An optimized molecular potential for carbon dioxide

Zhigang Zhang
The Key Laboratory of Mineral Resources, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, 100029, China

Zhenhao Duan
The Key Laboratory of Mineral Resources, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, 100029, China and Department of Chemistry, 0340 University of California, San Diego, La Jolla, California 92129

(Received 27 December 2004; accepted 6 April 2005; published online 6 June 2005)

An optimized molecular potential model for carbon dioxide is presented in this paper. Utilizing the established techniques of molecular-dynamics and histogram reweighting grand canonical Monte Carlo simulations, this model is demonstrated to show excellent predictability for thermodynamic, transport, and liquid structural properties in a wide temperature-pressure range with remarkable accuracies. The average deviations of this new model from experimental data for the saturated liquid densities, vapor densities, vapor pressures, and heats of vaporization are around 0.1%, 2.3%, 0.7%, and 1.9%, respectively. The calculated critical point is almost pinpointed by the new model. The experimental radial distribution functions ranging from 240.0 to 473.0 K are well reproduced as compared to neutron-diffraction measurements. The predicted self-diffusion coefficients are in good agreement with the nuclear-magnetic-resonance measurements. The previously published potential models for CO2 are also systematically evaluated, and our proposed new model is found to be superior to the previous models in general. © 2005 American Institute of Physics.

[DOI: 10.1063/1.1924700]

I. INTRODUCTION

Next to H2O, CO2 is the most important fluid in biological, chemical, or geochemical processes. Knowledge of the thermodynamic, dynamic, and microscopic properties of CO2 or CO2-bearing mixtures is essential in the understanding of the versatile mechanisms in these processes. For example, its thermodynamic properties, such as the pressure-volume-temperature (PVT) relations and phase behavior over large temperature-pressure (TP) range, are fundamental in the interpretations of many geochemical processes in the evolution of the Earth and other planets; the data of liquid-vapor phase equilibrium are very useful for supercritical CO2 extraction of chemicals; and the chemical properties of CO2 mixing with water are indispensable for the safe storage of CO2 in aquifer and ocean for the purpose of the reduction of CO2 emission into the air.

For decades, the properties of CO2 have been extensively studied by theorists and experimenters. However, all the experimental data of CO2 compiled together only cover part of TP space in nature, especially for various CO2-bearing mixtures, experimental data are even scarcer. In order to interpolate and extrapolate the limited data beyond data range, theorists developed different kinds of equation of state (EOS). With elaborate calibrations of the parameters in these equations, some well-established EOS can be used to accurately reproduce the experimental data.1–3 However, their extrapolation beyond experimental scope is limited.

With the development of computational algorithms and the improvement of computational resources, molecular-dynamics/Monte Carlo (MD/MC) simulations have become increasingly powerful tools in the predicting of physical chemical properties of fluids for the following reasons: (1) MD/MC simulation depends little on experimental data and has far better predictability than such thermodynamic models as EOS. (2) Through MD/MC simulation, we can directly look into microscopic properties, which are generally difficult to observe experimentally. (3) MD/MC can be utilized as a versatile tool to predict various thermodynamic, transport, and structural properties and act as a peculiar role between the experiments and theories.

Molecular interaction potential (IP) is crucial in the MD/MC simulation. As a matter of fact, the lack of appropriate intermolecular potential functions is often quoted as the most important barrier for applications of atomistic simulation methodologies to the problems of industrial and geochemical interests. In order to simulate the properties of the system CO2–H2O with high accuracies and reliabilities, we have systematically evaluated the potential models of water and found that simple point-charge extended (SPCE) model which was proposed based on very few experimental data under room temperatures and pressures, shows remarkable accuracy under high temperatures and pressures.4 As a continuous effort, we comprehensively evaluate different potential models proposed for carbon dioxide in the literature. The aim of our evaluation was to find the best choice of the potential model for carbon dioxide, which would show similar high accuracies under high temperatures and pressures while keeping good predictability of the phase behaviors.
Unfortunately, although a number of potential models have been proposed for carbon dioxide, none of them can fully meet our requirements. Among them, modified extended primitive (EPM2) model gives the most accurate prediction of phase coexistence.\textsuperscript{5} However, as shown in the following sections, systematic overestimations of volumetric properties are found when we comprehensively analyze the simulation results with EPM2. A potential model proposed by Errington shows much better extrapolation behaviors under high temperatures and pressures.\textsuperscript{6} However, it only gives a rough description of the phase equilibria near the critical point.

Optimization of the potential models has turned out to be nontrivial. As far as we know, up to now there is no general and simple routine to find the global minimum in the course of parameter optimizations. In most cases the refinement of potentials involves time-consuming and tedious adjustments with trials and errors over the parameter spaces. Nevertheless, we notice two facts: (1) New experimental data and first-principle simulations are available since the publications of previous potential models and these results can be used to refine the parameters for more accurate predictions. (2) New simulation methodologies have been proposed for the thermodynamic properties with unexpected precisions never seen before. For example, with the histogram reweighting technique, the phase behaviors of fluids can be predicted within much smaller uncertainties. These high precisions greatly facilitate the optimizations over the existing potential models. Based on these facts, we made extensive investigations in the optimization of a new potential model for carbon dioxide. The optimized potential is expected to show improved accuracies and better transferability for different properties while keeping the formula consistent with SPCE water model for the convenience of our further research on the mixtures.

In the following section, we briefly review the existing potential models for carbon dioxide and describe the optimization procedure of our potential model; subsequently, the methodologies and the simulation details are presented; then we give a detailed discussion over the simulation results of carbon dioxide with the new potential and other best-known potentials, including thermodynamic, structural, and dynamical properties. Finally, some conclusions are drawn.

II. POTENTIAL MODELS

A large number of efforts have been devoted to the development of an accurate potential model for carbon dioxide. The simplest model is the spherical model with only short-range interactions. This kind of models has great advantage of computational efficiency and easy to parametrize with some statistical theories.\textsuperscript{7} However, the transferability of these models is limited. Moreover, they cannot provide any microscopic structural information related to the molecular angular distributions. Accordingly site-site interaction models are the most popular choice for carbon dioxide. These models designate interaction centers on the three atoms. At the same time, in order to characterize the typical anisotropic feature of carbon dioxide, the substantial quadrupole moment is generally explicitly supplemented to the potential models\textsuperscript{8–10} or decomposed into partial charges.\textsuperscript{5,6,11,12} We adopted the site-site potential models with partial charges in this study for their remarkable predictabilities for different properties and for the convenience of our further research on its mixture with SPCE water model.

