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Properties of fluids under multiphysical coupling and frequency-dependent rock physics modeling

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Abstract

In fluid underground storage and seismic monitoring, accurately characterizing the physical properties of fluid-bearing rocks under multiphysical coupling is crucial. However, in deep geological environments, fluids often exist in a supercritical state with highly nonlinear acoustic properties. Moreover, most existing models lack a unified framework for multiple gas types, often treating fluid properties as constants, which does not adequately reflect their actual state. This study proposes a method for constructing a frequency-dependent rock physics model for fluid-bearing rocks. Three equations of state were used to calculate the density, bulk modulus, and acoustic velocity of carbon dioxide, methane, and hydrogen, which were then compared with reference data from the National Institute of Standards and Technology. The properties of brine under varying temperature and pressure conditions were derived from the Batzle–Wang model, and the properties of mixed fluids were obtained using Wood's equation, before being integrated into a sandstone matrix. To account for inelastic behavior, the Johnson and White models were applied to analyze the effects of fluid distribution on compressional wave velocity and the attenuation factor under different conditions. The results show that the acoustic properties of fluids are significantly influenced by phase changes. This frequency-dependent rock physics model improves upon most conventional models that treat fluid properties as fixed constants, enabling more accurate calculation of acoustic properties in deep environments. It thus provides a theoretical basis for underground fluid storage and monitoring in practical applications.

Keywords: Multiphysical coupling; Supercritical fluids; Equations of state; Geological storage of carbon dioxide/methane/hydrogen; Johnson model; White model

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1. Introduction

Energy security and the sustainable development of the ecological environment are global issues. Over the past 150 years, the increase in atmospheric carbon dioxide (CO₂) concentration has contributed to a global average temperature rise of 0.3–0.6

°C.¹ The construction of a new energy system urgently requires vigorous development of renewable energy and effective management of carbon emissions. In this context, utilizing underground geological formations for the large-scale sequestration and storage of CO₂, methane (CH₄), and hydrogen (H₂) has become a key technological pillar supporting the energy transition, ensuring energy security, and achieving deep decarbonization. Among these, CO₂ geological sequestration stands as one of the most feasible and scalable technological pathways for serving global carbon neutrality goals.² Underground CH₄ gas storage represents the most mature and largest-scale practice of underground energy storage today, directly contributing to energy security.³ As a clean and renewable energy source, hydrogen plays a significant role in the global energy transition.⁴ Underground H₂ storage is a strategic technology for the future hydrogen-based society, offering clean energy solutions in sectors such as transportation and power generation, and enabling large-scale reductions in greenhouse gas emissions.

However, the effective implementation of these underground energy storage technologies relies on accurate monitoring of the distribution and migration of the sequestered fluids. The key to achieving this monitoring lies in establishing robust rock physics models, which must fully consider the influence of the supercritical state on fluid properties and be capable of characterizing the differences in acoustic properties among the three gases. In early rock physics, research on the propagation of elastic waves in fluid-containing porous media was primarily based on the assumption of macroscopic homogeneity. Biot⁵ first provided a theoretical framework for elastic wave propagation in fluid-saturated porous media, analyzing the acoustic characteristics of fluid-saturated porous permeable media. The work of Batzle and Wang⁶ provided a reliable quantitative calculation method for the acoustic properties of hydrocarbon gases, crude oil, and brine. Murphy⁷ verified that the Wood's⁸ equation can be used to calculate the effective modulus of two-phase fluids. In the study of wave propagation in porous media, White⁹ first introduced the concept of mesoscopic heterogeneity. Johnson¹⁰ then provided a closed-form analytical expression to approximate frequency-dependent physical quantities in fluid-saturated porous media.

