The Phase Diagram of Carbon Dioxide from Correlation Functions and a Many-body Potential

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ABSTRACT

The phase stability and equilibria of carbon dioxide is investigated from 125 – 325K and 1 – 10,000 atm using extensive molecular dynamics (MD) simulations and the Two-Phase Thermodynamics (2PT) method. We devise a direct approach for calculating phase diagrams in general, by considering the separate chemical potentials of the isolated phase at specific points on the P-T diagram. The unique ability of 2PT to accurately and efficiently approximate the entropy and Gibbs energy of liquids thus allows for assignment of phase boundaries from relatively short (~ 100ps) MD simulations. We validate our approach by calculating the critical properties of the flexible Elementary Physical Model 2 (FEPM2), showing good agreement with previous results. We show, however, that the incorrect description of the short-range Pauli force and the lack of molecular charge polarization leads to deviations from experiments at high pressures. We thus develop a many-body, fluctuating charge model for CO₂, termed CO₂-Fq, from high level quantum mechanics (QM) calculations, that accurately captures the condensed phase vibrational properties of the solid (including the Fermi resonance at 1378 cm⁻¹) as well as the diffusional properties of the liquid, leading to overall excellent agreement with experiments over the entire phase diagram. This work provides an efficient computational approach for determining phase diagrams of arbitrary systems and underscore the critical role of QM charge reorganization physics in molecular phase stability.

1. INTRODUCTION

Carbon dioxide is an essential chemical, both environmentally and industrially. Human driven climate change has been largely attributed to the growing concentration of CO₂ in the atmosphere[1]; data from the Intergovernmental Panel on Climate Change and research studies [2, 3] indicate that CO₂ has the highest Radiative Forcing value, and is the greatest contributor to global warming and the greenhouse effect. Industrially, there is widespread use of supercritical carbon dioxide (SCCO₂), which has superior mass transfer properties, is non-toxic, cheap, and easy to recycle.[4] In heavy metal extraction, SCCO₂ is widely applied as the extracting solvent due to its high removal efficiency.[5] In the synthesis of Rhodium, Silver, and Copper nanoparticles, SCCO₂ provides a unique environment to homogenize these systems.[6-8] Additionally, SCCO₂ can serve as a highly selective anti-solvent in polymer synthesis, since most organic solvents show high mutual solubility with SCCO₂.[9]

In all these industrially and environmental processes, knowledge of the chemical and physical properties of CO₂ at various temperature / pressure conditions is essential, especially at extreme (high temperature and pressure) conditions. Experimental studies at these extreme conditions usually involve shock experiments,[10-12] yet these are challenging to perform in a laboratory setting as it requires highly specialized equipment. Computer simulations, employing Molecular Dynamics (MD) and/or Monte-Carlo approaches, are complementary techniques that are in principle more straightforward to perform than experiments. These simulations have been aided by the development of efficient, empirical forcefields,
fitted to reproduce the properties of homogenous phases, as well as phase equilibria. Of particular note is the Elementary Physical Model 2 (EPM2),[13] which was developed to predict the liquid-vapor coexistence curve and critical properties of CO₂. The performance of the EPM2 over the entire phase diagram has not previously been reported, however.

Evaluating of the entire phase diagram is important since it is the ultimate metric for determining the accuracy and transferability of interaction potentials. Various computational approaches have been employed to meet this challenge, ranging from simulations in the Gibbs ensemble,[14] calculations of the latent heat across the phase boundaries and application of the Clausius-Clapeyron equation,[15] Thermodynamic Integration calculations,[16] phase-coexistence simulations,[17] and recent attempts using advanced ensemble sampling and order parameters.[18] Yet in spite of these advances, calculating the full P-T phase diagram is still a computationally expensive proposition. Moreover, while evaluation of the relative Gibbs energy of the various phases is essential, calculations of other useful thermodynamic potentials, such as entropy and heat capacity, are either difficult to obtain in the former or require additional, extensive simulations to obtain the latter.

In this study, we develop an approach for rapidly determining phase diagrams, based on explicit calculations of the entropy, enthalpy and Gibbs energy of competing phases in isolation, using the Two-phase thermodynamic (2PT) model. [19-22] The attractiveness of this approach is that it allows for the generation of the P-T phase diagram from short MD simulations, usually ~ 20ps after equilibration. Our previous work has shown that the 2PT method predicts the properties of CO₂ along the saturated vapor-liquid coexistence curve in good agreement with experiments, using the EPM2 model. Here, we expand on that study and show that by considering the thermodynamic properties of the CO₂ crystal, one can obtain good agreement compared to experiments along the entire P-T phase diagram at little extra computational cost. Moreover, our approach allows for the straightforward elaboration of the separate entropic and enthalpic energies across the phase boundaries, gaining further insights into the nature of phase transitions. Finally, we develop a new Quantum-Mechanics (QM) based, fluctuating charge forcefield, termed CO₂-FQ, which leads to improved performance over the phase diagram and allow us to quantify the role of intermolecular charge renormalization on phase stability.

