

## A Fully Flexible Potential Model for Carbon Dioxide<sup>\*</sup>

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**Abstract** A fully flexible potential model for carbon dioxide has been developed to predict the vapor-liquid coexistence properties using the NVT-Gibbs ensemble Monte Carlo technique (GEMC). The average absolute deviation between our simulation and the literature experimental data for saturated liquid and vapor densities is 0.3% and 2.0%, respectively. Compared with the experimental data, our calculated results of critical properties (7.39 MPa, 304.04 K, and 0.4679 g·cm<sup>-3</sup>) are acceptable and are better than those from the rescaling the potential parameters of elementary physical model (EPM2). The agreement of our simulated densities of supercritical carbon dioxide with the experimental data is acceptable in a wide range of pressure and temperature. The radial distribution function estimated at the supercritical conditions suggests that the carbon dioxide is a nonlinear molecule with the C=O bond length of 0.117 nm and the O=C=O bond angle of 176.4°, which are consistent with Car-Parrinello molecular-dynamics (CPMD), whereas the EPM2 model shows large deviation at supercritical state. The predicted self-diffusion coefficients are in agreement with the experiments.

**Keywords** molecular simulations, radial distributions, fully flexible potential model, carbon dioxide

### 1 INTRODUCTION

Carbon dioxide, especially, supercritical carbon dioxide (ScCO<sub>2</sub>) is widely studied as a “green solvent” in chemical reaction and catalysis because it is non-flammable, inexpensive, nontoxic, and has exceeding miscible ability.

In order to improve the precision of physical models for solute solubility and reaction rates in a liquid and supercritical carbon dioxide, a model should include intermolecular interactions between carbon dioxide molecules and/or other solutes. For decades, the most acceptable models are fully rigid models, such as the rescaling the potential parameters of the elementary physical model (EPM2) [1], one of three different atom-atom intermolecular potentials developed by Murthy, Singer, and McDonald (MSM) [2, 3], and transferable potentials for phase equilibria (TraPPE) [4], and several optimized potential models with improvement in some aspects [5–7] have been proposed. For example, Vrabec *et al.* [5] developed the two-centers+quadrupole model that predicted saturated vapor pressures with a better precision (10%) than the EPM2 model. Draghi *et al.* [7] added bond stretching and bending potentials and developed a fully flexible model on the basis of the EPM2 model, however, there were 11% and 15% average deviation of the saturated pressure and the saturated vapor density, respectively.

Although several potential models have been proposed for carbon dioxide, unfortunately, none of them can meet all requirements. *Ab initio* and Car-Parrinello molecular-dynamics (CPMD) calculations on charged

CO<sub>2</sub> clusters [8, 9], and neutron diffraction experiments on supercritical carbon dioxide [9–11] have shown a similar deviation. The CPMD simulations of carbon dioxide have been employed within a plane-wave-basis density functional theory (DFT). Comparing with neutron diffraction experiments, the CPMD simulations [8] on the microscopic structure of carbon dioxide are quite good, while they are unable to describe the phase behaviors accurately since they have employed only 32 molecules in the system.

The aim of this study is to find a suitable potential model for carbon dioxide, which will accurately predict both the microscopic structure and the phase behavior under high and low temperatures and pressures. For the proposed model, the ways to obtain the parameters, the methodologies, and the simulation details were provided. The simulation results of carbon dioxide obtained by the present potential and the best-known potential EPM2 were discussed, including vapor-liquid equilibria (VLE), structural properties, PVT properties, and dynamic properties.

### 2 POTENTIAL MODELS

In this study, carbon dioxide is treated as a fully flexible molecule. The known models (the EPM2, MSM, TraPPE) are all rigid models, which fix the O=C=O angle to be 180° and the C=O bond length, and cannot give the three representative geometries that are the slipped-parallel, T-shaped, and crossed geometries for ScCO<sub>2</sub>. The T-shaped geometry for ScCO<sub>2</sub> is dominant, especially at high density [9, 12, 13].