Regarding underground fluid modeling for storage, Picotti *et al.*¹¹ and Carcione *et al.*¹² calculated gas properties using equations of state (EoS) and analyzed changes in seismic response before and after CO₂ injection. The former described the seismic characteristics of reservoir rocks saturated with CO₂, CH₄, and brine, while the latter constructed an integrated model capable of predicting

changes in seismic signals following CO₂ injection. In terms of field measurements and experimental studies, Wang *et al.*¹³ and Oldenburg¹⁴ noted that the phase changes of CO₂ and its injection can lead to significant changes in pore pressure and density. Xue *et al.*¹⁵ found that injecting gaseous CO₂ into a reservoir significantly alters the seismic wave attributes of the reservoir. Daniele *et al.*¹⁶ suggested that within rock–brine and hydrogen storage systems, the structural and trapping capacity of H₂ reservoirs is generally higher than that of CO₂ and CH₄ reservoirs. Carcione *et al.*¹⁷ emphasized that obtaining accurate acoustic property data is crucial for implementing underground storage and monitoring. Depleted reservoirs and saline aquifers possess the potential for the required storage capacity. Meanwhile, Heinemann *et al.*¹⁸ indicated that in studies on storing H₂ in such reservoirs, gas injection should be conducted under supercritical pressure to avoid the presence of a gaseous phase. Ali *et al.*¹⁹ further highlighted that due to its thermodynamic properties, such as specific heat capacity and entropy, H₂ becomes a practical energy source in many industrial applications.

While previous research has achieved significant progress, applying rock physics models to the practical monitoring of multiple gas storage (e.g., CO₂, CH₄, and H₂) still faces several core challenges. Firstly, regarding the accurate calculation of complex fluid acoustic properties, when fluids are in deep geological environments, CO₂ and CH₄ tend to exist in a supercritical state, whereas H₂ generally does not. This leads to highly nonlinear acoustic behaviors, making it difficult to determine their precise property parameters.²⁰ Secondly, traditional EoS exhibit significant errors when calculating properties such as density and bulk modulus, which directly impact the reliability of input parameters for subsequent rock physics models and result in distorted seismic response predictions.²¹ Furthermore, most existing rock physics models are developed for specific single gases, such as CO₂ storage or CH₄ exploration scenarios.²² There is a lack of a unified modeling framework, and fluid parameters are often treated as constants within the models. This significantly reduces the models' adaptability to varying environmental conditions and prevents a systematic comparison and prediction of the differences in seismic responses among the three key gases—CO₂, CH₄, and H₂—under varying depths, temperature–pressure conditions, and different patch morphologies.

Based on the aforementioned background and challenges, this study aims to develop a systematic, accurate, and universally applicable frequency-dependent rock physics model. First, by comparing the van der Waals EoS, the Peng–Robinson EoS, and its modified form

(MPR EoS) for calculating the acoustic properties of CO₂, CH₄, and H₂—and validating them against the National Institute of Standards and Technology (NIST) database—the most accurate EoS is selected to simulate the P-wave velocity, density, and viscosity of gases under varying temperature and pressure conditions corresponding to depth. Subsequently, the Batzle–Wang model is employed to calculate the seismic P-wave velocity, density, and viscosity of brine. The three gases are then mixed with brine to simulate the actual fluid mixture in rock pores, and Wood's⁸ equation is used to derive the equivalent P-wave velocity, density, and viscosity of the mixed fluid.

To capture the inelastic behavior of the rock, the Johnson model is introduced for analysis, with the seismic frequency set to 30 Hz. For comparison, the White model is also applied to systematically examine the suitability of both models in describing fluid states in deep geological environments and to provide practical criteria for selecting between them in real reservoir scenarios. This research not only offers a unified rock physics framework for modeling the underground storage of CO₂, CH₄, and H₂, but also provides theoretical references and practical recommendations for selecting seismic interpretation and monitoring models tailored to different reservoir conditions.

2. Gas acoustic properties

In the calculation of thermodynamic properties of gases, the primary factors are temperature and pressure. However, as these vary with formation depth, a constant geothermal gradient G may be adopted to quantitatively describe the changes in temperature and pressure with depth. The change in temperature can be expressed as:

$$T_c = T_0 + Gz \quad (1)$$

where z represents formation depth, T_c denotes the temperature at depth, and T_0 denotes the surface temperature (at zero depth), with an average surface temperature of approximately 15 °C. Therefore, in this study, $T_0 = 15$ °C. Similarly, for the constant geothermal gradient G , its common value ranges between 20–30 °C/km. For computational convenience, $G = 30$ °C/km is adopted in this study.

