Microscopic Mechanism of Variations in Physical Parameters of Natural Gas Containing CO₂ at Ultrahigh Temperature and High Pressure

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ABSTRACT: Owing to limitations imposed by the experimental requirements, it is difficult to carry out pressure−volume−temperature experiments on CO₂-containing natural gas in high-temperature and ultrahigh-pressure gas reservoirs. Relevant research is also insufficient, which has led to a lack of clarity in current understanding of the microscopic mechanism of variations in the deviation factor of high-CO₂ natural gas under high-temperature and ultrahigh-pressure conditions. This has greatly limited the development of natural gas reservoirs containing CO₂. To reveal the microscopic mechanism of variations in the deviation factor of natural gas containing CO₂ as a function of pressure under high-temperature and high-pressure conditions, by physical simulation experiments, the deviation factors of samples of sour natural gas with known CO₂ contents from the Ledong gas reservoir were determined. Then, according to the idealized parameters of the physical experiment, a molecular model of natural gas containing CO₂ was established using molecular simulation methods. Changes in molecular density, molecular volume, nonbonding interaction energy, potential energy, and kinetic energy during variations in the deviation factor of a CO₂-containing natural gas system as a function of pressure under ultrahigh-temperature and high-pressure conditions were quantitatively studied. Using molecular simulation techniques, it was found that the changes in total energy, kinetic energy, and potential energy between molecules are the internal factors that cause variations in the deviation factor of natural gas systems containing CO₂ under ultrahigh-temperature and high-pressure conditions. The results show that the increase of carbon dioxide content in natural gas will cause the total energy of natural gas molecules to decrease when the pressure is constant. This means that the higher the CO₂ content in natural gas, the easier it will be compressed. This study should lay the foundation for investigating the mechanisms of the occurrence of CO₂-containing natural gas, as well as facilitating the exploitation of CO₂-containing natural gas.

1. INTRODUCTION

A substantial amount of research has been carried out on the behavior of the fluid phase in conventional gas reservoirs, but there have been few studies of the behavior of the fluid phase in gas reservoirs at abnormally high temperatures and high pressures. Owing to the limitations of experimental conditions, there has been no experience of production from such gas reservoirs. In the case of these particular types of gas reservoirs, research is needed into the presence or absence of specificity in the behavior of the fluid phase in the reservoir. In 2011, Bian et al. studied the influence of the water content of natural gas on the gas compression factor. The experimental results showed that the water content of natural gas will reduce the compression factor of the gas. Furthermore, the Peng−Robinson, Hall−Yarborough, and Soave−Benedict−Webb−Rubin equations were used to calculate the compression factors of natural gas with and without water, which confirmed the reliability of the experimental conclusion. In 2014, Yu conducted pressure−volume−temperature (PVT) experiments on samples of gas condensate containing CO₂ at 120.1 °C and 31.58 MPa and found that an increase in the molar fraction of the CO₂ component of the gas condensate system would reduce the compression factor. In 2015, Jia conducted an experiment on the high-pressure physical properties of high-CO₂ fluids, measured the high-pressure physical properties of fluids with different CO₂ contents at different temperatures and pressures, and analyzed the law of changes in density and viscosity in the near-critical region of high-CO₂ natural gas. In 2017, Guo and Wang conducted PVT phase state experiments on anhydrous...
and water-containing acidic gas at high temperatures and high pressures and found that the water content of acidic gas had no effect on the gas compression factor, and changes in temperature had little effect on the gas compression factor. These experiments had high requirements for experimental equipment and were time-consuming and high cost. In 2019, Hu et al.\textsuperscript{5} conducted a comparative PVT experiment on gas condensate at a formation temperature of 110.4 °C and a pressure of 35 MPa and found that the dew point pressure of the gas condensate in dense porous media was 9.42% higher than the value measured in a PVT cylinder. In 2019, Ran\textsuperscript{6} studied the phase characteristics of CO\textsubscript{2}-containing natural gas in tight gas reservoirs and found that as the CO\textsubscript{2} content increased, the gas compression factor decreased significantly and, as the pressure increased, the natural gas counteracted the PVT characteristics in the porous medium. The relative volume of the natural gas in the PVT cylinder was reduced, and the decrease at a high pressure was much smaller than that at a low pressure. The CO\textsubscript{2} content and core permeability had little effect on the pressure—volume curve. In 2020, Xie et al.\textsuperscript{7} used samples from a high-water-cut tight-condensate gas reservoir to carry out phase behavior experiments in a PVT cylinder at 34 MPa and 78 °C, but the temperature and pressure referred to in the experiment and the model that was established were too low to meet the application requirements.