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Therefore, it may be useful to update the rigid models to a fully flexible model [7]. The total potential energy of the system is calculated by

$$U_{\text{total}} = U_{\text{intramolecular}} + U_{\text{intermolecular}} \quad (1)$$

The non-bonded interactions are described by pair wise-additive Lennard-Jones (L-J) 12-6 potentials and Coulombic interactions of partial charges.

$$U_{\text{intermolecular}}(r_{ij}) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \quad (2)$$

where,  $r_{ij}$ ,  $\varepsilon_{ij}$ ,  $\sigma_{ij}$ ,  $q_i$ ,  $q_j$ , and  $\varepsilon_0$  are the separation, L-J well depth, L-J size, partial charges, and permittivity of free space, respectively, for the pair of atoms  $i$  and  $j$ . The parameters for unlike L-J interactions are determined by Lorentz-Berthelot combining rules [13].

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (3)$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \quad (4)$$

The long-range interactions using a Group based summation method [14–16] were compared with the Ewald summation. The intramolecular part consists of harmonic bond stretching and bond angle vibration terms in the equation below

$$U_{\text{intramolecular}} = \frac{1}{2} k_r (r - r_0)^2 + \frac{1}{2} k_\theta (\theta - \theta_0)^2 \quad (5)$$

where,  $r$ ,  $r_0$ ,  $\theta$ , and  $\theta_0$  are the measured bending length, the equilibrium bending length, the measured bending angle, and the equilibrium bending angle, respectively; and  $k_r$  and  $k_\theta$  are the force constants.

The force field parameters are obtained using the optimization method proposed by Zhang [6] and Khare *et al.* [16]. Firstly, we understand how the parameters affect the simulations results. The initial force constants are obtained from quantum chemical calculations, and the other initial parameters are obtained from the EPM2 model. For example, the PVT properties at supercritical conditions for carbon dioxide are calculated to get a prerequisite knowledge of the parameter spaces. Then, the Lennard-Jones parameters of oxygen or carbon atom are changed, and the PVT properties of carbon dioxide that are the most sensitive to the Lennard-Jones parameter of oxygen atoms are slightly changed to get good results. The analysis of the carbon dioxide structure shows that the equilibrium bending length is short, which is consequently increased. The process described above was repeated to obtain all the optimized parameters that were different from the initial parameters. All the parameters for carbon dioxide in this study are listed in Table 1.

### 3 SIMULATION DETAILS

#### 3.1 Phase equilibrium simulations

Pure component vapor-liquid equilibria were obtained using the NVT-Gibbs ensemble Monte Carlo (GEMC) method [17] with periodic boundary conditions. The intra and intermolecular force field parameters adopted are shown in Table 1. The simulation system contained 400–500 molecules. Simulations for the vapor-liquid equilibria at high temperature consisted of  $1.2 \times 10^7$  moves, and longer simulations ( $1.5 \times 10^7$ ) were required at low temperatures. The ratio of the different types of Monte Carlo moves was 13%–16% translation moves, 13%–16% rotation moves, 8%–12% volume moves, and the rest were transfer moves that were employed. The temperature increases with the decreasing of the ratio of transfer moves. A cutoff distance of 1.05 nm was used for the non-bonded interactions, with long-range corrections applied beyond this distance for the van der Waals interactions. Initial configurations were based on the face centered cubic (fcc) lattice. Then, enough Monte Carlo cycles ( $1 \times 10^4$  moves) at an elevated temperature were used to “melt” the crystal structure, and the system was then “cooled” to the desired temperature.

