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Exploring the Thermodynamics and Dynamics of CO₂ Using Rigid Models

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Abstract: Understanding the behavior of carbon dioxide (CO₂) under varying thermodynamic conditions is essential for optimizing processes such as Carbon Capture and Storage (CCS) and supercritical fluid extraction. This study employs molecular dynamics (MD) simulations with the EPM2 and TraPPE-small force fields to examine CO₂ phase behavior, structural characteristics, and transport properties across a temperature range of 228–500 K and pressures from 1 to 150 atm. Our findings indicate a good agreement between simulated and experimental liquid–vapor coexistence curves, validating the capability of both force fields to model CO₂ accurately in a wide range of thermodynamical conditions. Radial distribution functions (RDFs) reveal distinct interaction patterns in liquid and supercritical phases, while mean squared displacement (MSD) analyses show diffusivity increasing from 5.2×10^{-9} m²/s at 300 K to 1.8×10^{-8} m²/s at 500 K. Additionally, response functions such as the heat capacity effectively capture phase transitions. These findings provide quantitative insights into CO₂ phase behavior and transport properties, enhancing the predictive reliability of simulations for CCS and related industrial technologies. This work bridges gaps in the CO₂ modeling literature and highlights the potential of MD simulations in advancing sustainable applications.

Keywords: carbon dioxide; phase behavior; molecular dynamics; EPM2 force field; TraPPE force field; thermophysical properties; LAMMPS; subcritical and supercritical isobars



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1. Introduction

Carbon dioxide (CO₂) is one of the most studied molecules in modern science, primarily due to its dual role in climate change and as a critical component in industrial processes. As a major greenhouse gas, CO₂ contributes significantly to global warming, and its atmospheric concentration has increased by over 50% since the pre-industrial era [1]. In fact, understanding the behavior of CO₂ under varying thermodynamic conditions is essential for developing effective mitigation strategies. In particular, CO₂ plays a central role in Carbon Capture and Storage (CCS) technologies, which aim to reduce the amount of CO₂ released into the atmosphere by capturing it from industrial emissions and storing it in geological formations or porous materials [2–6]. The efficiency of these processes relies heavily on a precise understanding of CO₂'s phase behavior and transport properties at distinct conditions [7].

In addition to its environmental implications, CO₂ has emerged as a versatile compound with numerous industrial applications. An example is its use as a supercritical fluid

in supercritical fluid extraction (SFE), a process increasingly employed in food, pharmaceutical, and material industries. When CO₂ is above its critical temperature (304.25 K) and critical pressure (73.8 atm), it enters a supercritical state, where it exhibits unique properties that combine the diffusivity of a gas with the solvation power of a liquid [8–10]. This makes supercritical CO₂ (scCO₂) an ideal solvent for a variety of applications, from natural product extraction to advanced material synthesis [11,12]. Its low toxicity, non-flammability, and environmentally benign nature make scCO₂ an attractive alternative to traditional organic solvents, positioning it as a “green” solvent in the context of sustainable industrial processes [13–15]. In this direction, one of the most significant uses of scCO₂ is in extracting essential oils, flavors, and active pharmaceutical ingredients from natural sources. The supercritical fluid acts as a highly efficient solvent, selectively dissolving desired compounds while leaving behind unwanted residues [16–18]. This process increases both yield and purity while avoiding the environmental and health risks associated with traditional organic solvents. For instance, in the food industry, scCO₂ is used to extract caffeine from coffee beans, flavors from herbs, and pigments from plants, all while preserving the quality of the final product [16,19]. Moreover, scCO₂ is widely employed in the pharmaceutical industry for the extraction of active ingredients from medicinal plants, offering a cleaner and more efficient alternative to traditional extraction methods that rely on toxic solvents [17,20].

Another area where CO₂ plays a crucial role is in its application as a processing solvent for polymers and materials [21–24]. Due to its tunable properties, scCO₂ can be used to control the morphology and crystallinity of polymers during synthesis, allowing for the creation of materials with specific properties tailored to particular applications. This has been particularly useful in the development of biodegradable polymers and other environmentally friendly materials. Additionally, scCO₂ is used as a medium for chemical reactions, where it can act as both a solvent and a reactant [25]. Its role in catalysis is especially noteworthy, facilitating efficient mass transfer and enabling cleaner product separation in green chemistry applications. Also, chemical methods such as the use of scale inhibitors have proven effective in controlling salt precipitation in oilfields [26–28]. These approaches could be integrated with CO₂ injection techniques, where CO₂-induced pressure and temperature changes may exacerbate scaling issues. A combined strategy could mitigate scale formation while enhancing oil recovery, offering a more robust solution for long-term reservoir management.

Despite the broad range of applications, there are research gaps in understanding CO₂'s complex phase behavior under varying thermodynamic conditions. Understanding these behaviors is particularly crucial for optimizing industrial processes such as CCS and SFE, where accurate predictions of phase transitions and transport properties can significantly enhance efficiency and cost-effectiveness. This highlights the necessity of precise computational approaches to complement experimental techniques. Significant changes in density, viscosity, and solubility as CO₂ transitions from subcritical to supercritical states further reinforce this need. Computational studies of CO₂ have a long history, and recent decades have seen a significant increase in the development of force field models. This growth enables a comprehensive study of subcritical and supercritical isobars.

Molecular dynamics (MD) simulations have emerged as a powerful method for investigating the microscopic properties of CO₂. This methodology enables the calculation of phase equilibria, transport properties, and structural information that are often difficult to obtain experimentally. The present study leveraged two well-established force fields—Elementary Physical Model 2 (EPM2) and Transferable Potentials for Phase Equilibria (TraPPE-small) [29,30]—to simulate CO₂ behavior under subcritical and supercritical isobars. The EPM2 model was specifically developed to accurately reproduce liquid-phase properties of CO₂, focusing on phase equilibria, density, and critical point data. It uses

site-specific interactions for carbon and oxygen atoms and is tuned for pure CO₂ systems. On the other hand, the TraPPE-small model was designed for broader applicability, including gas-phase and mixture simulations. Its transferable nature enables it to simulate CO₂ in mixtures with hydrocarbons or other compounds, making it ideal for industrial applications where CO₂ coexists with other species.