Limited by the experimental conditions of high temperature and high pressure and by traditional macroscopic experimental methods, researchers have focused on the interpretation of macroscopic experimental laws. Few scientists have explained changes in the phase state of CO\textsubscript{2}-containing natural gas in terms of a microscopic mechanism. This has made the understanding of the phase change characteristics and phase change mechanisms of CO\textsubscript{2}-containing natural gas under ultrahigh-temperature and high-pressure conditions insufficiently clear, which has greatly limited plans for the development of ultrahigh-temperature and high-pressure CO\textsubscript{2}-containing natural gas reservoirs. In the process of modern scientific research, computational techniques have become the main methods used in research on microscopic mechanisms. The molecular dynamics simulation method is a comprehensive technology that combines physics, mathematics, and chemistry; it has the characteristics of a wide range of uses, high precision, and strong reliability and is often used to study various microscopic mechanisms. However, hardly anyone has conducted systematic research on the microscopic mechanisms of the phase change of CO\textsubscript{2}-containing natural gas. In 2017, Yan\textsuperscript{8} used molecular dynamics simulation methods to study the movement and aggregation of CO\textsubscript{2} molecules as the temperature and pressure changed near the critical point and explained the corresponding macroscopic phase and physical properties of CO\textsubscript{2} in microscopic terms. Same year, Javad Kondori\textsuperscript{9} introduced the theory on the molecular dynamics simulation and its application in various decomposition methods. It shows that because of the limitations of existing experimental and theoretical approaches, development of more accurate theoretical models and equations of state (EOSs) is inevitable. In 2019, Moiseeva et al.\textsuperscript{10} provided a method to determine the compressibility factor based on molecular dynamics simulations with the Lennard-Jones potential. Statistical analysis shows that the molecular dynamics method has the smallest error and is suitable for determination of z-factor of mixtures with methane content more than 90%. In 2021, Zeng et al.\textsuperscript{11} used molecular simulation methods to determine the phase state of CO\textsubscript{2} in nanoparticles under pressure and found that as the pressure increases the density of CO\textsubscript{2} in the free state in the pores also increases. A transition layer appears between the adsorption layer and the free CO\textsubscript{2}. However, this study was limited to a single CO\textsubscript{2} phase. In 2021, Tang et al.\textsuperscript{12} analyzed the factors influencing methane diffusion from a microscopic point of view. The inhibitory effect of CO\textsubscript{2} on the diffusion of CH\textsubscript{4} molecules in coal was stronger than that of H\textsubscript{2}O, but the mechanism of action was not analyzed from the perspective of molecular dynamics.

At present, the development of CO\textsubscript{2}-containing natural gas in high-temperature and ultrahigh-pressure gas reservoirs is still in its infancy. Therefore, the current understanding of variations in the deviation factor of CO\textsubscript{2}-containing natural gas with pressure under conditions of high temperature and ultrahigh pressure is not sufficiently thorough. For these reasons, this study took the Ledong high-temperature and ultrahigh-pressure offshore gas reservoir as its research object. This gas reservoir has the characteristics of a formation temperature as high as 190 °C, a formation pressure coefficient of greater than 2.1, a low formation hydrocarbon fluid content, and a high CO\textsubscript{2} content of acidic gas. By physical simulations, the deviation factor of natural gas containing CO\textsubscript{2} under high-temperature and high-pressure conditions was determined. A molecular simulation method was also used to establish a mixed molecular model of natural gas containing CO\textsubscript{2}. By fitting the model density on the basis of verifying the applicability of the force fields in the mixed molecular model, the molecular density, molecular volume, nonbonding interaction energy, and potential energy of CO\textsubscript{2}-containing natural gas systems under high-temperature and ultrahigh-pressure conditions during changes in pressure were determined. At the same time, the innovation of this article is to reveal how CO\textsubscript{2} affects the natural gas deviation factor through total energy, kinetic energy, and potential energy. The law of change in kinetic energy, for example, revealed the microscopic mechanism of the effect of the CO\textsubscript{2} content on the deviation factor of natural gas and laid the foundation for investigating the mechanisms governing the occurrence of CO\textsubscript{2}-containing natural gas, as well as facilitating the exploitation of CO\textsubscript{2}-containing natural gas.