Regarding pore pressure, it is primarily influenced by depth, lithology, fluid properties, and geological structure. For simplicity, we adopt the hydrostatic pressure assumption, expressed as:

$$P_c = P_0 + P_b gz \quad (2)$$

where P_c represents the pore pressure at depth z , P_0 is the standard atmospheric pressure, P_b is the average brine density from the surface to depth z , and g is the gravitational acceleration.

In this study, $P_b = 1,030$ kg/m³ and $g = 9.8$ m/s². This approach allows for the determination of the values of temperature and pressure—the two factors exerting the most significant influence on thermodynamic properties—as they vary with depth.

Once temperature and pressure are determined, the thermodynamic parameters of supercritical-state fluids—such as those of CO₂, CH₄, and H₂—can generally be calculated using the van der Waals EoS.²³ Although experimental measurements can also be employed to obtain these thermodynamic parameters,²⁴ this study focuses on computational modeling approaches. The VDW equation is expressed as:

$$P_c = \frac{RT_c}{V-b} - \frac{a}{V^2} \quad (3)$$

where P_c represents the gas pressure, V is the molar volume (in m³/mol), R is the universal gas constant (taken here as $R = 8.31$ J/mol), and a and b are the attraction and repulsion parameters, respectively, which depend primarily on the specific compound.²⁵ The parameters a and b are further defined as follows:

$$a = \frac{R^2 T_{cr}^2}{P_{cr}} \Omega_a \quad (4)$$

$$b = \frac{RT_{cr}}{P_{cr}} \Omega_b \quad (5)$$

where T_{cr} and P_{cr} represent the critical temperature and critical pressure of the gas, respectively, and $\Omega_a = 0.4218$ and $\Omega_b = 0.125$ are dimensionless constants specific to the EoS. For this gas EoS, the molar volume of the gas in **Equation 3** can be solved by simultaneously applying **Equations 1–5**.

Safari and Zahedi²⁶ proposed a modified version of the cubic EoS, known as the corrected Peng–Robinson equation (CPR). Unlike the VDW equation, CPR introduces a temperature-dependent term α into the attraction parameter a , making it a function of temperature rather than a constant. This modification significantly improves predictions of vapor pressure and liquid density. Furthermore, by incorporating the acentric factor to account for molecular polarity differences, CPR achieves markedly higher accuracy in describing vapor–liquid equilibrium compared to VDW. As a result, it

has become a widely adopted basis for many industrial calculations. The general form of the CPR equation is as follows:

$$P = \frac{RT_c}{(V-b)} - \frac{a\alpha(T_c)}{V^2 + 2Vb - b^2} \quad (6)$$

$$T_r = \frac{T_c}{T_{cr}} \quad (7)$$

$$\alpha(T_c) = (1 + m[1 - \sqrt{T_r}])^2 \quad (8)$$

$$m = \begin{cases} 0.37464 + 1.54226\omega - 0.26992\omega^2 & \omega \leq 0.49 \\ 0.379642 + 1.487503\omega + 0.164423\omega^2 \\ + 0.016666\omega^3 & \omega > 0.49 \end{cases} \quad (9)$$

where $\alpha(T_c)$ is a dimensionless temperature-dependent correction factor introduced to improve vapor pressure predictions, T_r is the reduced temperature, and ω is the acentric factor.

