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Vapor–Liquid Interfacial Properties of CO₂ Mixtures for Sequestration Applications: Molecular Simulations, Classical Density Functional Theory, and Equations of State

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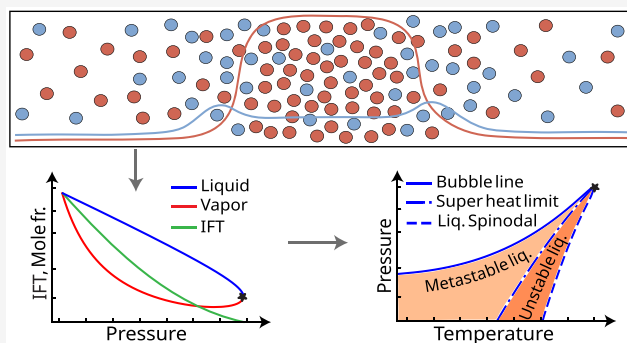


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Supporting Information

ABSTRACT: Experimentally determining interfacial tension (IFT) for compositions relevant to CO₂ transport is challenging. We address this using molecular dynamics (MD) simulations and perturbed-chain statistical associating fluid theory (PC-SAFT) equation of state with classical density functional theory. We compute phase equilibria and interfacial properties of pure CO₂ and CO₂–CH₄, CO₂–Ar, CO₂–N₂, and CO₂–H₂ mixtures at 220–273 K. Both approaches accurately estimate CO₂ phase equilibria and IFTs. For binary mixtures, phase equilibria computed using PC-SAFT agree well with experiments when $k_{ij} \neq 0$. IFTs computed from PC-SAFT depend strongly on k_{ij} , while MD simulations systematically overpredict IFTs. The IFT decreases with increasing pressure, least pronouncedly for H₂-containing mixtures. Binary mixtures exhibit interfacial enrichment of the light boiling component, decreasing with increasing temperature and pressure. Semiempirical Parachor and Winterfeld–Scriven–Davis models capture IFT–pressure trends with mixture-dependent accuracy. These results improve predictions of metastable limits and provide key insights for fast-transient multiphase CO₂ flow modeling.



1. INTRODUCTION

Carbon dioxide CO₂ is a major greenhouse gas that drives global warming.^{1,2} Carbon capture and storage (CCS) has become an essential process to reduce CO₂ emissions.^{3,4} Efficient transportation of CO₂, either by pipelines or ships, plays a central role in connecting capture facilities with storage reservoirs.⁵ The CO₂ obtained from capture processes is rarely pure and its composition depends on the capture technology and the source stream, often carrying trace components from flue gas or syngas.⁶ Major impurities present in the CO₂ streams are noncondensable impurities such as Ar, N₂, H₂, and CH₄.^{7–11} These impurities can affect phase stability. For economic transportation, CO₂ streams must be maintained in a dense single phase.^{12–14} This requirement is particularly challenging during transient operations, where pressure and temperature fluctuate and impurities can shift the phase boundaries.^{6,15} While steady-state operation targets a dense phase, systems often encounter startup, shutdown, depressurization, and planned maintenance, which can lead to the occurrence of two-phase flows in CO₂ transportation systems.¹⁶ At such conditions, accurate knowledge of the thermodynamic and transport properties of impure CO₂ mixtures becomes indispensable for modeling their flow and phase behavior.^{6,17}

Experimental determination of thermodynamic and transport properties for multicomponent mixtures is costly and time-consuming, resulting in limited and scarce experimental data for impure CO₂ mixtures.^{6,18–20} In addition to experimental measurements for these systems, molecular simulations with classical force fields have proven to be a powerful tool for computing thermodynamic and transport properties.^{21–24} Experiments and molecular simulations are complemented by models such as Equation of State (EoS),^{25–28} Extended Corresponding States (ECS),²⁹ friction theory,³⁰ and other empirical correlations.^{31–33} For instance, Lasala et al.³⁴ measured the phase equilibria of CO₂–N₂, CO₂–Ar, and CO₂–O₂ binary mixtures at 218–253 K and pressures up to 160 bar, and successfully modeled the phase equilibria with Peng–Robinson (PR) and Soave–Redlich–Kwong (SRK) cubic EoS using advanced mixing rules. In our previous study,²¹ we performed Monte Carlo (MC) and Molecular Dynamics (MD) simulations of multicomponent

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CO₂ mixtures to compute densities, thermal expansion coefficients, isothermal compressibilities, heat capacities, Joule-Thomson coefficients, speed of sound, and viscosities at 235–313 K and pressures between 20 and 200 bar, and compared with the GERG-2008 EoS.²⁷ In addition to bulk thermodynamic and transport properties, interfacial properties of CO₂ mixtures have also been investigated in numerous studies.^{35–39} To illustrate a few, Chow et al.³⁷ measured interfacial tensions of H₂O + H₂ and H₂O + H₂ + CO₂ mixtures at 298–448 K and pressures up to 450 bar and developed empirical correlations to calculate IFTs. In a previous study, Chow et al.³⁵ measured IFTs of H₂O + CO₂, H₂O + Ar, H₂O + N₂, H₂O + CO₂ + N₂, and H₂O + CO₂ + Ar mixtures at 298–473 K and pressures up to 600 bar and compared with Statistical Associating Fluid Theory (SAFT)-VR Mie EoS^{40,41} in combination with Square Gradient Theory (SGT).^{42–44} The SAFT-VR Mie EoS^{40,41} combined with SGT^{42–44} predicted IFTs for systems containing H₂O, CO₂, Ar, and N₂ in good agreement with experiments. Numerous studies have measured IFTs of binary and ternary systems such as CO₂–water,^{35,37–39} CO₂–brine,³⁶ H₂O–dilute gases (N₂, Ar, and H₂)³⁷ and CO₂–hydrocarbon mixtures,⁴⁵ and compared with theoretical models such as classical Density Functional Theory (cDFT),^{46–49} Density Gradient Theory (DGT),^{43,50} SGT,^{42–44} Linear Gradient Theory (LGT),⁵¹ and the Parachor model^{52,53} in combination with EoS. Most of these studies have focused on reservoir-relevant systems where water is the dominant component in the system. IFTs of pipeline-relevant mixtures have been scarcely investigated, where H₂O concentrations must remain below 500 ppm to prevent hydrate formation and corrosion inside CO₂ transportation systems.^{11,54} Experimental and molecular simulation data on IFT for binary CO₂ mixtures containing dilute gases are extremely limited. To the best of our knowledge, the only available study is by Schenk et al.,⁵⁵ in which IFTs of CO₂–CH₄ mixtures at 223–233 K and 20–60 bar were computed using both experiments and molecular simulations, and good agreement was found between the two approaches.

The vapor–liquid interfacial tension (IFT) is an important property in governing bubble stability, droplet formation, and interphase heat and mass transfer^{56–59} in CO₂ transportation systems. For example, during depressurization of a CO₂-rich mixture through valves or nozzles, the liquid or dense-phase CO₂-rich stream may experience a delayed phase change and remain in a metastable state instead of vaporizing spontaneously.^{60,61} In Computational Fluid Dynamics (CFD) simulations, neglecting this delayed phase change leads to inaccurate predictions of mass flow rates and pressure, which in turn results in incorrect evaluation of forces on pipelines and the associated risk of Running Ductile Fracture (RDF).^{54,62} Phase change delay is modeled in CFD simulations by estimating the metastable limits of the fluid.^{60,63} These states exist between the binodal (saturation line) and the theoretical thermodynamic limit of stability, known as the spinodal.⁵⁷ Beyond the spinodal, the fluid can no longer remain metastable, and phase separation occurs spontaneously (unstable regime).^{56,57} In practice, however, phase change typically sets in earlier than the spinodal, at the so-called Superheat Limit (SHL) for liquids and Supercool Limit (SCL) for vapors, which represent practical metastable limits.⁶⁰ Phase transitions in these metastable regions occur via either homogeneous or heterogeneous nucleation.^{56,57,61} Heterogeneous nucleation is facilitated by surfaces and impurities, and

its rate is strongly affected by geometrical factors such as the surface roughness.^{56,57} It is typically represented in models through empirical correlations tailored to the system geometry.^{56,57} Homogeneous nucleation arises within the bulk fluid and is commonly described using Classical Nucleation Theory (CNT).^{54,60,63,64} In CNT, the nucleation rate is expressed in an Arrhenius form, with the free energy barrier for forming a critical nucleus (bubble or droplet) evaluated using the capillarity approximation, which assumes that the IFT of a curved interface is equal to that of the planar interface.⁵⁶ The SHL and SCL are then estimated by applying a nucleation rate criterion, namely by identifying the conditions at which CNT predicts that at least one critical nucleus forms within the system volume over the relevant observation time.⁵⁶ Since this estimation relies strongly on the accuracy of IFT data,⁵⁴ reliable prediction of both IFTs and metastability limits is essential for modeling the multiphase flow behavior in CO₂ transport systems.

In this study, we computed the vapor–liquid interfacial properties of pure CO₂ and four binary mixtures, namely CO₂–N₂, CO₂–Ar, CO₂–CH₄, and CO₂–H₂ using MD simulations, the Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) EoS combined with the cDFT,⁵⁵ and semiempirical models.^{33,52,66} To compute IFTs of pure components, the Guggenheim–Katayama equation^{33,67,68} were used. The Parachor^{52,53} and Winterfeld–Scriven–Davis (WSD)^{66,69} models were used to compute IFTs of binary mixtures. To quantify the effect of impurities, the computed IFTs of the binary mixtures were compared with those of pure CO₂. The IFTs obtained from semiempirical models were then used with phase equilibria to estimate the SHL and SCL for both pure CO₂ and the CO₂ binary mixtures using the CNT. Using this approach, phase equilibria, IFT, and metastable limits are examined by combining EoS based methods, cDFT, and MD simulations. This enables the influence of impurities on SHL and SCL to be quantified through direct comparison with pure CO₂ superheat and supercool limits. This study presents a comprehensive evaluation of models for computing IFTs, ranging from molecular simulations to simplified theoretical approaches, with direct relevance to CO₂ transport systems.

The manuscript is organized as follows: the methodology used to compute phase equilibria and IFTs using MD simulations, PC-SAFT EoS with the cDFT, and semiempirical models are explained in Section 2. In Section 3, we present the validation and the results of the computed phase equilibria and IFTs of pure CO₂ and binary CO₂ mixtures. We also analyze the effect of impurities on IFT and report the IFTs obtained from the Parachor and WSD models. In Section 4, our key findings are summarized.

2. METHODOLOGY

2.1. MD Simulation

MD simulations were performed with the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS: version August 2024) package⁷⁰ to compute IFTs of pure CO₂ and CO₂ mixtures with CH₄, N₂, Ar, and H₂ as impurities. The TraPPE^{71,72} force fields were used to model CO₂ and CH₄. N₂ and H₂ are simulated using force fields of Vrabec et al.⁷³ and Köster et al.,⁷⁴ respectively. The force field from García-Pérez et al.⁷⁵ was used for Ar. CO₂ and N₂ are represented by three-site and two-site flexible models, respectively. For CO₂, bond-

stretching and angle-bending terms were included to make the TraPPE⁷¹ force field fully flexible, with parameters adopted from Perez-Blanco and Maginn.⁷⁶ The bond-stretching parameter for N₂ was taken from Wang et al.⁷⁷ Force fields of H₂, Ar, and CH₄ are described by single-site models consisting of one Lennard–Jones (LJ) interaction site with no point charges. The force field parameters of CO₂, Ar, N₂, H₂, and CH₄ are listed in the Section S1 of the Supporting Information. Intermolecular interactions were modeled by a pairwise-additive 12–6 Lennard–Jones (LJ) potential combined with long-range Coulombic interactions. The corresponding total potential energy U of the system is given as^{78,79}

$$U = \sum_{i=1}^{N-1} \sum_{j=i+1}^N \left(4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right) + \sum_{\text{bonds}} k_r (r - r_0)^2 + \sum_{\text{angles}} k_\theta (\theta - \theta_0)^2 \quad (1)$$

where N denotes the number of atoms, ϵ_{ij} is the LJ energy parameter between atoms i and j , σ_{ij} is the LJ size parameter between atoms i and j , q_i and q_j are the partial charges of atoms i and j , respectively. ϵ_0 is the permittivity of free space. k_r and k_θ are the bond and angle force constants. r and θ are the bond length and bond angle. r_0 and θ_0 are the equilibrium bond length and equilibrium value of the angle. The first term in eq 1 corresponds to van der Waals interactions (intermolecular), and the second term represents Coulombic interactions (intermolecular). The third and fourth terms describe bond stretching and angle bending, modeled using harmonic potentials. For dissimilar atom pairs, the Lorentz–Berthelot (LB)^{78,79} mixing rules were used

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) \quad (2)$$

$$\epsilon_{ij} = (1 - k_{ij})(\epsilon_{ii}\epsilon_{jj})^{1/2} \quad (3)$$

where the indices ii and jj denote interactions between atoms of the same type, while ij refers to cross interactions between atoms of different types. k_{ij} is the binary interaction parameter of components i and j . In MD simulations, binary interaction terms were set to zero, $k_{ij}^{\text{MD}} = 0$.

The equations of motion were integrated using the velocity-Verlet algorithm with a time step of 0.5 fs.⁸⁰ A cutoff radius of 16 Å was used for the short-range LJ and long-range Coulombic interactions. Since this value exceeds $5\sigma_{\text{CO}_2}$, no tail corrections were applied for energy and pressure.⁸¹ This choice ensures an appropriate treatment of system inhomogeneity while maintaining MD simulations within an acceptable computational time. Long-range electrostatic interactions were handled using the Particle–Particle–Mesh (PPPM) method with a relative accuracy of 10^{-5} .^{78,82} To compute the vapor–liquid IFT, simulations were carried out in a parallelepiped box containing a liquid slab at the center with vapor regions on either side⁸³ as shown in Figure 1. The z -axis was chosen as the elongated dimension (normal to the vapor–liquid interface), with $L_x = L_y = 40$ Å, while L_z was varied between 5 and 25 times L_x , depending on liquid and vapor phase densities. The liquid slab thickness ranged from 80 to 120 Å, and periodic boundary conditions were applied in all directions. Temperature and pressure were controlled using a Nosé–Hoover thermostat and barostat^{78,84,85} with coupling

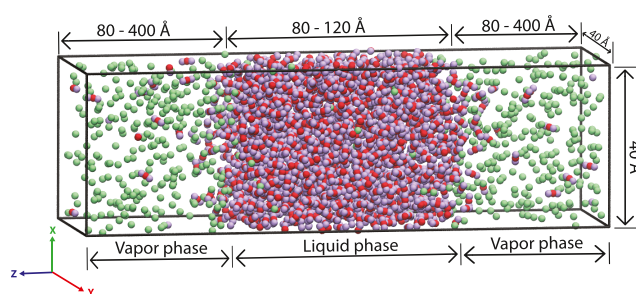


Figure 1. Schematic representation of the MD simulation box used in this study to compute phase equilibria and interfacial properties of pure CO₂ and binary CO₂ mixtures. For pure CO₂, the simulation box dimensions were fixed at $L_x = L_y = 40$ Å and $L_z = 240$ Å, as the simulations were performed in the NVT ensemble. For binary mixtures, L_x and L_y were fixed, while L_z was allowed to vary since the simulations were conducted in the NPT ensemble. The example shown here illustrates the CO₂–H₂ mixture at 220 K and 100 bar. The visualization was rendered in orthographic view using the Visual Molecular Dynamics (VMD) software.¹²⁶

constants of 0.1 and 1 ps, respectively. Initial configurations were generated in LAMMPS using liquid and vapor densities calculated from the multiparameter Helmholtz EoS of Span and Wagner²⁶ for pure CO₂ and the GERG-2008²⁷ multiparameter Helmholtz EoS for binary CO₂ mixtures, as implemented in the REFPROP v10.⁸⁶ According to the Gibbs phase rule,⁸⁷ a pure component system is characterized by a single independent thermodynamic variable, whereas a binary system requires two. In this study, IFTs of pure CO₂ were computed as a function of temperature with $N = 2000$ –2500 molecules. For CO₂ mixtures IFTs were evaluated as functions of temperature and pressure with $N = 2500$ –4000 molecules. Each simulation consisted of a 7–10 ns equilibration run followed by a 40 ns production run in the NVT ensemble for computing the IFTs of pure CO₂. For CO₂ mixtures, an equilibration run of 10–15 ns followed by a production run of 50–60 ns was performed in the $NAP_{zz}T$ ensemble for each simulation. In this ensemble, the interfacial area $A = L_x L_y$ is kept fixed, while the z -dimension of the simulation box is allowed to fluctuate to maintain a stable interface in the xy plane.⁸³

The IFT of a system is computed either from the ensemble-averaged diagonal components of the pressure tensor over the entire simulation box or from pressure profiles as a function of the z -coordinate. In this study, the ensemble-averaged diagonal pressure tensor components computed over the whole volume of the simulation box were used to calculate IFTs, where the IFT (γ) is given by

$$\gamma = \frac{\langle L_z \rangle}{2} \left[\langle P_{zz} \rangle - \frac{\langle P_{xx} \rangle + \langle P_{yy} \rangle}{2} \right] \quad (4)$$

The brackets $\langle \dots \rangle$ denote an ensemble average. $\langle P_{xx} \rangle$ and $\langle P_{yy} \rangle$ are the ensemble-averaged tangential components of the pressure tensor, while $\langle P_{zz} \rangle$ is the ensemble-averaged normal component. All components are evaluated over the entire simulation box volume with $\langle P_{zz} \rangle$ corresponding to the saturation pressure. $\langle L_z \rangle$ represents the box length averaged in the NPT ensemble and is used to compute the IFTs of binary systems. For pure systems, L_z is fixed (constant value) since simulations are performed in the NVT ensemble. As an

alternative to eq 4, IFTs of pure and binary systems can be computed using the Irving–Kirkwood formulation^{83,88}

$$\gamma = \frac{1}{2} \int_{-\infty}^{+\infty} \left[\langle P_{zz}(z) \rangle - \frac{\langle P_{xx}(z) \rangle + \langle P_{yy}(z) \rangle}{2} \right] dz \quad (5)$$

