Gibbs Ensemble Monte Carlo Simulations of Binary Mixtures of Methane, Difluoromethane, and Carbon Dioxide

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Gibbs ensemble Monte Carlo simulations were used to study the vapor—liquid equilibrium of binary mixtures of carbon dioxide + methane and carbon dioxide + difluoromethane. The potential forcefields we employ are all atomistic models, and have not previously been mixed together to study the vapor—liquid equilibrium of the binary mixtures. In addition, we characterize the microscopic structure of these liquid mixtures. In carbon dioxide + methane at 230 K and 56 bar, the microscopic structure of carbon dioxide in the mixture is the same as that in the pure liquid. In carbon dioxide + difluoromethane at 283 K and 56 bar, the presence of carbon dioxide does not noticeably perturb the liquid structure of difluoromethane, but the structure of carbon dioxide is subtly changed, due to a strong interaction between it and difluoromethane. The simulations in the isobaric—isothermal (NPT) ensemble agree well with the experimental data, except at the two extreme regions of the pressure range. The good agreement of most simulated state points with experimental data encourages one to develop more accurate potentials for predicting the thermodynamic properties of these systems as well as other complicated systems, which are less amenable to measurement by experiment.

I. Introduction

Non-ozone-depleting refrigerants have become increasingly important alternatives in industrial applications.¹ Carbon dioxide (CO_2) , methane (CH_4) , and diffuoromethane (CH_2F_2) are possible substitutes. However, CH₄ and CH₂F₂ are flammable fluids. CO₂ is a nonflammable fluid, but its freezing point is too high. Mixtures of $CO_2 + CH_4$ and $CO_2 + CH_2F_2$ are expected to have reduced flammability relative to pure CH_4 and pure CH_2F_2 and a lower freezing point than pure CO_2 , making them an attractive possibility. However, accurate knowledge of the thermophysical properties of these mixtures is necessary to evaluate the performance of refrigeration cycles. Knowledge of phase equilibria is usually obtained from experimental observation. Since the measurement of vapor-liquid equilibria is time-consuming and expensive, there is a demand to reduce the experimental work by employing suitable equations of state. Conventional approaches for predicting phase equilibria properties use empirical equations of state such as the Peng-Robinson equation of state.² Although equations of state can be an excellent tool, they depend on a range of experimental data to evaluate parameters, and often lack predictive power for complex systems.

A promising alternative is computer simulation based on molecular modeling, which can predict vapor—liquid equilibria of fluid systems under a wide range of conditions, and also provides insight into the microscopic structure of the systems. There has been much progress in the development of molecular simulation methods and forcefields, which allows one to predict the phase behavior of real fluids with great accuracy.^{3–6} Computer simulations can even be used to predict behavior at conditions under which experimental data are difficult or impossible to obtain. Several techniques have been proposed, such as the NPT + test particle method,³ Gibbs ensemble Monte Carlo (GEMC),⁴ Gibbs—Duhem integration,⁵ and histogram reweighting grand canonical Monte Carlo.⁶ Intermolecular potentials play a crucial role in obtaining accurate predictions

of properties. Molecular potential parameters are optimized using experimental data for the pure system, and often mixture potential parameters are determined using a combining rule. The potential parameters can also be determined from *ab initio* calculations. There are a large variety of molecular models for pure fluids. We have chosen to use in our work simple molecular potentials that have been shown in the literature to model vapor liquid equilibrium properties of pure substances accurately.

Liu and Beck applied the GEMC method to binary and ternary mixtures containing CH₄, ethane, and CO₂,⁷ which were modeled as one- or two-center Lennard-Jones plus quadrupole (for CO₂) fluids. Their results were compared to those obtained by Vrabec and Fischer⁸ using the NPT + test particle method and the same potentials. Both methods agree well with experimental data, and these independent results imply that the methods are effective and comparably accurate. Recently, Vrabec et al.⁹ presented a set of molecular models for 267 binary mixtures, including the mixtures $CO_2 + CH_4$ and $CO_2 + CH_2F_2$, for the simulations of vapor-liquid equilibria. Although these potential models predict the vapor-liquid equilibria for mixtures $CO_2 + CH_4$ and CO_2 $+ CH_2F_2$ quite well, they are highly simplified, consisting of a one-center Lennard-Jones potential for CH4, two-center Lennard-Jones plus quadrupole for CO₂, and one-center Lennard-Jones plus dipole for CH₂F₂. Thus, they can provide only limited structural information. Here, we apply the GEMC method to the same binary systems $CO_2 + CH_4$ and $CO_2 + CH_2F_2$ but with atomistic intermolecular pair potentials (atomic charges and Lennard-Jones sites on each atom), to demonstrate the ability of these simple potentials to predict the vapor-liquid equilibrium of the binary systems and to study their microscopic structure.