Owing to the large fluctuations near the critical point, it is not possible to determine its location explicitly. Simulation data at subcritical conditions are used to estimate the critical point by invoking the following scaling law

$$\rho_l - \rho_g = A(T - T_c)^\beta \quad (6)$$

where,  $\rho_l$  is the liquid density,  $\rho_g$  is the vapor density,  $A$  is a constant,  $T_c$  is the critical temperature, and  $\beta = 0.325$  is the critical exponent [1]. The law of rectilinear diameters is

$$\frac{\rho_l - \rho_g}{2} = \rho_c + B(T - T_c) \quad (7)$$

where,  $B$  is a constant, and  $\rho_c$  is the critical density. The critical pressures were found by extrapolating the vapor pressure curve to the critical temperature. The vapor pressures were fitted to the semi-empirical equation [18]

$$\ln P = a_0 + \frac{a_1}{T} + a_2 \times T + a_3 \times T^2 \quad (8)$$

where,  $a_0$ – $a_3$  are the fitting constants.

#### 3.2 Pressure, self-diffusion coefficient, and structure of pure carbon dioxide

In our molecular dynamics simulations, 400

Table 1 Parameters for carbon dioxide in this study

| $R_{C=O}/\text{nm}$ | $\theta_{O=C=O}/(^{\circ})$ | $\sigma_{C}/\text{nm}$ | $\sigma_{O}/\text{nm}$ | $k_r/\text{kJ}\cdot\text{mol}^{-1}\cdot\text{nm}^{-2}$ | $k_\theta/\text{kJ}\cdot\text{mol}^{-1}\cdot\text{rad}^{-2}$ | $\varepsilon_{C}/\text{K}$ | $\varepsilon_{O}/\text{K}$ | $q_{O}/e$ | $q_{C}/e$ |
|---------------------|-----------------------------|------------------------|------------------------|--|--|----------------------------|----------------------------|-----------|-----------|
| 0.1162              | 180                         | 0.2800                 | 0.3028                 | 6  | 110  | 28.14                      | 80.37                      | -0.3258   | 0.6516    |

molecules were placed in a cubic simulation box. The conventional periodic boundary conditions and minimum image conventions were used in the simulations. Velocity Verlet algorithm was adopted to propagate the statistical trajectory. Long-range electrostatic forces and energies were calculated *via* the group based method, which was compared with the Ewald method in calculating the pressures of VLE. The constant number of atom, pressure and temperature ensemble molecular dynamics (NPT-MD) simulations proposed by Khare *et al.* [14–16] were used to calculate the vapor pressures (the saturated pressures), and then the pressure-density data were fitted linearly to determine the vapor pressure corresponding to the equilibrium vapor density from coexisting calculations. The NPT-MD ensemble was also used to calculate the dynamic properties, and the self-diffusion coefficients were calculated by the Einstein equation [19]:

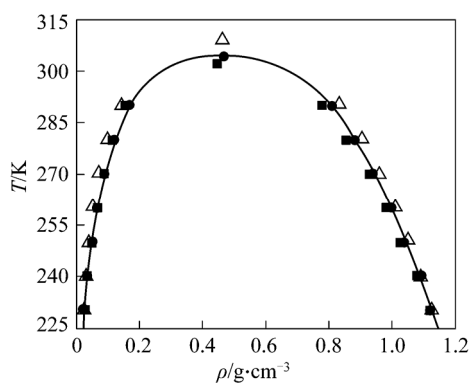
$$D = \lim_{t \rightarrow \infty} \frac{1}{6t} [r_i(t) - r_i(0)]^2 \quad (9)$$

where,  $r_i(t)$  is the molecular position  $i$  at time  $t$ , and the  $r_i(0)$  is the initial position.

The constant number of atom, volume and temperature ensemble molecular dynamics (NVT-MD) ensemble was used to investigate the structural properties of pure carbon dioxide. All the simulations were run at the time step of 1 fs for 120 ps, using the method of Andersen and Berendsen for the temperature control and the pressure control, respectively. The choice of the simulation length, number of molecules, *etc.*, in this study is made on the basis of Ref. [14–16].