$\langle P_{xx}(z) \rangle$, $\langle P_{yy}(z) \rangle$, and $\langle P_{zz}(z) \rangle$ denote the ensemble-averaged pressure tensor profiles as a function of z -coordinate. To compute these profiles, the simulation box was divided into 100 to 300 bins along the z -coordinate. The factor of 2 in eqs 4 and 5 accounts for the two interfaces present in the simulation box. Equations 4 and 5 yield identical IFTs for a given thermodynamic state, and this has been verified for pure CO₂ in Section S5 of the Supporting Information. The same binning approach was also applied to calculate the density profiles, $\rho(z)$, along the z axis. The bulk liquid density (ρ^L) and vapor density (ρ^V) were computed by fitting $\rho(z)$ to the following hyperbolic tangent function⁸³

$$\rho(z) = \rho^V + \frac{\rho^L - \rho^V}{2} \left[\tanh\left(\frac{z - z_R}{D}\right) - \tanh\left(\frac{z - z_L}{D}\right) \right] \quad (6)$$

where z_R and z_L denote the position of the vapor–liquid interface (Gibbs-dividing surface) on the left and right sides.⁸³ D is the interface width, and it is related to the 10/90 effective interfacial thickness (L_{10}^{90}) definition proposed by Lekner and Henderson⁸⁹ via the relation $L_{10}^{90} \approx 2.19D$.⁸¹ The parameter L_{10}^{90} is defined as the distance between the positions where the local density reaches 10% and 90% of the bulk density differences

$$L_{10}^{90} = z(\rho_{90}) - z(\rho_{10}) \quad (7)$$

$$\rho_{10} = \rho^V + 0.1(\rho^L - \rho^V) \quad (8)$$

$$\rho_{90} = \rho^V + 0.9(\rho^L - \rho^V) \quad (9)$$

Computing bulk densities of binary mixtures by fitting the density profiles $\rho_i(z)$ to eq 6 can be inaccurate due to the interfacial enrichment near the interface.⁹⁰ To overcome this limitation, we used a plateau-detection method. In this approach, the spatial derivative of the average $\rho_i(z)$ is evaluated as a function of the z coordinate. Bulk regions are identified as plateaus where the derivative $d\rho/dz$ remains close to zero within a relative tolerance of 10^{-5} , corresponding to constant density in either the vapor or liquid phase. By isolating and averaging these plateau regions, the saturated vapor and liquid densities are obtained without being biased by possible interfacial enrichment. The computed bulk densities were used to calculate the mass fractions of the liquid and vapor phases.⁹⁰ For a binary mixture with components $i = 1, 2$, the mass fraction w_i^k of component i in phase k is defined as

$$w_i^k = \frac{\rho_i^k}{\sum_{j=1}^2 \rho_j^k}, \quad k \in \{L, V\} \quad (10)$$

where ρ_i^k is the bulk density of component i in phase k . The mole fractions were obtained from the liquid and vapor mass fractions using

$$x_i^L = \frac{w_i^L/M_i}{\sum_{j=1}^2 w_j^L/M_j}, \quad y_i^V = \frac{w_i^V/M_i}{\sum_{j=1}^2 w_j^V/M_j} \quad (11)$$

where M_i is the molar mass of the component i .

2.2. Classical Density Functional Theory + PC-SAFT

The interfacial properties of pure CO₂ and CO₂ mixtures were computed using the FeO_s v0.8 framework,⁶⁵ in which EoS models are integrated with cDFT. EoS models are used to compute thermodynamic properties of homogeneous phases (phase equilibria),^{18,19} but the modeling of inhomogeneous systems with density gradients, such as fluid interfaces, is not possible.^{17,91} By coupling EoS with cDFT, the FeO_s⁶⁵ approach enables the modeling of spatial inhomogeneities. In cDFT, the liquid–vapor interface is represented as a mesoscopic region where the density smoothly varies from the bulk liquid to the bulk vapor value.^{49,65} The theory is formulated by expressing the grand potential as a functional of the density profile, which incorporates both ideal and nonideal interaction contributions.^{49,65} The equilibrium density profile is then obtained by minimizing this functional, i.e., by setting its functional derivative with respect to the density to zero, which enforces a constant chemical potential across the interface.^{49,65} Once the equilibrium profile is known, interfacial properties such as density gradients, interfacial thicknesses, and IFTs can be directly computed.^{49,65} In this study, the PC-SAFT^{28,92} was used as the EoS model. The PC-SAFT EoS is a molecular based approach that represents fluids as chains of spherical segments and accounts for dispersion and association interactions. For pure CO₂ and binary CO₂ mixtures, a simplified PC-SAFT EoS formulation without explicit quadrupolar contributions was employed. In this formulation, quadrupolar effects are implicitly implemented through fitting of the pure component PC-SAFT parameters to experimental data.⁹³ This simplified treatment may contribute to deviations in the predicted critical properties.⁹⁴ For more details regarding the cDFT and PC-SAFT EoS, the reader is referred to refs^{46–49,92}

The phase equilibria of pure CO₂ and CO₂ binary mixtures were computed using the PC-SAFT EoS.^{28,92} For binary mixtures, the optimized binary interaction parameters, k_{ij} , were required in the Lorentz–Berthelot (eq 3) mixing rules to accurately model the experimental vapor–liquid equilibrium (P_{xy}) data available in the literature.^{34,95–100} In FEO_s,⁶⁵ the optimization was carried out by adjusting k_{ij} using nonlinear least-squares minimization, where the calculated equilibrium pressures and compositions were fitted to reproduce the experimental data. The quality of each fit was evaluated through the Mean Absolute Percentage Deviation (MAPD), defined as

$$\text{MAPD} = \frac{1}{N} \sum_{n=1}^N \left| \frac{q_n^{\text{EoS}} - q_n^{\text{exp}}}{q_n^{\text{exp}}} \right| \times 100\% \quad (12)$$

where q denotes the target property (pressure, composition distance, or chemical potential) and N is the total number of data points. The k_{ij} value corresponding to the lowest MAPD was selected and used in the FEO_s framework to compute IFTs of CO₂ mixtures. The PC-SAFT parameters of CO₂, CH₄, N₂, Ar, and H₂ used to compute P_{xy} diagram, IFTs are listed in Section S2 of the Supporting Information.

2.3. Parachor Model

IFTs of pure fluids were evaluated using the Guggenheim–Katayama equation^{33,86,101,102} (as implemented in the REFPROP v10 program by the National Institute of Standards and Technology) expressed as

$$\gamma(T) = \sum_{i=0}^{k-1} s_i \left(1 - \frac{T}{T_c}\right)^{n_i} \quad (13)$$

where k denotes the total number of summation terms, s_i and n_i are fluid specific coefficients, and T_c is the critical temperature of the pure component.^{67,68} The fluid-specific parameters k , s_i , n_i , and T_c used in this study were taken from the works of Cachadiña et al.⁶⁷ and Mulero et al.,⁶⁸ which are listed in Section S3 of the Supporting Information. IFTs of mixtures (γ_{mix}) was calculated using the Parachor model,^{52,53,103,104} expressed as

$$\gamma_{\text{mix}} = \left(\rho_{\text{mix}}^L \sum_{j=1}^N \sum_{i=1}^N x_i x_j \mathcal{P}_{ij} - \rho_{\text{mix}}^V \sum_{j=1}^N \sum_{i=1}^N y_i y_j \mathcal{P}_{ij} \right)^n \quad (14)$$

with the cross-Parachor term defined as

$$\mathcal{P}_{ij} = (1 - \delta_{ij}) \frac{\mathcal{P}_i + \mathcal{P}_j}{2} \quad (15)$$

where N is the number of components in the mixture, n is the exponent constant of the Parachor model ($n = 3.87$),^{53,86} ρ_{mix}^L and ρ_{mix}^V are the liquid and vapor phase densities of the mixture in mol/cm³, and x_i and y_i denote the mole fractions of component i in the liquid and vapor phases, respectively, $\mathcal{P}_i$ is the Parachor number of component i , and δ_{ij} represents the binary interaction parameter of the Parachor model.^{53,86} The parameter $\mathcal{P}_i$ is obtained from the relation

$$\gamma^{1/n} = \mathcal{P}_i (\rho^L - \rho^V) \quad (16)$$

where ρ^L and ρ^V are the liquid and vapor densities of the pure fluid, expressed in mol/cm³, at the mixture temperature (T_{mix}), and γ is the pure fluid IFT computed using eq 13. For numerical stability, if $T_{\text{mix}} > 0.9 \times T_c$, $\mathcal{P}_i$ is computed at $0.9 \times T_c$ following the approach implemented in REFPROP v10.⁸⁶ The calculation of IFTs using the Parachor model requires the EoS⁵³ to compute the necessary thermodynamic properties, including ρ^L , ρ^V , $\mathcal{P}_i$, x , and y . In this study, the GERG-2008 EoS²⁷ was used to obtain these properties.

2.4. Winterfeld–Scriven–Davis (WSD) Model

The Winterfeld–Scriven–Davis (WSD) model presents an approximate theory for determining the planar interfacial tension of multicomponent, polyatomic fluids.⁶⁶ It extends the Fowler–Kirkwood–Buff framework by Kirkwood, Buff and Fowler^{88,105} by simplifying the rigorous statistical-mechanical expression for calculating IFT through the assumption of pairwise additive intermolecular potentials.^{66,88,105} The WSD model provides a practical approach for estimating IFTs of nonaqueous mixtures using IFTs of pure components and can be generalized to multicomponent systems as

$$\gamma_{\text{mix}} = \sum_{\alpha,\beta} \left(\frac{\rho_{\alpha}^L - \rho_{\alpha}^V}{\rho_{\alpha}^{0,L} - \rho_{\alpha}^{0,V}} \right)^2 \gamma_{\alpha}^0 \delta_{\alpha,\beta} + \Phi_{\alpha,\beta} \left[\left(\frac{\rho_{\alpha}^L - \rho_{\alpha}^V}{\rho_{\alpha}^{0,L} - \rho_{\alpha}^{0,V}} \right) \left(\frac{\rho_{\beta}^L - \rho_{\beta}^V}{\rho_{\beta}^{0,L} - \rho_{\beta}^{0,V}} \right) \right] \sqrt{\gamma_{\alpha}^0 \gamma_{\beta}^0} \quad (17)$$

where γ_{mix} is the interfacial tension of the mixture, indices α and β labels for the chemical components in the mixture, and the summation in eq 17 runs over all component pairs ($\alpha, \beta = 1, 2, \dots, N$). The parameters γ_{α}^0 and γ_{β}^0 represent IFTs of pure

components α and β , respectively. Similarly, $\rho_{\alpha}^{0,L}$, $\rho_{\alpha}^{0,V}$, $\rho_{\beta}^{0,L}$, and $\rho_{\beta}^{0,V}$ correspond to the equilibrium liquid and vapor molar densities in mol/cm³ of the pure components α and β , respectively. The parameters ρ_{α}^L , ρ_{α}^V , ρ_{β}^L , and ρ_{β}^V denote the liquid and vapor molar densities of α and β components in the mixture.⁶⁶ The term $\Phi_{\alpha,\beta}$ is the cross-interaction or mixing parameter that accounts for nonideal interactions between dissimilar molecules, and for nonaqueous, weakly polar fluids, $\Phi_{\alpha,\beta} \approx 1$.⁶⁶ The Kronecker delta $\delta_{\alpha,\beta}$ equals one when $\alpha = \beta$ (pure-component contribution) and zero otherwise.⁶⁶

The WSD model provides accurate predictions for nonaqueous mixtures and serves as a reliable semiempirical framework in cases where molecular correlation data are unavailable.^{66,69} However, the formulation becomes less accurate when the mixture temperature exceeds the critical temperature of one or more components present in the mixture. For a binary system, eq 17 equals to

$$\gamma_{\text{mix}} = \left(\frac{\rho_1^L - \rho_1^V}{\rho_1^{0,L} - \rho_1^{0,V}} \right)^2 \gamma_1^0 + \left(\frac{\rho_2^L - \rho_2^V}{\rho_2^{0,L} - \rho_2^{0,V}} \right)^2 \gamma_2^0 + 2\Phi \left[\left(\frac{\rho_1^L - \rho_1^V}{\rho_1^{0,L} - \rho_1^{0,V}} \right) \left(\frac{\rho_2^L - \rho_2^V}{\rho_2^{0,L} - \rho_2^{0,V}} \right) \right] \sqrt{\gamma_1^0 \gamma_2^0} \quad (18)$$

which further reduces to

$$\gamma_{\text{mix}} = \left(\frac{\rho_1^L - \rho_1^V}{\rho_1^{0,L} - \rho_1^{0,V}} \right)^2 \gamma_1^0 \quad (19)$$

when the mixture temperature is higher than the critical temperature of component 2. Equation 19 implies that the supercritical component has no effect on IFT, which is physically unrealistic. In practice, the presence of a supercritical component is expected to decrease the IFT between the liquid and vapor phases of the subcritical component, due to the weakening of cohesive forces between unlike molecules, an effect analogous to that of a surfactant. To account for this behavior, an empirical correction term is introduced in this study, which should decrease IFT as the concentration of the supercritical component increases. The correction factor can be conveniently expressed in terms of the liquid phase mole fraction of the supercritical component as $1 - x_2^L$, where x_2^L is the mole fraction of component 2 in the liquid phase, equivalently given by $x_2^L = \rho_2^L / (\rho_1^L + \rho_2^L)$. The corrected expression for the IFT of a binary mixture is given by

$$\gamma_{\text{mix}} = \left(\frac{\rho_1^L - \rho_1^V}{\rho_1^{0,L} - \rho_1^{0,V}} \right)^2 \gamma_1^0 \left(1 - \frac{\rho_2^L}{\rho_1^L + \rho_2^L} \right) \quad (20)$$

2.5. Classical Nucleation Theory (CNT)

The Superheat Limit (SHL) and Supercool Limit (SCL) for CO₂ and binary CO₂ mixtures were evaluated using Classical Nucleation Theory (CNT), which relates the work required to form a critical bubble or droplet to the nucleation rate J .⁵⁶ The nucleation rate per unit volume and time is written in an Arrhenius form⁵⁶

$$J = K \exp \left(-\frac{\Delta G^*}{k_B T} \right) \quad (21)$$

where ΔG^* is the free energy barrier at the critical radius r_c of the bubble or droplet, k_B is the Boltzmann constant, T is the

absolute temperature, and K is the kinetic prefactor. Within the capillarity approximation of CNT, i.e., by assuming a planar IFT (γ) and bulk densities and chemical potentials inside the nucleus, ΔG^* is defined as

$$\Delta G^* = \frac{4\pi\gamma r_c^2}{3} \quad (22)$$

For superheated liquid (bubble nucleation), the nucleation driving force is the liquid tension, which is the pressure deficit of the liquid relative to equilibrium.

$$\Delta P = P^{\text{sat}}(T, z) - P_c > 0 \quad (23)$$

where $P^{\text{sat}}(T, z)$ is the saturation pressure of the fluid at temperature T and composition z , and P_c is a metastable liquid pressure at which J is evaluated. At the critical radius r_c of the bubble, the liquid tension exactly balances the Laplace pressure $2\gamma/r$, yielding the standard CNT expression for r_c

$$r_c^{\text{bubble}} = \frac{2\gamma}{P^{\text{sat}}(T, z) - P_c} \quad (24)$$

For supersaturated vapor (droplet nucleation), the driving force is the bulk free energy density $\rho_n^L k_B T \ln(P_c/P^{\text{sat}}(T, z)) > 0$, where ρ_n^L is the liquid number density. Balancing the Laplace pressure and bulk free energy density terms at r_c leads to

$$r_c^{\text{droplet}} = \frac{2\gamma}{\rho_n^L k_B T \ln(P_c/P^{\text{sat}}(T, z))} \quad (25)$$

For a detailed derivation, see ref 56. The kinetic prefactor K for bubble formation in liquid and droplet formation in vapor is calculated by following the approximate expressions used by Aursand et al.⁶⁴ and Skarsvåg et al.⁵⁴

$$K^{\text{bubble}} \approx \rho_n^L \sqrt{\frac{2\gamma}{\pi m}}; \quad K^{\text{droplet}} \approx \frac{(\rho_n^V)^2}{\rho_n^L} \sqrt{\frac{2\gamma}{\pi m}} \quad (26)$$

where ρ_n^V is the vapor number density and m is the mass per molecule. For binary mixtures, we adopt the effective mass, m_{eff} instead of m in eq 26

$$\sqrt{1/m_{\text{eff}}^{\text{bubble}}} = \sum_{i=1}^{N_c} \frac{x_i^L}{\sqrt{m_i}}; \quad \sqrt{1/m_{\text{eff}}^{\text{droplet}}} = \sum_{i=1}^{N_c} \frac{y_i^V}{\sqrt{m_i}} \quad (27)$$

where x_i^L is the liquid mole fraction and y_i^V is the vapor mole fraction of component i . N_c denotes the number of components in a mixture. The P_{SHL} and P_{SCL} limits are obtained by solving $J = J_{\text{cr}}$ for the metastable pressure P_c at a given T and z . The resulting P_c equals the P_{SHL} for bubbles in liquid and P_{SCL} for droplets in vapor. In this study, we adopt $J_{\text{cr}} = 10^{12} \text{ m}^{-3} \text{ s}^{-1}$, which is the same value of J_{cr} used by Aursand et al.⁶⁴ and Skarsvåg et al.⁵⁴ to estimate P_{SHL} and P_{SCL} of pure CO_2 and multicomponent CO_2 mixtures.