To validate our choice of the molecular potentials, we performed simulations with the canonical version of the GEMC method (NVT-GEMC) to calculate the phase equilibria properties of the pure components (see the Supporting Information). Then, the isothermal—isobaric version of GEMC (NPT-GEMC) was used to simulate the phase equilibria properties of the binary

mixtures. The simulations are compared with experimental data from the literature and data from NIST¹⁰ including density, pressure, heat of vaporization, and equilibrium mole fraction. One of the main advantages of computer simulation is that it affords an insight into the microscopic structure of the simulated systems. For the mixture of $CO_2 + CH_4$, we use the simulations at 230 K and 56 bar to probe the saturated liquid structure. Since under these conditions the mole fraction of CO₂ is twice that of CH₄, the structure of the liquid mixture should be dominated by CO_2 . Therefore, we compare the mixture with CO_2 under the same conditions to investigate the influence of the CH₄ solute. For the mixture $CO_2 + CH_2F_2$, we use the simulations at 283 K and 23 bar. Under these conditions, the mole fraction of CH_2F_2 is nearly double that of CO_2 , and we compare the structure of this liquid mixture with pure CH₂F₂. The effect of pressure on the structures of both liquid mixtures is also investigated. Two established methods, which are often used to analyze the microscopic structure of substances, are employed. The radial distribution function (RDF) probes the occurrence of an atom at a distance from another atom. Peaks in an RDF are associated with solvation shells or specific neighbors. The orientational distribution function (ODF) gives information about the distribution of average angles between a pair of molecules at a given separation.

II. Methods

The GEMC simulation technique⁴ was employed to study the vapor-liquid equilibrium of both pure and binary mixtures of components. Often, NVT-GEMC is used to determine the saturation properties of pure fluids, and NPT-GEMC is used to determine the phase equilibrium properties of mixtures. Hence, in our study, NVT-GEMC was used to determine the coexistence curves of CO₂, CH₄, and CH₂F₂ and NPT-GEMC was used to determine the vapor-liquid equilibria for the binary mixtures $CO_2 + CH_4$ and $CO_2 + CH_2F_2$. In NVT-GEMC and in NPT-GEMC, two phases at equilibrium are simulated at a given temperature with a fixed number of molecules. Two cubic simulation boxes are needed, one for each phase. The thermodynamic requirements for phase equilibria are that each region should be in internal equilibrium, and that the temperature (T), pressure (P), and chemical potential (μ) of all components should be the same in both phases. The phase equilibrium is achieved by performing three types of trial Monte Carlo (MC) moves: particle displacements (including translating and rotating particles) within each box to satisfy internal equilibrium, volume change (NVT-GEMC) or volume rearrangement (NPT-GEMC) to equalize the pressure, and particle transfer to equalize the chemical potentials. In NVT-GEMC, the total volume of the system cannot change and an increase in the volume of one box must be matched by a decrease in the volume of the other, whereas, in NPT-GEMC, the volumes of the two boxes change independently to keep the pressure constant.

The quality of the results of a computer simulation depends on the potential models describing the interactions between the molecules of the studied substances. Much effort has been devoted to the development of an accurate potential for CO₂. In our simulations, the rigid fixed-point-charge elementary physics model (EPM) was employed, due to its widespread use.¹¹ This potential includes pairwise interactions between all atoms, with a Coulomb and a Lennard-Jones component:

$$\mathbf{U} = \sum_{a \in A} \sum_{b \in B} 4\varepsilon_{ab} \left[\left(\frac{\sigma_{ab}}{r_{ab}} \right)^{12} - \left(\frac{\sigma_{ab}}{r_{ab}} \right)^{6} \right] + \sum_{a \in A} \sum_{b \in B} \frac{q_{a}q_{a}}{r_{ab}}$$
(1)

where sites *a* belong to molecule *A*, sites *b* belong to molecule *B*, and the separation between sites *a* and sites *b* is r_{ab} . ε_{ab} is the well depth for short-range interactions, σ_{ab} is the core diameter for the Lennard-Jones potential, and *q* is the partial charge of each site. The atomic charges (q_a , q_b) reproduce the experimental quadrupole moment; the Lennard-Jones parameters are fitted to reproduce the experimental pressure and internal energy at 239 K.

To enable combination with the CO_2 model, potentials for CH_4 and CH_2F_2 with the same functional form are required. Here, for CH_4 , we used the transferable potentials for phase equilibria with explicit hydrogen atoms (TraPPE-EH) model:¹² the CH_4 molecule has five Lennard-Jones interaction sites, which are located at the carbon atom and the centers of the CH bonds. For CH_2F_2 , we used a five-center Lennard-Jones plus charge model,¹³ in which the values of the Lennard-Jones parameters were fitted to the experimental vapor—liquid equilibrium properties of CH_2F_2 . The parameters are summarized in Tables 1 and 2. For the Lennard-Jones interactions between unlike atoms, the Lorentz—Berthelot combining rules were used. Thus, the Lennard-Jones interactions were calculated using the arithmetic mean of the core diameters and the geometric mean of the potential well depths.

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \tag{2}$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \tag{3}$$

III. Simulation Details

The molecules were inserted at random positions in both boxes, which introduced overlaps in the initial configurations. Before the volume change and particle transfer moves take place, 10 000 MC displacement steps were used to remove the overlaps. Calculations within the canonical ensemble were performed to determine the coexistence curves of the pure components. In all pure component simulations, 500 molecules

TABLE 1:	Structure	of the	Molecular	Models
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	bond length (Å)	angle (deg)
СО	1.149	
CH (CH ₄)	1.100	
$CH (CH_2F_2)$	1.090	
CF	1.370	
∠OCO		180.0
\angle HCH (CH ₄)		107.8
\angle HCH (CH ₂ F ₂)		113.8
∠FCF		108.6

TABLE 2: Potential Parameters of the Molecular Models

molecule	atom/group	ε/k_b (K)	σ (Å)	<i>q</i> (e)
carbon dioxide	С	28.129	2.757	0.6512
	0	80.507	3.033	-0.3256
methane	С	0.01	3.31	0.0000
	CH	15.3	3.31	0.0000
difluoromethane	С	42.000	3.460	0.3850
	Н	29.000	2.200	0.0490
	F	37.000	2.950	-0.2410