In this direction, we conducted, in this work, a comprehensive evaluation of CO₂ behavior using the EPM2 and TraPPE-small force fields across a wide range of pressures and temperatures, offering a detailed comparison of their performance under subcritical, critical, and supercritical conditions. We analyze both thermodynamic and dynamic properties, including response functions such as heat capacity and the Widom line, as well as transport properties like mean squared displacement and viscosity, emphasizing their relevance for industrial applications such as CCS and SFE.

This paper is organized as follows: In Section 2, we discuss the CO₂ models and the details of our simulations. In Section 3, we present and discuss our findings, and Section 4 outlines our conclusions and their implications.

2. The Models and Computational Details

Several potential models have been developed to accurately represent the behavior of CO₂ under varying conditions [7,29–31]. The most widely used are site–site interaction models, which describe interactions among the three atoms belonging to distinct CO₂ molecules. In this study, we employed two of such models: the Elementary Physical Model 2 (EPM2) and the Transferable Potentials for Phase Equilibria (TraPPE-small) [29,30]. The interaction potential between atoms in distinct CO₂ molecules is modeled using a combination of Lennard-Jones (LJ) and Coulomb potentials. The Lennard-Jones potential, given by Equation (1), describes van der Waals interactions:

$$U_{ij}^{LJ}(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right], \quad (1)$$

where ϵ_{ij} is the Lennard-Jones energy parameter (in kilojoules per mole, kJ/mol), and σ_{ij} and r_{ij} are the distance parameters (in angstroms, Å) and also the separation between atoms i and j [32,33]. This equation is fundamental to modeling the short-range repulsion and long-range attraction between particles in CO₂ simulations.

Electrostatic interactions are modeled using the Coulomb potential, shown in Equation (2):

$$U_c(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}. \quad (2)$$

where q_i and q_j are the atomic charges (in elementary charge units, e), r_{ij} is the separation distance (in angstroms, Å), and ϵ_0 is the permittivity of free space (8.854×10^{-12} C²/J·m) of the electric field [32]. This equation captures long-range interactions crucial for accurately simulating CO₂ dynamics.

Bonded interactions in CO₂ are modeled using harmonic potentials for bond length and angle. The bond potential governs the distance between bonded atoms, and the angle potential maintains the bond angles within the molecule [32]. Since the vibrational modes are relevant only at high temperatures, above 10⁴ K, it is usual to constrain the vibrations, creating the so-called rigid models, like the ones employed in this study [34]. Algorithms like SHAKE or LINCS can constrain the bond lengths and angles, ensuring structural stability during simulations—here, the SHAKE algorithm was employed [35]. This approach ensures the stability of the rigid CO₂ models used in this study.

The main difference between the models came from the LJ σ and ϵ parameters and for the charge residue in each atom, as listed in Table 1. One of the main differences is that the TraPPE force field was developed for mixtures (transferable force field), while the EPM2 was designed without this focus on transferability to mixtures. The former is ideal for calculations with lower computational cost, as it is more efficient in its implementation. On the other hand, the EPM2 demonstrates greater computational complexity due to its more detailed calculation of intermolecular interactions. Choosing both force fields for this study is interesting because one proves to be more advantageous where the other presents limitations, thus together providing a comprehensive result.

Table 1. Parameters of the models used to simulate CO₂ in this work.

Model	d_{OC} (Å)	ϵ_{C-C}/k_b (K)	α_{C-C} (Å)	ϵ_{O-O}/k_b (K)	α_{O-O} (Å)	q_C (e)	q_O (e)
EPM2	1.149	28.129	2.757	80.508	3.033	+0.6512	−0.3256
TraPPE-small	1.160	27.0	2.800	79.0	3.050	+0.700	−0.350

The cutoff distances for non-bonded interactions are also distinct in these models. The EPM2 uses a specific mathematical form (exponential-6 potential) that approximates the van der Waals interactions for systems like carbon dioxide. The exponential decay of the interactions means that the forces between particles drop off more rapidly with distance. As a result, a shorter cutoff distance (10 Å) might be sufficient to capture most of the significant interactions without losing much accuracy. The choice of 10 Å balances computational efficiency and the need to model interactions accurately. On the other hand, the TraPPE-small model is designed for small molecules and is often used in simulations involving a variety of substances, including hydrocarbons, CO₂, and other fluids, and typically, it decays more slowly compared to the EPM2 model. This slower decay might necessitate a longer cutoff distance (in this work, we employ 15 Å) to ensure that the longer-range interactions are captured accurately, especially for small, less polar molecules where these interactions are important. Long-range electrostatic interactions were computed using the particle–particle–particle–mesh (PPPM) method for greater efficiency and accuracy in large-scale simulations [36].

Simulations were carried out using the molecular dynamics (MD) software package LAMMPS 3 Mar 2020 [37], freely available at lammmps.org in the *NPT* ensemble, with temperature and pressure regulated by the Nosé–Hoover thermostat and barostat [33]. The Velocity–Verlet algorithm with a time step of 1 fs was used to integrate the equations of motion [38]. The initial configuration was built from a topology file and expanded to a simulation box containing 512 CO₂ molecules. After an equilibration phase of 1 ns, the system evolved for 1.0 ns, with thermodynamic properties recorded every 0.1 ns.

The EPM2 and TraPPE-small models were used to simulate over 12 isobars between 1 atm and 150 atms, covering the subcritical and supercritical CO₂ experimental isobars. Distinct heating ramps from 228 K to 500 K were performed for each isobar, while data analyses of temperature, volume, density, viscosity, radial distribution functions ($g(r)$), and mean squared displacements (*MSD*) were carried out using log files obtained from LAMMPS and post-processing scripts as described in our previous works [39–43].

To analyze the phase transitions and the locus of the maximum of response functions close to the critical point at the fluid phase, we calculated the specific heat at constant pressure C_p , which was calculated as in Equation (3):

$$C_p = \frac{1}{N} \left(\frac{\partial H}{\partial T} \right)_p, \quad (3)$$

where $H = U + PV$ is the enthalpy (in kilojoules per mole, kJ/mol, with V is the mean volume from NPT simulations), T is the temperature (in kelvins, K), N is the number of molecules, and P is the pressure (in atmospheres, atm). The derivatives are obtained from statistical fluctuations [32]. This parameter aids in identifying critical behavior near the fluid phase's critical point.