3. RESULTS AND DISCUSSION

In this section, the Vapor–Liquid Equilibrium (VLE) and interfacial properties of pure CO_2 and binary CO_2 mixtures computed from MD simulations, cDFT, EoS, and semi-empirical models are discussed. The computed phase equilibria from MD simulations and the PC-SAFT EoS were compared with the multiparameter Helmholtz EoS of Span and Wagner²⁶ for pure CO_2 , as implemented in REFPROP v10⁸⁶ and with experimental data^{34,95–100} for binary CO_2 mixtures. For binary

CO_2 mixtures, IFTs computed from MD simulations and the PC-SAFT EoS + cDFT are presented combined with the phase equilibria (P_{xy} diagram) for three different temperatures. The P_{xy} diagrams and IFTs of CO_2 binary mixtures were computed from the PC-SAFT EoS + cDFT, for both $k_{ij} = 0$ and $k_{ij} \neq 0$. The k_{ij} values were determined by fitting the phase equilibria to experimental data^{34,95–100} at each temperature and are therefore temperature dependent. The methodology used for obtaining k_{ij} and the experimental data used for fitting are presented in Sections S7 and S8 of the Supporting Information. The values of k_{ij} used in this study to compute the phase equilibria and interfacial properties are listed in Table 1. To obtain reliable statistics from MD simulations, 10

Table 1. Binary Interaction Parameters (k_{ij}) of CO_2 – CH_4 , CO_2 –Ar, CO_2 – N_2 , and CO_2 – H_2 at Different Temperatures to Compute Phase Equilibria (P_{xy} Diagram) and Interfacial Properties from the PC-SAFT EoS^{28,92} Combined with cDFT^a

binary mixture	$T/[\text{K}]$	$k_{ij}/[-]$
CO_2 – CH_4	230.0	0.0519
	250.0	0.0541
	270.0	0.0566
CO_2 –Ar	223.07	0.0317
	253.28	0.0295
	273.26	0.0240
CO_2 – N_2	220.0	−0.0164
	250.0	−0.0294
	273.12	−0.0699
CO_2 – H_2	220.0	−0.0594
	250.0	0.0474
	273.1	0.0538

^aThe binary interaction parameters were obtained by fitting to experimental data reported in the literature.^{34,95–100} Experimental data for the CO_2 – CH_4 mixtures were taken from Wei et al.⁹⁶ at 230, 250, and 270 K. For the CO_2 –Ar mixtures, the experimental data were taken from Lasala et al.³⁴ at 223.07 K and from Coquelet et al.⁹⁷ at 253.28 and 273.26 K. Experimental data for the CO_2 – N_2 mixtures at 220, 250, and 273.12 K were obtained from Brown et al.,⁹⁹ Al-Sahhaf et al.,⁹⁸ and Lasala et al.,³⁴ respectively. Experimental data for the CO_2 – H_2 mixtures were taken from Tsang and Street¹⁰⁰ at 220 and 250 K and from Fandiño et al.⁹⁵ at 273.1 K.

independent simulations with different initial configurations were performed for each temperature, and the results were analyzed using block averaging over 5 blocks to compute mean values and uncertainties of VLE and interfacial properties of pure CO_2 . For binary systems, due to the computational costs, 2 independent simulations were performed at different initial configurations to compute the mean and uncertainty values of liquid mole fractions, vapor mole fractions, and interfacial properties at a given temperature and pressure. For clarity, the uncertainties in IFT and in the phase equilibria of the binary mixtures are omitted from the P_{xy} diagrams and are instead provided in Section S9 of the Supporting Information. To evaluate the accuracy of the computed bulk and interfacial properties of pure CO_2 and binary CO_2 mixtures, the Relative Percentage Deviation (RPD) and Maximum Absolute Relative Deviation (MARD) are used in addition to MAPD (eq 12). The RPD at a given state point i (temperature, pressure, or composition) is defined as

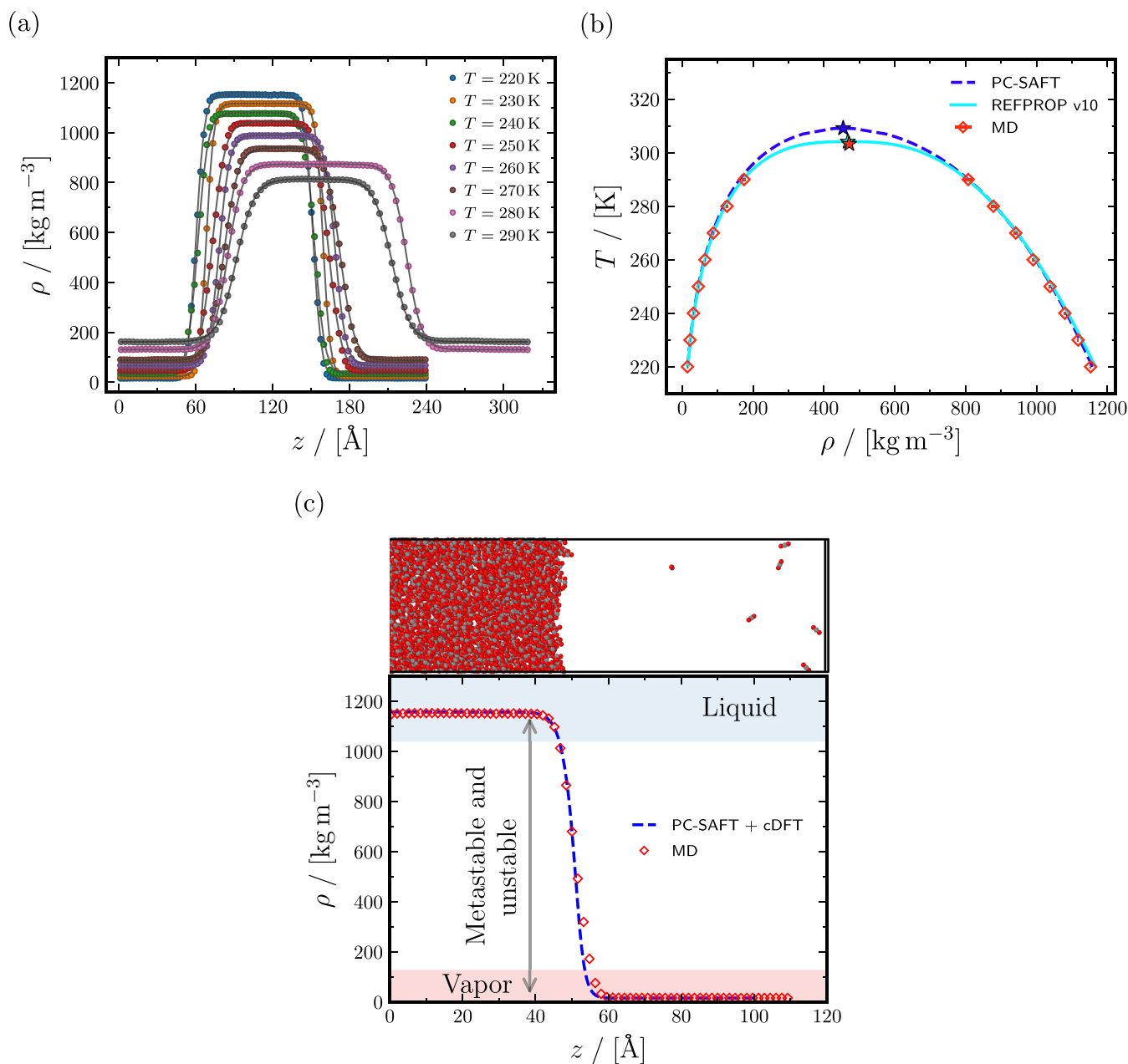


Figure 2. (a) Density profiles of pure CO_2 obtained from MD simulations, $\rho(z)_{\text{MD}}$, at temperatures 220 to 290 K in 10 K increments. (b) Comparison of CO_2 VLE densities computed from MD simulations (red symbols) with the PC-SAFT EoS + cDFT^{28,92} (blue line) and REFPROP v10 (Span and Wagner EoS^{26,86}) (cyan line). Star symbols denote the critical temperatures T_c estimated from MD simulations, the PC-SAFT EoS, and REFPROP v10. (c) Snapshot of the MD simulation box representing the coexistence of liquid and vapor phases (top) and comparison of the CO_2 density profile at $T = 220$ K obtained from MD simulations with the PC-SAFT EoS + cDFT.^{28,92} The liquid, vapor, metastable, and unstable density regions were determined using the definition of L_{10}^0 (eq 7). The visualization was rendered using the Open Visualization Tool (OVITO) software.¹²⁷

$$\text{RPD}_i = \frac{\chi_i^{\text{Comp.}} - \chi_i^{\text{Ref.}}}{\chi_i^{\text{Ref.}}} \times 100\% \quad (28)$$

where $\chi_i^{\text{Comp.}}$ is the value obtained from MD simulations, EoS, or semiempirical models, and χ_i^{ref} is the corresponding reference value (experiment, simulation, or semiempirical model). The MARD is then

$$\text{MARD} = \max_i \left| \frac{\chi_i^{\text{Comp.}} - \chi_i^{\text{Ref.}}}{\chi_i^{\text{Ref.}}} \right| \times 100\% \quad (29)$$

which represents the largest deviation across all state points, for example, IFTs of pure CO_2 over a full temperature range. The interfacial thickness of binary mixtures computed using MD simulations and the PC-SAFT EoS + cDFT are provided and discussed in Section S10 of the Supporting Information, as their detailed presentation involves numerous figures. The numerical values of phase equilibria and interfacial properties of pure CO_2 and binary CO_2 mixtures computed from MD simulations, PC-SAFT EoS + cDFT, and semiempirical models are provided in Sections S6 and S11 of the Supporting Information, respectively. The numerical values of SHL and SCL of pure CO_2 and binary CO_2 mixtures computed using

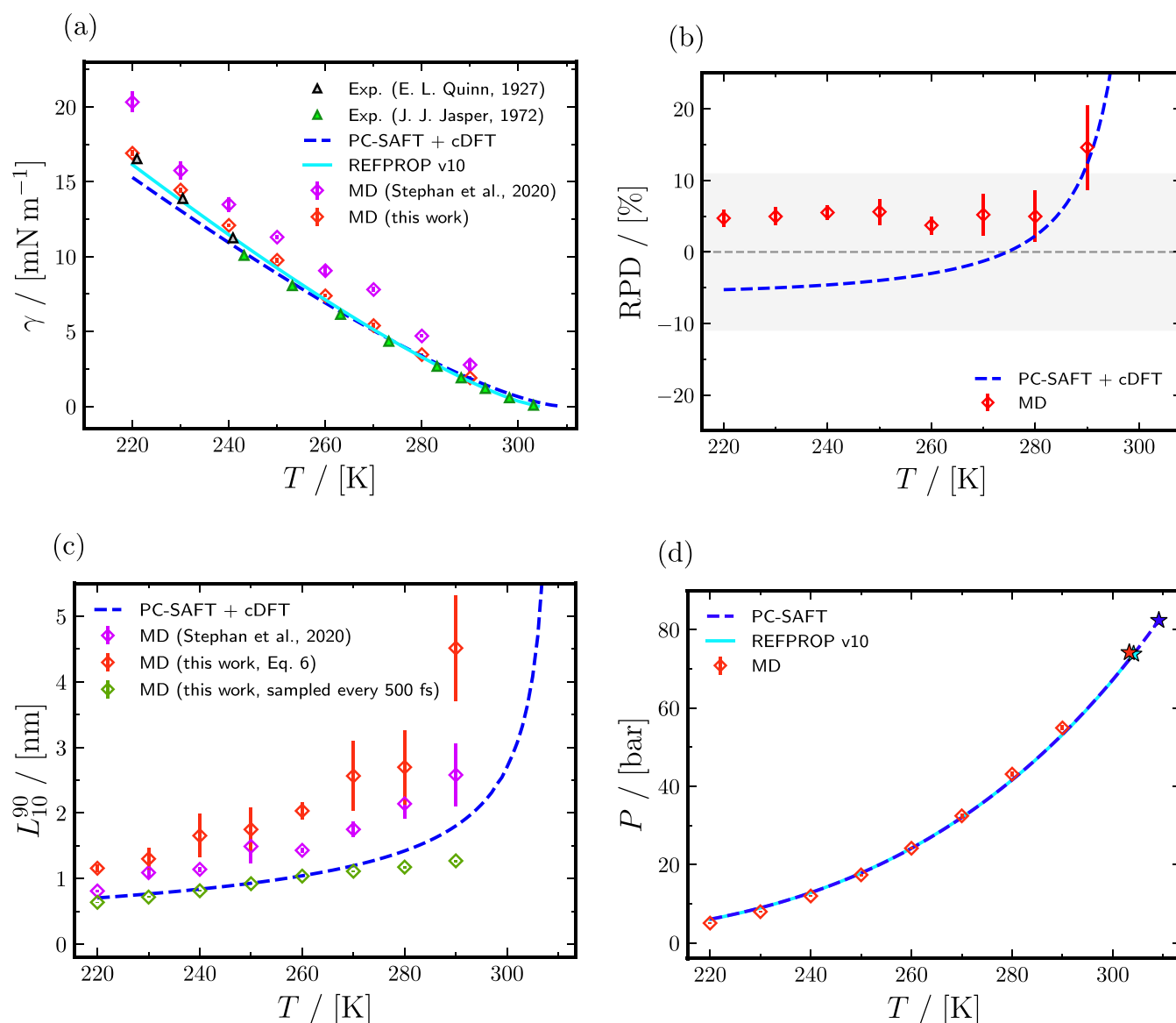


Figure 3. (a) Interfacial Tension (IFT) of CO₂ obtained from MD simulations and the PC-SAFT EoS + cDFT^{28,92} as a function of temperature and comparison with REFPROP v10,⁸⁶ MD simulations of Stephan et al.¹²⁸ using the force field of Merker et al.¹¹⁰ and experimental measurements of Quinn¹⁰⁸ and Jasper.¹⁰⁹ (b) Relative Percentage Deviation (RPD) of IFTs computed from MD simulations and the PC-SAFT EoS.^{28,92} The uncertainty region of 11.7% reported by Cachadiña et al.⁶⁷ is shown as a gray band. (c) Comparison of interfacial thickness L_{10}^0 of pure CO₂ computed from MD simulations and the PC-SAFT EoS + cDFT^{28,92} with MD simulations of Stephan et al.¹²⁸ In this work, L_{10}^0 of pure CO₂ were computed using two approaches: (1) using eq 6 and (2) by sampling the density profiles $\rho(z)_{MD}$ every 500 fs. (d) Comparison of CO₂ saturation pressures P^{sat} computed from MD simulations (red symbols) and PC-SAFT EoS^{28,92} (cyan line) with REFPROP v10⁸⁶ (blue line). Star symbols denote the critical pressure P_c estimated by MD using the Antoine equation,¹¹¹ PC-SAFT EoS,^{28,92} and REFPROP v10.⁸⁶

CNT are presented in Section S12 of the Supporting Information.

3.1. Pure CO₂

MD simulations were performed in the NVT ensemble using a two-phase system with a liquid slab between two vapor slabs to compute VLE and interfacial properties of pure CO₂, similar to the setup shown in Figure 1. Density profiles $\rho(z)_{MD}$ of pure CO₂, averaged over 40 ns, are shown in Figure 2a for 220–290 K in 10 K increments. Two system sizes were used: $L_z = 240$ Å with 2000 CO₂ molecules for 220–270 K, and $L_z = 320$ Å with 3000 CO₂ molecules for $T = 280$ and 290 K. Larger system sizes at $T = 280$ and 290 K were necessary to account for the significant density fluctuations noticed in MD simulations.⁷⁸ Coexistence densities were determined by fitting eq 6 to the

$\rho(z)_{MD}$ profiles shown in Figure 2a. The coexistence densities were also computed using the PC-SAFT EoS^{28,92} (computed using FeO_s) and the Span and Wagner EoS²⁶ (computed using REFPROP v10⁸⁶). As shown in Figure 2b, liquid and vapor densities from MD simulations and the PC-SAFT EoS were found to be in close agreement over the temperature range 220 to 290 K, when compared to the Span and Wagner EoS.²⁶ Vapor densities predicted by the PC-SAFT EoS were underestimated up to 290 K and overestimated at higher temperatures, while liquid densities were underestimated up to 280 K and overestimated at higher temperatures. For the temperature range 220 to 290 K, we observed maximum RPD values of approximately −5.5% at 290 K and −0.7% at 220 K for vapor densities, relative to the Span and Wagner EoS.²⁶

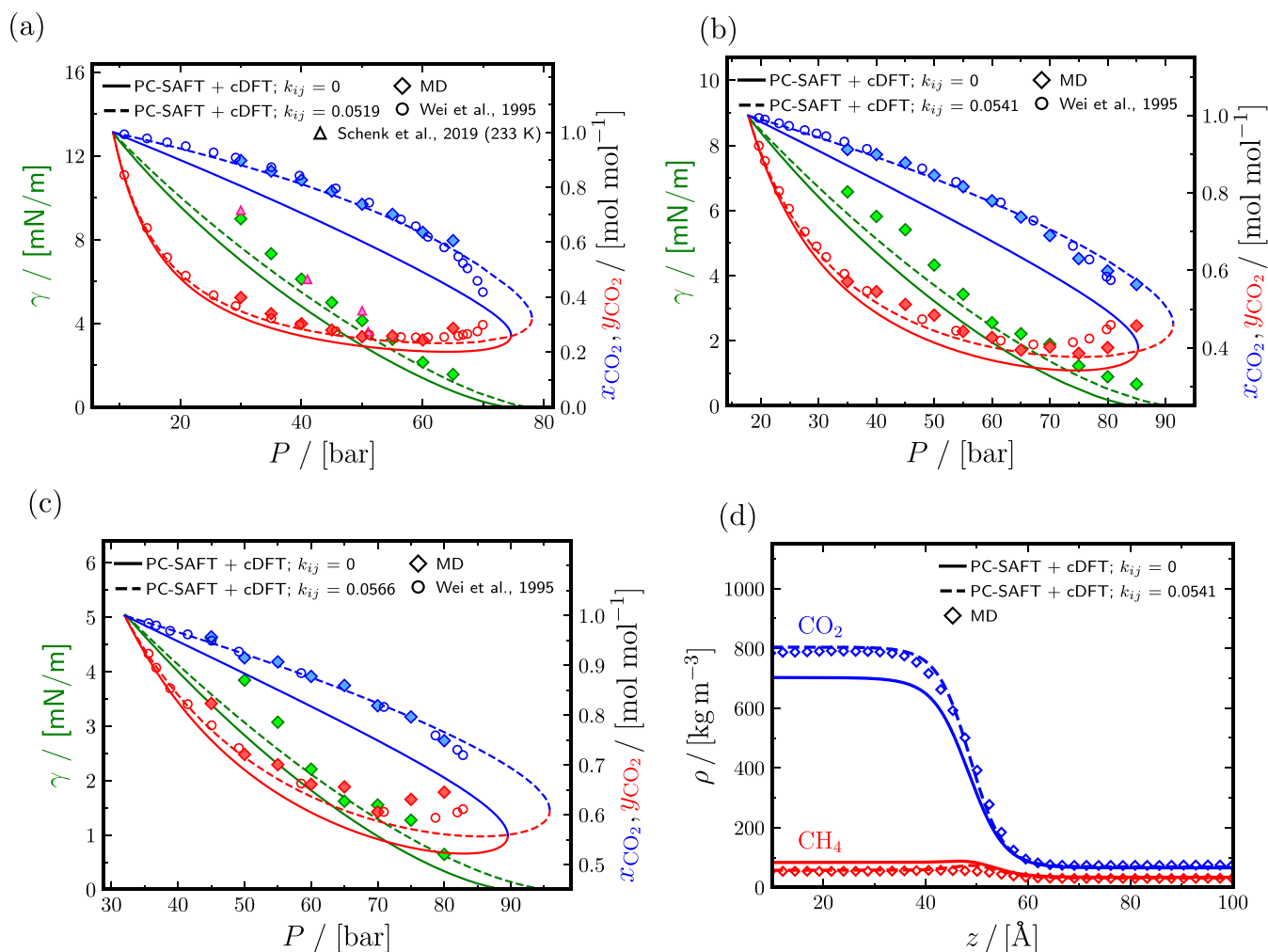


Figure 4. P - x_{CO_2} diagrams and IFTs of CO_2 – CH_4 mixtures at (a) 230 K, (b) 250 K, and (c) 270 K computed using the PC-SAFT EoS^{28,92} combined with cDFT, with $k_{ij} = 0$ and $k_{ij} \neq 0$, compared with experimental data^{55,96} and MD simulations. In subfigures (a–c), the left vertical-axis (green) represents the interfacial tension γ , while the right vertical-axis (red and blue) corresponds to the vapor and liquid mole fractions of CO_2 , respectively. (d) Comparison of density profiles at 250 K and 50 bar, computed using the PC-SAFT EoS^{28,92} combined with cDFT for $k_{ij} = 0$ and $k_{ij} \neq 0$, and from the MD simulation.