TABLE 3: Thermodynamic Properties Calculated from the Simulation of the Binary Mixture CO₂ + CH₄ at 230 K^a

P (bar)	$\rho_{\rm L}~({\rm kg/m^3})$	$\rho_{\rm V}~({\rm kg/m^3})$	$U_{\rm L}$ (kJ/mol)	U _V (kJ/mol)	X _A	УА
10.78	1100.7 (5.60)	23.33 (1.11)	-13.63 (0.08)	-0.419 (0.02)	0.992 (0.005)	0.777 (0.007)
14.53	1084.4 (7.70)	27.69 (1.61)	-13.40(0.10)	-0.477(0.04)	0.976 (0.006)	0.589 (0.005)
17.86	1069.5 (5.50)	31.77 (0.77)	-13.21 (0.09)	-0.526(0.02)	0.963 (0.008)	0.499 (0.003)
20.92	1053.5 (4.70)	35.58 (0.80)	-12.99(0.07)	-0.575 (0.02)	0.952 (0.004)	0.438 (0.006)
25.51	1033.6 (8.40)	42.67 (1.27)	-12.75 (0.12)	-0.685 (0.03)	0.933 (0.005)	0.392 (0.012)
29.16	1019.9 (10.9)	46.87 (1.13)	-12.57(0.14)	-0.739(0.02)	0.918 (0.009)	0.339 (0.008)
35.03	978.2 (19.0)	55.32 (2.81)	-12.04 (0.24)	-0.870 (0.05)	0.884 (0.010)	0.293 (0.009)
39.68	931.1 (19.1)	63.07 (2.22)	-11.45 (0.24)	-0.997 (0.04)	0.843 (0.013)	0.264 (0.010)
45.65	895.8 (20.5)	72.25 (4.20)	-11.02(0.35)	-1.146(0.07)	0.808 (0.011)	0.239 (0.008)
51.16	873.1 (21.1)	87.14 (4.80)	-10.74(0.27)	-1.367 (0.06)	0.786 (0.010)	0.238 (0.009)
56.40	833.3 (22.6)	99.12 (5.80)	-10.27(0.52)	-1.544(0.09)	0.748 (0.011)	0.230 (0.010)
58.85	785.3 (21.7)	103.63 (6.40)	-9.67 (0.26)	-1.613 (0.09)	0.705 (0.009)	0.225 (0.010)
60.86	729.6 (27.4)	110.07 (8.40)	-9.03(0.68)	-1.709(0.12)	0.658 (0.012)	0.217 (0.008)
63.53	672.7 (24.9)	120.14 (7.50)	-8.35 (0.53)	-1.869 (0.12)	0.607 (0.013)	0.219 (0.010)
65.86	635.6 (25.1)	127.63 (10.3)	-7.93 (0.44)	-1.968 (0.19)	0.575 (0.012)	0.214 (0.009)

^{*a*} *P*, saturated pressure; ρ , density; *U*, configurational potential energy; x_A , mole fraction of CO₂ in the liquid phase; y_A , mole fraction of CO₂ in the vapor phase. The numbers in parentheses indicate the statistical uncertainties.

were used. The binary mixtures were simulated in the isobaric-isothermal Gibbs ensemble, with 1000 molecules in the system. For pure components, simulations consisted of 120 000 MC cycles. For binary systems, simulations were extended to 200 000 MC cycles. The first 40 000 cycles in each simulation were used to equilibrate the system. Each MC cycle comprises an average of one translation move and one rotation move per molecule, one volume move, and 150 particle transfer moves. The densities of each box are chosen initially to give roughly equal partitioning of the particles between each box. The production period of each simulation was divided into 10 blocks, and the standard deviations of the simulations are calculated from these blocks. The acceptance ratios for the particle translations and rotations varied between 30 and 46% within the liquid phase and 36 and 88% in the vapor phase. The acceptance ratios for the volume change were between 41 and 75%. The low acceptance rate for molecule transfer, especially to the liquid phase, was one of the main challenges in the simulations. At low temperature, the acceptance ratios for the particle transfers were less than or equal to 0.1%. At other temperatures, they varied between 0.1 and 3%.

For the nonpolar systems CO₂, CH₄, and CO₂-CH₄, a spherical cutoff, r_{cut} , of 12 Å between molecules was used to truncate both the Lennard-Jones and the electrostatic part of the potential energy. Since the r^{-6} Lennard-Jones term still makes a significant contribution to the interaction energy beyond the cutoff distance, a long-range correction (tail correction)¹⁴ was used, where the long-range energy of a molecule is given by

$$E_{\text{tail}} = \frac{2}{3}\pi\rho(4\varepsilon\sigma^6)r_{\text{cut}}^{-3} \tag{4}$$

where ρ is the density of molecules in the box. The r^{-12} term decays rapidly with distance, so a correction to this term is unnecessary. For the polar systems CH₂F₂ and CO₂-CH₂F₂, Ewald summation with tinfoil boundary condition was used to calculate the long-range electrostatic interactions.¹⁵ Lennard-Jones nonbonded interactions were truncated at 12 Å, and a long-range correction was used for the r^{-6} term.