2. RESULTS AND DISCUSSION

2.1. Study of the Laws of Changes in Physical Parameters of Fluids under Ultrahigh-Temperature and High-Pressure Conditions. To fully study the changes in physical parameters of CO\textsubscript{2}-containing natural gas with changes in pressure under conditions of ultrahigh temperature and high pressure, in accordance with the national standard GB/T 26981-2011: Test method for reservoir fluid physical properties,\textsuperscript{13} CO\textsubscript{2}-containing natural gas was analyzed. The natural gas compression factor test clarifies the seepage mechanism of ultrahigh-temperature and high-pressure low-permeability gas reservoirs and the laws of changes in physical parameters of fluids under ultrahigh-temperature and high-pressure conditions. In addition, it provides a basis for revealing the microscopic mechanism of the phase change of natural gas containing CO\textsubscript{2} under ultrahigh-temperature and high-pressure conditions.

Under conditions of an experimental pressure of 90 MPa and an experimental temperature of 190 °C, the compression factor of natural gas containing CO\textsubscript{2} under ultrahigh-temperature and high-pressure conditions was determined. The CO\textsubscript{2} content in
the samples of natural gas was 0, 10, 35, 70, and 100%, respectively.

The experimental results are shown in Table 1 and Figure 1.

### Table 1. Results of Measurements of the Deviation Factor of Natural Gas

| Experimental pressure (MPa) | C1 + C2 | CO2 content in natural gas |
|----------------------------|---------|---------------------------|
|                            | 0%      | 10% | 35% | 70% | 100% |
| 90                         | 1.5443  | 1.5605 | 1.4923 | 1.4008 | 1.2605 |
| 80                         | 1.4567  | 1.4592 | 1.4022 | 1.3027 | 1.1837 |
| 60                         | 1.2865  | 1.2854 | 1.2074 | 1.1904 | 1.0358 |
| 40                         | 1.1311  | 1.1188 | 1.0792 | 0.9369 | 0.9097 |
| 20                         | 1.0157  | 0.9946 | 0.9733 | 0.8627 | 0.8625 |
| 12                         | 0.9930  | 0.9736 | 0.9665 | 0.8948 | 0.8927 |
| 6                          | 0.9896  | 0.9878 | 0.9782 | 0.9413 | 0.9381 |
| 3                          | 0.9930  | 0.9926 | 0.9833 | 0.9695 | 0.9672 |

**Figure 1.** Deviation factors $(Z)$ of samples of natural gas with different CO2 concentrations.

For natural gas with a CO2 content of 100%, the deviation factor was 0.9672 at a pressure of 3 MPa and 1.2605 at a pressure of 90 MPa; for natural gas with a CO2 content of 70%, the deviation factor was 0.9695 at a pressure of 3 MPa and 1.4008 at a pressure of 90 MPa; for natural gas with a CO2 content of 35%, the deviation factor at 3 MPa was 0.9833, and the deviation factor at 90 MPa was 1.4923; for natural gas with a CO2 content of 10%, the deviation factor at 3 MPa was 0.9930, and the deviation factor at 90 MPa was 1.6043. As shown in Figure 1, according to the experimental results, it was found that at the same pressure the deviation factor of natural gas with a high CO2 content decreased with an increase in the CO2 concentration. When the CO2 content was constant, the deviation factor of natural gas first decreased and then increased with an increase in pressure. The deviation factor of natural gas with different CO2 concentrations reached a minimum in the pressure range of 12–20 MPa. As the CO2 content increased, the minimum deviation factor exhibited a tendency to decrease and occur at a higher pressure. Hence, the higher is the CO2 content, the easier it is to compress natural gas containing CO2.

### 2.2. Study of the Microscopic Mechanism of the Phase Change of Natural Gas Containing CO2

The research described in this chapter started with natural gas containing CO2 and simulated the phase characteristics of methane, ethane, and CO2 under ultrahigh-temperature and high-pressure conditions. Molecular simulation methods were used to study the microscopic mechanism of the phase state of CO2-containing natural gas under ultrahigh-temperature and high-pressure conditions.