The system's dynamical properties were analyzed through the mean squared displacement (MSD), as defined in Equation (4):

$$\langle [\vec{r}(t) - \vec{r}(t_0)]^2 \rangle = \langle \Delta \vec{r}(t)^2 \rangle, \quad (4)$$

where $\vec{r}(t_0)$ and $\vec{r}(t)$ denote the positions of a particle at subsequent times t_0 and t , respectively (in angstroms, Å) [32]. The MSD relates to the diffusion coefficient D via the Einstein relation (Equation (5)):

$$D = \lim_{t \rightarrow \infty} \frac{\langle \Delta \vec{r}(t)^2 \rangle}{6t}. \quad (5)$$

where $\langle \Delta \vec{r}(t)^2 \rangle$ is the mean squared displacement (in square angstroms, Å²), and t is the time (in picoseconds, ps). This relation connects molecular motion to macroscopic diffusion properties [33].

Also, we evaluated the viscosity using the Green–Kubo formalism, expressed in Equation (6), as the autocorrelation function of the off-diagonal components of the stress tensor:

$$\eta = \frac{V}{k_B T} \int_0^\infty \langle P_{\alpha\beta}(0) P_{\alpha\beta}(t) \rangle dt, \quad (6)$$

where V is the system volume (in cubic angstroms, Å³), k_B is the Boltzmann constant (1.38×10^{-23} J/K), T is the temperature (in kelvins, K), $\langle P_{\alpha\beta}(0) P_{\alpha\beta}(t) \rangle$ denotes the components of the stress tensor (in atmospheres, atm), and t is the time (in picoseconds, ps) [44,45]. This formulation provides insight into the fluid's resistance to shear deformation.

Distinct isobars spanning pressures from 1 atm to 150 atm and temperatures from 228 K to 500 K were simulated for both subcritical and supercritical regimes. Thermodynamic properties, including density, viscosity, RDF ($g(r)$), MSD, and response functions, were extracted using LAMMPS and custom post-processing scripts [39,40]. These results enable detailed comparisons of CO₂ behavior across force fields and thermodynamic conditions.

3. Results

3.1. Thermodynamical Behavior

Guggenheim's seminal work [46] laid the foundation for analyzing gas–liquid coexistence behavior, particularly near the critical point where the liquid and vapor densities converge and become indistinguishable. This diagram is particularly useful because it highlights the coexistence of phases by showing how the liquid and vapor densities evolve as the system approaches the critical point along isobars. In the case of subcritical pressures, we observe two distinct branches: one corresponding to the liquid phase (high density) and the other to the vapor phase (low density). These branches converge as the temperature approaches the critical temperature T_c and the isobar is close to the critical pressure P_c , and at the critical point, both branches merge into a single density value. The CO₂ critical point is well established in the literature [47–50]: $P_c = 72.9$ atm and $T_c = 304.2$ K. Building on this approach, we begin our discussion by presenting the behavior of T versus ρ along subcritical, critical, and supercritical isobars for both models: TraPPE-small in Figure 1a and EPM2 in Figure 1b. For comparison, we also include the experimental results from [29] in both phase diagrams.

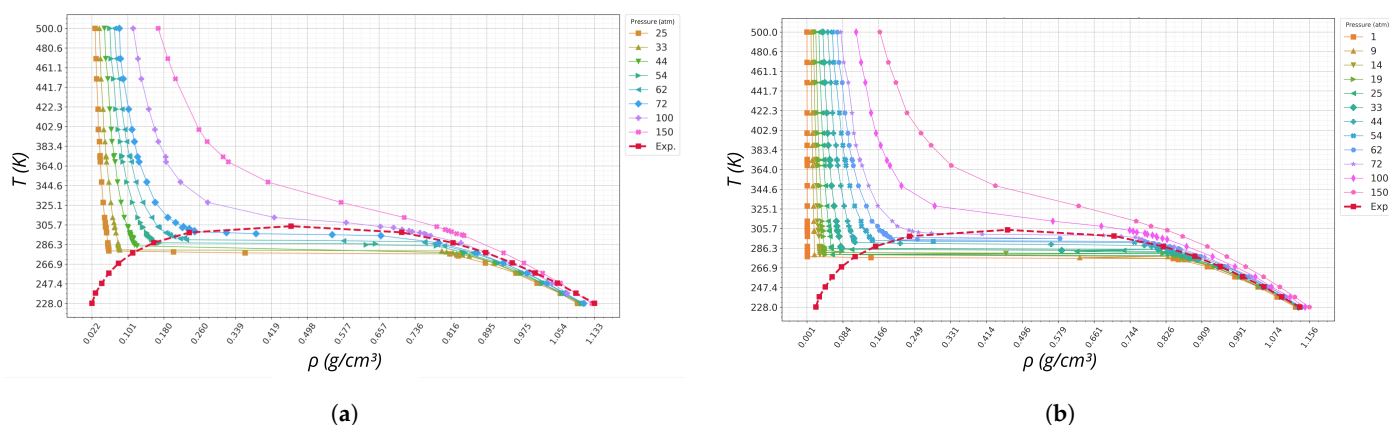


Figure 1. Temperature vs. density (T vs. ρ) isobars for CO_2 using the TraPPE-small (a) and EPM2 (b) models. The densities were estimated as the mean value along the simulations. Error bars are smaller than the points. The red dashed line represents the experimental coexistence line at saturation pressure, obtained from Ref. [29]. The simulations cover a pressure range of 1–150 atm, while the experimental coexistence line corresponds to equilibrium data under vapor–liquid conditions.

This coexistence region is important because it coincides with a liquid–vapor phase transition, which represents the temperatures and pressures where the system can exist in a low-density phase (gas phase) or a high-density phase (liquid phase) [48,51]. Our results align closely with the comprehensive equation of state provided by Span and Wagner [47], which demonstrated high accuracy in predicting CO_2 's vapor–liquid equilibrium properties. In particular, the EPM2 model's performance in capturing liquid-phase densities strongly reflects Span and Wagner's calibrated values for saturated liquid densities, emphasizing its reliability near the critical point. Additionally, TraPPE-small's gas-phase predictions corroborate findings by Potoff and Siepmann [30], who noted its accuracy in modeling low-density regions for multi-component systems.