#### 4 RESULTS AND DISCUSSION

Figure 1 shows the simulated coexistence envelopes, the experimental observations [20], and the literature simulation data [5, 21]. At 230 K, the deviations of the saturated liquid and vapor density are 0.5% and 17% (EPM2), and 0.2% and 18% (TraPPE), respectively. At 290 K, the maximums are 3.3% and 8.7% (EPM2), and 3.5% and 18.6% (TraPPE), respectively. The present model shows as good results as the



**Figure 1** Pure carbon dioxide phase equilibria  
— Exp. [20];  $\Delta$  TraPPE [6];  $\blacksquare$  EPM2 [21];  $\bullet$  this work

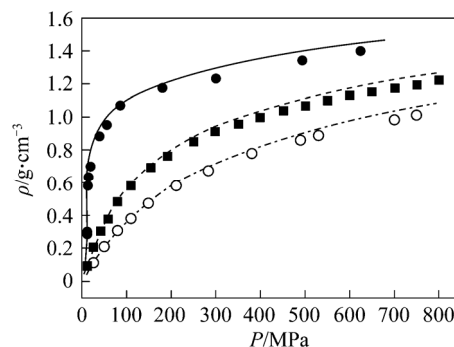
EPM2 and TraPPE models below 260 K. The deviations of the saturated liquid and vapor density by the present model are 0.6% and 1.3% (230 K), and 0.7% and 2.0% (290 K), respectively. The average absolute deviation by the EPM2, TraPPE, and the present model are 2.3% and 6.3%, 1.7% and 19.1%, and 0.3% and 2.0%, respectively. Generally, the present model produces improved saturated liquid and vapor density over the two well-known models in a wide temperature range, especially at higher temperatures.

The experimental data [20], the literature simulation data [1, 4, 6], and the predictions in this study for the critical properties are shown in Table 2. The EPM2 predictions agree with the experimental data for the critical density and pressure, however, there is significant deviation for the critical temperature. The critical pressure predicted by the MSM and TraPPE models is either considerably lower or higher than the experimental data. The critical properties obtained by the Errington and the present model agree with the experimental values. In this study, the deviation of  $T_c$ ,  $\rho_c$ , and  $P_c$  are only 0.09 K,  $0.0003 \text{ g}\cdot\text{cm}^{-3}$ , and 0.01 MPa, respectively.

**Table 2** Critical properties of carbon dioxide reproduced by different models

|               | $T_c/\text{K}$ | $\rho_c/\text{g}\cdot\text{cm}^{-3}$ | $P_c/\text{MPa}$ |
|---------------|----------------|--------------------------------------|------------------|
| Exp. [20]     | 304.13         | 0.4676                               | 7.38             |
| EPM2 [1]      | 313.4          | 0.4537                               | 7.34             |
| MSM [6]       | 303.2          | 0.4642                               | 7.17             |
| TraPPE [4]    | 306.2          | 0.4649                               | 7.77             |
| Errington [6] | 302.5          | 0.4728                               | 7.31             |
| this study    | 304.04         | 0.4679                               | 7.39             |

The simulated densities by the present model and the experimental data [20] from 5 to 800 MPa are shown in Fig. 2. The relative errors for other models increased almost parallel with increasing the pressures [5]. The largest deviation for the EPM2 model is almost 7% at 980.65 K and 800 MPa. Below 100 MPa, the simulated

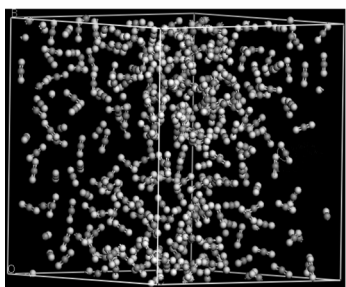


**Figure 2** Densities of supercritical carbon dioxide at different temperatures

— Exp. [20] at 315 K;  $\bullet$  this work at 315 K; - - - - Exp. [20] at 681.35 K;  $\blacksquare$  this work at 681.35 K; ····· Exp. [20] at 1100 K;  $\circ$  this work at 1100 K