#### 2.2.1. Results of Molecular Simulation Calculations

According to the single-molecule models of methane, ethane, and CO2, the NEAD force field, OPLS position, and CO2 force field were selected to build three simulation boxes with dimensions of 8.0 $\times$ 8.0 $\times$ 8.0 nm, into which a total of 1000 mixed molecules were inserted. The molecular composition of natural gas containing CO2 is listed in Table 2. A model of a methane–ethane–CO2 mixed molecular system with CO2 contents of 0, 10, 35, 70, and 100% was constructed, as shown in the left of Figure 2. The simulation temperature was set to 190 C , the simulation pressure to 3–90 MPa, the time step to 2 fs, and the number of simulation steps to 500,000 steps. The simulation gave the magnitudes of the changes as a function of pressure in the molecular density, molecular volume, non-bonding interaction energy, potential energy, kinetic energy, and other parameters of the CO2-containing natural gas mixed molecular system at the formation temperature. These parameters comprehensively reflect the microscopic mechanism of the phase change of CO2-containing natural gas (Table 2). The results of the simulation calculations are shown in Figures 2345.

#### Table 2. Molecular Composition of the Molecular Model of CO2-Containing Natural Gas

| Type of component/molecule | CO2 content of natural gas |
|---------------------------|---------------------------|
|                           | C1 + C2 | 10% | 35% | 70% | 100% |
| C1                        | 940     | 850 | 625 | 290 | 0    |
| C2                        | 60      | 50  | 25  | 10  | 0    |
| SUM                       | 1000    | 1000| 1000| 1000| 1000 |

At the formation temperature, the change in the total energy of the methane–ethane–CO2 mixed molecular system is shown in Figure 3. When the pressure increases from 3 to 90 MPa, the total energy of natural gas with 100% CO2 decreases from 1699.03 to 970.56 kJ/mol; the total energy of natural gas with 70% CO2 decreases from 1342.96 to 804.18 kJ/mol; the total energy of natural gas with 35% CO2 is reduced from 974.602 to 526.54 kJ/mol; the total energy of natural gas with 10% CO2 is reduced from 690.716 to 324.57 kJ/mol; and the total energy of natural gas with 0% CO2 is reduced from 574.198 to 236.238 kJ/mol. At the same pressure of natural gas, the total energy of the CO2 content decreased with an increase in the CO2 concentration.

**Figure 2.** Changes in total energy. The percentages refer to the CO2 contents.
mixed molecular system increases with an increase in the CO₂ content. In addition, when the CO₂ content is constant, the total energy of the mixed molecular system decreases with an increase in pressure but tends to remain unchanged above 80 MPa. It can be seen that the changes in total energy, kinetic energy, and potential energy between molecules are the internal causes of the changes in the deviation factor.

Figures 8910 show the results of molecular simulations of parameters of the natural gas systems containing CO₂.

As shown in Figure 4, when the pressure increases from 3 to 90 MPa, the nonbonding interaction energy of natural gas with 100% CO₂ decreases from $-60.85$ to $-766.13$ kJ/mol; the nonbonding interaction energy of natural gas with 70% CO₂ decreases from $-45.5334$ to $-620.7197$ kJ/mol; the nonbonding interaction energy of natural gas with 35% CO₂ is reduced from $-32.5171$ to $-453.8334$ kJ/mol; the nonbonding interaction energy of natural gas with 10% CO₂ is reduced from $-22.3950$ to $-365.5499$ kJ/mol; and the nonbonding interaction energy of natural gas with 0% CO₂ is reduced from $-19.37$ to $-338.78$ kJ/mol. Under high-pressure conditions, the mixed molecular system of natural gas containing CO₂ is compressed, and thus the density of molecules in the system, nonbonding interaction energy, and gravitational force increase, whereas the volume of the system decreases. This phenomenon is manifested by the fact that when the CO₂ content is constant, as the pressure increases the nonbonding interaction energy of the CO₂-containing natural gas mixed molecular system decreases, whereas at the same pressure the...
nonbonding interaction energy increases with an increase in the CO$_2$ content. The results show that the increase of carbon dioxide content in natural gas will cause the nonbonding energy and total energy of natural gas molecules to decrease when the pressure is constant. This means that the higher CO$_2$ content in natural gas, the easier it will be compressed.