2. METHODS

2.1 Background Theoretical Approach

2.1.1 Two-Phase Thermodynamic (2PT) Method for rapid evaluation of the Entropy and Gibbs Energy

Details of the 2PT method have been published elsewhere,[20, 21, 23] so we summarize the salient points here and direct the interested reader to our previous works [19, 24-26] and an overview in the methods sections of the supplementary materials. In 2PT, we represent the thermodynamics of a condensed phase liquid as a linear combination of two subsystems:

\[ Q = fQ^{\text{gas}} + (1-f)Q^{\text{solid}} \] (1)

where \( Q^{\text{gas}} \) represents the thermodynamics of a hard-sphere gas, in the limit that all the modes are diffusive and \( Q^{\text{solid}} \) is the thermodynamics of a Debye vibrating crystal, in the limit that all the modes are vibrational. In principle, the thermodynamic properties of these two subsystems can be obtained exactly from statistical mechanics.[27] In practice, we obtain the \( Q^{\text{gas}} \) at constant density, and temperature from the Carnahan-Starling equation of state,[28, 29] while \( Q^{\text{solid}} \) is obtained from the frequency dependent reweighting of the Density of States function (DoS, also known as the spectral density), as a Fourier transform of the velocity autocorrelation function [30] in MD simulations.

This superposition theory is based on early work by Eyring and Ree.[31] Lin and coworkers
showed that the partition (or “fluidicity”) factor $f$ in Equation 1, which determines the relative weight of each subsystems, can be obtained self-consistently from an MD simulation as a ratio of the computed self-diffusion constant to that of a hard-sphere fluid at the same temperature and density.[20] When applied to molecular systems, recent work has shown that in the limit of independent molecular motions, the total system thermodynamics can be obtained from linear combinations of the thermodynamics resulting from (self-)diffusional, librational (both solid-like translations and rotations) and internal vibrational contributions.[21, 24, 26] A recent extension by Desjarlais showed that the frequency dependent distribution DoS of the gas-subsystem can be better approximated using a Gaussian memory function, which leads to improved results compared to experiments.[22]

The ultimate utility of the 2PT method in the current context is that it has the correct asymptotic behavior (by construction), so it can be applied equally in determining the thermodynamic properties of solids, liquids and gases within the same computational framework. Previous work has shown 2PT to be efficient (only required $\sim 10 – 20$ ps trajectories), with acceptable accuracy compared to more exact, but computationally expensive, Thermodynamic Integration and Free Energy Perturbation schemes.[23] These advantages are leveraged presently to calculate the entire phase diagram of CO$_2$, from independent MD simulations of the three competing phases at specific temperatures and pressures.

2.1.2 Partial atomic charges from the Charge Equilibration (QEq) Method

Traditional empirical forcefield are usually based on partial atomic charges that are fixed, with the total electrostatic energy obtained by Coulomb’s law. While various approaches have been developed to obtain these atomic charges, in modern forcefields they are usually based on 1) population analysis of the QM wavefunction or electron density for isolated, gas-phase molecules or fragments; or 2) empirically fitted to reproduce the high order electrostatic moments (i.e., dipole, quadrupole, octupole, etc.) of the molecule. The choice of fixed atomic charges introduces some conceptual difficulties for performing simulations under conditions not explicitly considered during the charge parameterization, although modern forcefield can mitigate this somewhat by optimizing the two-body van der Waals potential. Indeed, applying this strategy, the properties of condensed phase systems using fixed charges can be reasonable under normal temperature and pressure (NTP) conditions. Specifically, in the case of CO$_2$, this strategy has led to the development of the EPM2 model, optimized to reproduce the critical properties.

Despite its attractiveness, the ability of fixed charge potentials to reliably predict the equilibrium thermodynamics far from NTP is not guaranteed and is in fact frequently compromised. This is partly due to the fact that highly compressed systems can minimize their total energy by redistributing the electron clouds around the atoms (i.e., the Pauli force), an effect that may not be correctly represented by analytic functions with power series decays, such as frequently used Lennard Jones 12-6 potentials. One approach for approximating QM charge reorganization physics is the application of polarizable forcefields. These can be generally classified as either inducible point dipole (PD),[32] classical Drude oscillators [33] or fluctuating charge (FC) [34] approaches. PD models, such as the AMOEBA [35] forcefield for example, have been successful in simulating biological systems [36], and, more recently, ionic liquids [37].