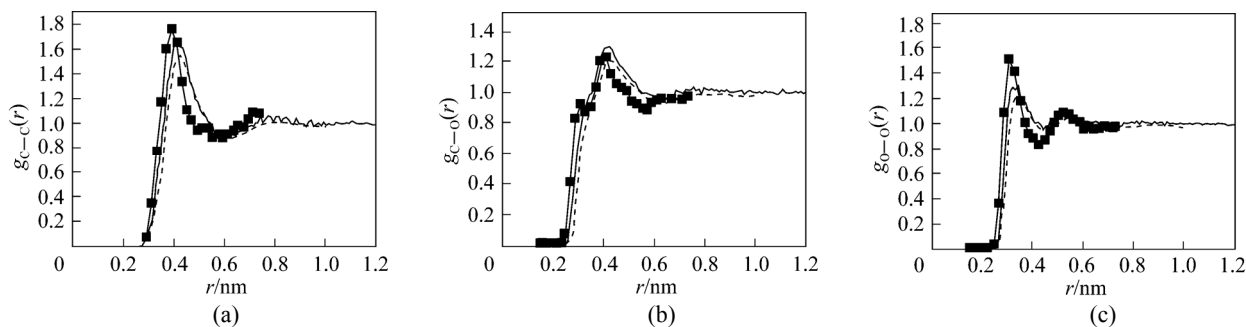
densities of the present model agree with the experimental data. In the range of 100 to 800 MPa, the deviations increase slightly, and the largest deviation is 5% at 1100 K and 800 MPa.

A snapshot of the configuration of 400 carbon dioxide molecules using NVT-MD at 318.15 K and  $0.703 \text{ g}\cdot\text{cm}^{-3}$  is shown in Fig. 3. The intramolecular C=O bond and the O=C=O angle for a randomly chosen carbon dioxide molecule at the supercritical condition can be obtained from Fig. 3. This indicates that the intramolecular C=O bond is 0.1167 nm, and the O=C=O angle is  $174.394^\circ$  instead of  $180^\circ$ , as noted by CPMD [8].



**Figure 3** Snapshot of  $\text{CO}_2$  under the supercritical state from the NVT-MD simulations (Oxygen atoms are in white, and carbon atoms are in gray)

The intermolecular C—C, C—O, and O—O pair correlation functions from the literature simulation data [8] and this study at 318.15 K and  $0.703 \text{ g}\cdot\text{cm}^{-3}$  are shown in Fig. 4. The essential features of the pair correlation functions such as the position of the first peak and the minimum are summarized in Table 3. The first neighbor C—C distance [Fig. 4 (a)] in this study is around 0.405 nm, and agrees with the CPMD calculation (0.39 nm), whereas there is a large deviation of the first minima by the EPM2 model (0.43 nm). The C—O and O—O pair correlation function [Figs. 4 (b) and 4 (c)] obtained by the EPM2 model shifts to larger distances, 0.12 nm and 0.04 nm. The present model improves the first peak value and the first minimum significantly. This may be owing to the fact that the EPM2 is a fully rigid model and does not agree with the  $\text{ScCO}_2$ .



**Figure 4** The radial distribution functions [ $g_{\text{C-C}}(r)$ ,  $g_{\text{C-O}}(r)$ , and  $g_{\text{O-O}}(r)$ ] calculated by the present model and the literature data for carbon dioxide

—■— CPMD; - - - EPM2; — this study

**Table 3** The structural features for  $\text{ScCO}_2$

| Quantity   | $g_{\text{C-C}}$ |              | $g_{\text{C-O}}$ |              | $g_{\text{O-O}}$ |              |
|------------|------------------|--------------|------------------|--------------|------------------|--------------|
|            | First peak/nm    | First min/nm | First peak/nm    | First min/nm | First peak/nm    | First min/nm |
| CPMD       | 0.39             | 0.55         | 0.31, 0.41       | 0.57         | 0.31             | 0.43         |
| EPM2       | 0.43             | 0.63         | 0.43             | 0.61         | 0.35             | 0.45         |
| this study | 0.405            | 0.565        | 0.415            | 0.605        | 0.325            | 0.445        |