IV. Results and Discussion

Vapor-Liquid Equilibria of Mixtures. The simulation results and experimental data for the vapor-liquid equilibrium



Figure 1. Vapor liquid equilibria of $CO_2 + CH_4$ at (a) 230 K and (b) 250 K: simulation (squares) versus experimental data (pluses).¹⁶

of the pure components are compared in the Supporting Information. The results are consistent with the literature.^{11–13} The simulated phase coexistence curves are in good agreement with experimental data. However, the saturated pressure and heat of vaporization of CO₂ deviate a little from the experimental values. Further discussion of the pure components is included in the Supporting Information. To match the temperatures at which the experimental data were measured, NPT-GEMC simulations of the binary systems were carried out at 230 and 250 K for $CO_2 + CH_4$ and at 283 and 293 K for $CO_2 + CH_2F_2$. Overall, within the statistical uncertainties (shown in parentheses in Tables 3-6), the simulation results are in good agreement with experimental data. The statistical uncertainties in the density of the mixtures were higher than those of the pure components. To mitigate this, twice as many molecules were employed in the mixtures as in the pure component systems.

 $CO_2 + CH_4$. The simulation results for the binary mixture CO₂ + CH₄ at 230 K are presented in Table 3. The calculated experimental P-x data¹⁶ are plotted in Figure 1a. At 230 K, the simulations correctly predict the solubility of CH₄ in both phases over a wide range of saturated pressures. Figure 1a shows that the simulations slightly overestimate the mole fraction of CH₄ in the vapor phase. However, within the uncertainties of the simulations, these values still agree quite well with the experimental data. The simulation results for the mixture CO₂ + CH₄ at 250 K are shown in Table 4 and plotted in Figure 1b. The statistical uncertainties in the densities are similar to those of the system at 230 K. The simulations at 250 K also overestimate the mole fraction of CH4 in the vapor phase. The deviations from experimental data for the vapor phase at this temperature are slightly larger than those at 230 K, perhaps caused by the limitations of the Lorentz-Berthelot combining rules. Some adjustable cross-interaction parameters may improve

TABLE 4: Thermodynamic Properties Calculated from the Simulation of the Binary Mixture CO₂ + CH₄ at 250 K^a

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P (bar)	$\rho_{\rm L} ~({\rm kg}/{\rm m}^3)$	$\rho_{\rm V}~({\rm kg/m^3})$	$U_{\rm L}$ (kJ/mol)	U _V (kJ/mol)	XA	УА
20.71	1028.4 (6.60)	49.21 (0.90)	-12.42 (0.09)	-0.851 (0.03)	0.991 (0.002)	0.878 (0.003)
23.15	1014.5 (6.70)	50.08 (2.41)	-12.24(0.09)	-0.827 (0.06)	0.980 (0.003)	0.772 (0.002)
24.88	1002.6 (5.52)	51.80 (2.10)	-12.09(0.07)	-0.837(0.04)	0.971 (0.004)	0.702 (0.004)
27.59	991.2 (9.13)	55.66 (2.03)	-11.96(0.12)	-0.877(0.04)	0.961 (0.005)	0.661 (0.004)
29.64	979.7 (8.82)	58.27 (2.21)	-11.81(0.12)	-0.916 (0.04)	0.953 (0.006)	0.618 (0.007)
31.31	971.2 (7.30)	60.17 (3.17)	-11.70(0.09)	-0.939(0.06)	0.945 (0.007)	0.582 (0.009)
34.46	964.0 (7.84)	65.71 (2.92)	-11.61 (0.11)	-0.998(0.05)	0.937 (0.009)	0.555 (0.008)
38.36	934.2 (10.3)	71.58 (1.00)	-11.25(0.15)	-1.093(0.03)	0.913 (0.010)	0.502 (0.009)
42.00	920.7 (15.6)	78.38 (2.20)	-11.08(0.20)	-1.189(0.04)	0.899 (0.011)	0.477 (0.010)
47.92	903.2 (16.9)	88.28 (1.89)	-10.87(0.21)	-1.327(0.04)	0.880 (0.011)	0.440 (0.009)
53.78	832.4 (20.7)	96.26 (5.48)	-10.01(0.25)	-1.424(0.08)	0.826 (0.010)	0.388 (0.008)
61.50	797.2 (19.9)	117.7 (6.51)	-9.60(0.28)	-1.727 (0.10)	0.791 (0.011)	0.371 (0.010)
67.15	708.3 (23.3)	129.7 (7.91)	-8.58(0.54)	-1.88(0.11)	0.718 (0.012)	0.347 (0.009)
73.99	652.5 (25.8)	150.0 (8.5)	-7.92(0.33)	-2.148(0.12)	0.672 (0.011)	0.341 (0.010)
76.84	614.3 (26.3)	168.9 (15.6)	-7.52 (0.35)	-2.401 (0.41)	0.639 (0.012)	0.343 (0.012)

^{*a*} *P*, saturated pressure; ρ , density; *U*, configurational potential energy; x_A , mole fraction of CO₂ in the liquid phase; y_A , mole fraction of CO₂ in the vapor phase. The numbers in parentheses indicate the statistical uncertainties.