In this work, we consider FC models, due to their inherent simplicity and intuitiveness. FC models aim to address the fundamental problem of assigning partial charges to atoms within a molecule, while simultaneously minimizing the electrostatic energy, under constraints of fixed overall system charge. The most popular schemes are based on the electronegativity equalization principle of Sanderson [38], which incorporates Mulliken electronegativities [39] $\chi$ and Parr–Pearson hardness [40] $\eta$. Here, the total electrostatic energy $E(q)$ of an atom is represented as a Taylor series expansion of the charge $q$:

$$E(q) = E_0 + q \chi + q^2 \eta + \ldots$$
\[
\chi_i = \left( \frac{\partial E}{\partial q} \right) = \frac{1}{2} \left( IP_i + EA_i \right) = -\mu_i; \quad \eta_i = \frac{1}{2} \left( \frac{\partial^2 E}{\partial q^2} \right) = \frac{1}{2} \left( IP_i - EA_i \right) \tag{2}
\]

where IP is the ionization potential, EA is the electron affinity and \( \mu \) is the chemical potential. The subscript \( i \) represents as the \( i \)th atom and the difference between IP and EA represents as the idempotent, \( J \).

Equation 2, in effect, represents the many-body, quantum mechanical electron density in a highly simplified basis. The coulomb interactions are either calculated by means of an analytic screened coulomb function in the popular EEM scheme [41], as the overlap of Slater-type \( ns \) orbitals in QEq [42-44], or more recently, as overlaps of 1s Gaussian type orbitals with atomic polarization in PPEq. [45, 46] We note that the many-body nature of FC models arises from the fact that the computed partial atomic charges are obtained self-consistently and include contributions from the self-energy as well as the interactions with other neighboring atoms. These charges are usually recalculated every step, and so varies smoothly as the local environment around the atom changes during an MD simulation. In principle, there are only two universal parameters for each element (\( \chi \) and \( \eta \)) that can be used to reproduce the electrostatic energy of arbitrary systems. In practice, these parameters are somewhat system specific, and we present a new parameter set for CO\(_2\), which we combine with various other potential energy surfaces derived from high level QM calculations, to produce the CO\(_2\)-Fq forcefield.

2.2 Computational Details

2.2.1. Description of Initial Systems

For simulations employing the FEPM2 forcefield, the initial structure of a CO\(_2\) crystal was obtained from the ICSD [47, 48] (database code ICSD 16428), with the cubic space group 205 (Pa-3) and lattice constant a=5.624 Å. We generated a 4x4x4 supercell (256 molecules) with the initial simulation cell of 22.496 Å in \( x \), \( y \) and \( z \) directions. To represent the liquid phase, we generated an amorphous CO\(_2\) structure (256 molecules), initially at a density of 1.185 g/cm\(^3\) and an initial simulation cell of 23.86 x 23.86 x 27.84 Å\(^3\). For simulations of the saturated vapor/liquid at the vapor-liquid coexistence (VLE) conditions, an amorphous structure with 252 molecules was used, with initial densities obtained from the NIST database.[49] Gas systems, which are not at saturated vapor condition, contained more molecules (512 amorphous molecules) to provide enough molecule-collisions to converge the thermodynamics. When using the CO\(_2\)-Fq forcefield, a smaller crystal cell, with 108 CO\(_2\) molecules in 3x3x3 structure (16.872 Å in \( x \), \( y \) and \( z \) directions), was used. In the corresponding liquid simulations, we used a cell with 108 amorphous molecules at all conditions except for the VLE condition, where we used a cell with 125 molecules.

2.2.2. The Flexible-EPM2 Carbon Dioxide Forcefield

The FEPM2 parameters are shown in Table 1. The valence interactions (i.e. the C-O bond stretching and angle bending motions) are modelled as harmonic springs, which is normally sufficient to provide a similar potential energies surface compared to QM for small displacements [13]:

\[
E_{valence} = E_{bonds} + E_{angles} = K_b (x - x_0)^2 + K_\Theta (\Theta - \Theta_0)^2 \tag{3}
\]

where \( x_0 \) is the equilibrium C-O bond length and \( \Theta_0 \) is the equilibrium O-C-O angle. The value of the \( K_b \) and \( K_\Theta \) force constants are taken from our previous work [19] and Ref [13], respectively. The van der Waals interactions are described with a Lennard-Jones 12-6 potential (LJ).
\[ E_{\text{vdw}}^{12-6} = 4\varepsilon \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \] (4)

with interaction energies \( \varepsilon \) and equilibrium distances \( \sigma \) taken from our previous work.[19]

### Table 1: FEPM2 force field parameters for CO

| Atom Charge (e) | Van der Waals (LJ) | Bond (Harmonic) | Angle (Harmonic) |
|-----------------|---------------------|-----------------|------------------|
|                 | \( \varepsilon \) (K) | \( \sigma \) (Å) | \( x_0 \) (Å) | \( K_b \) (kcal/mol Å\(^2\)) | \( \theta_0 \) (degree) | \( K_\theta \) (kcal/mol/radian\(^2\)) |
| C 0.65\( \sigma \) | C 28.13 2.757 | C-O 1.149 1284 | O-C-O 180 147.8 |
| O -0.32\( \sigma \) | O 80.51 3.033 |                 |                  |