In contrast to such EoS, Hekayati *et al.*²⁷ proposed a more advanced computational approach. Instead of modifying the form of **Equation 6**, this method identifies new, more precise α functions for different gases to replace the generic α function. The specific forms are as follows, for CO₂:

$$\alpha(T_c) = A_1 + \ln(P_r)(A_2 + A_3 \ln(T_r) - A_4 \ln(T_r^2) - A_5 \sin(A_6 \ln(P_r^2) - A_7 \sin(\ln(T_r))) \quad (10)$$

where

$$P_r = \frac{P}{P_{cr}} \quad (11)$$

For CH₄ and H₂, α can be written as:

$$\alpha(T_c) = \exp(B_1 T_r + B_2 \ln(T_r) + B_3 (1 - \sqrt{T_r})) \quad (12)$$

where $A_1 = 1.0010$, $A_2 = 0.0524$, $A_3 = 0.2315$, $A_4 = 0.1286$, $A_5 = 0.3258$, $A_6 = 0.0704$, $A_7 = 0.9461$, $B_1 = 0.039$, $B_2 = 0.0473$, and $B_3 = 0.8514$. It is important to note that, in order to distinguish between the two computational methods, the algorithm is classified as follows: if $\alpha(T_r)$ in **Equation 6** adopts the form given in **Equation 9**, the method is referred to as the CPR algorithm; if $\alpha(T_r)$ is determined by solving **Equations 11** and **12** simultaneously, the method is termed the MPR

algorithm. By solving the above system of equations, the molar volume of the target gas can be obtained. The mass density of the gas is then given by:

$$\rho_g = \frac{M}{V} \quad (13)$$

where M is the molar mass and V represents the molar volume of the gas, obtained by solving **Equations 1–5** simultaneously.

Based on the physical parameters of the three gases listed in **Table 1** and the NIST Chemistry WebBook,²⁸ the mass density variation of the gases with depth can be calculated using the three different methods described above. The results are presented in **Figure 1**, which also allows for a comparison of the accuracy among these methods.

To calculate the variation of gas velocity with depth, the bulk modulus of the gas must also be determined. For acoustic waves with frequencies below approximately 1 GHz, a more physically reasonable approximation is the adiabatic compression model. This model assumes that the entropy of the gas remains essentially constant during compression.²⁹ The relationship between the isentropic bulk modulus and the isothermal bulk modulus is given by:

$$C_s = \frac{G}{\gamma} \quad (14)$$

where C_s represents the isentropic bulk modulus, G denotes the isothermal bulk modulus, and γ is the adiabatic index (heat capacity ratio), which primarily depends on temperature and pressure.³⁰ For the VDW algorithm, **Equation 3** yields:

$$K_g = \frac{\gamma}{G} = \gamma \left\{ \frac{VRT_c}{(V-b)^2} - \left(\frac{2a}{V^2} \right) \right\} \quad (15)$$

For the CPR and MPR algorithms, **Equation 6** yields:

$$K_g = \frac{\gamma}{G} = \gamma \left\{ \frac{VRT_c}{(V-b)^2} - V \left(\frac{2a\alpha(V+b)}{V^2 + 2Vb - b^2} \right)^2 \right\} \quad (16)$$

After calculating K_g , the velocity and related acoustic expressions for the gas can be determined.³¹ The velocity formula is given by:

$$V_g = \sqrt{\frac{K_g}{\rho_g}} \quad (17)$$

Using the velocity calculation method (Equation 17), the velocity curves for the three gases under the three EoS can be obtained, as shown in Figures 2–4.

For the three gases considered, their key physical properties are listed in Table 1.

Table 1. Critical properties, molar mass, and acentric factor of the three gases

Substance	T_{cr} (K)	P_{cr} (MPa)	V_{cr} (cm ³ /mol)	Molar mass (g/mol)	ω
CO ₂	304.12	7.37	94.07	44.010	0.225
CH ₄	190.56	4.56	98.60	16.043	0.011
H ₂	33.25	1.30	65.00	2.016	−0.2202

Abbreviations: CH₄: Methane; CO₂: Carbon dioxide; H₂: Hydrogen.