The MARD of the PC-SAFT EoS, relative to the Span–Wagner EoS,²⁶ was ca. 0.3% for liquid densities and ca. 2.5% for vapor densities. Liquid densities were underestimated in MD simulations, with a maximum RPD of ca. 1% at 220 K, and were overestimated from 280 K to T_c . Vapor densities were underestimated up to 280 K and overestimated at higher temperatures, with a maximum RPD of ca. –6% at 220 K. The MARD was ca. 1% for liquid densities and ca. 3% for vapor densities. From the coexistence densities computed from MD simulations, T_c and ρ_c were calculated using the scaling law¹⁰⁶ and the law of rectilinear diameter⁵¹ (see Section S4 of the Supporting Information). Compared to the Span and Wagner EoS, MD predicts a slightly lower value of T_c (ca. 0.2%), whereas the PC-SAFT EoS yields a higher estimate (ca. 1.7%), consistent with previous studies that showed the PC-SAFT EoS tends to overestimate critical properties.^{28,107} Figure 2c presents the comparison of CO_2 density profiles at 220 K obtained from MD and PC-SAFT EoS + cDFT, and it also includes a representative snapshot of the MD simulation (top), showing the liquid phase in equilibrium with its vapor phases. To enable direct comparison with the density profiles from the PC-SAFT EoS + cDFT, $\rho(z)_{\text{MD}}$ (computed with $L_z = 240$ Å,

i.e., 120 Å per interface) was scaled to a reference length of 110 Å so that both methods could be compared on the same spatial basis. Both approaches agree well with each other in describing the bulk liquid, vapor, and interfacial regions, while the metastable region provides a smooth transition between the two phases. Multiparameter EoS models, such as the Span and Wagner²⁶ and GERG-2008,²⁷ are known to produce multiple artificial Maxwell loops,¹⁷ which hinder a smooth phase transition. For this reason, the PC-SAFT EoS^{28,92} was selected for estimating interfacial properties of CO_2 and binary CO_2 mixtures.

Figure 3a shows IFTs of pure CO_2 as a function of temperature computed from MD simulations and the PC-SAFT EoS + cDFT and their comparison with experimental measurements of Quinn¹⁰⁸ and Jasper,¹⁰⁹ REFPROP v10⁸⁶ (Guggenheim–Katayama equation³³), and MD simulations of Stephan.⁹¹ The coefficients required to compute IFTs using the Guggenheim–Katayama equation³³ are fitted with 125 experimental values by Cachadiña et al.⁶⁷ which also includes the experimental measurements of Quinn¹⁰⁸ and Jasper.¹⁰⁹ The fitted coefficients suggested by Cachadiña et al.,⁶⁷ which is used in REFPROP v10,⁸⁶ are reported to have a maximum

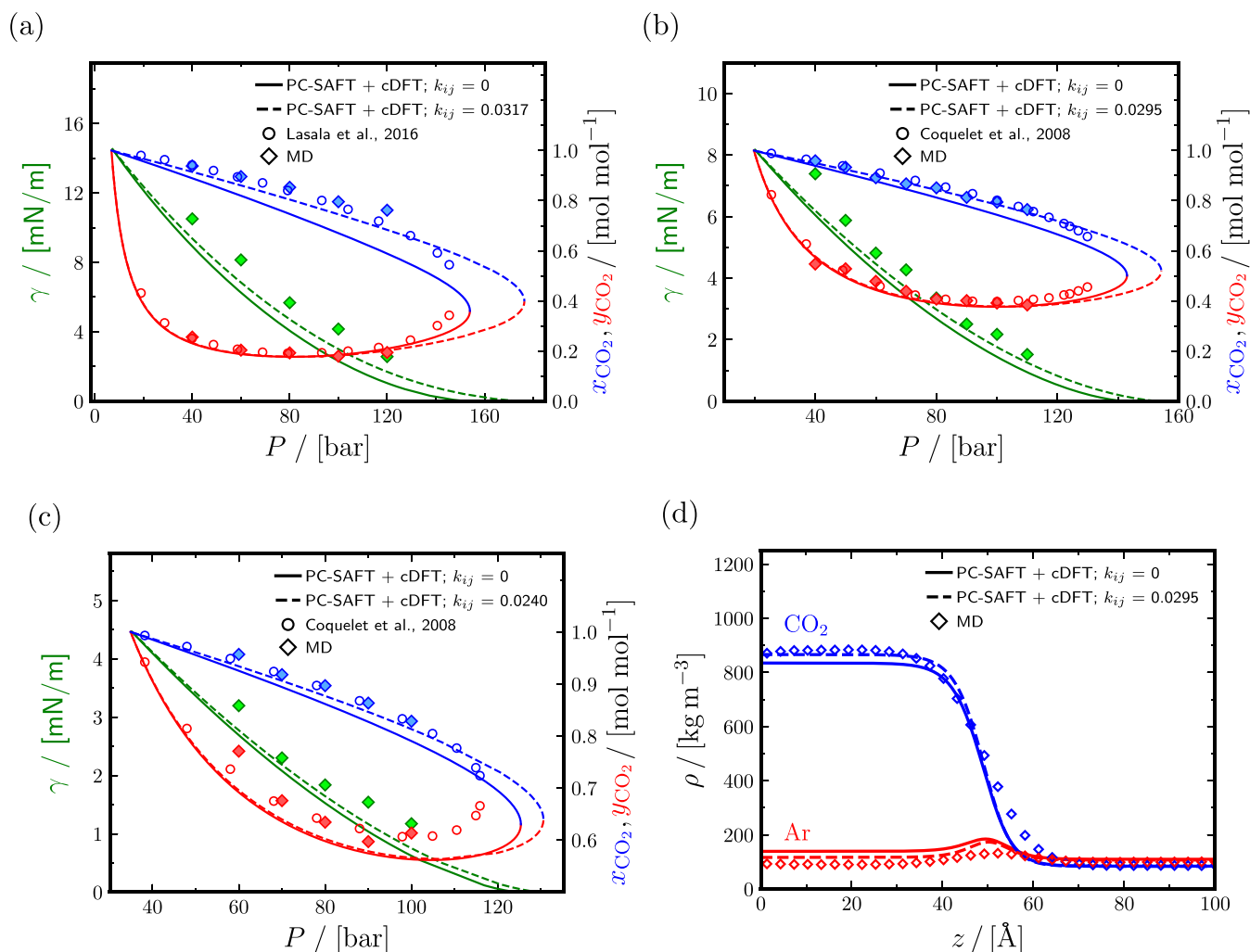


Figure 5. P - xy diagrams and IFTs of CO₂-Ar mixtures at (a) 223.07 K, (b) 253.28 K, and (c) 273.26 K computed using the PC-SAFT EoS^{28,92} combined with cDFT, with $k_{ij} = 0$ and $k_{ij} \neq 0$, compared with experimental data^{34,97} and MD simulations. In subfigures (a–c), the left vertical-axis (green) represents the interfacial tension γ , while the right vertical-axis (red and blue) corresponds to the vapor and liquid mole fractions of CO₂, respectively. (d) Comparison of density profiles at 250 K and 70 bar, computed using the PC-SAFT EoS^{28,92} combined with cDFT for $k_{ij} = 0$ and $k_{ij} \neq 0$, and from the MD simulation.

RPD of 11.7% at 280.15 K. Using the Guggenheim-Katayama equation (eq 13)³³ with the coefficients of Cachadiña et al.⁶⁷ as reference, the IFTs computed from MD simulations with the TraPPE force field⁷¹ were overestimated, consistent with findings of Stephan⁹¹ where the force field of Merker et al.¹¹⁰ was used for IFTs computation. The PC-SAFT EoS + cDFT underestimates IFTs up to 274 K and tends to overestimate at higher temperatures ($T > 274$ K). Figure 3b shows the RPD of MD and the PC-SAFT EoS + cDFT computed using eq 28. The maximum uncertainty reported by Cachadiña et al.⁶⁷ was taken as the uncertainty range for comparison. As shown in Figure 3b, IFTs computed from MD simulations with the TraPPE force field⁷¹ remain within the uncertainty range except at 290 K, where large density fluctuations cause deviations larger than 11.7%. Similarly, the RPD of the PC-SAFT EoS + cDFT lies within the uncertainty range for temperatures less than 290 K, and diverges at temperatures larger than 290 K. The RPD values from MD simulations of Stephan⁹¹ are not included in Figure 3b since all points fall outside the uncertainty range. We computed the interfacial thickness of pure CO₂ from MD simulations with the TraPPE force field⁷¹ and from the PC-SAFT EoS + cDFT using the

definition of $L_{10}^{90,89}$ (eq 7), and compared the results with values reported by Stephan⁹¹ (Merker et al.¹¹⁰ force field), as shown in Figure 3c. Stephan⁹¹ computed the interfacial thickness from ensemble-averaged density profiles of MD simulations using the same L_{10}^{90} definition.⁸⁹ In this work, we applied two approaches: (1) using eq 6 to compute L_{10}^{90} ($L_{10}^{90} \approx 2.19D^{81}$), and (2) sampling L_{10}^{90} every 500 fs (i.e., every 1000 time steps), since we observed the lateral movement of the liquid slab. The results from both approaches are shown in Figure 3c, with eq 6 represented by red symbols and the L_{10}^{90} values sampled every 1000 time steps represented by green symbols. In all cases, the interfacial thickness increases with temperature and diverges at T_c . The values obtained from eq 6 and those reported by Stephan⁹¹ overestimate L_{10}^{90} at all temperatures, whereas the values sampled every 500 fs agree well with the PC-SAFT EoS + cDFT, except at 290 K. We did not report RPD and MARD, since no reference experimental data or model to compute the L_{10}^{90} for pure CO₂ were available in literature. Using the same simulation setup as for the computation of coexistence densities, IFTs, and interfacial thickness of pure CO₂, we computed the saturation pressures P_{sat} as a function of temperature. Figure 3d compares P_{sat} obtained from MD

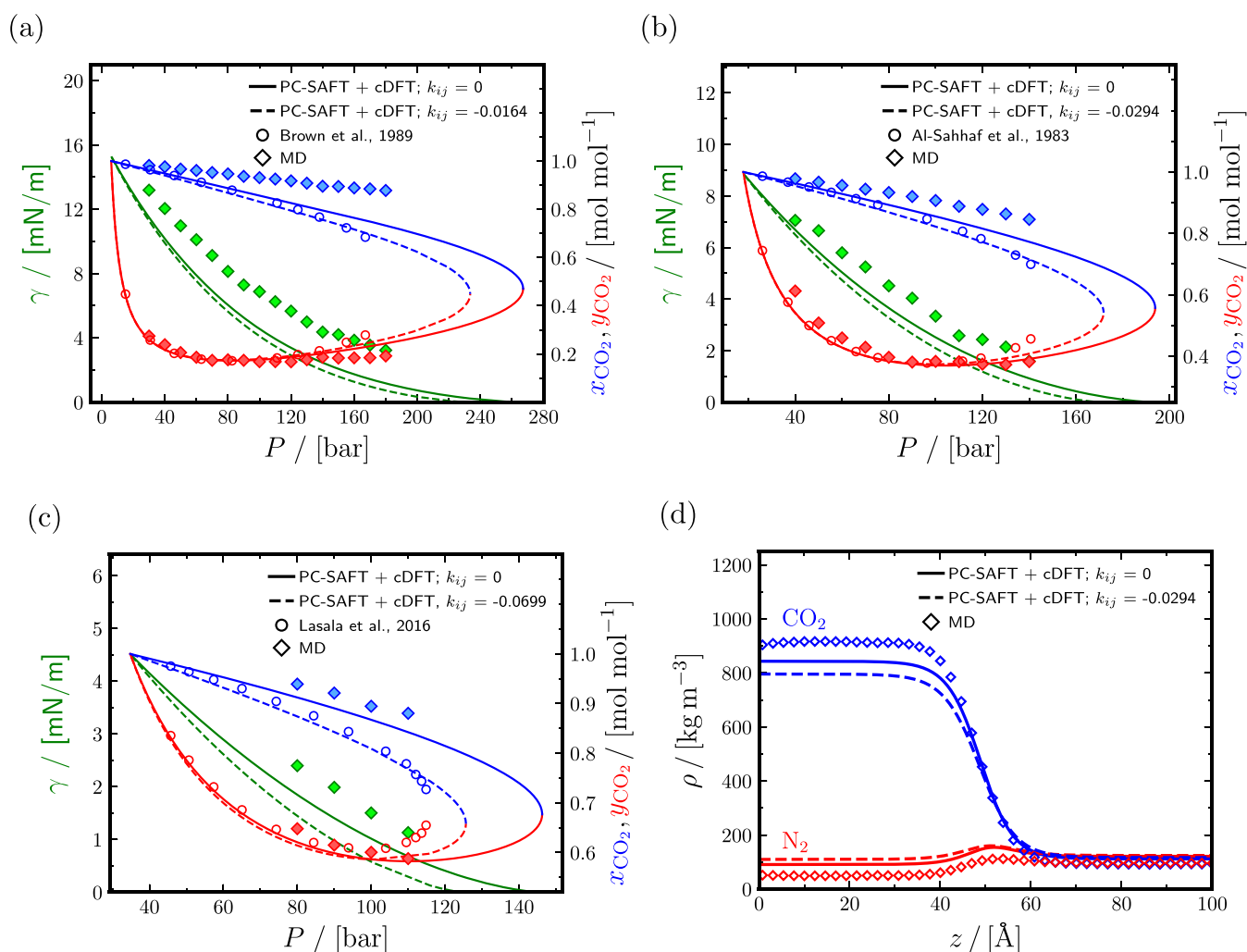


Figure 6. P_{xy} diagrams and IFTs of $\text{CO}_2\text{--N}_2$ mixtures at (a) 220 K, (b) 250 K, and (c) 273.12 K computed using the PC-SAFT EoS^{28,92} combined with cDFT, with $k_{ij} = 0$ and $k_{ij} \neq 0$, compared with experimental data^{34,98,99} and MD simulations. In subfigures (a–c), the left vertical-axis (green) represents the interfacial tension γ , while the right vertical-axis (red and blue) corresponds to the vapor and liquid mole fractions of CO_2 , respectively. (d) Comparison of density profiles at 250 K and 90 bar, computed using the PC-SAFT EoS^{28,92} combined with cDFT for $k_{ij} = 0$ and $k_{ij} \neq 0$, and from the MD simulation.

simulations and the PC-SAFT EoS with the Span and Wagner EoS.²⁶ MD simulations underestimated P_{sat} below 260 K and overestimated it above this temperature, yielding a maximum RPD of ca. 16% at 220 K and a MARD of ca. 6%. The large RPD at 220 K arises from relatively low P_{sat} at this low temperature. Conversely, the PC-SAFT EoS overpredicted up to 234 K and underpredicted above that temperature, with a maximum RPD of ca. 0.5% at 220 K and a MARD of ca. 0.2% in the range 220 to 290 K. The saturated vapor pressure at T_c was estimated by fitting the $P_{\text{sat}}(T)$ data from the MD simulations with the Antoine equation¹¹¹ and extrapolating the fit to T_c (see Section S4 of the Supporting Information). The saturated vapor pressure at T_c computed from both MD simulations and the PC-SAFT EoS were found to be overestimated by ca. 0.4% and ca. 12%, respectively, when compared to the Span and Wagner EoS.²⁶