Both models clearly capture the gas–liquid coexistence region. Since we utilize the NPT ensemble, Figure 1a,b show the coexistence of a low-density phase and a high-density phase at the same temperature for subcritical pressures and temperatures. In particular, both models also exhibit points within the metastable/coexistence region. Interestingly, the TraPPE-small model more accurately reproduces the gas phase branch of the coexistence curve, even at lower temperatures, but performs less well in predicting the density along the liquid phase branch [30]. Additionally, the critical isobar for TraPPE-small (72 atm) lies below the true critical point [49,50]. In contrast, the EPM2 model's critical isobar aligns more closely with the experimental critical point and better captures the liquid-phase densities, although it shows weaker agreement in the low-density branch [29].

The T vs. ρ phase diagram is directly interconnected with the P vs. ρ phase diagram, which provides complementary information about the behavior of a system along the coexistence line up to the critical point, where the gas and liquid phases become indistinguishable. Both models' predictions are consistent with experimental critical point data reported by Duschek et al. [49] and Michels et al. [48]. For example, the EPM2 model accurately aligns with the critical density and pressure values established in these studies, further validating its parameterization for pure CO_2 . In contrast, TraPPE-small exhibits a slight underestimation of critical isobar pressures, a trend also observed in similar transferable force fields designed for broader applicability [30].

As we vary the pressure along an isotherm, we observe distinct regions that correspond to the liquid phase, vapor phase, and the phase coexistence region, known as the binodal curve. Near the critical temperature T_c , this coexistence region shrinks and eventually disappears at the critical point. The critical point is characterized by the fact that the isotherm ($T = T_c$) is tangent to the binodal curve at a single point, where the liquid and

vapor densities become equal. The T vs. ρ phase diagram is directly interconnected with the P vs. ρ phase diagram, shown in Figure 2a,b. It provides complementary information about the behavior of the system along the coexistence line up to the critical point, where gas and liquid phases become indistinguishable [47,48]. As in the T vs. ρ diagram, both models exhibit the coexistence of two distinct densities at a single pressure along isotherms, showing good agreement with experimental results [29,49]. Although even better agreement could be achieved by running longer simulations with a larger number of particles, this analysis demonstrates that these relatively simple models can effectively capture and represent the overall thermodynamic behavior of CO₂.

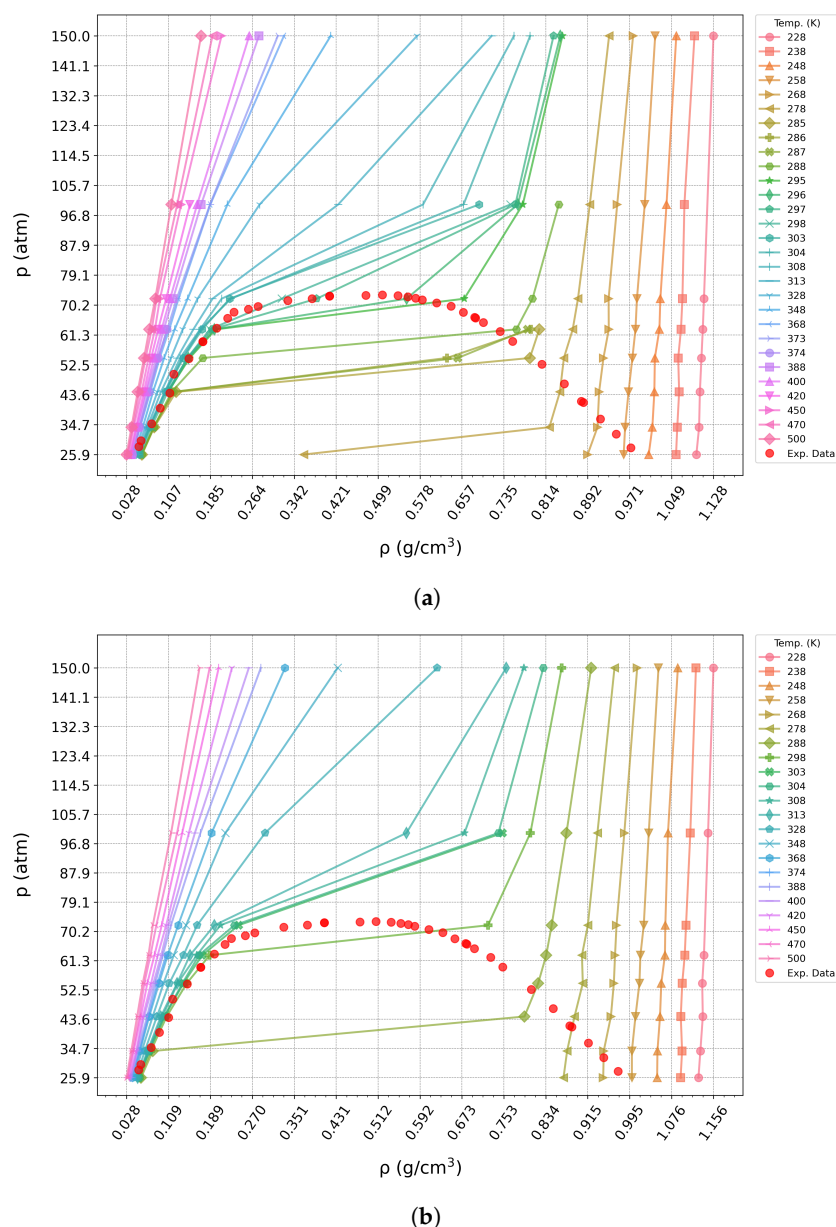


Figure 2. P vs. ρ diagrams for CO₂ using the TraPPE-small (a) and EPM2 (b) models. The simulations were performed over a temperature range of 228–500 K. Experimental points obtained from Ref. [49] correspond to isothermal measurements near the CO₂ critical region.

Despite their minor differences—such as in the LJ parameters and partial charges—the EPM2 and TraPPE-small models consistently reproduce key experimental features. For instance, the EPM2 model excels in predicting liquid-phase densities, whereas TraPPE-small better captures gas-phase properties, particularly at lower temperatures [29,30,52].

The distinction between the models aligns with the previous literature, where Harris and Yung [29] highlighted EPM2's superior accuracy in reproducing liquid-phase densities and phase equilibria. Conversely, TraPPE-small's transferable nature enables more versatile applications, particularly in multi-component systems, as emphasized by Potoff and Siepmann [30]. These findings reinforce the complementary strengths of both models in addressing specific aspects of CO₂ thermodynamics.