In the development of site-site potential, there are several commonly used start points: (1) Fitting to the experimental data of gas phase, such as second virial coefficient.\textsuperscript{1,3,14} (2) Fitting to the \textit{ab initio} simulation results.\textsuperscript{15–18} (3) Fitting to the lattice parameters of solid states.\textsuperscript{8,11} Potential models derived from \textit{ab initio} simulation results may be promising in the optimization but still call for further clarifications of the ambiguities from the noticeable uncertainties of the calculated results.\textsuperscript{15} Among our evaluated potential models which were directly parametrized from these start points, the potential model proposed by Murthy, Singer, and McDonald\textsuperscript{8,11} (MSM) shows fairly good predictability for various properties. However, according to our calculations discussed below, the MSM model provides only a fair description of the vapor-liquid equilibria and has room for the improvement of liquid volumetric properties.

A number of the potential models for carbon dioxide can be regarded as the descendants of MSM.\textsuperscript{5,19–22} Among them, EPM2 model is the most famous for its remarkable accuracy of phase equilibrium.\textsuperscript{5} Nevertheless, as will be shown in Sec. III, EPM2 shows inferior predictability of the volumetric properties compared with its predecessor MSM. Another variation of MSM is a most recent potential proposed by Potoff and Siepmann\textsuperscript{12} and is abbreviated as TraPPE in the following descriptions. According to our evaluations, this potential cannot predict both volumetric properties and phase behaviors with sufficient accuracies. Errington proposed a model for carbon dioxide with the exponential-6 potential functions, which shows improved accuracies for the \textit{PVT} properties at high densities.\textsuperscript{5} But two facts limit the popularity of this model: (1) The predicted saturated vapor densities at higher temperatures near the critical point are much larger than those of experiments. This pathological feature in the near critical region has greatly limited its applications. (2) The exponent-6 form of its potential function hinders its mixing with the most popular and successful pairwise-additive models for water, such as the famous SPCE, transferable intermolecular potential (TIP4P), etc.

All of the models discussed in this study are rigid with the angle of OCO fixed as 180°. The potential functions can be formulated as a summation of short-range interaction between three atoms and Coulombic interaction between charges:

\[
u(1,2) = u_{\text{short}}(1,2) + u_{\text{Coul}}(1,2)
= \sum_{i=1}^{s} \sum_{j=2}^{d} u_{\text{short}}(r_{ij}) + \sum_{i=1}^{s} \sum_{j=2}^{d} \frac{q_{i} q_{j}}{r_{ij}},
\]

where \(r_{ij}\) is the separation between two atoms and \(q_{i}\) and \(q_{j}\) are the partial charges designated on the center of each atom. For MSM (Refs. 8 and 11) (as modified by Geiger \textit{et al.}\textsuperscript{20}), EPM2,\textsuperscript{5} TraPPE,\textsuperscript{12} and the model proposed in this study, short-range interactions are calculated with Lennard-Jones function,
corresponding states. By scaling the parameters and \( s \) were expected to be enlarged according to the theorem of the value of \( s \). We found an appropriate value for the Lennard-Jones potential, estimated to be higher than the experiments. In order to reduce the critical points, we slightly decreased the \( s \) parameters of the exponential-6 potential. Note that in the Monte Carlo simulations, Eq. (3) would result in nonphysical negative values at very close distance. An additional cutoff distance \( r_{\text{cut}} \) should be enforced and \( r_{\text{cut}} \) can be calculated by solving the smallest positive value of \( dU_{\text{short}}^{\text{exp}}(r)/dr = 0 \). All of these parameters and the carbon–oxygen bond lengths are summarized in Table I.

The potential model for carbon dioxide in this study was previously discussed with a prerequisite knowledge of the carbon dioxide properties. We performed a serial of simulations in the vicinity of the parameter spaces. After comprehensive analysis over the potential and \( r_{\text{cut}} \) and \( \alpha \) are parameters for the exponential-6 potential. Note that in Monte Carlo simulations, Eq. (3) would result in nonphysical negative values at very close distance. An additional cutoff distance \( r_{\text{cut}} \) should be enforced and \( r_{\text{cut}} \) can be calculated by solving the smallest positive value of \( dU_{\text{short}}^{\text{exp}}(r)/dr = 0 \). All of these parameters and the carbon–oxygen bond lengths are summarized in Table I.

The potential model for carbon dioxide in this study was proposed on the basis of extensive simulations. As a first step, we carried out a number of simulations with the MSM and EPM2 potential model to get a prerequisite knowledge of the parameter spaces. After comprehensive analysis over the simulated liquid volumes, we found that MSM gives a systematical overestimation of about 1.5% while EPM2 lowers the overestimation to about 2.0%. In the meantime, we also performed a serial of simulations in the vicinity of the parameters of the MSM and EPM2 and found that the volumetric properties of carbon dioxide are most sensitive to the core diameter of oxygen atoms \( \sigma_{\text{OO}} \) in Eq. (2)]. Increasing the value of \( \sigma_{\text{OO}} \) would generally increase the molar volume of the system and this would be the predominant reason for the larger overestimations of EPM2. Based on these experiences, we slightly decreased the \( \sigma_{\text{OO}} \) of MSM. As expected, we found an appropriate value for \( \sigma_{\text{OO}} \) to eliminate the systematical errors for the volumetric properties of liquid carbon dioxide. However, this adjustment turned out to result in significant deviations of phase behaviors. The critical point was estimated to be higher than the experiments. In order to rectify these deviations, the core diameters (including \( \sigma_{\text{OO}} \)) were expected to be enlarged according to the theorem of corresponding states. By scaling the parameters and minor trials and errors, a new set of parameters can be found with good phase behaviors. On the basis of these parameters, the value of \( \sigma_{\text{OO}} \) was again slightly decreased and the process described above was repeated. After several iterations of these processes, we found the parameters were approximately converged and finally got the optimized parameters for carbon dioxide as listed in Table I.