3.2. Binary CO_2 Mixtures

The phase equilibria (P_{xy} diagrams) and IFTs for four binary mixtures $-\text{CO}_2\text{--CH}_4$, $\text{CO}_2\text{--Ar}$, $\text{CO}_2\text{--N}_2$, and $\text{CO}_2\text{--H}_2$ computed from MD simulations and from the PC-SAFT EoS combined with cDFT using both $k_{ij} = 0$ and $k_{ij} \neq 0$ at different

temperatures are shown in comparison with experimental P_{xy} data^{34,95–100} in Figures 4a–4c, 5a–5c, 6a–c, 7a–7c. MD simulations at low pressure limit of the phase envelope (i.e., at high vapor mole fraction) were not feasible because the vapor phase became too dilute to maintain a stable vapor–liquid interface within a single simulation box. Hence, MD simulations were considered at pressures where stable two-phase equilibrium could be maintained for computing P_{xy} diagrams and IFTs. The experimental P_{xy} data reported in the literature for binary mixtures considered in this study were measured at different temperatures, namely 230 K for $\text{CO}_2\text{--CH}_4$, 223.07 K for $\text{CO}_2\text{--Ar}$, and 220 K for $\text{CO}_2\text{--N}_2$. Hence, IFTs and P_{xy} diagrams of binary mixtures were computed using MD simulations and the PC-SAFT EoS + cDFT, at the experimentally available temperatures as shown in Table 1. The k_{ij} s of binary mixtures obtained by fitting the experimental P_{xy} data^{34,95–100} at different temperatures are also presented in Table 1. It is clear from all the P_{xy} diagrams (Figures 4a–4c, 5a–5c, 6a–c and 7a–7c) that the phase equilibria computed from the PC-SAFT EoS with $k_{ij} \neq 0$ has a good agreement with experimental measurements^{34,95–100} compared to the PC-SAFT EoS with $k_{ij} = 0$. To quantify the deviations in liquid and

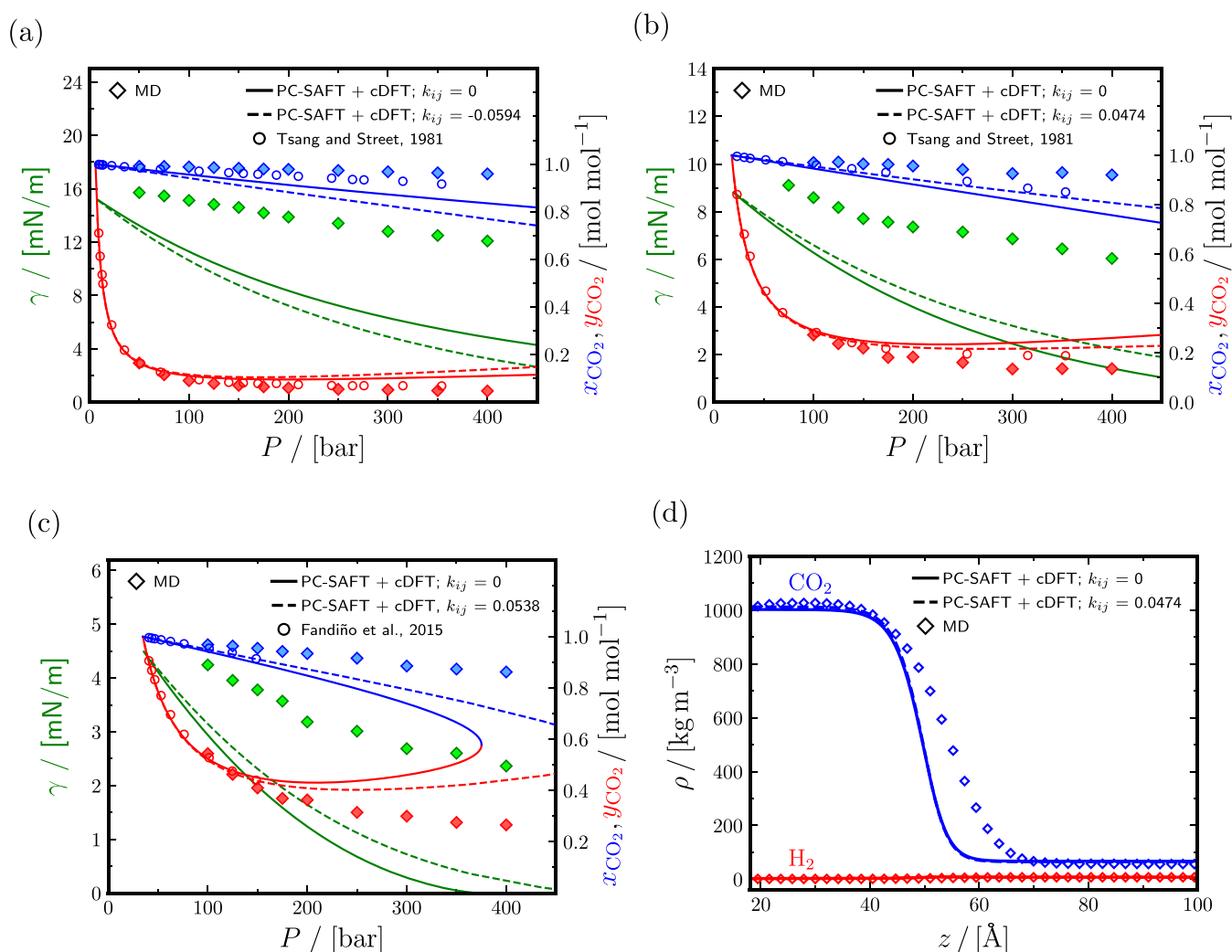


Figure 7. P_{xy} diagrams and IFTs of CO₂-H₂ mixtures at (a) 220 K, (b) 250 K, and (c) 273.1 K computed using the PC-SAFT EoS^{28,92} combined with cDFT, with $k_{ij} = 0$ and $k_{ij} \neq 0$, compared with experimental data^{34,100} and MD simulations. In subfigures (a–c), the left vertical-axis (green) represents the interfacial tension γ , while the right vertical-axis (red and blue) corresponds to the vapor and liquid mole fractions of CO₂, respectively. (d) Comparison of density profiles at 250 K and 100 bar, computed using the PC-SAFT EoS^{28,92} combined with cDFT for $k_{ij} = 0$ and $k_{ij} \neq 0$, and from the MD simulation.

vapor mole fractions predicted by the PC-SAFT EoS relative to experimental data, the mean absolute percentage deviation defined in eq 12 (MAPD) is used. Similarly, MAPD is used to compare the liquid and vapor mole fractions and IFTs predicted by the PC-SAFT EoS relative to those obtained from MD simulations. IFTs computed using the PC-SAFT EoS + cDFT with $k_{ij} \neq 0$ are underestimated for all binary mixtures compared to MD simulations. The MAPD is an appropriate measure for quantifying these deviations than RPD. The analysis of P_{xy} data between MD simulations and experimental measurements was not quantified because the experimental data points were not available exactly at the same discrete pressure values used in the simulations. The experimental IFTs of CO₂-CH₄ mixture at 233 K of Schenk et al.,⁵⁵ were used to compare IFTs computed from MD and the PC-SAFT EoS + cDFT at 230 K. Except for the experimental measurements reported by Schenk et al.,⁵⁵ experimental data on IFTs of binary mixtures discussed in literature are very limited, to the best of our knowledge. This scarcity has also been highlighted by Skarsvåg et al.⁵⁴ In addition to the P_{xy} diagrams, we also computed the density profiles of CO₂-CH₄, CO₂-Ar, CO₂-

N₂, and CO₂-H₂ from MD simulations, and the PC-SAFT EoS + cDFT with $k_{ij} = 0$ and $k_{ij} \neq 0$. We compared the density profiles for a single thermodynamic state point (at a particular temperature and pressure) for each binary mixture. For binary mixtures, the enrichment of the Light Boiling Component (LBC), such as CH₄, Ar, N₂, and H₂, was noticed in both MD simulations and the PC-SAFT EoS + cDFT. The enrichment of the LBC at the interface was evaluated using the definition¹¹²

$$E_i = \frac{\max(\rho_i(z))}{\max(\rho_i^L, \rho_i^V)} \quad (30)$$

where, $\rho_i(z)$, ρ_i^L , and ρ_i^V denote the density profile, liquid density, and vapor density of component i , respectively. Equation 30 provides the ratio between the maximum interfacial density of a component i and its corresponding maximum bulk phase densities.¹¹² By definition, $E_i > 1$ indicates interfacial enrichment, whereas $E_i = 1$ signifies presence of no interfacial enrichment. For all the binary mixtures investigated in this study, E_1 (E_{CO_2}) is equal to 1,

indicating that CO₂ does not accumulate at the interface. In contrast, E_2 represents the enrichment of the LBC, and values greater than 1 indicate that the LBC becomes more concentrated at the interface than in either bulk phases. Enrichment is strongest at lower pressures with a high liquid mole fraction and decreases as pressure increases.¹¹² In this work, we present the density profiles in Figures 4d, 5d, 6d and 7d at relatively low pressures compared to the critical pressure of the mixture. Density profiles are shown at 250 K for CO₂–CH₄, CO₂–N₂, and CO₂–H₂, and at 253.28 K for CO₂–Ar, enabling a consistent assessment of enrichment across different LBC within the same temperature range. The bulk liquid and vapor densities of the binary mixtures studied in this work are not reported. Readers are referred to our previous study²¹ for details and discussion on the computation of bulk densities using Monte Carlo^{113–115} simulations in the Gibbs ensemble,^{116,117} rather than by simulating two coexisting phases within a single simulation box.

3.2.1. CO₂–CH₄. The P_{xy} diagrams of CO₂–CH₄ mixtures at 230, 250, and 270 K are shown in Figure 4a–4c and compared with the experimental data of Wei et al.⁹⁶ The liquid mole fractions predicted by the PC-SAFT EoS with $k_{ij} \neq 0$ at 230, 250, and 270 K show good agreement with the experimental data of Wei et al.,⁹⁶ yielding a MAPD below 5%, excluding the points near the critical pressures (i.e., $P < 65$, 75, and 80 bar for 230, 250, and 270 K, respectively). The critical pressures predicted by the PC-SAFT EoS are generally overestimated compared to experimental values,^{28,92} therefore, data near the critical region were excluded from the analysis. Similarly, the liquid mole fractions obtained using the PC-SAFT EoS with $k_{ij} \neq 0$ maintain a MAPD of less than 5% across the considered pressure range. When comparing the MD simulations with the PC-SAFT EoS with $k_{ij} \neq 0$ as a reference state point, the MAPD of liquid mole fractions and vapor mole fractions were ca. 2% for 230, 250, and 270 K. The MAPD of vapor mole fraction was also found to be ca. 5% for 250, and 270 K, whereas at 230 K it was ca. 7%. Along with the P_{xy} diagrams of CO₂–CH₄ presented in Figure 4a–4c, the IFT values computed using the PC-SAFT EoS + cDFT, with $k_{ij} = 0$ and $k_{ij} \neq 0$, are compared with the results from MD simulations. The results clearly show that the IFT decreases with increasing pressure and decreasing liquid mole fraction for 230, 250, and 270 K. The PC-SAFT EoS combined with cDFT and $k_{ij} \neq 0$ generally underpredicted the IFTs, except at 270 K and 65 bar. For all temperatures, the MAPD remained below 14%. Data points near the critical pressure were excluded from the analysis because evaluating the MAPD at very low IFT values ($<1 \text{ mN m}^{-1}$) leads to disproportionately large errors. In addition to the comparison of IFTs computed from MD simulations and the PC-SAFT EoS combined with cDFT, the experimental measurements of Schenk et al.,⁵⁵ at 233 K are shown in Figure 4a. IFTs predicted by the MD simulations show good agreement with the experimental data reported by Schenk et al.,⁵⁵ A slight underestimation is observed, which we attribute to the temperature difference between the IFTs measured at 233 K and those computed at 230 K.

We computed the density profiles of the CO₂–CH₄ mixture at 250 K and 50 bar using MD simulations and the PC-SAFT EoS coupled with cDFT, and present them in Figure 4d. A comparison of these density profiles shows that the PC-SAFT EoS + cDFT with $k_{ij} = 0.0541$ provides better agreement with the MD simulation than with $k_{ij} = 0$. The density profile from the MD simulation also accurately reproduces the interfacial

thickness, which was averaged over 60 ns. The plateau regions in the MD density profile, corresponding to the bulk liquid and vapor phases, show good agreement with the densities predicted by the PC-SAFT EoS. However, the liquid density of CO₂ obtained from the MD simulation is underestimated by a RPD of ca. 2% compared to the PC-SAFT EoS + cDFT results with $k_{ij} = 0.0541$. A slight interfacial enrichment ($E_{\text{CH}_4} \approx 1.1$) is observed in the density profiles obtained from the MD simulation. An enrichment of $E_{\text{CH}_4} \approx 1.3$ is observed in the PC-SAFT EoS combined with cDFT using $k_{ij} = 0.0541$ at 250 K and 50 bar.

3.2.2. CO₂–Ar. The P_{xy} diagrams of CO₂–Ar mixtures at 223.07, 253.28, and 273.26 K, computed from the PC-SAFT EoS and MD simulations, are shown in Figure 5a–5c. The computed P_{xy} diagrams were compared with the experimental data of Lasala et al.³⁴ for 223.07 K and Coquelet et al.⁹⁷ for 253.28 and 273.26 K. The P_{xy} diagrams computed from the PC-SAFT EoS with fitted k_{ij} agreed well with the experimental P_{xy} data^{34,97} at all three temperatures. The liquid and vapor mole fractions estimated by the PC-SAFT EoS with fitted k_{ij} exhibited MAPDs of less than 2% and 5%, respectively, for both 253.28 and 273.26 K. However, the MAPDs were slightly higher at 223.07 K, with ca. 3% for the liquid mole fractions and 6% for the vapor mole fractions. This analysis excluded data points close to the critical pressure, corresponding to P values below 120, 110, and 100 bar for 223.07, 253.28, and 273.26 K, respectively, to ensure consistency across conditions. A similar comparison was also performed for the P_{xy} diagrams and IFTs computed from MD simulations. The liquid mole fractions computed from MD simulations agreed closely with the experimental measurements of Coquelet et al.⁹⁷ and Lasala et al.,³⁴ consistent with the results obtained from the PC-SAFT EoS with fitted k_{ij} . The MAPDs of liquid and vapor mole fractions computed from the PC-SAFT EoS with $k_{ij} \neq 0$ were 2% and 6%, respectively, at 253.28 and 273.26 K compared to MD simulations, whereas at 223.07 K, the MAPDs were ca. 6% and 7% for the liquid and vapor mole fractions, respectively. The higher MAPDs of the PC-SAFT EoS with $k_{ij} \neq 0$ at 223.07 K were also reflected in the estimation of IFTs, where the MAPD was close to 18%, whereas at 253.28 and 273.26 K, the MAPDs were ca. 12% and 14%, respectively.

We computed the density profile of the CO₂–Ar mixture at 253.28 K and 70 bar using MD simulations and the PC-SAFT EoS with cDFT. The results are shown in Figure 5d. From the comparison of the density profiles, it is clear that the density profiles computed from the PC-SAFT EoS + cDFT with $k_{ij} = 0.0295$ and $k_{ij} = 0$ have a better agreement with the MD simulation. The density profile computed from MD simulation (averaged for 60 ns), shown in Figure 4d overestimated the interfacial thickness compared to the PC-SAFT EoS + cDFT with $k_{ij} = 0.0295$ and $k_{ij} = 0$. The MD simulation accurately predicted the CO₂ liquid and vapor densities and Ar vapor density, whereas the Ar liquid density was underpredicted by ca. 7% compared to the PC-SAFT EoS + cDFT with $k_{ij} = 0.0295$. At the interface, a slight enrichment of Ar is noticed in Figure 5d in both MD simulation and the PC-SAFT EoS + cDFT with $k_{ij} = 0.0295$ and $k_{ij} = 0$. The MD simulations and the PC-SAFT EoS + cDFT yielded E_{Ar} values of approximately 1.3 and 1.5, respectively.

3.2.3. CO₂–N₂. The P_{xy} diagrams of CO₂–N₂ mixtures at 220, 250, and 273.12 K, computed using the PC-SAFT EoS and MD simulations, are compared with the experimental data

of Brown et al.,⁹⁹ Al-Sahhaf et al.,⁹⁸ and Lasala et al.³⁴ in Figure 6a–6c. Compared to CO₂–CH₄ and CO₂–Ar, CO₂–N₂ binary interaction parameters are negative, which means the liquid and vapor mole fractions, IFTs and density profiles shown in Figure 6 are overestimated compared to $k_{ij} = 0$. To quantify the deviations between the experimental measurements^{34,98,99} and the PC-SAFT EoS with $k_{ij} \neq 0$, as well as between the MD simulations and the PC-SAFT EoS with $k_{ij} \neq 0$, we excluded data points near the critical region. This analysis was carried out to avoid disproportionate errors caused by the overestimation of the critical pressure by the PC-SAFT EoS^{28,92} and from IFTs values lower than 1 mN m⁻¹. The excluded pressure ranges correspond to values below 160, 150, and 100 bar for 220, 250, and 273.12 K, respectively. The MAPD of liquid and vapor mole fractions computed from the PC-SAFT EoS with $k_{ij} \neq 0$ were found to be ca. 1% and 2%, respectively, compared to experimental measurements^{34,98,99} for all temperatures. Comparing the liquid and vapor mole fractions between MD simulations and the PC-SAFT EoS with $k_{ij} \neq 0$, a large MAPD up to ca. 9% and 8%, respectively, were observed for all the temperatures. Large deviation in the liquid mole fraction computed from MD simulations compared to experimental measurements^{34,98,99} and the PC-SAFT EoS observed in Figure 6a–c is due to exclusion of the binary interaction parameter ($k_{ij}^{\text{MD}} = 0$) in MD simulations for CO₂–N₂ mixture at 220, 250, and 273.12 K. Due to the use of $k_{ij}^{\text{MD}} = 0$, the IFTs computed from MD simulations were overestimated, with MAPDs of ca. 36%, 35%, and 50% at 220, 250, and 273.12 K, respectively. The overprediction of both liquid mole fractions and IFTs clearly indicates that MD simulations deviate significantly from the PC-SAFT EoS with $k_{ij} \neq 0$. To achieve accurate predictions of liquid mole fractions and IFTs, the appropriate k_{ij}^{MD} values should be determined by constructing a k_{ij}^{MD} matrix and validating the resulting thermodynamic properties with experimental data. The inclusion of k_{ij}^{MD} is particularly important for the CO₂–N₂ mixture because the combination of force fields used for CO₂⁷¹ and N₂⁷³ does not accurately capture the unlike interactions when applying the LB mixing rules. It should also be noted that k_{ij}^{MD} differs from k_{ij}^{EoS} , and therefore, the same value cannot be assumed for both. In this study, no k_{ij}^{MD} corrections were applied due to the high computational cost associated with their determination. Assuming $k_{ij}^{\text{MD}} = 0$ is reasonable for the other mixtures examined in this study, however, for the CO₂–N₂ mixture, it results in a noticeable overprediction of IFTs.