As shown in Figures 1–4, the analysis reveals that, in terms of gas density variation with depth, the mass density of CO₂ increases rapidly around 800 m before the growth rate slows down, whereas the densities of CH₄ and H₂ exhibit a steadily rising trend with overall stable growth. Regarding velocity, the velocity of CO₂ first decreases and then increases with depth. The velocity of CH₄ also shows a slight initial decrease followed by an increase, while the velocity of H₂ rises continuously and remains the highest among the three gases. Furthermore, by examining the velocity trends of the three gases, it can be observed that the CO₂ velocity profile exhibits a distinct change around 800 m. This is because CO₂ transitions into a supercritical state within this depth range, where its phase exists between gaseous and liquid states, resulting in unstable properties. Consequently, its density increases rapidly, while its velocity shows an initial decline followed by an upward trend. This pattern can be more conveniently observed in Figure 6. Meanwhile, comparative analysis indicates that the MPR algorithm demonstrates higher accuracy and better agreement with the NIST data compared to the other two algorithms.

Figure 5 shows the comparative precision of the MPR algorithm against the alternatives. It can be observed that the agreement between calculated and reference data for CO₂ and H₂ is highest when using the MPR method. For the density parameter of CH₄, the CPR algorithm yields relatively more accurate results. However, in terms of

velocity prediction, the MPR algorithm exhibits the highest accuracy, showing near-perfect alignment with the NIST data. Therefore, given that the MPR algorithm achieves the highest computational accuracy for both density and velocity parameters across the three gases, it will be uniformly adopted for calculating the thermodynamic properties of gases in all subsequent analyses, ensuring both computational consistency and reliability.

Additionally, in the computational process, the specific heat ratio γ plays multiple critical roles in thermodynamic properties and influences the variation of gas velocity curves. To assess its impact on the calculation results, the specific heat ratio γ for the three gases is plotted, as shown in Figures 6–8.

As shown in Figures 6–8, the observed trend where the velocity of CO₂ initially decreases and then increases around a depth of 800 m can be attributed to variations in its heat capacity ratio. These changes indicate that CO₂ reaches its critical state at this depth, resulting in the characteristic velocity profile. Similarly, variations in the heat capacity ratios of CH₄ and H₂ also influence their respective velocity trends and the calculation of their bulk moduli.

Regarding the viscosity properties of gases, the Lohrenz–Bray–Clark model³² was employed to model and calculate the viscosities of the three gases. The principal calculation procedure is as follows:

$$\left[(\eta_g - \eta_0)\xi + 10^{-4}\right]^{0.25} = \sum_{j=0}^4 a_j \left(\frac{\rho_g}{\rho_{cr}}\right) \quad (18)$$

$$\xi = T_{cr}^{1/6} M^{-1/2} P_{cr}^{-2/3} \quad (19)$$

$$\eta_0 = \begin{cases} 34 \cdot 10^{-5} T_r^{0.94} / \xi & T_r \leq 1.5 \\ 17.78 \cdot 10^{-5} (4.58 T_r - 1.67)^{5/8} / \xi & T_r > 1.5 \end{cases} \quad (20)$$

$$\rho_{cr} = \frac{M}{V_{cr}} \quad (21)$$

where $a_0 = 0.10230$, $a_1 = 0.023364$, $a_2 = 0.058533$, $a_3 = -0.040758$, and $a_4 = 0.0093324$. The results of these calculations are shown in Figure 9.

As shown in Figure 9, while minor differences exist between the Lohrenz–Bray–Clark model calculations and the NIST dataset, the overall agreement remains strong. In terms of viscosity variation with depth, the viscosities of all three gases increase as depth rises, with CO₂ exhibiting the fastest growth rate. Around 1 km depth, its rate of increase reaches a maximum and subsequently levels off.