### III. SIMULATION DETAILS

We adopted two kinds of simulations in this study: the \( PVT \) properties, structural properties, and the dynamical properties were calculated with a \( NPT \) molecular-dynamics program proposed in our previous study; for the phase behavior, we carried out histogram reweighting grand canonical Monte Carlo simulations. We briefly describe the simulation algorithms and computational details below.

#### A. Molecular-dynamics simulations

As suggested by Martyna et al., the following equations of motion were adopted to propagate the MD trajectories with the isothermal-isobaric ensemble:

\[
\dot{\mathbf{r}}_i = \mathbf{F}_i/m_i + \eta_i^2 \mathbf{r}_i + \eta_i \mathbf{p}_i - (\xi + 3\eta_0^2)(\mathbf{r}_i - \mathbf{i} \mathbf{p}_i),
\]

\[
\eta = (\rho_{\text{inst}} - \rho_{\text{des}})\exp(3\eta_0^2)k_B T_{\text{des}}
\]

\[
+ \frac{1}{N} \sum_{i=1}^{N} m_i (\mathbf{r}_i - \mathbf{i} \mathbf{p}_i)^2 k_B T_{\text{des}} - \xi \eta.
\]

\[
\dot{\xi} = \frac{1}{N} \sum_{i=1}^{N} m_i (\mathbf{r}_i - \mathbf{i} \mathbf{p}_i)^2 + 3 \eta_0^2 k_B T_{\text{des}}
\]

\[
- (f + 1) k_B T_{\text{des}} \sqrt{Q},
\]

\[
\eta = \ln V^{1/3},
\]

where \( \mathbf{r}_i, \mathbf{F}_i \) and \( m_i \) are the position, force, and mass of the \( i \)th particle, respectively; \( \dot{\xi} \) and \( \eta \) are the thermostat and barostat variables, with two corresponding parameters of \( Q \) and \( T_p \) to adjust the fluctuation of temperature and pressure; \( V \) is the volume; \( f \) is the degree of freedom of the simulated system with \( N \) particles; \( k_B \) is the Boltzmann constant; \( P_{\text{des}} \) and \( T_{\text{des}} \) are the desired/external pressure and temperature; and \( P_{\text{inst}} \) is the instantaneous pressure, which is calculated from atomic virial \( W = 1/3 \sum_i \mathbf{F}_i \mathbf{r}_i \).
\[ P_{\text{inst}} = \frac{1}{3V} \sum_{i=1}^{N} m_i (r_i - \bar{r}_i)^2 + \frac{W}{V}. \] 

In all of our molecular-dynamics simulations, 256 molecules were placed in a cubic simulation box. The conventional periodic boundary conditions and minimum image conventions were used in the simulations to calculate interatom distances. Long-range electrostatic forces and energies were calculated with the Ewald summation. Long-range corrections to the Lennard-Jones interactions were made with the formulations presented by Zhang and Duan. Velocity Verlet algorithm was adopted to propagate the statistical trajectory, which was described in detail in the Appendix of our previous paper. The geometries of CO\(_2\) molecules were constrained with the RATTLE method. The oxygen atoms were set as primary atoms in the propagation of MD trajectory and the positions of the carbon atoms were calculated as the midpoint of the other two oxygen atoms. Note that the forces acting on the carbon atoms should be carefully transformed to the primary oxygen atoms for consistency as suggested by Ciccotti et al. Parameters of \( Q \) and \( t_p \) in Eq. (4) were adjusted to control the fluctuation of temperature and pressure according to the suggestion of Martyna et al. with a typical value of 5.0 kJ ps\(^{-2}\)/mol for \( Q \) and 5.0 ps for \( t_p \). When \( t_p \) was set as an extremely large number, the volume of the system would not change and the MD trajectories would be propagated in an NVT ensemble. The time step of all the simulations was set as 1.0 fs. Simulations were initiated from the configurations “melted” from the face-centered-cubic lattice structure or the previous equilibrated configurations at similar densities. The instantaneous volumes were recorded and counted into the statistical average for about 50 ps after a 10–20-ps preequilibrium simulation. At lower temperatures and pressures, longer simulations (to 80 ps) were performed to ensure the convergence of the simulation and sufficient statistical reliability.

As discussed in our previous paper, the simulation results show good reliability and are in good agreement with prior workers. We carefully checked the possible finite-size effect and the adequacy of the simulation lengths. Little differences were found when we increased the system size from 256 to 512 molecules. As the total simulation time increased from 50–80 to 200 ps, the simulation results of volumetric and structural properties were almost identical. So we conclude that our choice of the system size and simulation length should be appropriate.

### B. Histogram reweighting grand canonical Monte Carlo (HRGCMC) simulation

Since the advent of histogram reweighting technique, determinations of the phase coexistence envelope and critical parameters with computer simulations have been greatly simplified with remarkable precisions. Detailed pedagogical descriptions about this technique can be found in a number of excellent reviews. The basic idea of this technique is to link different thermodynamic states with a global estimation of microcanonical partition function.

From a grand canonical Monte Carlo (GCMC), simulation in which the temperature \((T)\) and volume \((V)\) and the chemical potential \((\mu)\) are fixed, the microcanonical partition function \(\Omega(N,V,E)\) can be calculated with the collected two-dimensional histogram \(f(N,E)\),

\[ \Omega(N,V,E) = f(N,E)\exp(\beta E - \beta \mu N)C, \]

where \(\beta = 1/k_B T\), \(C\) is a constant related to the total grand canonical partition function \(\Xi(\mu, V, T)\) of a specific simulation. Equation (6) can be regarded as a local estimation of microcanonical partition function. In most cases, the histogram \(f(N,E)\) collected in a simulation only covers a limited range of particles and energies and this would result in erroneous estimation of \(\Omega(N,V,E)\) out of this range.

Multiple histogram reweighting technique elegantly overcomes this problem with a linear combination of the local estimations of \(\Omega(N,V,E)\) with multiple histograms \(f_i(N,E)\) at different \(\beta_i\) and \(\mu_i\) \((i = 1, 2, \ldots, R)\),

\[ \Omega(N,V,E) = \sum_{i=1}^{R} W_i(N,E)f_i(N,E)\exp(\beta_i E - \beta_i \mu_i N), \]

where \(W_i(N,E)\) are appropriate weights. Ferrenberg and Swendsen determined the weights by minimizing the variance of \(\Omega(N,V,E)\) contributed from local estimations and got the following expression for the global estimation of \(\Omega(N,V,E)\):

\[ \Omega(N,V,E) = \frac{\sum_{i=1}^{R} f_i(N,E)}{\sum_{i=1}^{R} K_i \exp(-\beta E + \beta \mu_i N - C_i)} , \]

where \(K_i\) is the total number of observations for run \(i\), \(C_i\) is the constant.