#### 2.2.3. FEPM2 Molecular Dynamics Simulations

All MD simulations were performed using the LAMMPS[50] engine. For the FEPM2 model, we initiated our simulations with 500 steps of conjugated gradient (CG) minimization. Afterwards, 10ps Langevin dynamics was applied, to heat up a system to a defined temperature. This was followed by isothermal / iso-baric dynamics (NPT) at the relevant pressure. To ensure equilibrium conditions, we then conducted twice 5ns of Langevin dynamics, followed by another 3ns of canonical (NVT) dynamics using a Nose-Hoover thermostat. For simulations involving the gas-phase systems, we did not perform NPT dynamics for maintaining the density property. The real space cutoffs for the Lennard-Jones and coulomb potentials were 9Å and 10Å, respectively. The long-range electrostatic were calculated with the particle-particle particle-mesh approach, with force tolerance of \( 10^{-4} \). We verified that this force tolerance was adequate by performing simulations with force tolerances of \( 10^{-6} \) and \( 10^{-8} \), which produced identical results.

#### 2.2.4. FEPM2 Thermodynamics of the Solid and Liquid Phases

After equilibration, we ran an additional 200ps NVT simulation, with the trajectory (atomic positions and velocities) saved every 4fs. The thermodynamics were then obtained from an in-house code that implements the 2PT method.[51] Uncertainties in our measurements were obtained from statistical average from 10 independent simulation of 200ps each.

#### 2.2.5. FEPM2 Thermodynamics of the Gas Phase

Two different procedures were employed to obtain the thermodynamics of the gas phases. First, we considered a low-density gas with a large number (512) of molecules and calculated the thermodynamics using the 2PT method over a 2ns sampling window. We verified that this approach has enough molecular collisions to converge the VAC and produce converged thermodynamics (Figure 1b). Secondly, we considered a high-density gas near the vapor-liquid coexistence condition, and approximated the Gibbs energies based on simulation results of the saturated vapor thermodynamics and the ideal gas equation:

\[ S = S_{\text{sat}} - R \ln \left( \frac{P}{P_{\text{sat}}} \right) \]
\[ E = E_{\text{sat}} \] (5)

where \( S, P, E, \) and \( R \) are denoted as entropy, pressure, internal energy, and gas constant, respectively, \( S_{\text{sat}} \) and \( E_{\text{sat}} \) are the entropy and internal energy respectively of a saturated vapor system at a certain
temperature condition.

### 2.2.6. Construction of the CO₂-Fq Forcefield

We obtained the intra- / inter- molecular parameters of CO₂ from quantum mechanics calculations via the Q-Chem 5.2 package [52] at the aug-cc-pVTZ/MP2 level of theory. The C-O bond stretching was obtained by fitting the QM energies (Table S1) to a morse potential: 

\[ E_{\text{bond}} = D_e \left[ 1 - \exp \left( -\alpha (r - r_0) \right) \right]^2 \]  

(6)

with bond energy \( D_e \), equilibrium distance \( r_0 \) and curvature \( \alpha \).

The O-C-O angle bending was obtained by fitting the QM energies to a harmonic potential:

\[ E_{\text{angle}} = K_\theta (\Theta - \Theta_0)^2 \]  

(7)

with force constant \( K_\theta \) and equilibrium angle \( \Theta_0 \).

The van der Waals interactions were obtained from fitting the QM binding energies of three different dimer configurations to the universal nonbonded function (UNB) [53, 54] (Table S2):

\[ E_{\text{vdw}} = -D_e \exp \left[ -\beta \left( \frac{r - R}{L} \right) \right] \sum_{n=0}^{5} \alpha_n \left( \frac{r - R}{L} \right)^n \]  

(8)

where the \( R_e, D_e, \) and \( L \) are the equilibrium distances, the binding energies, and the scaling lengths, respectively. In keeping with a previous study,[53] the parameters series (\( \beta, \alpha_0, \alpha_1, \alpha_2, \alpha_3, \alpha_4, \alpha_5 \)) were defined as (1.00348500, 1.0, 1.02009000, 0.01678480, 0.00327294, 0.00365706, 0.00106613). We employed the UNB functional form here as it gave better fits to the QM binding energies compared to the more popular Lennard Jones, Exponential-6 or Morse potentials. The QEq parameters for carbon and oxygen in Equation 2 were fitted to reproduce the gas phase quadrupole moment of CO₂ from QM. The full set of parameters that defined the CO₂-Fq model is given in Table 2.