These differences highlight the models' design goals: EPM2 is tailored for pure CO₂ systems with a focus on accurately reproducing the critical point, whereas TraPPE-small is optimized for broader applications, including mixtures, making it more versatile in capturing gas-phase behavior [29,30]. The ability of both models to achieve strong experimental agreement across phases underscores their robustness and reliability for studying CO₂ in various thermodynamic states.

To gain deeper insights into their predictive capabilities, it is essential to analyze how these models represent the energetic behavior of CO₂, particularly the variation of energy along distinct isobars. Such an analysis would further clarify their effectiveness in describing the microscopic mechanisms underlying phase transitions and critical phenomena.

By evaluating the specific heat capacity along the isobars, C_p , as shown in Figure 3a,b for the TraPPE-small and EPM2 models, respectively, we observe that this thermodynamic response function exhibits a discontinuity at the liquid-gas phase transition for both models. The behavior of C_p observed in our study mirrors the trends reported by Span and Wagner [47], who utilized caloric data to refine CO₂ equations of state. Additionally, the peaks in C_p along the critical isobar, indicative of the Widom line, align well with the experimental observations of Duschek et al. [49]. These findings underscore the capability of both models to capture critical phenomena and thermodynamic response functions with high fidelity. Consistent with the behavior expected in a first-order phase transition. As the system approaches the critical point, this discontinuity evolves into a peak at the critical pressure, reflecting the inflection in the isobar and the absence of latent heat, characteristic of the continuous nature of the transition beyond the critical point. In the supercritical regime, the maxima in C_p corresponds to the Widom line, which terminates at the gas-liquid critical point.

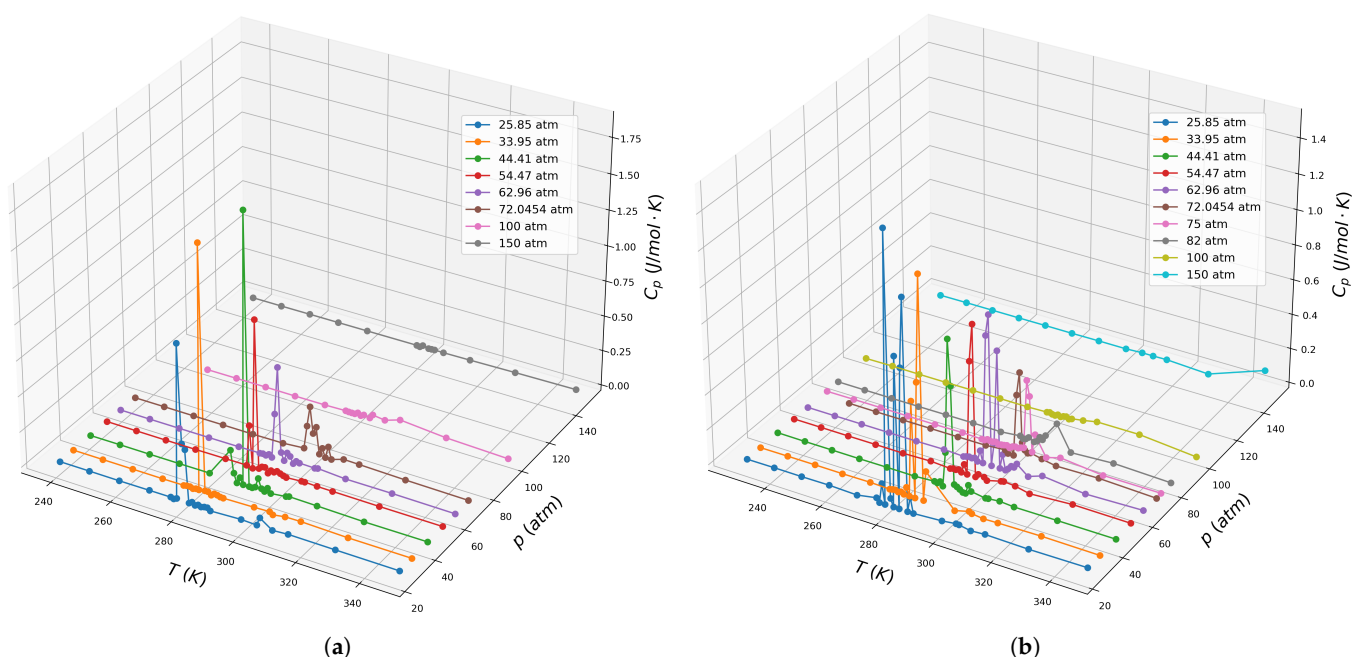


Figure 3. Specific heat capacity (C_p) as a function of temperature and pressure for CO₂ using two different models: TraPPE-small (a) and EPM2 (b).

Both the TraPPE-small and EPM2 models effectively capture this behavior despite their parameter differences. The accurate identification of the Widom line by both models highlights their capability to describe the crossover between liquid-like and gas-like behaviors in the supercritical regime. This further underscores their utility in studying phase transitions and critical phenomena in CO₂ across a wide range of thermodynamic conditions.

3.2. Dynamical Behavior

The mean squared displacement (MSD) analysis enable us to distinguish between different dynamic regimes as a system transitions from a gas-like, highly diffusive phase to a liquid-like, less diffusive phase. The trends observed in the MSD results align well with prior findings in supercritical fluid dynamics. McHugh and Krukoniš [53] emphasized that the transition from gas-like to liquid-like behavior in supercritical CO₂ is characterized by a continuous decrease in diffusivity, reflecting the smooth nature of this regime. The sharp reduction in MSD at subcritical pressures, particularly near the critical point, mirrors the phenomena of critical slowing down [33], where large fluctuations in molecular motion dominate. In the subcritical region, a clear demarcation between these two phases is evident: the denser liquid phase exhibits significantly lower mobility, whereas the gas phase features more mobile molecules. This behavior is clearly illustrated in Figure 4a at lower pressures, such as $P = 25.85$ atm.