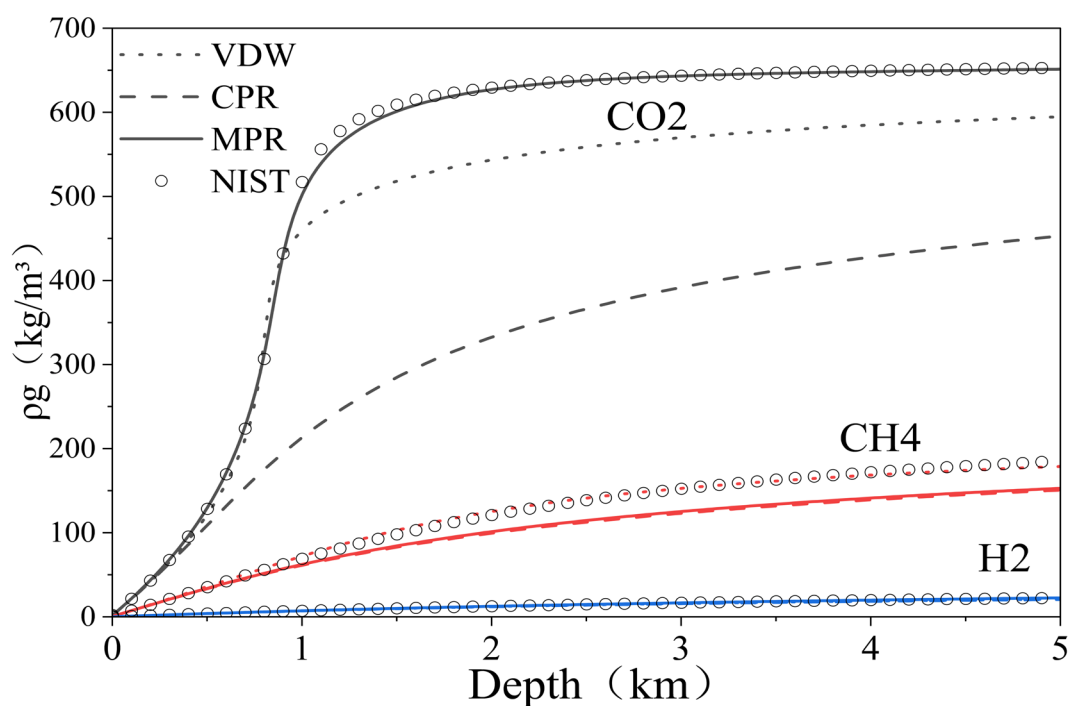


Figure 1. Graph of mass density versus depth for three gases under three equations of state. The solid lines represent the values calculated by the equations of state, whereas the circles indicate the reference data obtained from the NIST Chemistry WebBook for comparison.

Abbreviations: CH_4 : Methane; CO_2 : Carbon dioxide; CPR: Corrected Peng–Robinson; H_2 : Hydrogen; MPR: Modified Peng–Robinson; NIST: National Institute of Standards and Technology; VDW: Van der Waals.