**Table 2 CO₂-Fq force field parameters.**

|                | C-C | O-O | C-O |
|----------------|-----|-----|-----|
| Van der Waals (UNB) |     |     |     |
| \( R_e \) (Å) | 5.42252 | 3.00361 | 3.64660 |
| \( D_e \) (kcal/mol) | 0.04138 | 0.43302 | 0.11315 |
| \( L \) (Å) | 0.69526 | 0.33056 | 0.47565 |
| Electrostatic (QEq) |     |     |     |
| \( \chi \) (eV) | 5.34300 | 9.19962 |     |
| \( J \) (eV) | 10.12600 | 16.07839 |     |
| \( R \) (Å) | 0.75900 | 0.40344 |     |
| Bond (Morse) |     |     |     |
| \( r_0 \) (Å) | 1.17257 |     |     |
| \( \alpha \) (1/Å) | 2.07474 |     |     |
| \( D_e \) (kcal/mol) | 262.239 |     |     |
| Angle (Harmonic) |     |     |     |
| \( \Theta_0 \) (degree) | 180 |     |     |
| \( K_\theta \) (kcal/mol/radian²) | 55.6154 |     |     |
2.2.7. CO₂-Fq MD Solid/Liquid Simulations and Thermodynamics

In simulating the CO₂-Fq solid and liquid phase systems, we followed a similar procedure to section 2.2.3., expect that the system electrostatics were obtained from the overlap of Gaussian 1s orbitals via the PQEq implementation in LAMMPS (pqeq method 0). We found that application of the Generalized Langevin equation (GLE)[55, 56] to thermostat the system lead to a better distribution of energies at equilibrium. After an initial 500 steps of CG minimization, we performed 10ps of dynamics using the GLE thermostat followed by simulations in the NPT ensemble in order to stabilize the system at a specific temperature and pressure. Afterwards, we performed 3ns NVT dynamics with the GLE thermostat and another 0.5ns dynamics with the Nose-Hoover thermostat for further equilibration. The real space cutoffs for the UNB and QEq potentials were 10Å and 12.5Å, respectively, and we applied a Taper function to the QEq energies and forces to ensure zero energies and forces at the cutoff. The GLE matrix was tuned to enforce “Smart sampling”,[57] with Ns=6 additional degrees of freedom. Similar to section 2.2.4., atomic trajectory information of CO₂-Fq solid and liquid systems were collected for 200ps NVT dynamics. The 200ps trajectory information was further applied in 2PT thermodynamics analysis.

2.2.8. CO₂-Fq Thermodynamics of the Gas Phase

The QEq approach equalizes the charges in the thermodynamic limit, leading to spurious long-range charge transfer between molecules.[44, 58] This complicates simulations of gas phase systems. Thus, we obtained the CO₂-Fq gas-phase reference energies at specific points on the P-T diagram by applying the ideal gas law, Equation 9, and the minimized energy of the isolated molecule at 0K:

\[ S = S^0 - R \ln(P/P_0) \]

\[ E = E_{\text{min}} + E_{\text{kinetic}} + C_p(T - T_0) \]  

(9)

where the \( S^0 \) is the ideal gas entropy at 1atm, \( E_{\text{min}} \) is the minimum energy of the system at 0 K, \( E_{\text{kinetic}} \) is the kinetic energy (temperature correction), and \( C_p \) is the constant pressure heat capacity correction.

2.2.9. Determination of the Phase Boundaries

We obtained the phase boundaries by explicitly considering the per-molecule Gibbs energy (i.e. the chemical potential \( \mu \) for a single component system: \( \mu(T, P) = g = G/N \)) of the respective phases at specific points in the P-T diagram. The most stable phase was determined to be the one with the lowest chemical potential. We employed a multi-resolution approach to efficiently obtain the phase diagram: initial simulations were performed on a coarse sampling of the P-T space. At specific pressures, once a phase transition was detected, we first approximated the location of the phase transition temperature(s) by linear interpolation between adjacent points, followed by further simulations around this temperature in smaller temperature increments. Critical points were treated as special cases, as detailed below.

2.2.10. Determining the Critical Point from the Vapor-Liquid Coexistence curve

A variety of approaches can be used to determine the critical point, such as the discontinuity of constant pressure heat capacity, \( C_p \)[59] or the discontinuity in relaxation times[60]. In this work, we determine the critical point via the VLE curve, [61] exploiting the fact that as the density increases, the temperature at VLE conditions will increase initially and further decrease, with the turnover point being the critical temperature.
3. RESULTS AND DISCUSSION

3.1 Spectral Density function of CO₂

We first tested the convergence of the 2PT method for describing the thermodynamics of CO₂, by considering the VAC function. Normally, for a solid, liquid, or saturated-vapor system, the VAC function converges to zero on the timescale of a few picosecond. A low-density gas, on the other hand, requires longer convergence times, due to the low collision probability between molecules. Figure 1 presents the VAC function of CO₂ described by the FEPM2 and CO₂-Fq models, where we find convergence times of ~ 20ps for the solid and liquid systems and ~ 500ps for the gas. This result validates our computational approach, where the sampling windows (200ps and 2ns respectively) are several factors greater than these typical correlation times.