As shown in Figure 5, when the pressure increases from 3 to 90 MPa, the molecular potential energy of natural gas with 100% CO$_2$ decreases from 357.078 to $-372.142$ kJ/mol; the molecular potential energy of natural gas with 70% CO$_2$ decreases from 223.588 to $-312.837$ kJ/mol; the molecular potential energy of natural gas with 35% CO$_2$ is reduced from 118.707 to $-329.575$ kJ/mol; the molecular potential energy of natural gas with 10% CO$_2$ is reduced from 22.008 to $-343.617$ kJ/mol; and the molecular potential energy of natural gas with 10% CO$_2$ is reduced from $-20.4092$ to $-359.942$ kJ/mol. The molecular kinetic energy of natural gas with 100, 70, 35, 10, and 0% CO$_2$ is basically unchanged. When the CO$_2$ content is constant, with an increase in pressure the decrease in potential energy in the mixed molecular system is much greater than the increase in kinetic energy. Therefore, the total energy of the mixed molecular system decreases with an increase in pressure. According to the simulation results for the mixed molecular system, when the potential energy is greater than 0 kJ/mol in the pressure range of 0–20 MPa, the intermolecular force acts as a repulsive force and the volume increases. Therefore, the resulting macroscopic behavior is that the deviation factor of CO$_2$-containing natural gas decreases with an increase in pressure in the range of 0–20 MPa. As the pressure continues to increase, the potential energy becomes less than 0 kJ/mol. Under these conditions, the intermolecular force acts as a gravitational force and the volume decreases. Therefore, the resulting macroscopic behavior is that the deviation factor of CO$_2$-containing natural gas increases with an increase in pressure. Because the absolute value of the potential energy of the system increases with an increase in the CO$_2$ content at the same pressure, as shown in the upper part of Figure 5, at the macroscopic level the deviation factor of natural gas containing CO$_2$ decreases with an increase in the CO$_2$ content at the same pressure. Molecular kinetic energy is still dominant in the CO$_2$-containing natural gas mixed molecular system and is more affected by temperature. Therefore, the molecular motion in the mixed molecular system accelerates with an increase in pressure, and the probability of molecular collisions increases, but the overall change is not significant. At the same pressure, the higher is the CO$_2$ content in the mixed molecular system, the higher is the molecular kinetic energy, as shown in the lower part of Figure 5.

2.2.2. Analysis of Energy Contribution. To further study the contribution of each energy to the variation of the deviation factor of CO$_2$ natural gas under ultrahigh temperature and high pressure conditions. It is necessary to make a graph of the relationship between different energies and deviation factors, as shown in Figures 6–7,8,9,10,11,12,13,14,15,16.

As you can see from Figures 6–7,8,9,10,11, intermolecular total energy, kinetic energy, and potential energy between molecules have the most significant impact on the deviation factor of natural gas systems containing CO$_2$ under ultrahigh-temperature and high-pressure conditions. Furthermore, the data are tested for outliers, and the sensitivity of the contribution of each energy is analyzed. The analysis results are shown in Table 3. According to the sensitivity analysis results, the influence degree of the change of pressure or CO$_2$ content on the energy of different gas mixtures can be obtained. It can be found that the
potential energy is most affected by pressure, and the change of potential energy is linear with CO₂ content φ₂; the total energy is most affected by the content of CO₂, and the change of total energy is linear with the current pressure \( P \); the change of kinetic energy is only affected by CO₂ content. When the initial pressure is set to 1 MPa and the initial CO₂ content is 1%, the potential energy of the mixed gas molecules increases by \(-4.2476\) kJ/mol for each increase in the pressure of 1 MPa; for every 1% increase in CO₂ content, the total energy increases by \(10.7262\) kJ/mol, and the kinetic energy increases by \(7.479\) kJ/mol. Thus it can be concluded that the changes in total energy, kinetic energy, and potential energy between molecules are the internal factors that cause variations in the deviation factor of natural gas systems containing CO₂ under ultrahigh-temperature and high-pressure conditions.

3. CONCLUSIONS

(1) In this study, under conditions of 190 °C and 3–90 MPa, the deviation factors of natural gas with CO₂ contents of 0, 10, 35, 70, and 100% were determined. It was found that the deviation factor of natural gas containing CO₂ first decreases and then increases with an increase in pressure. When the temperature and pressure remain unchanged, the deviation factor of natural gas decreases with an increase in the CO₂ content.

(2) Using molecular simulation techniques, it was found that the changes in total energy, kinetic energy, and potential energy between molecules are the internal factors that cause variations in the deviation factor of natural gas systems containing CO₂ under ultrahigh-temperature and high-pressure conditions. At the same pressure, the higher is the CO₂ content of natural gas, the higher is the intermolecular density and the smaller is the molecular volume in a mixed molecular system. The total energy of a mixed molecular system increases with an increase in the CO₂ content, and the absolute value of the potential energy of the system increases with an increase in the CO₂ content. At the macroscopic level, at the same pressure the deviation factor of natural gas containing CO₂ decreases with an increase in the CO₂ content.