TABLE 5. Thermouynamic ropernes Calculated from the Simulation of the Dinary Mixture $CO_2 + CH_2\Gamma_2$ at 20	${}_{2}\mathbf{F}_{2}$ at 283]	$+ \mathbf{C}$	CO_2	Mixture	Binary	of the	Simulation	from th	Calculated	Properties	iermodynamic	TABLE 5:
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P (bar)	$\rho_{\rm L}~({\rm kg/m^3})$	$\rho_{\rm V}~({\rm kg/m^3})$	$U_{\rm L}$ (kJ/mol)	$U_{\rm V}$ (kJ/mol)	x_{A}	УА
12.42	1026.9 (7.8)	31.83 (2.19)	-15.66 (0.12)	-1.06 (0.09)	0.059 (0.002)	0.179 (0.008)
16.17	1019.7 (2.8)	39.75 (2.10)	-15.17(0.05)	-1.13(0.07)	0.158 (0.003)	0.378 (0.015)
23.18	999.9 (4.2)	54.78 (2.85)	-14.11(0.08)	-1.15(0.07)	0.362 (0.013)	0.636 (0.014)
27.88	989.7 (4.7)	64.67 (3.64)	-13.56 (0.09)	-1.23(0.07)	0.469 (0.007)	0.727 (0.011)
34.82	956.2 (3.8)	79.66 (4.92)	-12.32(0.05)	-1.35 (0.09)	0.685 (0.003)	0.852 (0.009)
37.56	940.1 (3.5)	91.47 (3.69)	-11.75 (0.05)	-1.50 (0.07)	0.784 (0.004)	0.898 (0.009)

^{*a*} *P*, saturated pressure; ρ , density; *U*, configurational potential energy; x_A , mole fraction of CO₂ in the liquid phase; y_A , mole fraction of CO₂ in the vapor phase. The numbers in parentheses indicate the statistical uncertainties.



Figure 2. Vapor liquid equilibria of $CO_2 + CH_2F_2$ at (a) 283 K and (b) 293 K: simulation (circles) versus experimental data (pluses).¹⁸

the simulation.⁹ At applied vapor pressures lower than 20 bar or greater than 75 bar, the simulations are no longer able to reproduce the phase coexistence properties, as they approach a single phase region, due to the finite size effect. The finite size effect occurs when a simulation, which constrains fluctuations to the box length used, cannot capture the fluctuations in thermodynamic properties.^{14,17}

 $CO_2 + CH_2F_2$. CO₂ is modeled as a three-center Lennard-Jones plus point charges fluid, and CH₂F₂ is modeled as a fivecenter Lennard-Jones plus point charges fluid (see Table 2). Both potential models have been fitted to experimental data to reproduce the vapor—liquid equilibrium properties but have not previously been mixed together. The present work shows that these two potentials can be used together to predict the phase equilibrium properties of the binary mixture CO₂ + CH₂F₂. The results at 283 K are presented in Table 5, and the calculated and experimental P-x data¹⁸ are compared in Figure 2a. The width of the two-phase region of this mixture is smaller than that of the CO₂ + CH₄ binary mixture. The statistical uncertainties in the densities are smaller than those of CO₂ + CH₄, but the uncertainties in the mole fraction of CO_2 in both the vapor and liquid phases are about the same. Within the uncertainties, the simulations accurately reproduce the experimental vaporliquid equilibrium data in most of the state points. The simulation results cannot be obtained at the two extremes of the pressure range, due to finite size effects, as discussed previously for $CO_2 + CH_4$.

Table 6 presents the simulation results for the binary mixture of $CO_2 + CH_2F_2$ at 293 K. These data are plotted and compared with experimental P-x data¹⁸ in Figure 2b. The uncertainties in the densities at this temperature are slightly higher than those at 283 K, especially in the density in the vapor phase at high pressure. There is excellent agreement between simulation and experimental values for the vapor—liquid equilibrium properties in all simulated state points, but as in other systems, the simulations are not capable of predicting the phase equilibrium properties at the two extremities of the pressure range. Nevertheless, the combination of these two potential models with a simple mixing rule still yields satisfactory results.

Microscopic Structure of Liquid Mixtures.

 $CO_2 + CH_4$. Figure 3 compares the RDFs of CO₂ molecules in the pure liquid and CO₂ in the liquid mixture CO₂ + CH₄ at 230 K and 56 bar. There is not much difference, which suggests the presence of the CH₄ solute does not alter the structure of CO₂ very much. Figure 4 compares the RDFs of CO₂-CO₂, CO₂-CH₄, and CH₄-CH₄ in the liquid mixture CO₂ + CH₄ at two state points: 230 K and 40 bar and 230 K and 65 bar. The shapes and heights of the RDFs of the CO₂-CO₂ and CO₂-CH₄ interactions are nearly independent of the concentration and pressure, but the first peak of the CH₄-CH₄ RDF at 40 bar is higher than that at 65 bar, which indicates that CH₄ aggregates at low pressure. In pure CO₂ at 230 K and 56 bar, the coordination number in the first solvation shell is 12. In the CO₂ + CH₄ mixture under the same conditions, the coordination

TABLE 6: Thermodynamic Properties Calculated from the Simulation of the Binary Mixture CO₂ + CH₂F₂ at 293 K^a

P (bar)	$\rho_{\rm L} ~({\rm kg}/{\rm m}^3)$	$\rho_{\rm V}~({\rm kg/m^3})$	$U_{\rm L}$ (kJ/mol)	U _V (kJ/mol)	x_{A}	УА
17.13	988.1 (5.60)	43.78 (3.25)	-14.91(0.08)	-1.34(0.12)	0.085 (0.009)	0.221 (0.008)
22.13	981.4 (11.1)	56.39 (2.21)	-14.42(0.16)	-1.43(0.07)	0.191 (0.010)	0.410 (0.014)
26.13	959.8 (11.1)	65.22 (2.24)	-13.30(0.24)	-1.32(0.05)	0.262 (0.008)	0.553 (0.009)
29.30	939.9 (12.1)	72.68 (2.25)	-12.81(0.21)	-1.27(0.08)	0.362 (0.009)	0.669 (0.020)
35.30	903.6 (13.7)	89.17 (2.40)	-11.85 (0.21)	-1.59(0.06)	0.586 (0.010)	0.779 (0.007)
40.47	914.8 (13.7)	111.7 (7.54)	-11.82 (0.21)	-1.92(0.19)	0.627 (0.011)	0.799 (0.008)
45.00	900.3 (13.2)	122.7 (6.67)	-11.30(0.15)	-2.00(0.12)	0.749 (0.008)	0.858 (0.009)
48.74	888.7 (11.9)	142.7 (10.7)	-10.85 (0.15)	-2.22 (0.28)	0.838 (0.011)	0.907 (0.009)