![Graphs showing VAC function for FEPM2 and CO₂-Fq models for solid/liquid and gas systems](image)

Figure 1 The CO₂ total VAC function of (a) FEPM2 solid/liquid density systems at 240K,100atm, (b) FEPM2 gas density system at 1atm, 250K and (c.) CO₂-Fq solid/liquid density systems at 240K,100atm. The zoomed inset of (c) demonstrates the VAC function details within 0 – 4 ps.

The associated DoS of liquid CO₂ are shown in Figure 2. Here we separately consider the independent motions that contribute to the DoS: translations, rotations and internal vibrations. We apply the 2PT method to the translations and rotations, and separately show the distribution of modes from diffusive (gas-like) and from librational (solid-like) motions. The purely vibrational degrees of freedom at equilibrium are analogous to the non-equilibrium response of the system when excited by Raman and infrared radiation,[62] providing a 1:1 mapping between molecular thermodynamics and spectroscopy. We find that the vibrational spectrum of the solid and liquid phases CO₂ described with the FEPM2 forcefield are in reasonable agreement with the experimental asymmetric and symmetric bond stretching frequencies. However, the FEPM2 angle bending force constant (taken from the work of Trinh at el. [10]), leads to a 60% increase in the O-C-O bond bending frequency, compared to experiments (1102 cm⁻¹ vs 667.38 cm⁻¹, respectively). Additionally, the FEPM2 model is unable to reproduce the Fermi resonance peak, which results from a coupling between the O-C-O angle bending and the C-O bond stretching (i.e. cross terms), observed experimentally. Conversely, we find that the full QM-derived CO₂-Fq model produces improved vibrational properties compared to experiments (Table S3) and remarkably, captures the Fermi resonance, with two peaks at 1278 cm⁻¹ and 1378 cm⁻¹, even though the cross term was not included in the parameterization.
3.2 The Thermodynamic Properties of Carbon Dioxide

3.2.1 Thermodynamics of Crystalline CO$_2$

We now turn our attention to the thermodynamics of crystalline CO$_2$ at low temperatures, which is a more stringent test of the (gas-phase) derived interaction potentials. Specifically, we consider the calculated entropy potential, which we compare to a purely theoretical model computed from empirical parameters (Table S4) and Equation 10:

$$\Delta S = \int dS = \int dH/T - \int VdP/T + \Delta H_{\text{phase-change}}/T_{\text{phase-change}}$$

$$= \int C_p^{G}/T \, dT + \int C_p^{L}/T \, dT + \int C_p^{S}/T \, dT - nR \int dP/P + \Delta H_{\text{vap}}/T_{\text{vap}} + \Delta H_{\text{fus}}/T_{\text{fus}}$$

$$= \int C_p^{G}/T \, dT + \int C_p^{S}/T \, dT - nR \int dP/P + \Delta h_{\text{sub}}/T_{\text{sub}}$$

(10)

where $C_p$ is the constant pressure heat capacity, the superscript $G$, $L$, and $S$ represent gas, liquid and solid, respectively. $\Delta H$ is the phase change enthalpy, the subscript vap, fus, and sub represent vaporization, fusion, and sublimation, respectively. The number of moles of CO$_2$ in a system is denoted by $n$, $R$ is the gas constant, and $P$ is the pressure. We note that the 2PT entropy applies the quantum harmonic oscillator weighting function to each of the (classical) modes, a hybrid approach that produces “quantum” entropies.
in very good agreement with experiment for a variety of liquid systems at ambient conditions [19, 22-26, 63-66]. Of course, the 2PT method is equally applicable to purely solid and gas systems, which are the limiting cases of the theory. We demonstrate this by noting that the fluidicity factors for the crystalline solids are small, as expected, but slowly increasing with increasing temperature.

We find that the calculated entropies are in very good agreement with the theoretical model at low temperatures (Table 3). Overall, the entropy of the CO$_2$-Fq model is larger than FEPM2, reflecting the additional degree of freedom (fluctuating partial atomic charge) in the former. This ultimately leads to an overestimation of the entropy, compared to the thermodynamic model, by $\sim 5 – 10\%$. Encouragingly, the temperature of the translational, rotational, and internal vibrational modes was consistent with the system temperatures, verifying equipartition and thermal equilibration and further validating our computational approach. Indeed, we found that application of a stochastic thermostat (Langevin or GLE) was necessary for proper mode thermal equilibration for these nanosized systems on the nanosecond timescale. Application of deterministic thermostats (Nose-Hoover) required an order of magnitude longer simulation to achieve proper mode equilibration, even though the overall temperature of the system and the per-molecule distribution of total kinetic energy converged in much shorter timescale.