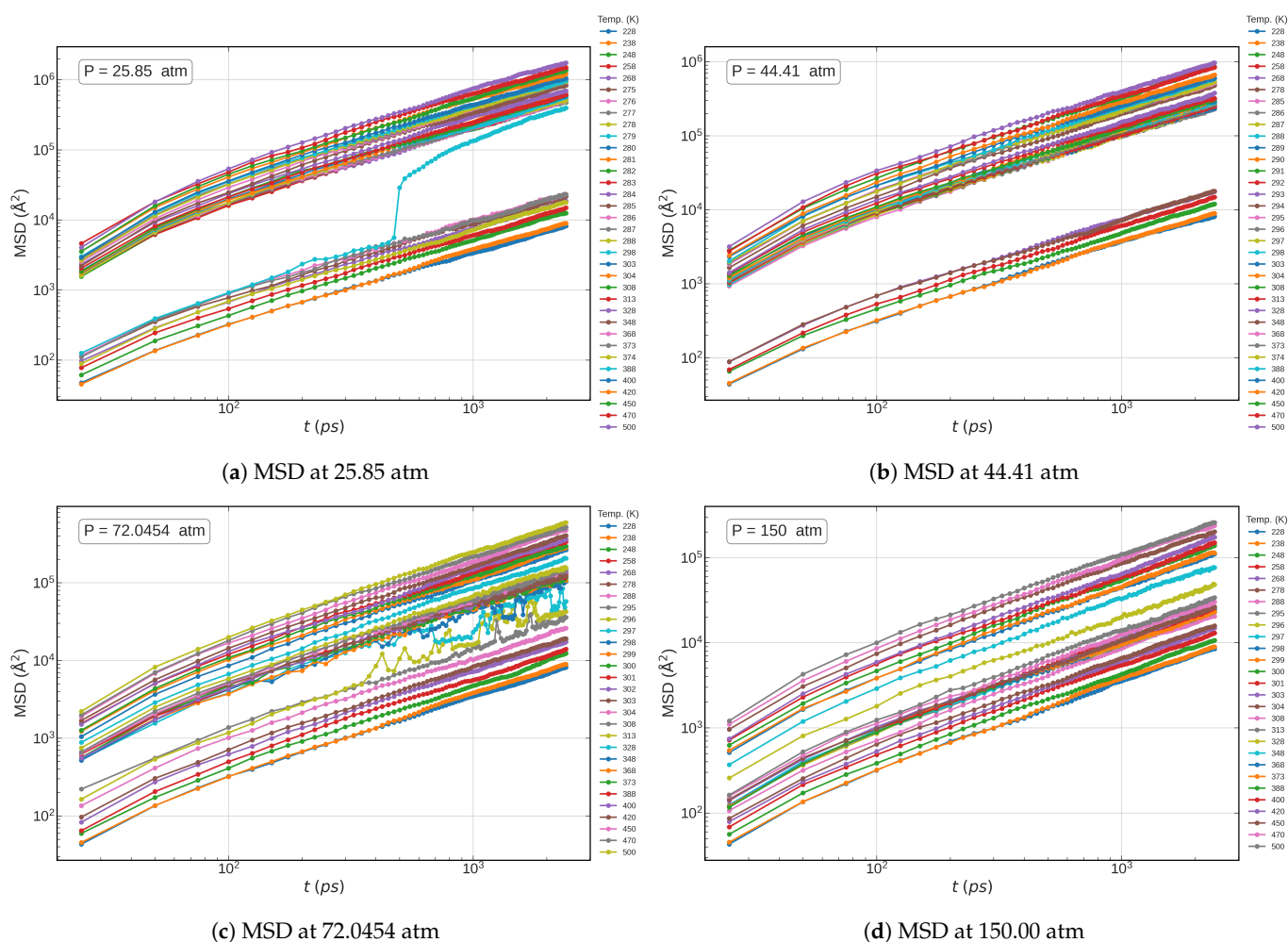


Figure 4. Mean squared displacement (MSD) for CO₂ at different pressures using the TraPPE force field.

As the pressure increases, the dynamics begin to shift. Along the isobar at $P = 44.41$ atm, depicted in Figure 4b, the distinction between the MSD values of the gas

and liquid phases becomes less pronounced. Furthermore, as the system approaches the critical point, large fluctuations emerge in the long-time correlation, reflecting the critical slowing down characteristic of phase transitions. These critical fluctuations are consistent with the observations of Michels et al. [52], who highlighted the role of intermolecular forces in driving dynamic heterogeneity near the critical region. Moreover, the alignment of our MSD trends with experimental diffusion coefficients further underscores the reliability of both TraPPE-small and EPM2 models for studying phase-transition dynamics. This behavior is particularly evident along the critical isobar, as shown in Figure 4c.

In the supercritical region, such as at $P = 150$ atm (Figure 4d), the dynamic distinction between liquid-like and gas-like diffusive regimes persists; however, there is no abrupt discontinuity between the phases. This smooth transition in the supercritical region aligns closely with the findings of McHugh and Krukons [53], who noted that the interplay between density and diffusivity results in a continuous crossover rather than a sharp phase separation. Such behavior is crucial in supercritical fluid extraction processes, as highlighted by Reverchon [54], where the solvation dynamics depend strongly on diffusivity and density variations. Instead, the transition appears smooth, indicative of the continuous nature of supercritical fluids.

Similarly, the EPM2 model successfully captures the dynamics across both subcritical and supercritical isobars, as reflected in the corresponding MSD profiles shown in Figure 5a–d. However, while these findings demonstrate the model's ability to differentiate between dynamic regimes, they do not confirm whether the models can accurately predict experimentally measurable dynamic properties, such as diffusion coefficients or viscosity.