We computed the density profile of the CO₂–N₂ mixture at 250 K and 90 bar using MD simulations and the PC-SAFT EoS coupled with cDFT, and present the results in Figure 6d. The density profiles obtained from the PC-SAFT EoS + cDFT with $k_{ij} = -0.0294$ show good agreement with the MD simulation, except for an overprediction of the liquid phase densities by ca. 11% for CO₂ and 35% for N₂. This overprediction can be attributed to the use of $k_{ij}^{\text{MD}} = 0$. Since the MD simulations overpredict the bulk densities, the resulting density difference between the two phases, which is an important factor governing the IFT,^{52,105} is also overestimated. This contributes directly to the overprediction of IFTs noticed in Figure 6a–6c. The density profile obtained from MD simulations, averaged over 80 ns, was found to accurately reproduce the interfacial thickness when compared with the results from the PC-SAFT EoS + cDFT using $k_{ij} = 0$ and $k_{ij} = -0.0294$. A minor enrichment of N₂ is observed at the interface, with E_{N_2} values of ca. 1.05% and 1.2% predicted by

the MD simulation and the PC-SAFT EoS + cDFT with $k_{ij} = -0.0294$, respectively.

3.2.4. CO₂–H₂. The P_{xy} diagrams of the CO₂–H₂ mixture at 220, 250, and 273.1 K, computed using the PC-SAFT EoS and MD simulations, are shown in Figure 7a–7c along with the experimental data from Tsang and Street¹⁰⁰ and Fandiño et al.⁹⁵ Experimental data^{95,100} were limited to 354, 884, and 148.67 bar at 220, 250, and 273.1 K, respectively. MD simulations were performed up to 400 bar, but comparisons of liquid and vapor mole fractions and IFTs were restricted to pressures below the experimental limits. At 220 K, the limited data yielded a negative value of k_{ij} , leading to poor predictions of P_{xy} diagrams and IFTs relative to both experiments and the PC-SAFT EoS results with $k_{ij} = 0$. In sharp contrast, MD simulations matched experimental P_{xy} data well, although mole fractions could not be directly compared due to differing pressure points. At 250 K, the PC-SAFT EoS with $k_{ij} \neq 0$ showed good agreement with both experimental and MD results, yielding liquid and vapor mole fractions with MAPDs below 1% and 7%, respectively, compared to the experimental data.¹⁰⁰ MD simulations overpredicted the liquid and vapor mole fractions by 6% and 32%, respectively, compared to the PC-SAFT EoS with $k_{ij} \neq 0$, showing RPDs exceeding 50% for y_{CO_2} values lower than 0.2 at pressures above 250 bar. At 273.1 K, the PC-SAFT EoS with $k_{ij} \neq 0$ accurately reproduced the experimental data, with MAPDs of 0.3% and 2% for the liquid and vapor mole fractions, respectively, whereas the MD simulations slightly overpredicted these values by 3% and 4%. However, at 273.1 K and pressures above 150 bar, the P_{xy} diagram changes noticeably when $k_{ij} = 0.0538$ compared to the results with $k_{ij} = 0$. This deviation arises from the limited experimental data,⁹⁵ which impacts the reliability of k_{ij} and, consequently, the predicted phase equilibria and IFTs. Although the experimental liquid and vapor mole fractions agree reasonably well with the PC-SAFT EoS + cDFT and MD simulations at 220 and 250 K (Figure 7a,b), IFTs estimated by the two methods differ substantially, with MAPDs of ca. 40% at 220 K and 33% at 250 K. This suggests that the observed deviations in IFTs may arise either from limitations in the PC-SAFT EoS + cDFT model or from the force field used for H₂, even though the liquid and vapor mole fractions were predicted accurately. The discrepancy becomes more pronounced at 273.1 K, likely due to the combined influence of uncertainties in the IFT predictions (from both the PC-SAFT EoS + cDFT and the force field) and the k_{ij} values.

The density profile of CO₂–H₂ mixture at 250 K and 100 bar computed from MD simulation and the PC-SAFT EoS combined with cDFT are shown in Figure 7d. From the density profiles comparison, it is clear that the density profiles computed from the PC-SAFT EoS + cDFT with $k_{ij} = 0.0541$ and $k_{ij} = 0$ are consistent with the MD simulation. The density profile of MD simulations obtained by averaging 80 ns, shown in Figure 7d, overpredicts the interfacial thickness due to the presence of fluctuation and slight lateral movement of the liquid slab. The MD simulation accurately predicted the vapor densities of both CO₂ and H₂, and the liquid densities of CO₂ and H₂ were overestimated by ca. 1.4% and underestimated by ca. 50%, respectively, compared to the PC-SAFT EoS + cDFT. The MD simulation accurately predicted the vapor densities of both CO₂ and H₂. The liquid density of CO₂ was overestimated by ca. 1.4%, while that of H₂ was underestimated by about 50% compared to the PC-SAFT EoS

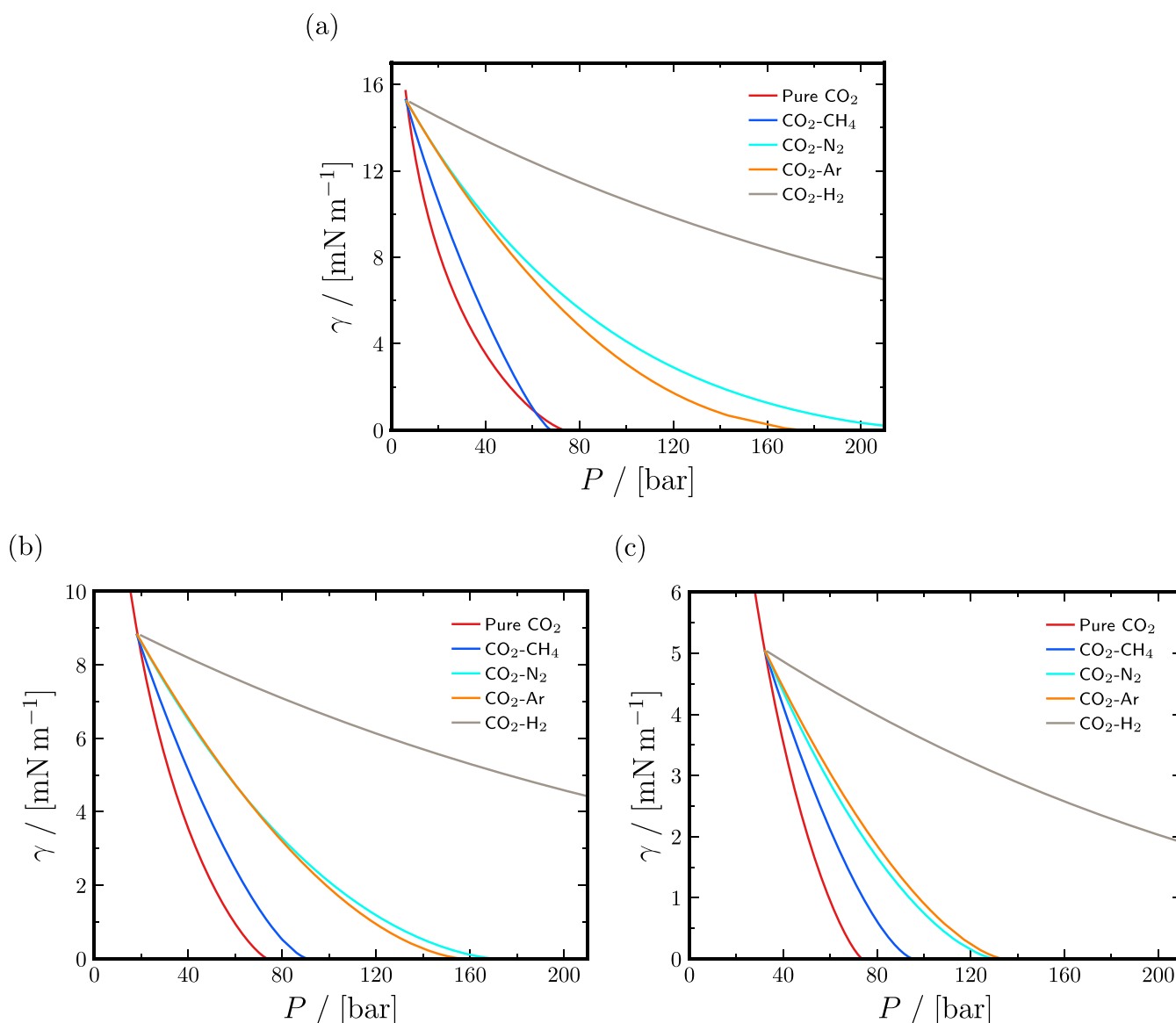


Figure 8. Comparison between pure CO₂ IFTs evaluated at the saturation pressure, $P^{\text{sat}}(T)$, and the IFTs of CO₂–CH₄, CO₂–N₂, CO₂–Ar, and CO₂–H₂ mixtures evaluated at the imposed pressure, P , for (a) 220 K, (b) 250 K, and (c) 270 K. All IFTs are computed using the PC-SAFT EoS^{28,92} with $k_{ij} \neq 0$ in combination with cDFT.

combined with cDFT. The apparent 50% underestimation of the H₂ liquid density in both the PC-SAFT EoS + cDFT and MD simulations is primarily due to its very low absolute density values, corresponding to a relative difference between 1 kg m^{−3} and 2 kg m^{−3}. The difference in density profiles computed from the PC-SAFT EoS + cDFT with $k_{ij} = 0.0474$ and $k_{ij} = 0$ was insignificant. The MD simulation shows no noticeable interfacial enrichment ($E_{\text{H}_2} \approx 1$). The PC-SAFT EoS + cDFT with $k_{ij} = 0.0474$ predicts a minor enrichment ($E_{\text{H}_2} \approx 1.1$) at 250 K and 100 bar.

To summarize, the PC-SAFT EoS with binary interaction parameters (k_{ij}) obtained from experimental P_{xy} data provided excellent agreement for the phase equilibria of the CO₂–CH₄, CO₂–Ar, and CO₂–N₂ mixtures, except for the well-known overprediction of critical pressures by PC-SAFT.^{28,92} The CO₂–H₂ system exhibited noticeable deviations due to the limited availability of experimental data for determining accurate k_{ij} values. MD simulations showed good agreement

with experimental phase equilibria for the CO₂–CH₄, CO₂–Ar, and CO₂–H₂ mixtures but deviated for CO₂–N₂, where the absence of a binary interaction parameter in the MD simulations resulted in overpredicted CO₂ liquid-phase compositions. For the phase equilibria at the corresponding temperatures and pressures, IFTs of the CO₂–CH₄ and CO₂–Ar mixtures obtained from MD simulations and from the PC-SAFT EoS combined with cDFT were in good agreement. In sharp contrast, for the CO₂–N₂ and CO₂–H₂ mixtures, the IFTs values predicted by the two approaches differ significantly. Additionally, the density profiles of the CO₂–CH₄, CO₂–Ar, and CO₂–N₂ mixtures obtained from MD simulations and from the PC-SAFT EoS combined with cDFT were compared at similar IFT magnitude ($\gamma = 4 \text{ mN m}^{-1}$) 250 K, except for the CO₂–Ar system, which was evaluated at 253.28 K. This showed that the enrichment at the interface is dependent on the impurity (LBC) component present in the mixture. It is expected to have larger enrichment at low pressures and high IFT,¹¹² but for CO₂–H₂ mixture the

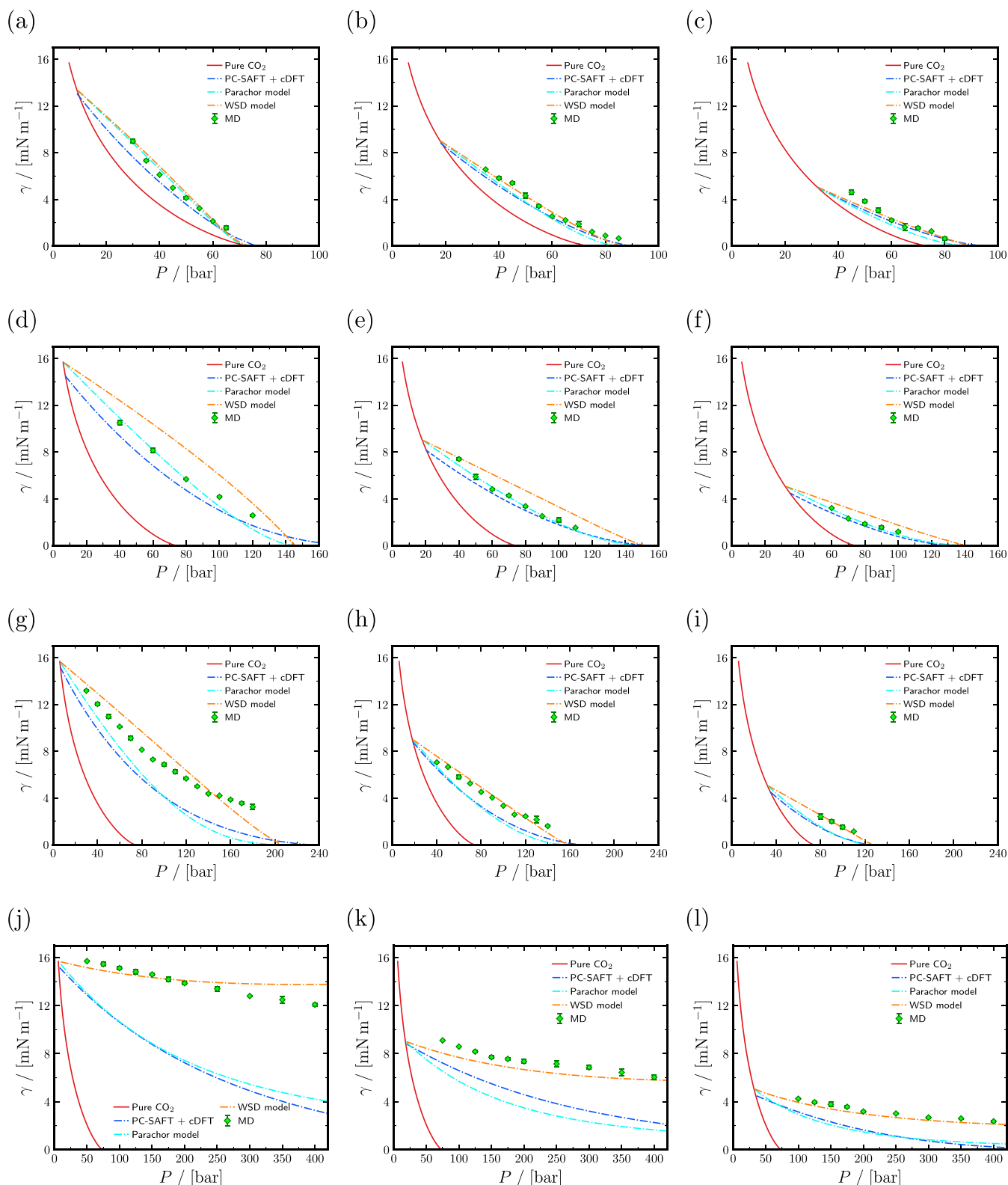


Figure 9. Comparison of IFTs computed from the PC-SAFT EoS^{28,92} with k_{ij} s combined with cDFT, Parachor model,⁵² Winterfeld–Scriven–Davis (WSD) model,⁶⁶ and MD simulations of CO₂–CH₄ mixtures at (a) 230 K, (b) 250 K, and (c) 270 K, CO₂–Ar mixtures at (d) 223 K, (e) 253.3 K, and (f) 273.3 K, CO₂–N₂ at (g) 220 K, (h) 250 K, and (i) 273.12 K and, CO₂–H₂ mixtures at (j) 220 K, (k) 250 K, and (l) 273.12 K.

enrichment of H₂ was observed to be insignificant at $\gamma = 8$ mN m^{−1} at 250 K and 100 bar. The enrichment of the LBC in the CO₂–CH₄, CO₂–Ar, and CO₂–N₂ mixtures, obtained from both MD simulations and the PC-SAFT EoS combined with cDFT for $k_{ij} = 0$ and $k_{ij} \neq 0$, is presented in Section S10 of the

Supporting Information. Interfacial thicknesses for all mixtures, computed from MD simulations and from the PC-SAFT EoS combined with cDFT using $k_{ij} = 0$ and $k_{ij} \neq 0$, are provided in Section S10 of the Supporting Information. The results show

that the interfacial thickness ranges from 0.35 to 2 nm for all binary mixtures, except in the vicinity of the critical pressure.