(3) The results show that the increase of carbon dioxide content in natural gas will cause the total energy of natural gas molecules to decrease when the pressure is constant. This means that the higher CO₂ content in natural gas, the easier it will be compressed.
4. EXPERIMENTAL SECTION OR COMPUTATIONAL METHODS

4.1. Research of the Physical Simulation Experiment.

4.1.1. Experimental Equipment and Sample Preparation.

(1) French ST company PVT experimental device: the rated working temperature $\geq 200^\circ\text{C}$, and temperature control was accurate to within less than 0.5 $^\circ\text{C}$; the rated working pressure $\geq 150$ MPa, and pressure control accuracy to 0.1 MPa; the rated working volume $\leq 240$ mL, and volume control accuracy to 0.0001 mL. Compared with the traditional PVT experimental device, the device has the characteristics of high precision and a high degree of automation. The data are automatically collected by a computer, and the data obtained in the experiment are reliable. The device as shown in the left of Figure 1.

(2) Agilent 7890A gas chromatograph: this was used to analyze components of natural gas containing air and CO$_2$, as shown in the right of Figure 12.

(3) Gas meter: the capacity was greater than or equal to 1000 cm$^3$, and the maximum resolution was less than or equal to 1 cm$^3$.

To investigate the influence of changes in the CO$_2$ content of natural gas on the deviation factor, also known as the compression factor, of natural gas, according to the method of controlling variables, different amounts of CO$_2$ were charged into samples of natural gas with the same composition, and three kinds of natural gas with different contents of CO$_2$ were thus obtained. In these experiments, samples of CO$_2$-free natural gas from the Ledong gas reservoir were used, and the contents of hydrocarbon components of this gas were determined by chromatography, as listed in Table 4. After CO$_2$ was added to the natural gas defined in Table 4 to give samples of natural gas with different CO$_2$ contents, these were subjected to chromatographic determination. The components of samples of natural gas with different CO$_2$ contents are listed in Table 5.

4.1.2. Experimental Method Used To Determine the Compression Factor. The deviation factor of natural gas refers into samples of natural gas with the same composition, and three kinds of natural gas with different contents of CO$_2$ were thus obtained. In these experiments, samples of CO$_2$-free natural gas from the Ledong gas reservoir were used, and the contents of hydrocarbon components of this gas were determined by chromatography, as listed in Table 4. After CO$_2$ was added to the natural gas defined in Table 4 to give samples of natural gas with different CO$_2$ contents, these were subjected to chromatographic determination. The components of samples of natural gas with different CO$_2$ contents are listed in Table 5.

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| component | content (%) |
|-----------|-------------|
| C$_1$     | 94.3704     |
| C$_2$     | 4.0149      |
| C$_3$     | 1.0485      |
| iC$_4$    | 0.2889      |
| nC$_4$    | 0.1292      |
| iC$_5$    | 0.0664      |
| nC$_5$    | 0.0342      |
| C$_6$     | 0.0476      |
| Sum       | 100         |

Table 3. Analysis Results of Different Energy Contributions$^{44}$

| pressure, +1 MPa | add 1 unit (kg/m$^3$) | volume (nm$^3$) | potential energy (kJ/mol) | kinetic energy (kJ/mol) | non-bond interaction (kJ/mol) | total energy (kJ/mol) |
|-----------------|-----------------------|----------------|----------------------------|-------------------------|-------------------------------|----------------------|
|                 | $\varphi_t$ $\times$ |                | $\ln(\varphi_t)$         | $P_t$                   | $P_t$                         | $P_t$                 |
| 2.7139 + 0.06   |                        | 215.436        | -4.209 - 0.0386 $\times$  | $\varphi_t$             | -3.9637 - 0.0401 $\times$ $\varphi_t$ | -3.759 - 0.04457 $\times$ $\varphi_t$ |
| 2.7739          |                        | -174.4034      | -4.2476                    | $P_t$                   | -4.0038                      | -3.80357 |
| 0.3957 + 0.06   |                        |                | -0.04                      | $P_t$                   | -0.9239 - 0.0401 $\times$ $P_t$ | 10.9726 |
| 0.4557          |                        |                |                           | $P_t$                   | -0.9640                      | 10.9726 |