| T [K] | Theoretical entropy [J/mol/K] | FEP2 | CO$_2$-Fq |
|-------|-------------------------------|------|-----------|
|       | T Decomposition from 2PT [K] | 2PT entropy [J/mol/K] | fluidity factor | T Decomposition from 2PT [K] | 2PT entropy [J/mol/K] | fluidity factor |
| 50    | $T_{\text{trans}} = 47.07$ | $S_q = 14.38$ | $f_{\text{trans}} = 0.0327785$ | $f_{\text{rot}} = 0.011844$ | $T_{\text{trans}} = 49.53$ | $S_q = 20.31$ | $f_{\text{trans}} = 0.0033372$ | $f_{\text{rot}} = 0.018596$ |
| 100   | $T_{\text{trans}} = 96.60$ | $S_q = 38.23$ | $f_{\text{trans}} = 0.041886$ | $f_{\text{rot}} = 0.021889$ | $T_{\text{trans}} = 94.21$ | $S_q = 43.94$ | $f_{\text{trans}} = 0.0045095$ | $f_{\text{rot}} = 0.034896$ |
| 150   | $T_{\text{trans}} = 146.21$ | $S_q = 56.4$ | $f_{\text{trans}} = 0.0053767$ | $f_{\text{rot}} = 0.029656$ | $T_{\text{trans}} = 149.59$ | $S_q = 63.96$ | $f_{\text{trans}} = 0.0051085$ | $f_{\text{rot}} = 0.057985$ |

The subscripts of trans, rot, and vib represent the translation, rotation, and vibration modes of 2PT, respectively. $S_q$ is the quantum entropy obtained from 2PT analysis.

As a further check of equilibration, we note that the distribution of C-O bond lengths is normal and can be fit to a Gaussian function with near zero skewness (2nd moment) and kurtosis (3rd moment) (Figure 3).
3.2.2 Carbon Dioxide Thermodynamic properties at Vapor-Liquid Coexistence (VLE) conditions and Critical Point

In Figure 4, we plot the density - temperature relationship of the saturated liquid and saturated vapor systems. The VLE density increases monotonically with temperature until a certain condition (i.e., critical density) is met, after which, the VLE density decreases monotonically with temperature. Thus, along the VLE curve, that saturated vapor becomes more liquid-like and saturated liquid becomes more gas-like as they approach the critical point. In fact, we note that besides the density - temperature characteristics at the VLE condition, the 2PT fluidicity-factor (f-factor) can be used to determine the critical point. This is demonstrated in Figure 4b for the FEPM2 model, where we find that the turning point of the curves (infinite slope) is in excellent agreement with the critical point determined from the density. At this point, the system can be described as equally liquid-like and gas-like, and the separate phases become indistinguishable.
Figure 4 a) The density – temperature relationship along the VLE curve and the critical point of CO₂ simulated with the FEPM2 and CO₂-Fq models (solid data points). Dashed curves are cubic spline fits to the calculated data. b) The translational (trans) and the rotational (rot) fluidicity factors of FEPM2 model along the VLE curve.

Based on the results in Figure 4, we calculate a critical temperature ($T_c$) and a critical density ($\rho_c$) $T_c=303.1$ K, $\rho_c=10.133$ mol/l for the FEPM2 model. This can be compared to Harris et al.’s work [61] ($T_c = 313.4$ K and $\rho_c = 10.31$ mol/l) for the original rigid EPM2 model. Further, we calculate $T_c=302.5$ K, $\rho_c=9.9883$ mol/l for the CO₂-Fq model. Both are in a good agreement with NIST database values ($T_c=304.18$ K, $d_c=10.6$ mol/l). Detailed 2PT simulated data and experimental values are shown in Table S5.

3.3 The Carbon Dioxide Phase Diagram based on phase stability and the 2PT method

As previously elaborated, we constructed the phase diagram by explicitly considering the Gibbs energy of the isolated phases at specific points on the P-T diagram. Such an approach is only possible due to the ability to compute the absolute entropy of the phases from short MD simulations using the 2PT method. This last point is important, since near the phase boundaries, we can expect significant fluctuations in the thermodynamic potentials over long-term dynamics. In fact, for 1st order phase transitions, the Gibbs energy function is discontinuous near the phase boundary. In Figure 5 we plot the Gibbs energy, entropy and enthalpy of liquid/solid systems for both FEPM2 and CO₂-Fq models as a function of temperature at 100atm, showing the system transitions from a solid ($G^S < G^L$) to a liquid ($G^S > G^L$). We note that the FEPM2 enthalpies are computed with quantum (zero-point energy) corrections, while CO₂-Fq enthalpies exclude the quantum corrections for consistency with the gas phase reference.