Once the microcanonical partition function has been determined, the unnormalized probability of a microstate (for a specific state) \(p(N,E;\mu,\beta)\) is
\[ \rho(N,E;\mu,\beta) = \Omega(N,V,E)\exp(-\beta E + \beta \mu N) \]
\[ = \frac{\sum_{i}^{N} \exp(-\beta E + \beta \mu N)}{\sum_{i=1}^{N} \exp(-\beta E + \beta \mu N)} \]
\[ \Xi(\mu,V,T) = \sum_{N} \sum_{E} \Omega(N,V,E)\exp(-\beta E + \beta \mu N). \]  
(9)

And the constants \( C_i \) can be calculated by

\[ C_i = \ln \sum_{N} \sum_{E} \rho(N,E;\mu_i,\beta_i). \]
(10)

Equations (9) and (10) can be iterated to get a convergent value for the probability function and all the relevant thermodynamic variables as a result.

In the GCMC simulation, the grand canonical distribution function \( \Xi(\mu,V,T) \) [equivalent to the normalization constant for Eq. (9)] can be calculated from

\[ \Xi(\mu,V,T) = \sum_{N} \sum_{E} \Omega(N,V,E)\exp(-\beta E + \beta \mu N). \]
(11)

Then with the following bridge equation the pressure can be calculated thereby

\[ \beta PV = \ln \Xi. \]
(12)

The phase coexistence can then be determined by finding the value of chemical potential with equal pressures.25

Our GCMC simulation began from near the critical point for a purpose of obtaining a broad covering range of the histogram. Several state points at 302.0 K and different chemical potentials were carried out. All of the volumes of the simulation box were specified as 10 000 Å³. Periodic boundary conditions with minimum image conventions were used. The configurational bias sampling technique was adopted to create or delete a carbon dioxide molecule in the

FIG. 2. A detailed comparison of the deviations of simulated volumes with different models (EPM2, MSM, Errington, TraPPE, and optimized model in this study) corresponding to the state points of Fig. 1.
FIG. 3. Comparisons between the simulated volumes with the different potential models and the experimental results by Juza et al. (Ref. 37) at high pressures from 200.0 to 400.0 MPa.

FIG. 4. Comparisons between the simulated volumes with the different potential models and the experimental results by Shmonov and Shmulovich (Ref. 40).
system. The Monte Carlo trajectory was generated by 40% particle displacement and 60% creation/annihilation with Metropolis acceptance criteria. $2 \times 10^7$ Monte Carlo steps were set to ensure a complete equilibrium and the histograms were collected for $6 \times 10^7$ Monte Carlo steps. With the collected histograms, we can give a prediction of the phase coexistence curve, which was found to be reliable in a limited distance below the critical point. The coexistence chemical potential (denoted as $\mu_{\text{coex}}$) at 290.0 K was estimated for the next simulations. After that, GCMC simulations were carried out at a second temperature of 290.0 K and three chemical potentials in the vicinity of the predicted coexistence chemical potential ($\mu_{\text{coex}} + \Delta \mu$, $\mu_{\text{coex}}$ and $\mu_{\text{coex}} + \Delta \mu$, where $\Delta \mu$ is a suitable increment for chemical potential).

### TABLE II. Coexistence properties of the optimized potential model in this study. Experimental data of saturated densities and pressures are selected from Duschek et al. (Ref. 47). The numbers in parentheses are the standard deviations of five independent HRGCMC calculations and can be regarded as the conservative estimations of corresponding uncertainties.

<table>
<thead>
<tr>
<th>$T$</th>
<th>$\rho_l$(kg/m$^3$)</th>
<th>$\rho_v$(kg/m$^3$)</th>
<th>$P$(MPa)</th>
<th>$\Delta H_{\text{vap}}$(kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>230</td>
<td>1125.83(0.57)</td>
<td>1128.77</td>
<td>0.897(0.017)</td>
<td>13.90(0.05)</td>
</tr>
<tr>
<td>240</td>
<td>1086.67(0.26)</td>
<td>1088.94</td>
<td>1.288(0.011)</td>
<td>13.19(0.06)</td>
</tr>
<tr>
<td>250</td>
<td>1044.54(0.33)</td>
<td>1045.99</td>
<td>1.788(0.002)</td>
<td>12.40(0.06)</td>
</tr>
<tr>
<td>260</td>
<td>998.13(0.56)</td>
<td>998.86</td>
<td>2.413(0.015)</td>
<td>11.51(0.05)</td>
</tr>
<tr>
<td>270</td>
<td>945.89(0.63)</td>
<td>945.80</td>
<td>3.179(0.034)</td>
<td>10.46(0.04)</td>
</tr>
<tr>
<td>280</td>
<td>883.84(0.82)</td>
<td>883.56</td>
<td>4.108(0.051)</td>
<td>9.17(0.03)</td>
</tr>
<tr>
<td>290</td>
<td>804.70(1.65)</td>
<td>804.66</td>
<td>5.233(0.063)</td>
<td>7.45(0.04)</td>
</tr>
</tbody>
</table>

$\rho_l$ and $\rho_v$ are saturated liquid and vapor densities, respectively.

$P$ is the saturation pressure.

$\Delta H_{\text{vap}}$ is the heat of vaporization.

FIG. 5. Simulated coexistence envelopes of different models and comparisons with experiments (Ref. 2): (a) the optimized potential model in this study; (b) EPM2; (c) the potential model proposed by Errington; (d) MSM; and (e) TraPPE. The uncertainties of the saturated properties in the subcritical region are not larger than the size of the symbols.
which explored the distribution of particles and energies around the coexistence phase envelope. Then with the combined information of these histograms, a more accurate estimation of the phase behavior can be expected to further down subcritical region. This process continued until the full curve of phase coexistence was finally determined.