$^{44}P_t$—current pressure, MPa; $\varphi_t$—CO$_2$ content in mixed gas, %.
to the ratio of the volume occupied by the real gas to the volume occupied by the same amount of an ideal gas at the same temperature and pressure and varies with the gas composition, pressure, and temperature. In addition to the PVT experimental method, the determination of the deviation factor of natural gas can also be achieved via several different calculation methods. At low pressures, natural gas closely follows the ideal gas law. However, when the pressure increases, especially when the temperature of the gas is close to its critical temperature, there will be a large deviation between the real volume of the gas and that of an ideal gas. The magnitude of this deviation is referred to as the deviation factor, which is represented by the symbol Z. In other words, at a certain pressure P and temperature T, the quotient obtained by dividing the actual volume of n moles of natural gas by the volume of n moles of an ideal gas at the same pressure P and temperature T is the deviation factor of the natural gas. In this study, the PVT experimental method was used to determine the deviation factor of ultrahigh-temperature, high-pressure, and high-CO2 natural gas. The experimental steps were as follows:

1. First, the airtightness of the ST high-pressure PVT instrument was checked. Second, a sample of the spiked gas containing 35% CO2 was transferred to the instrument. Finally, the pressure was increased to 90 MPa, and the temperature was maintained at 190 °C until the system pressure stabilized.
2. Constant-pressure mode was used to set the high-pressure displacement pump, the displacement pump piston was retracted to its initial position, and the initial readings of the high-pressure displacement pump and the gas meter were recorded.
3. The valve on top of the high-pressure container was opened, about 30 cm3 of high-pressure gas was slowly released while the pressure was maintained, and the top valve was then closed. At this time, the final readings of the high-pressure displacement pump and the gas meter, the room temperature, and the atmospheric pressure were recorded. The compression factor Z was calculated as follows:

\[
Z = \frac{P_i \times (V_0 - V_i) \times T_p}{P_r \times V_G \times T_k}
\]

where \( P_i \) is the experimental pressure (MPa), \( V_0 \) is the initial reading of the metering pump (mL), \( V_i \) is the final reading of the metering pump (mL), \( T_p \) is the standard temperature (K), \( P_r \) is the standard pressure (MPa), \( V_G \) is the reading of the gas meter reading (mL), and \( T_k \) is the experimental temperature (K).

### 4.2. Research of Molecular Simulation

#### 4.2.1. Research Basis of the Microscopic Mechanism

Molecular dynamics methods are used for systems containing many particles (atoms or molecules). Given the interaction potential, initial conditions, and boundary conditions between particles, Lagrangian equations or Newtonian equations of motion are used for numerical integration to deduce the motion process of each particle in the system and determine the trajectories of the microscopic particles.

In this study, the GROMACS package was used for molecular simulation. This software can use molecular dynamics, stochastic dynamics, or path integration methods to simulate any molecule in a solution or crystal, minimize molecular energy, and analyze molecular conformation. Its simulation package includes the NEAD particle force field, the OPLS methane position, which was employed in the research described in this paper, and the CO2 force field.

The general simulation process in GROMACS can be divided into the following three stages:

1. Preprocessing stage: coordinate files, topological structure files, and balance parameter files of the simulated object are generated, the model is built, and 1000 molecules are inserted into an 8.0 × 8.0 × 8.0 nm simulation box.
2. Simulation stage: first, the energy of the system is minimized to check whether the potential energy has converged, and then the NVT balance is performed to control the temperature, the NPT balance is performed to control the pressure, and the density is determined and compared with that in the experimental database.
3. Postprocessing stage: after the molecular dynamics simulation, GROMACS generates a series of files, which can be analyzed, and various data about the molecular system can be obtained.