^{*a*} *P*, saturated pressure; ρ , density; *U*, configurational potential energy; x_A , mole fraction of CO₂ in the liquid phase; y_A , mole fraction of CO₂ in the vapor phase. The numbers in parentheses indicate the statistical uncertainties.



Figure 3. Radial distribution functions of CO_2 in the pure liquid (solid lines) and in the $CO_2 + CH_4$ mixture (dashed line) at 230 K and 56 bar.



Figure 4. Radial distribution functions of the CO_2-CO_2 (solid lines), CO_2-CH_4 (dashed lines), and CH_4-CH_4 interactions (dotted lines) in the liquid mixture of $CO_2 + CH_4$ at (a) 230 K and 40 bar and (b) 230 K and 65 bar.

number of the first solvation shell of the CO_2-CO_2 interaction is 8 and that of the CO_2-CH_4 interaction is 3, making a total of 11. These two coordination numbers in both pure CO_2 and in the $CO_2 + CH_4$ mixture are quite close to each other, because CO_2 and CH_4 are about the same size. The ratio of the number of CH_4 molecules to the number of CO_2 molecules in the first solvation shell is about the same as the $CH_4:CO_2$ ratio of the liquid phase of the system (about 3:8).

Augmenting the RDFs, we use ODFs to characterize the environments around each type of molecule in the liquids. Figure 5a shows the distribution of the average angle between the CO bonds of pairs of CO₂ molecules at 230 K and 56 bar. Figure 5b shows the analogous plot for the distribution of the average angle between the CO bonds and the C–C distance between pairs of CO₂ molecules. In these figures, the radial axis represents the distance between the two carbon atoms of the CO₂ pairs. In Figure 5a, the peak appears at a C–C distance of 4.2 Å and an angle of 90°, indicating that the CO bonds of each pair of molecules prefer to be perpendicular. There are three maxima in Figure 5b. Two are located at a C–C distance of 4.2 Å and angles of 0 and 180°. A larger peak appears at a C–C distance of 4.2 Å and an angle of 90°. Combining the information, we can see that the molecules adopt a T-shaped



Figure 5. (a) Distribution of the average angle between CO vectors (θ_1) in CO₂ + CH₄ liquid mixture at 230 K and 56 bar. (b) Distribution of the average angle between CO bond and C–C vector from CO₂ to CO₂ (θ_2) in CO₂ + CH₄ liquid mixture at 230 K and 56 bar.



Figure 6. (a) T-shaped pair of CO_2 molecules. (b) The nearest neighbor interaction between CO_2 and CH_4 in the liquid mixture. The C–C distances are, respectively, 4.2 and 3.5 Å.

geometry (Figure 6a). The same analysis has been performed for pure CO_2 under the same conditions (see the Supporting Information). In the pure liquid, CO_2 also adopts a T-shaped geometry, in accord with the early study of Zhang et al.¹⁹ Thus, both the RDFs and the ODFs confirm that the microscopic structure of CO_2 is not influenced by the presence of CH_4 .



Figure 7. Distribution of the average angle between CO vector and C–C vector from CO₂ to CH₄ (γ) at 230 K and 56 bar.



Figure 8. Snapshot of the first solvation shell of $CO_2 + CH_4$ at 230 K and 56 bar (CO_2 is the central molecule).

Figure 7 shows the distribution of the average angle between CO bonds of CO₂ and the C–C vectors from CO₂ to CH₄. Details of the orientations of the CH bonds are omitted for brevity. This distribution tells us how CH₄ molecules are positioned around the CO₂ molecules in the liquid mixture. In Figure 7, there is a peak at a C–C distance of 3.5 Å and an angle of 90°. This suggests that CH₄ molecules preferentially populate a circle of radius 3.5 Å centered on the carbon atoms of CO₂ molecules, in the plane perpendicular to the CO₂ molecules (Figure 6b). A snapshot of the first solvation shell of CO₂ + CH₄ at 230 K and 56 bar is shown in Figure 8.

 $CO_2 + CH_2F_2$. For CO₂ + CH₂F₂, we use simulations at two state points—283 K and 23 bar, and 283 K and 37 bar—to study the effect of pressure on the structure of the liquid mixture. We then use the simulation at 283 K and 23 bar as an example to study the microscopic structure of this system. Under these conditions, the ratio of CO₂ to CH₂F₂ in the liquid is about 1 to 2. Therefore, we will compare the structure of this liquid mixture with the structure of pure liquid CH₂F₂ under the same conditions, since this mixture is dominated by CH₂F₂.