3.3. Effect of Impurities on IFT

The effect of impurities on IFT was evaluated by comparing IFTs of CO₂ binary mixtures with those of pure CO₂. The IFTs of the binary mixtures were obtained using the PC-SAFT EoS^{28,92} combined with cDFT and the k_{ij} parameters listed in Table 1. At temperatures where the k_{ij} values are not reported in Table 1, namely 220 K for CO₂–CH₄, 220, 250, and 270 K for CO₂–Ar, and 270 K for CO₂–N₂ and CO₂–H₂, the k_{ij} parameters were determined using a third-order polynomial fit to the values listed in Table 1. Details of the fitting procedure and the corresponding plots are provided in Section S8 of the Supporting Information. Results at 220, 250, and 270 K for CO₂–CH₄, CO₂–Ar, CO₂–N₂, and CO₂–H₂ are presented in Figure 8a–8c with the pure CO₂ IFTs. Pure CO₂ IFTs were computed using the eq 13 and using the coefficients of Cachadiña et al.⁶⁷ The pure CO₂ IFTs are plotted as a function of $\gamma(P^{\text{sat}})$ in Figure 8a–8c. The interfacial tension values $\gamma(P^{\text{sat}})$ for pure CO₂ were determined by converting the temperature dependent $\gamma(T)$ into a function of the saturated vapor pressure using $P^{\text{sat}}(T)$ values calculated from the Span and Wagner EoS.²⁶ Using $\gamma(P^{\text{sat}})$ of pure CO₂ as a reference, it can be observed from Figure 8a–c that IFTs of the binary mixtures are found over the entire two-phase region, from the onset of vapor–liquid phase separation up to the critical pressure of each binary system. At the pressure where the two-phase region starts for each binary mixture at a given temperature, IFT coincides with that of pure CO₂. This is because the liquid phase remains highly enriched in CO₂, with only negligible impurity content, as observed in the P_{xy} diagrams of Figures 4a–c, 5a–5c, 6a–6c and 7a–c. In this dilute impurity point, the impurity components (CH₄, Ar, N₂, and H₂) do not noticeably affect the IFT, and the mixture IFT values coincide with those of pure CO₂. At the dilute impurity point, the IFT can be approximated by the IFT of pure CO₂ evaluated at the saturation pressure of the binary mixture at that temperature. For example, in the CO₂–Ar system at 220 K, the two-phase region begins at ca. 8 bar (Figure 5a), where the liquid phase is nearly pure CO₂. At this pressure and temperature, the IFT of the CO₂–Ar mixture matches the pure CO₂ $\gamma(P^{\text{sat}})$, as shown in Figure 8a. Similar behavior is observed for other mixtures. The CO₂–N₂ and CO₂–H₂ systems enter the two-phase region at ca. 7 bar, while the CO₂–CH₄ mixture begins at ca. 10 bar at 230 K. At these pressures, the mixture IFTs coincide with the pure CO₂ IFTs. The same trend is observed at higher temperatures, as shown in Figure 8b,c, with the dilute impurity saturation pressures of the mixtures shifting to higher values as temperature increases.

Figure 8a–8c show that, as pressure increases at constant temperature, the CO₂-rich liquid phase is diluted by impurities, resulting in higher IFTs for the mixtures compared to pure CO₂. The magnitude of this increase depends on the volatility of the impurity component. Impurities with very low boiling points, such as H₂ and Ar, dissolve only weakly in the liquid phase and therefore exhibit the largest increase in IFT. Moderately volatile species, such as N₂, yield an intermediate response, whereas the most condensable impurity examined here, CH₄, mixes more readily with liquid CO₂ and consequently produces the smallest enhancement in IFT. In general, binary mixtures follow the trend CO₂–H₂ shows the largest increase in IFT, followed by CO₂–Ar and CO₂–N₂,

which exhibit similar behavior, while CO₂–CH₄ produces the smallest increase in IFT relative to pure CO₂. In addition, increasing the temperature reduces IFTs for both pure CO₂ and binary CO₂ mixtures, because larger temperatures weaken the interface and reduce the distinction between the liquid and vapor phases. In other words, the bulk density difference ($\rho^L - \rho^V$) decreases as the temperature increases. This leads to a decrease in the IFT.⁵²

3.4. Computation of IFT from Parachor and WSD Models

We computed IFTs for the CO₂–CH₄, CO₂–Ar, CO₂–N₂, and CO₂–H₂ binary mixtures using the semiempirical Parachor⁵² and WSD⁶⁶ models defined in eqs 14 and 20, respectively. IFTs computed from the Parachor and WSD were compared with IFTs obtained from the PC-SAFT EoS coupled with cDFT^{28,65,92} using the k_{ij} values listed in Table 1 and MD simulations. These comparisons were performed for the temperatures and mixtures given in Table 1, and the results are presented in Figure 9, where pure CO₂ IFTs were also included as a reference using the procedure described in Section 3.3. The Parachor and WSD models yield identical IFT values at the lowest pressure where the two phases coexist for the corresponding binary mixture and temperature, as well as at the critical pressure (where $\gamma \rightarrow 0$) for all binary systems shown in Figure 9a–9l. In contrast, the PC-SAFT EoS + cDFT tends to underestimate the IFTs near the low-pressure limit at the onset of the two-phase region when compared with the Parachor and WSD models. This deviation arises because the Parachor and WSD models are based on the GERG-2008 EoS,²⁷ whereas the cDFT approach uses the PC-SAFT EoS. In addition to the underestimation at the low pressure limit, the PC-SAFT EoS also tend to overestimate the two-phase pressure range.^{28,92} Therefore, only the Parachor and WSD models were compared quantitatively with the MD obtained IFT values, while the PC-SAFT EoS combined with cDFT was used for quantitative analysis. Additionally, IFT values at pressures close to the critical pressure were neglected for analysis to avoid disproportionate errors. Figure 9a–9l show that the Parachor and WSD models reproduce the expected decrease in IFT with increasing pressure. However, both models deviate from MD and PC-SAFT EoS + cDFT results, particularly in capturing the curvature of the IFT–pressure relationship. To assess the predictive performance of the Parachor and WSD models for all the binary mixtures shown in Figure 9a–9l, the MAPD values were evaluated relative to MD simulations for each binary system listed in Table 1.

Figure 9a–9c show IFTs of CO₂–CH₄ system at 230, 250, and 270 K. The Parachor model deviates by MAPDs of ca. 5%, 13%, and 30% at 230, 250, and 270 K, respectively, whereas the WSD model has MAPDs of ca. 8%, 4%, and 12% at 230, 250, and 270 K, respectively. At 230, 250, and 270 K, the WSD model generally predicts higher IFTs than the PC-SAFT EoS + cDFT for the entire pressure range, with deviations more pronounced at 230 K and diminishing near the critical region. The Parachor model aligns more closely with PC-SAFT EoS + cDFT than the WSD model. While both models exhibit a similar decreasing trend with pressure that parallels PC-SAFT EoS + cDFT, the WSD model consistently produces slightly higher IFTs than the Parachor model compared to the PC-SAFT EoS + cDFT. The WSD model shows better agreement with MD simulations than the PC-SAFT EoS + cDFT. Figure 9d–9f show IFTs of CO₂–Ar mixture at 223.07, 253.28, and 273.26 K. The WSD deviated by a MAPDs of ca. 34%, 31%,

and 36% at 223.07, 253.28, and 273.26 K, respectively. The Parachor model had considerable less MAPDs of ca. 6%, 5%, 6% at 223.07, 253.28, and 273.26 K, respectively. Compared to the PC-SAFT + cDFT, the Parachor model had a better agreement than the WSD model. At pressures less than 40 bar (Figure 9d–f), the Parachor model differed significantly with PC-SAFT + cDFT, while MD simulations had a better agreement. Figure 9g–9i show IFTs of CO₂–N₂ system at 220.07, 250, and 273.12 K. Compared to the PC-SAFT + cDFT, the Parachor model had a better agreement than the WSD model. The Parachor model insignificantly overestimated IFTs at pressures lower than ca. 80 bar in Figure 9g–9i and underestimated at pressures larger than ca. 80 bar. The Parachor model deviated by MAPDs of ca. 33%, 28%, and 49% compared to MD simulations at 220.07, 250, and 273.12 K, respectively, while the Parachor model had MAPDs of ca. 13%, 8%, and 3%. It is important to note that the MD simulations systematically overpredicted the IFTs, liquid mole fractions, and bulk densities relative to the PC-SAFT + cDFT results with $k_{ij} \neq 0$ in Figure 6, due to the use of $k_{ij}^{\text{MD}} = 0$. Consequently, the Parachor model showed higher MAPDs than the WSD model when compared with IFTs obtained from MD simulations. Figure 9j–9l show IFTs of CO₂–H₂ system at 220, 250, and 273.1 K. The WSD model shows good agreement with the IFTs obtained from MD simulations, with MAPDs of approximately 3.7%, 9.7%, and 9.5% at 220, 250, and 273.1 K, respectively. In contrast, the Parachor model exhibits significantly larger deviations, with MAPDs approaching 50% relative to the MD results. The Parachor model had a better agreement with PC-SAFT + cDFT compared to MD simulations. To summarize, the Parachor and WSD models yielded better IFT predictions for the CO₂–CH₄ mixtures, whereas the Parachor model provided more accurate IFT predictions for the CO₂–Ar and CO₂–N₂ mixtures. For the CO₂–H₂ mixtures, the WSD model provided better IFT predictions than both the Parachor model and the PC-SAFT + cDFT approach, particularly considering the limited experimental phase equilibria data available for determining the k_{ij} values at 220, 250, and 273.1 K.

3.5. Metastable Phase Boundaries of CO₂ and CO₂-Binary Mixtures

The metastable boundaries of pure CO₂ and impure CO₂ mixtures are essential for identifying when the fluid departs from equilibrium. These boundaries indicate the onset of mechanical and chemical nonequilibrium between phases during depressurization, decompression, or nozzle flow.^{62,118,119} A liquid can be expanded past its equilibrium boundary and still remain liquid for a short time.^{54,63,120} The point where it can no longer remain liquid is known as the SHL. Similarly, a vapor can be cooled or compressed past its equilibrium boundary and remain vapor until it reaches the SCL.⁶³ In this study, we compute the homogeneous metastable limits (SHL and SCL) of pure CO₂ and binary CO₂ mixtures using CNT.^{56,57} In practice, fluids undergo both homogeneous and heterogeneous nucleation. However, this study focuses on homogeneous nucleation since it is expected to dominate at larger temperatures, whereas heterogeneous nucleation is strongly influenced by surface properties and system geometry.¹²⁰ Compared to the other parameters discussed in Section 2.5 that are required to compute the SHL and SCL, the critical nucleation rate J and the interfacial tension (IFT) γ show the strongest sensitivity.⁵⁴ In particular, IFT has a

dominant influence because the free-energy barrier ΔG^* scales as γ^3 , which makes the SHL and SCL sensitive to small changes in IFT. In this study, the SHL and SCL were computed using a critical nucleation rate of $J = 10^{12} \text{ /m}^3\cdot\text{s}$, consistent with the approach of Skarsvåg et al.⁵⁴ and Aursand et al.⁶⁴ Skarsvåg et al.⁵⁴ demonstrated that changing the critical nucleation rate J by 6 orders of magnitude produced a very small change in the predicted SHL of CO₂ mixtures at low temperatures, where heterogeneous nucleation dominates. At high temperatures, where homogeneous nucleation dominates the nucleation process, the predicted SHL remained essentially unchanged. In this study, the SHL and SCL of pure CO₂ and CO₂ binary mixtures with 95 mol % CO₂ and 5 mol % CH₄, Ar, N₂, or H₂ are computed by solving the CNT using a constant nucleation rate of $J = 10^{12} \text{ /m}^3\cdot\text{s}$. IFT values of pure CO₂ required to compute the SHL and SCL were estimated using MD simulations, the PC-SAFT EoS,^{28,92} and the Guggenheim–Katayama equation (eq 13)^{33,67,86} with coefficients reported by Cachadiña et al.⁶⁷ (REFPROP v10). For CO₂–CH₄, CO₂–Ar, and CO₂–N₂ mixtures, we computed IFT values with the Parachor model,⁵² which agrees well with both MD simulations and the PC-SAFT EoS^{28,92} with $k_{ij} \neq 0$, as detailed in Section 3.4. Similarly, IFT values for CO₂–H₂ were obtained using the WSD model,⁶⁶ which agrees well with MD simulations. Although extending MD simulations to a broader temperature range would allow IFT values at saturation to be determined for each mixture and composition, such an extension is computationally intensive. The PC-SAFT EoS combined with cDFT also requires temperature-dependent values for $k_{ij}(T)$. Binary interaction parameters are typically expressed as temperature-dependent correlations obtained by fitting a limited number of k_{ij} values, such as the three values listed for each mixture in Table 1. Constructing a $k_{ij}(T)$ relationship from few data points can introduce substantial uncertainty at temperatures where no experimental measurements exist. For example, if k_{ij} is only available at 220 and 250 K, the interpolated k_{ij} at an intermediate temperature such as 225 K could be unreliable. For these reasons, we use the semiempirical Parachor and WSD models in this study to estimate IFT values for computing the SHL and SCL. We computed the saturation pressures, liquid and vapor number densities, and liquid and vapor mole fractions needed for the SHL and SCL estimation, using the Span and Wagner EoS²⁶ for pure CO₂ and the GERG-2008 EoS²⁷ for binary mixtures. In addition to the SHL and SCL, we also present the spinodal limits for pure CO₂ and binary CO₂ mixtures, computed using the PC-SAFT EoS. The spinodal marks the absolute thermodynamic stability limit of a single phase and corresponds to the points where the pressure–density curve reaches a local maximum or minimum, i.e., where $\frac{\partial p}{\partial \rho} = 0$.

Beyond this boundary, which corresponds to the region enclosed by the liquid and vapor spinodal lines, the homogeneous fluid becomes thermodynamically unstable, cannot suppress infinitesimal density fluctuations, and undergoes spontaneous phase separation through spinodal decomposition.^{56,57} The PC-SAFT EoS was chosen because multiparameter models such as Span and Wagner and GERG-2008 can introduce artificial Maxwell loops that distort the true thermodynamic stability boundary.¹⁷ Nevertheless, thermodynamic properties in metastable and unstable regions, including spinodal lines and IFTs, can also be computed from multiparameter EOSs using extrapolation techniques, such as

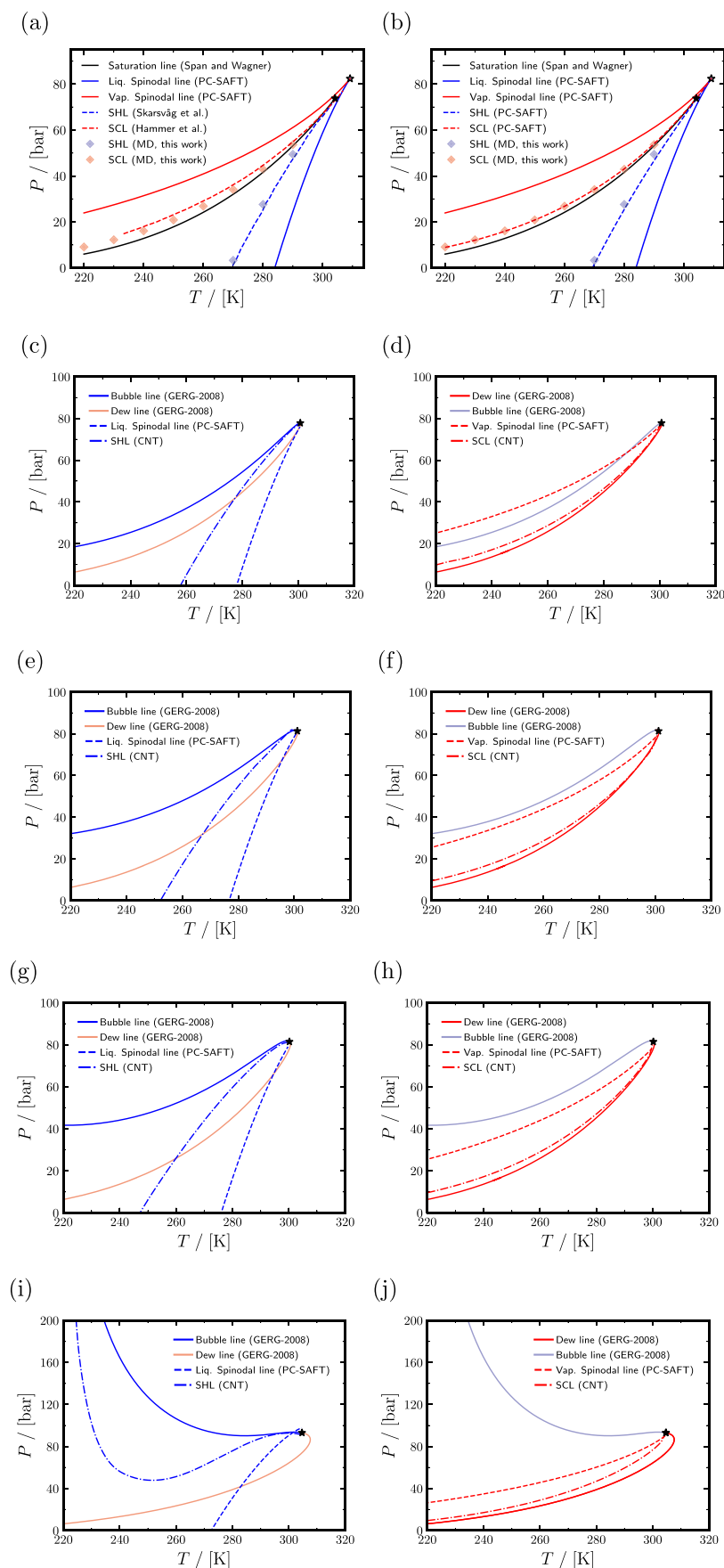


Figure 10. *PT* diagrams of pure CO₂ including the saturation line obtained from the Span and Wagner EoS,²⁶ the liquid and vapor spinodal lines from the PC-SAFT EoS,^{28,92} and the metastable limits (SHL and SCL) estimated using CNT⁵⁶ with IFTs computed from (a) MD simulations, together with the corresponding SHL and SCL from Skarsvåg et al.⁵⁴ and Hammer et al.⁶³ (b) Comparison of the SHL and SCL obtained using

Figure 10. continued

IFTs from the PC-SAFT EoS with the limits obtained from MD computed IFTs. (c–j) PT diagrams for binary CO_2 mixtures containing 95 mol % CO_2 and 5 mol % impurity. The bubble and dew lines are calculated using the GERG-2008 EoS,²⁷ and the spinodal lines are obtained from the PC-SAFT EoS.^{28,92} Metastable limits from the CNT⁵⁶ are determined using IFTs from the Parachor model for (c, d) $\text{CO}_2\text{--CH}_4$, (e, f) $\text{CO}_2\text{--Ar}$, and (g, h) $\text{CO}_2\text{--N}_2$, and using IFTs from the WSD model⁶⁶ for (i, j) $\text{CO}_2\text{--H}_2$. (c, e, g, and i) Include the dew and bubble lines together with the liquid spinodal and SHL, whereas (d, f, h, and j) include the dew and bubble lines together with the vapor spinodal and SCL. The area between the metastable and spinodal lines in (a–j) is the thermodynamically unstable area.