#### 4.2.2. Molecular Model Construction

According to the components of CO2-containing natural gas listed in Table 6, the main components are CO2-containing natural gas, namely, methane, ethane, and CO2. The model used the NEAD particle force field, the OPLS methane position, and the CO2 force field. Then, under conditions of 190 °C and 93.061 MPa, the applicability of

| Table 5. Composition of Natural Gas Containing CO2 |
|-----------------------------------------------|
| component | 10% | 35% | 70% | 100% |
| CO2       | 10.8021 | 35.2127 | 70.7815 | 100 |
| C1        | 84.3596 | 61.2938 | 27.6239 |   |
| C2        | 3.5179  | 2.5575  | 1.1467  |   |
| C3        | 0.8921  | 0.6416  | 0.2901  |   |
| iC4       | 0.1820  | 0.1029  | 0.0829  |   |
| nC4       | 0.1172  | 0.0919  | 0.0335  |   |
| iC5       | 0.0453  | 0.0236  | 0.0302  |   |
| nC5       | 0.0249  | 0.0398  | 0.0044  |   |
| C4        | 0.0588  | 0.0362  | 0.0069  |   |
| sum       | 100     | 100     | 100     | 100 |

| Table 6. Molecular Parameters of the Molecular Model of CO2-Containing Natural Gas |
|-----------------------------------------------|
| chemical name | chemical or linear formula | CAS number | force field |
|----------------|----------------------------|------------|-------------|
| carbon dioxide | CO2                       | 124-38-9   | CO2 force field |
| methane        | C1                         | 74-82-8    | NEAD        |
| ethane         | C2                         | 74-84-0    | OPLS        |

In this study, the GROMACS package was used for molecular simulation. This software can use molecular dynamics, stochastic dynamics, or path integration methods to simulate any molecule in a solution or crystal, minimize molecular energy, and analyze molecular conformation. Its simulation package includes the NEAD particle force field, the OPLS methane position, which was employed in the research described in this paper, and the CO2 force field.

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the CH$_4$–CO$_2$ and C$_2$H$_6$–CO$_2$ force fields under ultrahigh-temperature and high-pressure conditions was verified. The verification process is shown in Figure 15.

The average relative error in the simulation results was calculated using eq 2. The errors in the simulated density and simulated deviation factor are listed in Table 7.

$$E = \frac{1}{n} \sum_{i=1}^{n} \left( \frac{|W_i - V_i|}{V_i} \right)$$

### Table 7. Relative Errors in Molecular Parameters of the Molecular Model of CO$_2$-Containing Natural Gas

| chemical name                  | average relative error (%) | simulated density | simulated deviation factor |
|-------------------------------|---------------------------|-------------------|---------------------------|
| methane–CO$_2$                | 0.002383                  | 0.003682          | 0.004242                  |
| ethane–CO$_2$                 | 0.003682                  | 0.002383          |                           |
| natural gas with 35% CO$_2$   |                           |                   |                           |

The key parameters in this equation are defined as follows: $E$: average relative error; $V_i$: deviation factor at the $i$th experimental point; $V_i$: fitted value of the deviation factor; $n$: number of experimental points.

As shown in the left of Figure 15, the applicability of the CH$_4$–CO$_2$ force field was verified. At a formation temperature of 190 °C and a formation pressure of 84.38–93.06 MPa, the simulated density was strongly consistent with the corresponding NST experimental data. As shown in the right of Figure 15, the applicability of the C$_2$H$_6$–CO$_2$ force field was verified. At a formation temperature of 190 °C and a formation pressure of 84.38–93.06 MPa, the simulated density was consistent with the corresponding NST experimental data. On comparing the deviation factor of natural gas with a CO$_2$ content of 35% determined by simulation with the experimental value, it was found that the simulated value was strongly consistent with the experimental value. Finally, in combination with the results for the simulated density, it was proved that the force field parameters selected for the simulation are accurate and usable under conditions of ultrahigh temperature and high pressure. Using the EOS, the results from the molecular simulation were imported, and the deviation factor of natural gas with a CO$_2$ content of 35% was calculated. eq 3 was used for the calculation, and the results of the calculation are shown in Figure 16.

$$pV = nRT = \frac{m}{M}RT = \frac{N}{NA}RT$$

$$Z = \frac{V}{V_0}$$

The key parameters in the above equations are defined as follows: $p$: gas pressure (MPa); $M$: molecular mass; $m$: gas quality; $V$: volume of ideal gas (m$^3$); $n$: amount of substance (mol); $NA$: Avogadro constant = 6.022 × 10$^{23}$/mol; $R$: universal gas constant = 8.3145 J/(mol K); $T$: thermodynamic temperature (K); $N$: number of particles.

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**Author Contributions**

Y.F.W., the main researcher of the article, is responsible for the determination of the deviation factor of natural gas containing CO$_2$ molecular simulation research, and article writing; P.G., the instructor, provides directional guidance for the research ideas of the article. J.F.Z. is responsible for molecular model construction.

**Notes**

The authors declare no competing financial interest.

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