The RDFs of CH₂F₂ molecules in pure CH₂F₂ and in the liquid mixture of CO₂ + CH₂F₂ at 283 K and 23 bar are the same (Figure 9). The presence of CO₂ does not influence the structure of CH₂F₂, due to the strong interaction between CH₂F₂ molecules. The $g_{CC}(r)$ pair correlation function of CH₂F₂ exhibits the features of a closely packed system. There are two peaks in this function, at 4.2 and 8.1 Å. The coordination number up to





Figure 9. Radial distribution functions of pure CH_2F_2 (solid lines) and CH_2F_2 in the $CO_2 + CH_2F_2$ mixture (dashed lines) at 283 K and 23 bar.



Figure 10. Radial distribution functions of the CO_2-CO_2 (solid lines), $CO_2-CH_2F_2$ (dashed lines), and $CH_2F_2-CH_2F_2$ interactions (dotted lines) in $CO_2 + CH_2F_2$ at (a) 283 K and 23 bar and (b) 283 K and 37 bar.

the first minimum is 13, which agrees with the study of Jedlovszky and Mezei.²⁰ The shape and height of the first peaks for the CO₂-CO₂ and CO₂-CH₂F₂ interactions are not particularly sensitive to pressure and concentration (Figure 10), while the first peak for the CH_2F_2 - CH_2F_2 interaction is slightly higher at higher pressure. These results indicate that the CO₂-CO₂ and CO₂-CH₂F₂ interactions are quite invariant over the pressure range and CH₂F₂ aggregates slightly as the pressure increases. The peak of the first solvation shell of the $CO_2-CH_2F_2$ interaction is as high as that of the CO_2-CO_2 interaction and slightly lower than that of the CH₂F₂-CH₂F₂. Thus, the interaction between CO₂ and CH₂F₂ is quite strong. At higher pressure, CH₂F₂ molecules tend to aggregate together. At 283 K and 23 bar, the coordination numbers in the first solvation shell for the CH₂F₂-CH₂F₂ and CH₂F₂-CO₂ interactions are 8 and about 4, respectively.

Figure 11a shows the distribution of the average angle between CH_2F_2 dipoles at different C–C distances in the liquid mixture $CO_2 + CH_2F_2$ at 230 K and 23 bar. The dipole moments of the nearest neighbors in the first solvation shell have a strong preference for a parallel alignment, as indicated by a peak at 0°. The dipole moments also have a slight, but much weaker, preference for an antiparallel alignment. Figure 11b shows the distribution of the average angle between CH_2F_2 dipoles and vectors C–C from CH_2F_2 to CH_2F_2 at 283 K and 23 bar. Peaks at 180 and 0° are observed, which suggests that the dipole moments and the C–C vectors of the nearest neighbors in the first solvation shell are colinear. Figure 11c shows the distribution of the average angle between C–H bonds at 283 K and 23 bar. This figure reveals that, in the first solvation shell, the C–H



Figure 11. (a) Distribution of the average angle between CH_2F_2 dipoles (α_1) in the mixture $CO_2 + CH_2F_2$. (b) Distribution of the average angle between CH_2F_2 dipole and C-C vector from CH_2F_2 to CH_2F_2 (α_2) in the mixture $CO_2 + CH_2F_2$ at 283 K and 23 bar. (c) Distribution of the average angle between CH vectors (α_3) in the mixture $CO_2 + CH_2F_2$ at 283 K and 23 bar.



Figure 12. (a) The nearest neighbor interaction of CH_2F_2 in both pure CH_2F_2 liquid and in the mixture of $CO_2 + CH_2F_2$. (b) The nearest neighbor interaction of CO_2 and CH_2F_2 in the mixture of $CO_2 + CH_2F_2$.

bonds of CH_2F_2 molecules prefer a parallel alignment, which is indicated by a large peak at 0°. In addition, C–H bonds have a small preference for other angles. The distributions of the average angles between CH_2F_2 dipoles, CH_2F_2 dipoles, and C–C vectors from CH_2F_2 to CH_2F_2 and C–H bonds in pure CH_2F_2 under the same conditions were also studied (see the Supporting Information). The CH_2F_2 molecules maintain the same organization as in pure CH_2F_2 under the same conditions, which agrees well with the RDFs. This confirms that, under these conditions, CO_2 does not influence the interaction between CH_2F_2 molecules. The nearest neighbor interaction of CH_2F_2 in both pure CH_2F_2 and $CO_2 + CH_2F_2$ is shown in Figure 12a.

From the RDFs of this mixture, there are about four CO₂ molecules in the first solvation shell of CH_2F_2 . It is interesting to examine the arrangement of CO_2 in this solvation shell. Due to a strong interaction between it and diffuoromethane, we expect some changes in its arrangement compared with the arrangement in pure CO₂. Figure 13a shows the distribution of the average angle between the CH_2F_2 dipoles and the CO bonds of CO_2 in the $CO_2 + CH_2F_2$ liquid mixture at 283 K and 23 bar. There are two peaks at a C–C distance of about 4.2 Å; one is at 0° , and the other is at 180°. This means that these vectors have a preference for a parallel alignment. To have a clearer picture of the relative position of CO₂ molecules around the central CH_2F_2 molecules, we calculated the distribution of the average angle between CH₂F₂ dipoles and C-C vectors from CH₂F₂ to CO_2 in the $CO_2 + CH_2F_2$ liquid mixture (Figure 13b). There are two peaks: one is at about 4.2 Å and 0°, and the other is at about 3.8 Å and 180°. Thus, the C–C vector from CH_2F_2 to CO₂ and the molecular symmetry axes are preferentially collinear. The oxygen atoms of CO₂ can get slightly closer to the hydrogen atoms than to the fluorine atoms of CH₂F₂, and therefore, there is a difference in the C-C distance at 0 and 180° (Figure 12b).