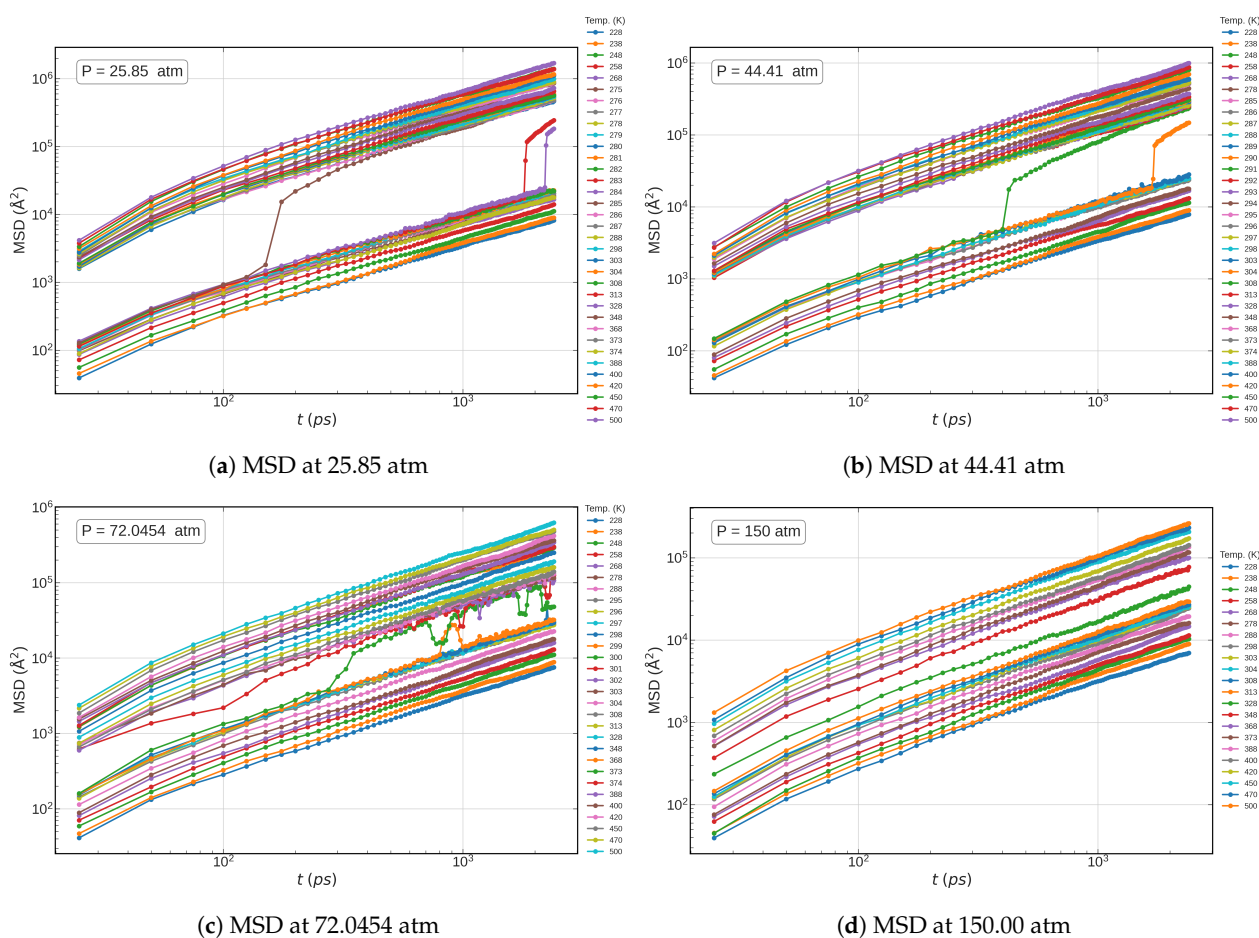


Figure 5. Mean squared displacement (MSD) for CO₂ at different pressures using the EPM2 force field.

The accurate reproduction of CO₂ diffusion and viscosity under subcritical and supercritical conditions is essential for numerous industrial applications. In CCS, supercritical CO₂ is transported efficiently due to its low viscosity, requiring precise modeling for pipeline design. Similarly, in supercritical fluid extraction (SFE), diffusion properties optimize the extraction of bioactive compounds. Viscosity and diffusion are also critical in polymer processing, where they affect material properties, and in catalytic reactors, where they enhance reaction efficiency. In geological storage, these properties govern CO₂ flow and dispersion in porous media, ensuring process safety and efficiency. Reliable models like EPM2 and TraPPE are, therefore, indispensable for designing and optimizing these applications.

To evaluate the predictive capability of these models, Figure 6a,b present the diffusion coefficient D and viscosity η as functions of pressure along various isotherms. The viscosity results are particularly significant, as they can be directly compared with experimental data from Ref. [52]. Our results for diffusion coefficients and viscosity closely follow the experimental trends reported by Michels et al. [52], particularly in capturing the sharp changes near the phase transition. The observed agreement further supports the parameterization of EPM2 and TraPPE-small models. Additionally, Frenkel and Smit [33] highlighted the role of particle correlations in influencing viscosity near the critical point, a behavior also evident in our findings.

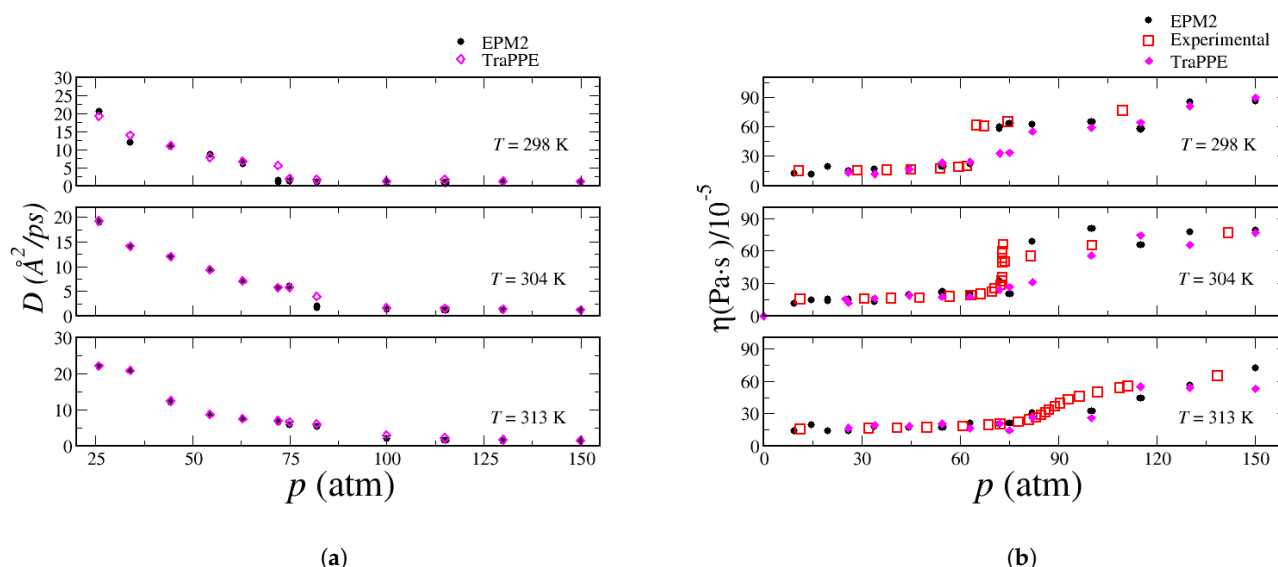


Figure 6. Diffusion coefficient (a) and viscosity (b) as a function of pressure for subcritical, critical, and supercritical temperatures. Experimental points obtained from Ref. [52].