Two issues should be addressed here. Firstly, when the temperature was lowered and the state point was located in the condensed liquid region, the number of trial positions for a creation/annihilation step should be increased to greatly enhance the statistical efficiency, which is important to validate Eq. (8) and (9). Secondly, from Eq. (6), the microcanonical partition function can only be calculated within an undetermined constant and this constant would be essential to the absolute value of pressure. This constant was suggested to be extrapolated from a linear fit to the histograms in the ideal-gas region, which entails an additional simulation with a histogram peaked at one particle to adequately sample the ideal-gas region.

IV. RESULTS AND DISCUSSION

A. Volumetric properties

Over the last century, a number of efforts have been devoted to the measurements of volumetric properties of carbon dioxide. In 1996, Span and Wagner systematically reviewed the available experimental densities over wide temperatures and pressures, which ranges from triple point to 1100 K and 800 MPa. Among these experimental data, most are in the pressure range from triple point to 100 MPa for the sake of industrial interest. In this region, the EOS proposed by Span and Wagner was claimed to be accurate with an accuracy of less than 0.2% (Ref. 2) and accordingly we regard the calculated volumes as experimental data. At higher pressures, several sets of experimental data were published by (1) Juza et al., 37 323–748 K, 70.0–400.0 MPa; (2) Michaels et al., 38 298–423 K, 7.5–315.8 MPa; (3) Tsiklis et al., 39 323–673 K, 200.0–700.0 MPa; and (4) Shmonov and Shmulovich, 40 681–980 K, 50.0–800.0 MPa. Since then, a few new data points were published but still are limited in this TP range 41 by the reason of difficulties encountered in the experiments. Under still higher temperatures and pressures, information of the volumetric properties of carbon dioxide can be obtained from the shock-induced measurements 43,44 or indirectly uncovered from the measured fugacity through reaction equilibria. 45,46 But these routines turn out to be inaccurate with remarkable uncertainties and show inconsistence with the experimental data mentioned above. 2

Figure 1 shows the simulated densities with the optimized potential in this study and compares them with the calculated densities by the EOS of Span and Wagner. 2 The overall agreement is very good, especially in the region of condensed carbon dioxide. Figure 2 gives a detailed com-

<p>| TABLE III. Coexistence properties of EPM2. Experimental data of saturated densities and pressures are selected from Duschek et al. (Ref. 47). |
|---------------------|---------------------|---------------------|---------------------|---------------------|</p>
<table>
<thead>
<tr>
<th>T</th>
<th>( \rho_s (\text{kg/m}^3) )</th>
<th>( \rho_c (\text{kg/m}^3) )</th>
<th>( P^\text{s} (\text{MPa}) )</th>
<th>( \Delta H_{\text{vap}} (\text{kJ/mol}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>230</td>
<td>1112.77</td>
<td>22.92</td>
<td>0.848</td>
<td>14.29</td>
</tr>
<tr>
<td>240</td>
<td>1088.94</td>
<td>32.55</td>
<td>1.224</td>
<td>13.55</td>
</tr>
<tr>
<td>250</td>
<td>1045.99</td>
<td>45.55</td>
<td>1.706</td>
<td>12.72</td>
</tr>
<tr>
<td>260</td>
<td>998.86</td>
<td>63.35</td>
<td>2.318</td>
<td>11.76</td>
</tr>
<tr>
<td>270</td>
<td>945.80</td>
<td>87.91</td>
<td>3.085</td>
<td>10.65</td>
</tr>
<tr>
<td>280</td>
<td>883.56</td>
<td>122.90</td>
<td>4.032</td>
<td>9.28</td>
</tr>
<tr>
<td>290</td>
<td>804.66</td>
<td>176.30</td>
<td>5.187</td>
<td>7.49</td>
</tr>
</tbody>
</table>

\( \rho_s \) and \( \rho_c \) are saturated liquid and vapor densities, respectively.

\( P^\text{s} \) is the saturation pressure.

\( \Delta H_{\text{vap}} \) is the heat of vaporization.

<p>| TABLE IV. Coexistence properties of MSM. Experimental data of saturated densities and pressures are selected from Duschek et al. (Ref. 47). |
|---------------------|---------------------|---------------------|---------------------|---------------------|</p>
<table>
<thead>
<tr>
<th>T</th>
<th>( \rho_s (\text{kg/m}^3) )</th>
<th>( \rho_c (\text{kg/m}^3) )</th>
<th>( P^\text{s} (\text{MPa}) )</th>
<th>( \Delta H_{\text{vap}} (\text{kJ/mol}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>230</td>
<td>1119.62</td>
<td>23.23</td>
<td>0.835</td>
<td>14.00</td>
</tr>
<tr>
<td>240</td>
<td>1088.94</td>
<td>32.67</td>
<td>1.206</td>
<td>13.32</td>
</tr>
<tr>
<td>250</td>
<td>1045.99</td>
<td>45.13</td>
<td>1.680</td>
<td>12.55</td>
</tr>
<tr>
<td>260</td>
<td>998.86</td>
<td>61.86</td>
<td>2.276</td>
<td>11.67</td>
</tr>
<tr>
<td>270</td>
<td>945.80</td>
<td>85.02</td>
<td>3.014</td>
<td>10.61</td>
</tr>
<tr>
<td>280</td>
<td>883.56</td>
<td>118.70</td>
<td>3.924</td>
<td>9.31</td>
</tr>
<tr>
<td>290</td>
<td>804.66</td>
<td>170.30</td>
<td>5.042</td>
<td>7.62</td>
</tr>
</tbody>
</table>

\( \rho_s \) and \( \rho_c \) are saturated liquid and vapor densities, respectively.

\( P^\text{s} \) is the saturation pressure.

\( \Delta H_{\text{vap}} \) is the heat of vaporization.
parison of the deviations of simulated volumes with different models (EPM2, MSM, TraPPE, potential model proposed by Errington, and optimized model in this study) corresponding to the state points of Fig. 1. From 223.0 to 323.15 K, our model generally predicts the volumes within an accuracy of 1.0%, which is the best among the evaluated models. At higher temperatures to 1073.15 K, the deviations are generally enlarged to around 1.0%–2.0%. At 1073.15 K, the model proposed by Errington begins to show its advantage but is actually comparable with our model. The overall evaluations in this TP region reveal the superiority of our model with relative errors decreased by about 1.0% as compared with the model of Errington and by 0.5% as compared with the other three models.

