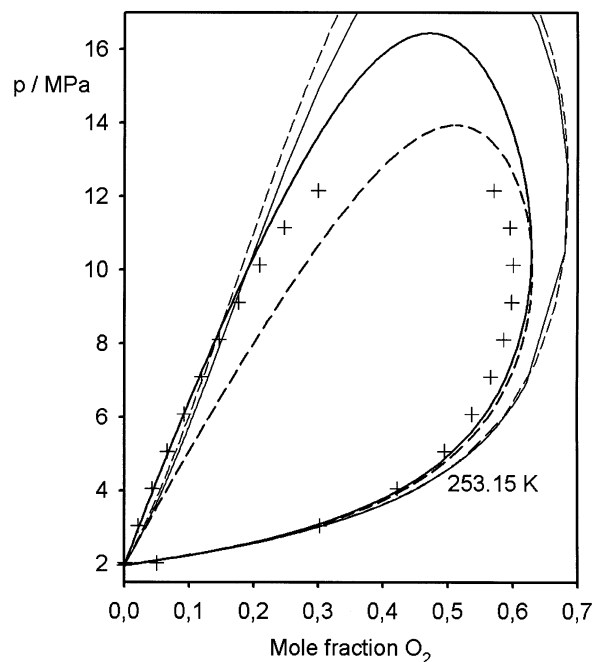


Figure B2. Vapor-liquid equilibria of the mixture $O_2 + CO_2$ at 253.15 K.

PC-SAFT equation of state and BACKONE equation of state compared to experimental data from Fredenslund and Sather (1970). Legend: cf. Figure B1.

equations of state are compared to experimental data in Figure B2. Prediction from the PC-SAFT equation of state is poor on the bubble line, whereas the BACKONE equation of state shows large deviations on the dew line that remain even in the case of adjustment of the binary parameter, k_{ij} . With adjusted k_{ij} , the PC-SAFT equation of state yields more reliable results on the bubble line, but shows deviations to high pressures for near-critical states, which is typical for the PC-SAFT equation of state.

Also saturated liquid densities were calculated with the PC-SAFT and the BACKONE equations of state for the binary systems investigated in this work. As expected, for many cases, these equations clearly yield better agreement with DDMIX data than the Peng-Robinson equation of state. However, there are some systems (such as nitrogen + carbon dioxide) for which these equations of state also give poor results, whereas the present molecular simulations show excellent agreement with the reference data.

From these findings we can conclude that the predictive power of the present molecular models is superior to the studied equations of state based on physical principles that account for molecular interactions. With adjusted binary parameters, these equations of state and the present molecular models describe the vapor-liquid equilibria with comparable quality.

Manuscript received Mar. 15, 2002, and revision received Feb. 4, 2003.