Figure 13. (a) Distribution of the average angle between the CH_2F_2 dipole and the CO bond (β_1) in $CO_2 + CH_2F_2$ liquid mixture at 283 K and 23 bar. (b) Distribution of the average angle between the CH_2F_2 dipole and the C-C vector from CH_2F_2 to CO_2 (β_2) in $CO_2 + CH_2F_2$ liquid mixture at 283 K and 23 bar.



Figure 14. (a) Distribution of the average angle between CO vectors (θ_1) in CO₂ + CH₂F₂ liquid mixture at 283 K and 23 bar. (b) Distribution of the average angle between the CO bond and C–C vector from CO₂ to CO₂ (θ_2) in CO₂ + CH₂F₂ liquid mixture at 283 K and 23 bar.

Figure 14 shows the distributions of the angle between the CO bonds of CO_2 and the angle between a CO bond of CO_2 and the C-C distance from CO_2 to CO_2 in the $CO_2 + CH_2F_2$ liquid mixture at 283 K and 23 bar. The radial distance is the distance between two carbon atoms of the CO₂ dimer. In Figure 14a, the highest level of probability appears at three positions. At a distance of about 3.5 Å, there are two peaks, at about 0° and at 180°. The last peak is found at a distance of about 4.2 Å and an angle of about 90°. These results indicate that the CO bonds of neighboring CO₂ molecules are either parallel or perpendicular to each other. In Figure 14b, we see a large peak at a distance of 4.2 Å and an angle of 90°, which means the CO bonds make a right angle with the plane that contains a C-C vector at a C-C distance of 4.2 Å. From this information, we can conclude that the preferred orientation of CO₂ molecules in the $CO_2 + CH_2F_2$ liquid mixture at 283 K and 23 bar is the



Figure 15. Snapshot of the first solvation shell of $CO_2 + CH_2F_2$ at 283 K and 23 bar (CH₂F₂ is the central molecule).

T-shaped geometry. However, it is not as dominant as in the pure CO₂ liquid and in the mixture CO₂ + CH₄ at 230 K and 56 bar. The peak corresponding to the T-shaped geometry (Figure 14a) is lower than the analogous peaks in pure CO₂ liquid (Figure 10a, Supporting Information) and in the mixture $CO_2 + CH_4$ at 230 K and 56 bar (Figure 5a). Also, a small proportion of the slipped-parallel geometry is preferred at short distance (about 3.5 Å), but it disappears as the distance increases. We do not see a clear preference for slipped-parallel structure in either pure liquid CO₂ or the CO₂ + CH₄ mixture at 230 K and 56 bar, but we do observe it in the CO₂ + CH₂F₂ mixture at 283 K and 23 bar. Therefore, CH₂F₂ has some influence on the structure of liquid CO₂. Figure 15 shows a snapshot of the first solvation shell of CO₂ + CH₂F₂ at 283 K and 23 bar.

V. Conclusion. The potentials used here for CO₂, CH₄, and CH₂F₂ are fitted to experimental data to reproduce the vapor-liquid equilibrium properties of the pure components, and have not previously been mixed with each other. The combination of these potentials with a simple mixing rule gives good agreement with experimental data for the vapor-liquid equilibrium properties of $CO_2 + CH_4$ and $CO_2 + CH_2F_2$ binary mixtures. In evaluating the performance of refrigeration cycles, knowledge of the vapor-liquid equilibrium is important, because the two main processes in refrigeration cycles are the condensation and the evaporation of the refrigerant. The simulations of these two binary mixtures will augment empirical and experimental data in this regard. For mixtures that are difficult to measure experimentally, one can be optimistic that molecular simulations can be used to calculate phase equilibria properties accurately. The NPT-GEMC method was used to simulate the vapor-liquid equilibrium properties of the binary mixtures. Molecular simulation gives us not only the thermodynamic properties of the system but also insight into the microscopic structure. The RDFs and ODFs reveal that pairs of CO₂ molecules adopt a T-shaped geometry in both pure CO₂ and the mixtures $CO_2 + CH_4$, but less so in $CO_2 + CH_2F_2$. In addition, the slipped-parallel structure of CO₂ occurs at short C-C distances (3.5 Å) in the mixture of $CO_2 + CH_2F_2$. The presence of CO_2 in the mixture does not influence the structure of CH_2F_2 . The dipole moments of CH_2F_2 of the nearest neighbors in the first solvation shell have a strong preference for a parallel alignment, and the C-H bonds of neighboring CH_2F_2 molecules also prefer a parallel alignment.

Although the family of forcefields used in our work reproduces the phase equilibria well for both pure substances and mixtures, the forcefield parameters are derived from fitting to the experimental data of pure substances at a fixed temperature, and may not be as accurate when mixed together or used to investigate under different conditions. The mixing rule is a very convenient approximation for unlike interactions, but there is no guarantee that it works for every mixture. Strictly speaking, we should calculate the potential parameters for every single interaction in the system, ideally from first principles. Work along these lines is in progress.^{21,22} We hope to see more *ab initio* forcefields in the future, as computational power continues to improve; this will provide a more comprehensive understanding of the molecular interactions at a microscopic scale.

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Supporting Information Available: Vapor–liquid equilibrium properties and microscopic structures of pure components (CO₂, CH₄, and CH₂F₂). This material is available free of charge via the Internet at http://pubs.acs.org.

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