Figure 3 shows the comparisons between the simulated volumes with the different potential models and the experimental results by Juza et al.\textsuperscript{37} from 200.0 to 400.0 MPa. All of the evaluated models give overestimations of volumes with different relative errors. Among them, the potential model proposed by Errington gives the best predictions with an accuracy of about 0.5%. Our model gives a little larger deviation of about 1.0%. MSM enlarges the deviations to about 1.5% and EPM2 goes further to about 2.0%. TraPPE gives an even larger relative error of about 3.0%, which implies the failure of TraPPE model at high pressures.

The trends observed in Fig. 3 can be extrapolated to higher pressures, as compared with the experimental results by Shmonov and Shmulovich\textsuperscript{40} in Fig. 4. As the pressure increased, the relative errors of different models are increased almost parallel. The largest deviation occurs at 980.65 K and 800.0 MPa, which is 4.5%, 5.6%, 6.3%, 6.6%, and 7.6% for the potential of Errington, the model proposed in this study, MSM, EPM2, and TraPPE, respectively. In the meantime, we notice a fact that all of the existing empirical EOS cannot give a good prediction of the volumes at higher pressures of Shmonov and Shmulovich\textsuperscript{40} if the EOS is accurate for the properties under lower pressures. As shown in Fig. 4, the EOS of Span and Wagner\textsuperscript{2} predicts the volumes with noticeable deviations, the maximum of which is 2.3% at 980.65 K and 800.0 MPa. It is plausible whether the data set of Shmonov and Shmulovich\textsuperscript{40} are reliable, which has also been suspected by prior workers.\textsuperscript{3} If we regard the EOS of Span and Wagner\textsuperscript{2} as a kind of smoothing model for these pathological data and compare it with simulated results with our model, the maximum deviation is estimated to be 3.3% and the averaged deviation is about 2.1%, which is satisfying by noticing the accurate phase behaviors described below.

**B. Phase behaviors**

The phase equilibria of carbon dioxide have been accurately described by different measurements.\textsuperscript{5} In this study we select the most recent experimental results of Duschek et al.,\textsuperscript{47} as the base line of our refinements and comparisons. For

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>230</td>
<td>1127.11</td>
<td>1128.77</td>
<td>19.10</td>
<td>23.27</td>
<td>0.710</td>
<td>0.893</td>
<td>15.23</td>
<td>14.44</td>
</tr>
<tr>
<td>240</td>
<td>1090.27</td>
<td>1088.94</td>
<td>27.30</td>
<td>33.30</td>
<td>1.044</td>
<td>1.283</td>
<td>14.51</td>
<td>13.63</td>
</tr>
<tr>
<td>250</td>
<td>1050.96</td>
<td>1045.99</td>
<td>38.09</td>
<td>46.65</td>
<td>1.476</td>
<td>1.785</td>
<td>13.71</td>
<td>12.73</td>
</tr>
<tr>
<td>260</td>
<td>1007.66</td>
<td>998.86</td>
<td>52.29</td>
<td>64.42</td>
<td>2.023</td>
<td>2.419</td>
<td>12.81</td>
<td>11.73</td>
</tr>
<tr>
<td>270</td>
<td>948.73</td>
<td>945.80</td>
<td>71.33</td>
<td>88.37</td>
<td>2.701</td>
<td>3.203</td>
<td>11.56</td>
<td>10.57</td>
</tr>
<tr>
<td>280</td>
<td>868.09</td>
<td>883.56</td>
<td>128.40</td>
<td>161.74</td>
<td>4.197</td>
<td>4.161</td>
<td>9.07</td>
<td>9.18</td>
</tr>
<tr>
<td>290</td>
<td>803.66</td>
<td>804.66</td>
<td>189.70</td>
<td>171.97</td>
<td>5.393</td>
<td>5.318</td>
<td>7.18</td>
<td>7.40</td>
</tr>
</tbody>
</table>

$\rho_s$ and $\rho_v$ are saturated liquid and vapor densities, respectively.

$\Delta H_{vap}$ is the heat of vaporization.
the clarity of our comparisons in the following descriptions, we smoothed the experimental data along the phase coexistence curve with the equations by Span and Wagner \( ^2 \) [presented as Eqs. (3.13)–(3.15) in their original paper], with standard deviation of less than 0.1%.

Table II presents the coexistence properties of the optimized potential model in this study, including saturated liquid and vapor densities, vapor pressures, and heats of vaporization. We carried out five sets of independent HRGCMC simulations with different initial configurations and calculated the standard deviations of these properties as conservative estimations of the uncertainties involved in these quantities. The overall agreements with the experiments are very good: the averaged absolute deviations are 0.1%, 2.3%, 0.7%, and 1.9% for saturated liquid densities, vapor densities, saturation pressures, and heats of vaporization, respectively. The accuracies of saturated liquid densities are remarkable within 0.3%.

Figure 5 shows the simulated coexistence envelopes of different models and experiments. Detailed data for the coexistence properties of EPM2, MSM, the potential of Errington, and TraPPE are listed in Tables III–VI, respectively. Compared with our model, EPM2 gives equivalent descriptions of the coexistence curve. Nevertheless, careful analysis shows that the EPM2 systematically underestimates the saturated liquid densities by about 0.7%, which is consistent with the original conclusion of Harris and Yung. \(^5\) The phase coexistence curve of MSM shows similar behaviors with a little larger deviation. As for the potential model proposed by Errington, the saturated liquid densities are well predicted within 0.4%. However, the accuracies of saturated vapor densities are not good enough and as the temperature increased to 290.0 K, this model gives an overestimation of about 10.3%. According to our calculations, the TraPPE model only gives a rough description of the phase coexistence curve, with the deviations for both liquid and vapor densities gradually increased as the temperatures increased and reached 3.5% and 18.6% for liquid and vapor densities, respectively, at 290.0 K.

Figure 6 gives a Clausius–Clapeyron plot of the saturated pressures versus temperatures of different potential models and experiments. \(^47\) For clarity, we only present the results of EPM2 and our potential in this plot. Both models show good and equivalent predictability of the vapor pressures.