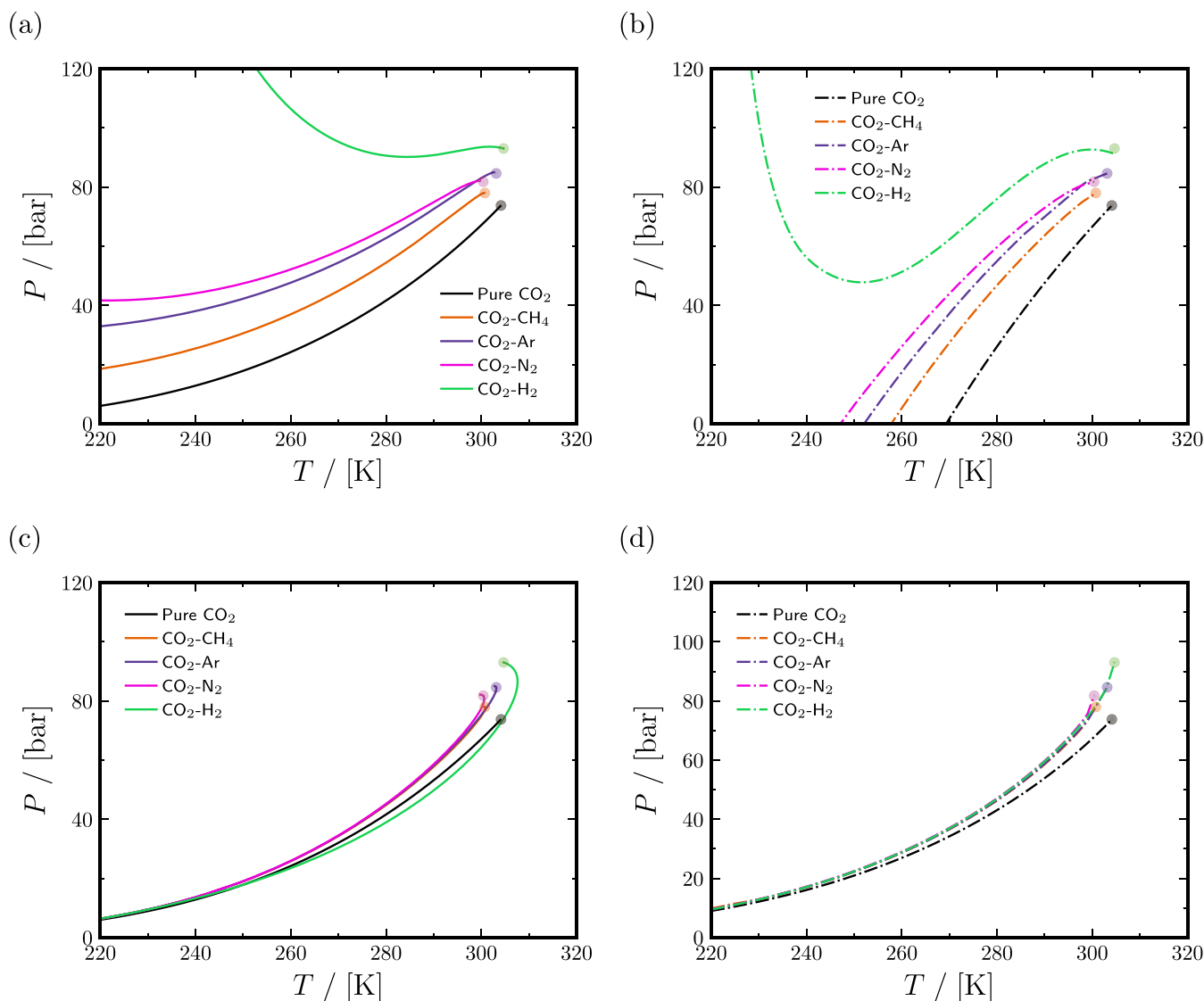


Figure 11. Comparison of (a) bubble and (c) dew lines of the $\text{CO}_2\text{--CH}_4$, $\text{CO}_2\text{--Ar}$, $\text{CO}_2\text{--N}_2$, and $\text{CO}_2\text{--H}_2$ binary mixtures containing 95 mol % CO_2 and 5 mol % impurity, computed using the GERG-2008 EoS,²⁷ with the saturation line of pure CO_2 computed using the Span and Wagner EoS.²⁶ Comparison of (b) SHL and (d) SCL lines of the same binary mixtures with the pure CO_2 SHL and SCL lines computed using CNT.⁵⁶

the isochoric pressure extrapolation with second-order temperature expansion proposed by Hammer et al.^{121,122} At realistic conditions, fluids do not typically reach the spinodal limit because nucleation initiates phase change earlier at the SHL and SCL.¹²⁰ This early onset of phase change has also been demonstrated experimentally for pure CO_2 .^{120,123} For a detailed description of spinodal lines estimation from EoS, the reader is referred to Keller et al.¹²⁴ and Aursand et al.⁶⁴

Figure 10a presents the PT phase diagram of pure CO_2 including the saturation line and spinodal lines computed from the Span and Wagner and PC-SAFT EoS, respectively. The

critical points of the Span and Wagner and PC-SAFT EoS are shown as a closed and open star marker, respectively. It is clear that the critical point of PC-SAFT EoS is overestimated, as are the spinodal lines. The region between the saturation curve and the liquid spinodal defines stable vapor and metastable liquid. The region between the vapor spinodal and the saturation curve defines stable liquid and metastable vapor. The area adjacent to the liquid spinodal corresponds to unstable liquid and stable vapor, whereas the region above the vapor spinodal corresponds to stable liquid and unstable vapor. In addition to the saturation and spinodal lines, the SHL and

SCL of pure CO₂ estimated using the CNT with IFT values computed from MD simulations are shown in Figure 10a. It is evident that the estimated SHL and SCL lines lie between the saturation curve and the spinodal limits, indicating that phase change proceeds through nucleation at these loci. The predicted SHL and SCL were validated with the results of Skarsvåg et al.⁵⁴ and Hammer et al.,⁶³ respectively. In both cases, the SHL and SCL obtained in this work were found to be slightly lower than the corresponding limits reported by Skarsvåg et al.⁵⁴ and Hammer et al.⁶³ In Figure 10b we also show the saturation line, spinodal lines, SHL, and SCL (computed using IFTs obtained from MD simulations) in addition to the SHL and SCL computed using IFTs obtained from the PC-SAFT EoS + cDFT. It is clear that the SHL predicted from the IFT values of the PC-SAFT EoS + cDFT is slightly overestimated when compared to SHL computed using IFTs obtained from MD simulation. This is due to the underestimation of IFTs computed from the PC-SAFT EoS + cDFT as shown in Figure 3a.3b. However, the SCL estimated using the IFTs computed from the PC-SAFT EoS + cDFT and MD simulations were in excellent agreement with each other. This implies that the SCL limit is not sensitive to the magnitude of IFT. The same argument can be made with the SHL and SCL limits estimated using IFTs computed from the Guggenheim–Katayama equation^{33,67,86} with coefficients reported by Cachadiña et al.⁶⁷ (REFPROP v10).

Figure 10c–10j shows the *PT* phase diagrams of CO₂–CH₄, CO₂–Ar, CO₂–N₂, and CO₂–H₂ binary mixtures containing 95 mol % CO₂ and 5 mol % impurities (CH₄, Ar, N₂, and H₂). The dew and bubble lines were computed using the GERG-2008 EoS, and the liquid and vapor spinodal lines were estimated using the PC-SAFT EoS. The critical points of binary mixtures were computed using the GERG-2008 EoS and shown as the closed markers in Figures 10 and 11. For clarity, Figure 10 excludes spinodal points above the critical point, which result from the PC-SAFT EoS overestimation of the critical point. To illustrate better, the SHL lines of CO₂–CH₄, CO₂–Ar, CO₂–N₂, and CO₂–H₂ are shown in Figure 10c,10e,10g,10i, respectively, with the bubble, dew, and liquid spinodal line. Similarly, the SCL lines of CO₂–CH₄, CO₂–Ar, CO₂–N₂, and CO₂–H₂ are shown in Figure 10d,10f,10h,10j, respectively, with the bubble, dew, and vapor spinodal line. The SHL lines adjacent to the bubble lines in Figure 10c,10e,10g,i mark the point at which the metastable liquid becomes thermodynamically unstable with respect to vapor formation, indicating the onset of homogeneous nucleation. Similarly, the SCL lines located above the dew lines in Figure 10d,f,10h,10j mark the point at which the metastable vapor becomes unstable with respect to liquid formation. For example, in the *PT* diagram of the CO₂–CH₄ mixture at 270 K (Figure 10c,10d), the liquid becomes unstable to vapor nucleation at ca. 28 bar, significantly lower than the equilibrium bubble pressure of ca. 44 bar. Similarly, the vapor becomes unstable to liquid nucleation at ca. 38 bar, slightly above the equilibrium dew pressure of ca. 37 bar. The area between the metastable limits (SHL and SCL) and the corresponding spinodal lines shown in Figure 10 is the thermodynamically unstable area, where infinitesimal density perturbations grow spontaneously and drive phase transition. In comparison with the SCL limits, the SHL limits show a more pronounced deviation from the corresponding saturation lines (bubble and dew lines), particularly at temperatures far from the critical temperatures of binary mixtures. A direct

comparison of the bubble lines of the CO₂ binary mixtures with the pure CO₂ saturation line is presented in Figure 11a, while Figure 11b compares the SHL lines of binary mixtures with the pure CO₂ SHL line. In both cases, the phase boundary shift follows the same trend, with the CO₂–H₂ mixture exhibiting the largest deviation from pure CO₂, followed by CO₂–N₂, CO₂–Ar, and CO₂–CH₄. The dew lines of the CO₂ binary mixtures, shown in Figure 11c, lie very close to one another and closely follow the pure CO₂ saturation line over the full two-phase temperature range, with noticeable deviations close to the critical region. The largest deviation compared to the pure CO₂ is observed for the CO₂–H₂. A similar behavior is observed for the SCL limits of binary mixtures shown in Figure 11d, where all mixtures exhibit nearly identical curves at low and intermediate temperatures. Interestingly, impurities do not introduce the systematic shifts seen in the SHL limits, indicating that the vapor phase metastable boundary is likely insensitive to impurities and thus the IFT. However, when compared with the pure CO₂ SCL line, the binary mixture SCL lines deviate substantially above ca. 270 K, where homogeneous nucleation dominates. This behavior indicates that a small 5 mol % impurity concentration can influence the instability of the vapor, despite the SCL lines of binary mixtures showing no significant difference. These findings indicate that the liquid-to-vapor transition through homogeneous nucleation is strongly influenced by both impurity type and concentration, whereas the vapor-to-liquid transition is primarily governed by concentration and exhibits minimal sensitivity to impurity type. The delay in phase transition, represented by the SHL and SCL lines estimated from the CNT, must be taken into account when modeling CO₂ flows undergoing decompression, depressurization, valve throttling, nozzle discharge, or flow through constrictions. The resulting *PT* diagrams, annotated with the saturation line, SHL, and SCL, provide essential insight into the thermodynamic behavior of two-phase CO₂ rich mixtures with impurities. The *PT* diagrams provide essential input for modeling two-phase CO₂ flows^{54,63} and for interpreting controlled laboratory studies, including vertical test section experiments that examine rapid phase transitions and nucleation behavior relevant to CCS injection systems.¹²⁵ Future work will focus on experiments that examine rapid phase transitions of CO₂ with impurities in the vertical test section.

4. CONCLUSIONS

In this study, we used MD simulations and the PC-SAFT EoS coupled with cDFT to compute the phase equilibria and interfacial properties of pure and CO₂–CH₄, CO₂–Ar, CO₂–N₂, and CO₂–H₂ binary CO₂ mixtures. The VLE and IFTs of pure CO₂ were validated with the Span and Wagner EoS²⁶ and the Guggenheim–Katayama³³ equation using the coefficients of Cachadiña et al.,⁶⁷ respectively. IFTs of pure CO₂ computed from MD simulations and the PC-SAFT EoS coupled with cDFT were within the maximum RPD of 11.7% reported by Cachadiña et al.,⁶⁷ except at temperatures close to the critical temperature. The interfacial thickness of pure CO₂ was found to range from approximately 0.5 to 2 nm for the temperature range of 220 to 290 K, based on both MD simulations and the PC-SAFT EoS combined with cDFT. The phase equilibria computed from MD simulations and the PC-SAFT EoS for CO₂–CH₄ mixtures at 230, 250, and 270 K and for CO₂–Ar mixtures at 223.1, 253.2, and 273.2 K showed good agreement with experimental data, except for the (well-known) over-

estimation of the critical pressures by the PC-SAFT EoS. For CO₂–N₂ mixtures at 220, 250, and 273.1 K, the PC-SAFT EoS with $k_{ij} \neq 0$ exhibited excellent agreement with experimental data, whereas MD simulations overpredicted the liquid mole fraction of CO₂ due to the absence of binary interaction parameters in the MD simulations. For CO₂–H₂ mixtures at 220, 250, and 273.1 K, the PC-SAFT EoS with $k_{ij} \neq 0$ produced phase envelopes that deviated significantly from the limited experimental data available, while MD simulations showed better agreement. At the same temperatures and pressures corresponding to the computed phase equilibria, the IFT values of CO₂–CH₄, CO₂–Ar, CO₂–N₂, and CO₂–H₂ systems were computed. IFTs of binary mixtures computed from MD simulations showed good agreement with the PC-SAFT EoS with $k_{ij} \neq 0$, but IFTs of CO₂–N₂ and CO₂–H₂ differed significantly. The interfacial thickness of the CO₂–CH₄, CO₂–Ar, CO₂–N₂, and CO₂–H₂ binary mixtures was found to range from approximately 0.35 to 2 nm, excluding the vicinity of the critical pressure, where the interfacial thickness diverges. The density profiles from MD simulations and the PC-SAFT EoS + cDFT agreed well for the CO₂–CH₄, CO₂–Ar, and CO₂–H₂ systems. However, for the CO₂–N₂ system, the density profiles from MD simulations differed from those predicted by the PC-SAFT EoS combined with cDFT due to $k_{ij}^{\text{MD}} = 0$. The enrichment of the impurities (LBC) at the interface was identified for all binary mixtures based on the density profiles obtained from MD simulations and the PC-SAFT EoS + cDFT. The enrichment of LBC decreased with increasing temperatures and pressures. We showed that the enrichment at the interface is dependent on the LBC in the mixture. The influence of impurities on IFT was assessed by comparing IFTs predicted using the PC-SAFT EoS combined with cDFT framework. For binary CO₂ systems, the IFTs initially coincide with those of pure CO₂ at the onset of phase separation, since the liquid phase is almost entirely CO₂ at that point. As pressure increases and impurities dissolve into the CO₂ rich liquid phase, the IFT increases compared to pure CO₂. The magnitude of this increase follows impurity volatility, with H₂ having the largest effect, followed by Ar and N₂ (similar), and then CH₄. It was also observed that increasing temperature leads to lower IFTs for all binary mixtures. To determine which semiempirical approach most accurately predicts interfacial tensions of binary mixtures considered in this study, the Parachor and WSD models were evaluated with IFTs obtained from MD simulations and the PC-SAFT EoS + cDFT framework. Both semiempirical models capture the overall IFT–pressure trend, but their quantitative accuracy varies depending on the mixture. The Parachor model performs best for the CO₂–Ar and CO₂–N₂ mixtures, while both models show strong agreement for the CO₂–CH₄ mixture. For the CO₂–H₂ mixtures, the WSD model provides the most reliable predictions compared to MD simulations. Based on the IFTs computed from the semiempirical models and their agreement with results from the PC-SAFT EoS + cDFT and MD simulations, we applied the Parachor and WSD models to estimate the SHL and SCL lines in the *PT* phase diagram. These estimates were made for binary CO₂ mixtures containing 95 mol % CO₂ and 5 mol % impurity (CH₄, Ar, N₂, or H₂). To validate the approach for predicting the metastable limits (SHL and SCL), we computed SHL and SCL for pure CO₂ using IFTs computed from MD simulations, the PC-SAFT EoS + cDFT, and the Guggenheim–Katayama correlation. The computed SHL and SCL lines differed slightly

from those reported in the literature.^{54,63} We compared the bubble, SHL, dew, and SCL lines of the binary mixtures with the saturation, SHL, and SCL lines of pure CO₂. The bubble line exhibited the largest shift for the CO₂–H₂ mixture, followed by CO₂–N₂, CO₂–Ar, and CO₂–CH₄, relative to pure CO₂. The SHL lines of the mixtures showed the same trend, as expected. In contrast, the SCL lines of the mixtures displayed negligible differences from one another and aligned closely with the pure CO₂ SCL line below 270 K. Near the critical region of each mixture, the SCL lines of all the binary mixtures exhibited noticeable deviations compared to the pure CO₂ SCL line. Our results demonstrate that the SHL depends on both the impurity type and its concentration, while the SCL is influenced primarily by the overall impurity concentration rather than the specific species present in the CO₂ stream. These findings emphasize that understanding IFT and its use in estimating metastable limits are crucial for modeling rapid phase transitions in CO₂ rich mixtures.

■ ASSOCIATED CONTENT

Data Availability Statement

All the raw and processed data supporting this work are available in the [Supporting Information](#).

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.5c04932>.

Raw VLE, interfacial properties, and metastable limit data of CO₂ binary mixtures ([ZIP](#))

Force field parameters used in MD simulations, PC-SAFT EoS parameters for VLE and interfacial properties computation, empirical correlation models to compute IFTs of pure components, VLE data of pure CO₂ obtained from MD simulations, details of interfacial tension computation from MD simulations, VLE and interfacial properties of pure CO₂, experimental P_{xy} data for binary CO₂ mixtures, binary interaction parameters (k_{ij}) used in PC-SAFT EoS computations, interfacial properties of binary CO₂ mixtures, phase equilibrium and interfacial properties data of binary CO₂ mixtures, superheat and supercool limit data of pure CO₂ and CO₂ binary mixtures ([PDF](#))

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D.R.: Simulations, data analysis, writing of original and revised manuscript. R.S.: Conceptualization, data analysis, co-supervision of project, proofreading of original and revised manuscript. M.R.: Conceptualization, data analysis, co-supervision of project, proofreading of original and revised manuscript. T.J.H.V.: Funding acquisition, conceptualization, data curation, main supervision of the project, writing of original and revised manuscript.

Notes

The authors declare no competing financial interest.

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