Both models capture the transition from the low-viscosity, high-diffusion gas phase to the liquid phase along the subcritical isotherm at $T = 298$ K. However, the EPM2 model exhibits better agreement with experimental data near the phase transition. Likewise, EPM2 provides a more accurate prediction of viscosity behavior at $T = 304$ K, the critical temperature. For both isotherms, the TraPPE model predicts the dynamical transition at higher pressures than observed experimentally. Along the supercritical isotherm at $T = 313$ K, both models consistently show a continuous transition from gas-like to liquid-like behavior, aligning well with experimental observations. These results underscore the models' strengths and limitations in predicting CO₂ dynamics under varying conditions. Overall, the dynamic behavior of CO₂ captured by these models is in strong agreement with foundational studies in supercritical fluid dynamics [52–54]. The ability of the TraPPE-small and EPM2 models to replicate critical phenomena and supercritical transitions reaffirms their utility for applications. These findings also align with the molecular insights provided

by Frenkel and Smit [33], emphasizing the importance of accurate force fields in predicting transport properties in supercritical systems.

4. Conclusions

In this study, we investigated the thermodynamic and dynamic behavior of CO₂ across a wide range of temperatures (228–500 K) and pressures (1–150 atm) using molecular dynamics (MD) simulations with two widely adopted rigid models: EPM2 and TraPPE-small. These simulations provided detailed insights into the phase transitions and transport properties of CO₂, encompassing subcritical, critical, and supercritical regimes.

Our findings demonstrate that both force fields accurately reproduce the liquid–vapor coexistence curve and critical behavior of CO₂. This agrees with previous studies that have validated the capability of EPM2 and TraPPE-small in describing phase equilibria and critical phenomena [29,30,52]. The TraPPE-small model exhibited superior performance in capturing the gas-phase dynamics, while the EPM2 model more accurately represented the liquid-phase densities. These observations are consistent with the models' design objectives, with TraPPE-small optimized for gas-phase and mixture simulations, and EPM2 focusing on pure CO₂ systems [30,46]. Despite their slight differences in parameterization—such as the Lennard-Jones parameters and partial charges—both models successfully replicate key experimental behaviors. Notably, the EPM2 model's critical isobar aligns closely with the experimental critical point, whereas the TraPPE-small model provides better agreement with gas-phase properties at lower temperatures. Experimental critical points for CO₂ are well documented, with $T_c = 304.25$ K and $P_c = 73.8$ atm [48,49]. These values served as benchmarks for our analysis and underscore the validity of our findings. Such complementary strengths highlight the robustness of both models in describing CO₂'s phase behavior.

The mean squared displacement (MSD) analysis further highlighted distinct diffusive regimes, with the gas-like phase exhibiting higher molecular mobility compared to the liquid-like phase. This behavior is consistent with theoretical predictions of diffusion dynamics near phase boundaries [33,51]. Near the critical point, large fluctuations in MSD were observed, consistent with critical slowing down [46]. In the supercritical regime, although liquid-like and gas-like behaviors persist, the transition between them is continuous, reflecting the absence of phase discontinuities [49].

The analysis of thermodynamic response functions, such as the specific heat capacity, revealed expected discontinuities at the liquid–gas phase transition for subcritical conditions. Similar observations of C_p behavior at phase transitions have been reported in both experimental and computational studies [29,52]. As the system approaches the critical point, these discontinuities evolve into maxima along the critical isobar, with the supercritical regime showing peaks associated with the Widom line. Both models consistently captured this behavior, further demonstrating their ability to accurately describe the critical phenomena of CO₂.

In conclusion, this study highlights the effectiveness of the EPM2 and TraPPE-small models in reproducing experimental phase behavior and transport properties of CO₂ despite their inherent differences. These findings align with experimental results reported in Ref. [49], reinforcing the reliability of these models in capturing CO₂ thermodynamics and dynamics under diverse conditions. These results not only enhance our fundamental understanding of CO₂ thermodynamics and dynamics but also provide valuable insights for optimizing industrial applications such as CCS and SFE. For example, the accurate modeling of CO₂ transport properties is critical for predicting permeability and solubility in geological formations for CCS, as well as maximizing solvation efficiency in SFE processes [12,52]. The demonstrated accuracy of these models reinforces their utility in

guiding the design and improvement of sustainable technologies leveraging CO₂ as a green solvent and industrial resource. Future work could focus on extending these models to study CO₂ behavior in complex mixtures or under extreme conditions to broaden their applicability in emerging industrial technologies.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/pr13010148/s1>: Table S1: Experimental Temperature and Density Data. Table S2: Temperature, Density, and Pressure — EPM2 Data. Table S3: Temperature, Density, and Pressure — TraPPE-small Data. Table S4: Density and Pressure Experimental Data. Table S5: Density, Pressure, and Temperature — EPM2 Data. Table S6: Density, Pressure, and Temperature — TraPPE-small Data. Table S7: Heat Capacity (Cp) as a Function of Temperature and Pressure — EPM2 Data. Table S8: Heat Capacity (Cp) as a Function of Temperature and Pressure — TraPPE-small Data. Table S9: Mean Squared Displacement (MSD) — Data for P = 25.85 atm. Table S10: Mean Squared Displacement (MSD) — Data for P = 44.41 atm. Table S11: Mean Squared Displacement (MSD) — Data for P = 72.0454 atm. Table S12: Mean Squared Displacement (MSD) — Data for P = 150 atm. Table S13: Mean Squared Displacement (MSD) — Data for P = 25.85 atm. Table S14: Mean Squared Displacement (MSD) — Data for P = 44.41 atm. Table S15: Mean Squared Displacement (MSD) — Data for P = 72.0454 atm. Table S16: Mean Squared Displacement (MSD) — Data for P = 150.0 atm. Table S17: Viscosity and Diffusion Data for T = 298 K. Table S18: Viscosity and Diffusion Data for T = 304 K. Table S19: Viscosity and Diffusion Data for T = 313.4 K. Inputs for lammps employed in this work.

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