We found that the fluctuations in the Gibbs energy were larger in the FEPM2 forcefield compared to CO₂-Fq, which led to larger uncertainties in the relevant phase boundaries. For example, at 100atm we were unable cleanly resolve the melting temperature ($T_m$) of the FEPM2 model by inspection, and instead had to determine $T_m$ by fitting to a cubic interpolation function, resulting in $T_m = 232 \pm 5$ K. The thermodynamics of the isolated phases are more well behaved in CO₂-Fq and the predicted $T_m = 217 \pm 1$ K is much better agreement with the experimental value of 218.6 K. Overall, we find a closer agreement with the experimental phase boundaries with the CO₂-Fq forcefield, especially in the high-pressure regime, which we attribute to an improved description of the repulsive inner wall by application of UNB nonbond potential over the Lennard Jones 12-6 potential in FEPM2.
**Figure 5** The thermodynamics of CO$_2$ described by the FEPM2 and CO$_2$-Fq models at 100 atm as the system undergoes a 1st order phase transition. The FEPM2 total Gibbs energy (a), the separate entropy (b), and enthalpy (c) contributions, and the CO$_2$-Fq total Gibbs energy (d), the separate entropy (e), and enthalpy (f) contributions are shown. The dashed green line and dashed blue line represent the fitted lines in determining the phase transition temperatures via interpolation (CO$_2$-Fq) and extrapolation (FEPM2). The dashed black lines demonstrate the simulated phase changes – FEPM2 of 232 K and CO$_2$-Fq of 217 K, which can be compared to the experimental value of 218.6 K - shown as the dashed gray lines.

In Figure 6 we present the entire phase diagram of CO$_2$, where the phase boundaries are taken as the points in P-T space where the phases have equal chemical potentials. Here again, we note that the larger fluctuations in the Gibbs energy of FEPM2 obscures exact determination of the phase boundaries, and so we apply to interpolation scheme employed in the previous section and considered two (or more) phases to have the same chemical potentials if the difference in the Gibbs energies ($\Delta G$) are within 5%. In the case of the CO$_2$-Fq model, we were able to resolve the phase boundaries with a much more stringent condition $\Delta G < 0.3\%$. 
Figure 6 The CO2 phase diagram, based on the Gibbs energy of the isolated solid, liquid and gas phases, using the FEPM2 (a) and the CO2-Fq (b) models. The superscript * means the ΔG is smaller than 5% between solid/liquid (S/L*), solid/gas (S/G*) or liquid/gas (L/G*) systems for the FEPM2, and smaller than 0.3% for the CO2-Fq model. The dashed blue curves are the simulated phase boundaries of FEPM2 and CO2-Fq models. The experimental reference is from the Global CCS Institute (solid black lines).

Overall, we find improved prediction of the phase diagram using the CO2-Fq model, compared to experiments. In addition to the improved van der Walls interaction mentioned previously, the additional charge degree of freedom in CO2-Fq leads to more a more accurate representation of the intermolecular physics by facilitating additional instantaneous dipole interactions that stabilizes the liquid. We also obtained encouraging results when considering the triple point. Our interpolation procedure yields an approximate triple point temperature ($T_t$) and the triple point pressure ($P_t$) of $T_t = 218.0 \pm 5.0$ K, $P_t = 8.2 \pm 1.1$ atm using the FEPM2 model and $T_t = 216.2 \pm 3.0$ K, $P_t = 5.5 \pm 0.5$ atm using the CO2-Fq model, both in good agreement with the experimental values from the NIST database: $T_t = 216.6$ K, $P_t = 5.12$ atm. Here again, the CO2-Fq model led to marked improved results compared to experiments, over FEPM2. While these results are indeed encouraging, we note that one potential limitation of the current approach is that stabilization of the isolated phases near the phase boundaries is rather difficult, even on the relatively short timescale of the 2PT trajectories. We overcome this here by interpolation near the phase boundaries, however this introduces some additional uncertainties in our calculations.

4. CONCLUSIONS AND OUTLOOK

In this work, we employed a fixed atom-charge model FEPM2 and a QM-derived fluctuating charge model CO2-Fq to calculate the phase diagram of CO2 from equilibrium MD simulations of the isolated phases and the 2PT method. We find that relatively short trajectories (~ 200ps) are sufficient for capturing the thermodynamics of the solid and liquid phases, while the gas phase require longer windows (~ 2ns). This means that the entire phase diagram was obtained from MD simulations on the ns timescale, and since the 2PT method does not incur any appreciable extra computational cost, this presents a rather efficient approach for determining phase diagram. Overall, the FEPM2 model predicts the phase behavior thermodynamics in reasonable agreement with experiments, especially at low temperatures and pressures. At higher pressures, the inability of the Lennard Jones 12-6 potential to adequately represent the repulsive Pauli forces and the inability to model charge renormalization within the molecule leads to larger deviations. The CO2-Fq thus improves on the FEPM2, by including the many body QM physics, leading to excellent agreement with experiments over the entire phase diagram. This improved description may be important for study CO2 in extreme environments, such as the controversial high pressure polymeric
phase [67, 68] and its associated thermodynamics.

This work provides an efficient approach for calculating phase diagrams, which should be applicable to arbitrary systems. We are currently applying to approach to study other homogeneous liquids, including water. Considerations of multi-component systems are a natural extension, and insights into the behavior of the separate entropic and enthalpic functions are currently being explored.

5. Supplementary Materials

See the supplementary material for complete information description of the 2PT and QEq methods and well as various tabulated energies in Tables S1 – S5.

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