The self-diffusion coefficient estimated by the present model and the experimental observations [22] are shown in Table 4. The self-diffusion coefficient at supercritical condition is important for chemical industries, particularly at 10–15 MPa. The best prediction of the present model is at 13.79 MPa and the predicted results are also reasonable with increasing the pressures in the supercritical condition.

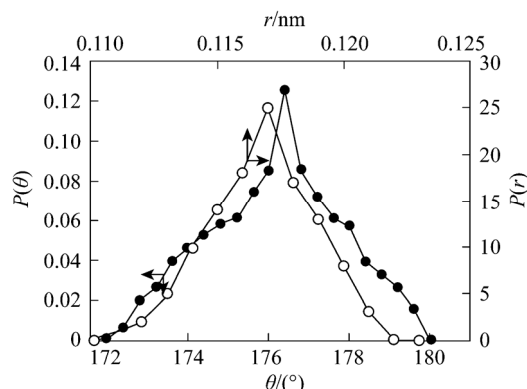
**Table 4** Self-diffusion coefficients estimated by this study and the experiments at 348.15 K

| $P/\text{MPa}$ | Self-diffusion coefficient $\times 10^8/\text{m}^2\cdot\text{s}^{-1}$ |            |
|----------------|---|------------|
|                | Exp. [22]   | This study |
| 3.84           | 32.5  | 30.48      |
| 13.79          | 5.51  | 5.50       |
| 49.85          | 1.84  | 2.32       |

The O=C=O angle and the C=O bond distributions at 318.15 K and  $0.703 \text{ g}\cdot\text{cm}^{-3}$  are shown in Fig. 5. The results show that the C=O bond length is 0.117 nm and the O=C=O bond angle is  $176.4^\circ$ , which are different from the values of 0.1162 nm and  $180^\circ$  at ambient condition [21], which agree with the *Ab initio* calculations and the neutron diffraction experiments [8, 10]. The simulation for carbon dioxide shows a deviation from the linear geometry under the supercritical state, and thus carbon dioxide possesses a dipole moment.

## 5 CONCLUSIONS

A new fully flexible potential model for carbon dioxide was optimized to reproduce experimental prop-



**Figure 5** The distribution of O=C=O angle and C=O bond

● O=C=O angle; ○ C=O bond

erties. The phase equilibrium of pure carbon dioxide was calculated by the GEMC over a wide temperature range. The densities of supercritical carbon dioxide and the structural properties (318.15 K and  $0.703 \text{ g}\cdot\text{cm}^{-3}$ ) for carbon dioxide were calculated using the present method. Radial distribution functions for  $\text{ScCO}_2$  were calculated. The critical properties were estimated from subcritical simulation data using the critical scaling laws.

The deviation of the saturated liquid and vapor densities for the present model are 0.6% and 1.3% (230 K), and 0.7% and 2.0% (290 K). The present model reproduces the critical properties ( $T_c$ ,  $\rho_c$ , and  $P_c$ ) within 0.09 K,  $0.0003 \text{ g}\cdot\text{cm}^{-3}$ , and 0.01 MPa, respectively. For supercritical carbon dioxide, the simulated densities agree with the experimental values below 100 MPa, and the largest deviation is 5% at 1100 K and 800 MPa. The calculation of structure shows that  $\text{ScCO}_2$  is a nonlinear molecule with the C=O bond length of 0.117 nm and the O=C=O bond angle of  $176.4^\circ$ , which is the reason for  $\text{ScCO}_2$  possessing a dipole moment. The present model has some advantages in reproducing the supercritical property, and will be useful for modeling separations in chemical industry.

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