The critical temperatures and densities were determined with the mixed-field technique suggested by Wilding. \(^48\) In order to estimate the critical pressure \( (P_c) \), the relation between saturated pressures \( (P_{sat}) \) and temperatures was fitted with the following equation: \(^36\)

\[
\ln P_{sat} = a_0 + a_1/T + a_2 T + a_3 T^2,
\]

where \( a_0-a_3 \) are the fitting constants. With this relation along with the calculated critical temperature, the critical pressure can be derived by extrapolations.

Table VII lists the calculated critical points of different models. To give a better understanding of the positions of these critical points, we also plotted them in Fig. 5. From Table VII and Fig. 5, the potential model in this study, along with EPM2 and MSM, gives good estimation of the critical point. As expected, the potential proposed by Errington predicts the critical point with discernible deviations from the experiments. TraPPE significantly overestimates the critical point. It should be addressed here that the critical parameters listed in Table VII are actually apparent properties for the specific system size adopted in this study. To get the precise estimations for infinite systems, the finite-size scaling technique can be utilized and thus a serial of additional simulations with larger system sizes should be carried out. \(^48\) Nevertheless, according to the experience of Errington, the finite-size effects are expected to be around 1.0%. \(^49\)

<table>
<thead>
<tr>
<th>( T_c (K) )</th>
<th>( \rho_s (kg/m^3) )</th>
<th>( P_c (MPa) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp. (^4)</td>
<td>304.1282±0.015</td>
<td>467.6±0.6</td>
</tr>
<tr>
<td>This study</td>
<td>304.0±0.7</td>
<td>467.0±2.9</td>
</tr>
<tr>
<td>EPM2</td>
<td>303.2</td>
<td>466.4</td>
</tr>
<tr>
<td>MSM</td>
<td>304.9</td>
<td>464.2</td>
</tr>
<tr>
<td>Errington</td>
<td>302.5</td>
<td>472.8</td>
</tr>
<tr>
<td>TraPPE</td>
<td>309.1</td>
<td>462.0</td>
</tr>
</tbody>
</table>

\(^{47}\)Reference 47.

\(^{49}\)Reference 47.

### C. Structural properties

Due to the typical anisotropic behaviors of carbon dioxide molecules, the structural properties of carbon dioxide have been studied through neutron-diffraction experiments \(^50-55\) or x-ray diffraction measurements. \(^56\) However, the measured radial distribution functions by different authors are not always consistent with each other for the uncertainties and statistical fluctuations involved in these experiments. \(^51,52\) Ricci and co-workers continuously and systematically carried out neutron-diffraction measurements on fluid carbon dioxide over wide temperature and density

---

**TABLE VII. Critical points of different models.** The uncertainties in the critical parameters of this study were estimated as the standard deviations of five independent HRGCMC calculations with the same system size.

---

**FIG. 6.** A Clausius–Clapeyron plot of the saturated pressures vs temperatures of EPM2 and the potential in this study and comparison with experiments (Ref. 47).
These can be regarded as the most comprehensive experimental structural properties for carbon dioxide up to now.

In order to compare the simulated structural properties of carbon dioxide with experiments, the neutron weighted radial distribution function \( g_n(r) \) was calculated by

\[
g_n(r) = 0.403g_{OO}(r) + 0.464g_{CO}(r) + 0.133g_{CC}(r),
\]

where \( g_{OO}(r), g_{CO}(r), g_{CC}(r) \) are the partial atom-atom distribution functions. \(^55\) From Fig. 7, the overall agreements between the experiments and simulation results are quite good. Almost all of the features in experimental radial distribution functions are well reproduced by the simulations with our model. Contributions from the partial atom-atom distribution functions are also shown.

The main features of these atom-atom pair distribution functions are summarized in Table VIII. From Fig. 7 and Table VIII, the atom-atom pair distribution functions are also shown. The overall agreements between the simulations and experimental data are quite good. Nevertheless, a noticeable feature of the neutron weighted distribution function is observed with a split of the first peak at low temperatures and high densities. When the temperature is increased and the density is decreased, this feature gradually diminishes to the change of slope (inflection) and finally almost disappears, which is mainly ascribed to the contributions from C–O and O–O distribution functions. The position of the first hump (or inflection) is found to be around 3.55 Å for all the three thermodynamic states examined in Fig. 7 and can be defined as the boundary of the first coordination shell of carbon dioxide.

To further disclose the structure within the first coordination shell, a cylindrical coordinate system is introduced. \(^57\) As shown in Fig. 8, the x axis is selected to pass through the mass centers of the three atoms of a carbon dioxide molecule and the origin is located at the carbon atom. When an oxygen atom is interested within the first coordination shell, the position \((x, y)\) is recorded on the plane determined by this atom and the frequency is accumulated as \( N(x, y) \). After a full statistics over all the molecules and the entire trajectories of a simulation, we computed the ensemble averaged number \( \langle N(x, y) \rangle \) and the number density \( n(x, y) \) was calculated by

\[
n(x, y) = \frac{\langle N(x, y) \rangle}{2\pi\delta y \delta x},
\]

where \( \delta x, \delta y \) determine the cylindrical unit shell on the position of \((x, y)\) (as indicated in Fig. 8). The calculated density profiles are presented as contours in Fig. 9. From

### Table VIII. Structural features of bulk carbon dioxide with the potential model in this study at three thermodynamic states.

<table>
<thead>
<tr>
<th></th>
<th>( g_{cc} )</th>
<th>( g_{co} )</th>
<th>( g_{oo} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a)</td>
<td>(b)</td>
<td>(c)</td>
</tr>
<tr>
<td>First peak (Å)</td>
<td>4.05</td>
<td>4.05</td>
<td>4.15</td>
</tr>
<tr>
<td>First min (Å)</td>
<td>5.65</td>
<td>5.95</td>
<td>5.85</td>
</tr>
<tr>
<td>Coordination number</td>
<td>11.1</td>
<td>9.8</td>
<td>9.3</td>
</tr>
</tbody>
</table>

FIG. 7. Comparison between the neutron weighted radial distribution functions \( g_n(r) \), obtained from simulations with the potential model in this study (full lines) and experiments (open circles): (a) 240.0 K, 40.416 cm\(^3\)/mol (Ref. 52); (b) 312.0 K, 52.825 cm\(^3\)/mol (Ref. 52); and (c) 473.0 K, 52.825 cm\(^3\)/mol (Ref. 51). The contributions from three partial atom-atom distribution functions are also shown.
these profiles, the T-shaped local configurations can be clearly imagined and are found to be predominant over wide temperatures and densities, which is consistent with the analysis of prior workers through experiments\textsuperscript{52} and ab initio simulations.\textsuperscript{58,59} Moreover, at low temperature and high density, a standard T-shape configuration with a vertical angle relative to the central molecule is preferred. As temperature increased and density decreased, the T-shape configuration is gradually distorted for the sake of thermal fluctuations.

D. Dynamical properties

Dynamic properties from simulations turn out to be much more sensitive to the selected potential model. Here we would give an illustrative discussion on the self-diffusion coefficients of carbon dioxide. The simulations of other dynamical properties are analogous and straightforward.

Self-diffusion coefficients were early measured by mass spectrometer and usually involved the use of tracer isotope.\textsuperscript{60,61} These measurements were generally limited in the gaseous region with low pressures and remarkable deviations between different data sets have been noticed.\textsuperscript{62} With the developments of experimental techniques [such as nuclear magnetic resonance (NMR)] and theories, measurements under higher pressures with dense gas and liquid phases are available with improved accuracies.\textsuperscript{63,64} Nevertheless, the uncertainties involved in these experiments are still obvious.

The self-diffusion coefficient was calculated from the “Einstein relation,”\textsuperscript{28}

\[
D = \lim_{t \to \infty} \frac{1}{6t} \langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \rangle, \tag{16}
\]

where \(\mathbf{r}_i(t)\) is the molecular position \(i\) at time \(t\) and \(\mathbf{r}_i(0)\) is the initial position, the bracket in Eq. (16) denotes ensemble average. In this calculation it is necessary to avoid the periodic image.

Figure 10 compares the predictability of self-diffusion coefficients with EPM2 and the potential model proposed in this study. Similar with the volumetric properties, the simulated self-diffusion coefficients agree better with experiments as the pressure increased. Furthermore, our potential shows slightly better accuracies than EPM2 by about 3.0% at the temperatures of 298.0 and 323.0 K. Nevertheless, after a comprehensive analysis of the simulation results over wide temperatures and pressures, we found this kind of superiority is limited in the range of about 273.0–373.0 K. At temperatures below 273.0 K, EPM2 gives better accuracies of self-diffusion coefficients. At temperatures higher than 373 K, both models give comparable predictions, as shown in Fig. 10.

V. CONCLUDING REMARKS

Optimization of the potential model has long been recognized as an important but nontrivial and even artistic job. For carbon dioxide, although a number of potential models have been proposed to reproduce different experimental properties, no one can be regarded as “perfect” to meet the insatiable appetites of different researchers. By noticing that none of the potential models available in the literature shows good predictability and transferability of volumetric properties and phase behaviors with sufficient accuracies simultaneously, it is our endeavor to find a better potential model for carbon dioxide in this study. On the basis of large number of computer simulations over the parameter spaces, the optimized potential model is expected to predict both volumetric properties and the phase coexistence envelope with improved accuracies.

Along with the optimized potential in this study, four other popular site-site potential models for carbon dioxide (EPM2,\textsuperscript{5} MSM,\textsuperscript{8,11,20} TraPPE,\textsuperscript{12} and the model proposed by Errington\textsuperscript{6}) have been comprehensively evaluated. For the volumetric properties of condensed phases with temperatures from 223.0 to 1073.15 K and pressures less than 100.0 MPa, our model generally gives the best predictions with relative errors lowered by about 1.0% as compared with the model of Errington and by 0.5% as compared with the other three.
models (Fig. 2). As pressures increased, the exponent-6 model of Errington shows better accuracies of about 0.5%. Our model gives a little larger deviation of about 1.0%. MSM enlarges the deviations to about 1.5% and EPM2 goes further to about 2.0%. TraPPE gives an even larger relative error of about 3.0%, which implies the failure of TraPPE model at high pressures (Figs. 3 and 4).

Among the five potential models examined in this study, our model gives the best predictions of phase behaviors. The saturated liquid densities, vapor densities, vapor pressures, and heats of vaporization are predicted with remarkable accuracies around 0.1%, 2.3%, 0.7%, and 1.9%, respectively. In particular, the critical point has been accurately reproduced. EPM2 shows comparable predictions but a systemati-
cal underestimation of about 0.7% for the saturated liquid densities at lower temperatures has been observed, as compared with 0.1% of our model. MSM reproduce the experimental phase behaviors with slightly larger deviations. While the predictions of saturated liquid densities are very good, the model proposed by Errington only gives a less accurate description of saturated vapor densities, which reaches to about 10.3% at 290.0 K and this would result in a noticeable deviation of the critical point. According to our calculations, TraPPE only gives a rough description of the phase behaviors and significantly overestimates the critical point (Tables II–VI and Fig. 5).

Subsequently, the structural properties have been studied with the optimized potential. Compared with neutron-diffraction measurements, the overall agreements between the experiments and simulation results with our model are remarkable (Fig. 7). A further analysis of the radial distribution functions reveals the effects of the temperature and density on the bulk structures, and the boundary of the first coordination shell of carbon dioxide has been defined accordingly. With a cylindrical coordination system introduced (Fig. 8), the T-shape configurations are found to be predominant but are gradually distorted as temperature increases and density decreases for the sake of thermal fluctuations (Fig. 9).

Finally, we give a brief discussion of the simulated dynamic property of self-diffusion coefficient. Our model gives the best prediction from 273.0 to 373.0 K (Fig. 10), while EPM2 shows better accuracies of self-diffusion coefficients at lower temperatures. At higher temperatures, both models give comparable predictions. The other models are inferior in the self-diffusion coefficient predictions.

ACKNOWLEDGMENTS

We would like to thank Dr. Errington and Dr. Panagiotopoulos for their constructive suggestions and valuable program codes for HRGCMC simulations. This work is supported by one of the authors (Z. D.) “Hundred Scientists Project” funds awarded by the Chinese Academy of Sciences and his Outstanding Young Scientist Funds (Grant No. 40225008) awarded by National Science Foundation of China and the funds from USA Grant No. NSF EAR-0126331.

4. Z. Zhang and Z. Duan, Phys. Earth Planet. Inter. 149, 335 (2005).