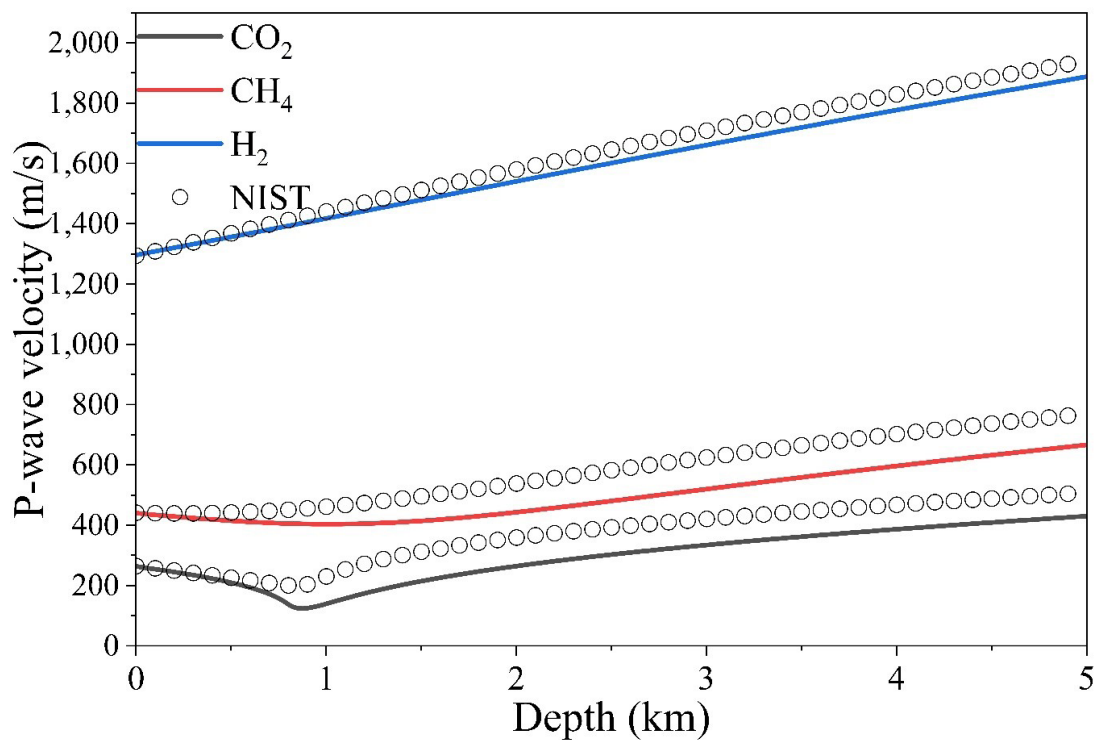


Figure 2. Graph of acoustic velocity versus depth for three gases under the van der Waals equation of state. The solid lines represent the values calculated by the equations of state, whereas the circles indicate the reference data obtained from the NIST Chemistry WebBook for comparison.

Abbreviations: CH_4 : Methane; CO_2 : Carbon dioxide; H_2 : Hydrogen; NIST: National Institute of Standards and Technology.

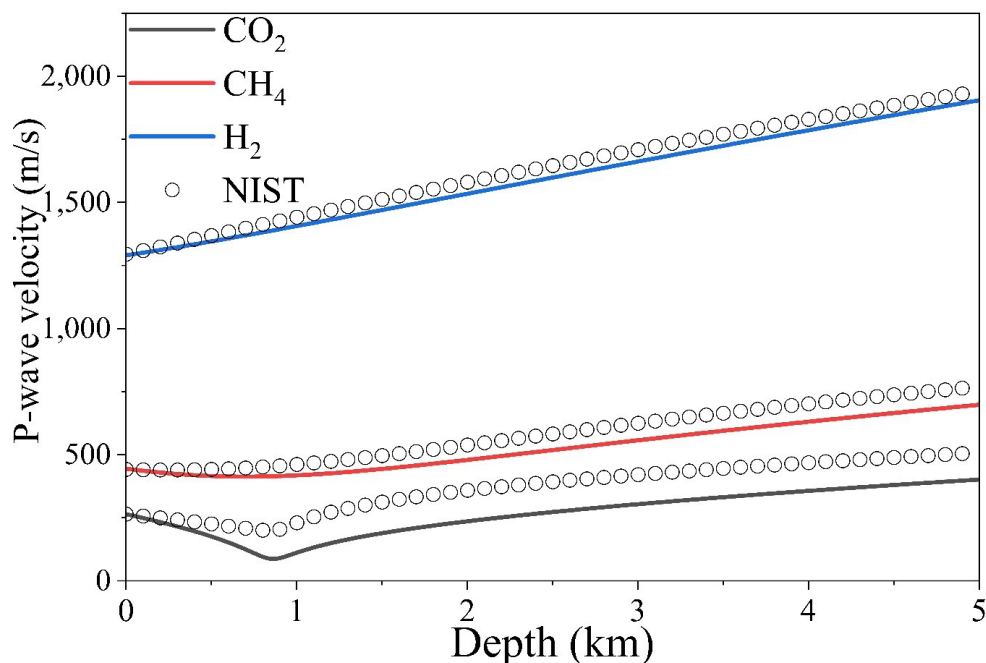


Figure 3. Graph of acoustic velocity versus depth for three gases under the corrected Peng–Robinson equation of state. The solid lines represent the values calculated by the equations of state, whereas the circles indicate the reference data obtained from the NIST Chemistry WebBook for comparison. Abbreviations: CH₄: Methane; CO₂: Carbon dioxide; H₂: Hydrogen; NIST: National Institute of Standards and Technology.

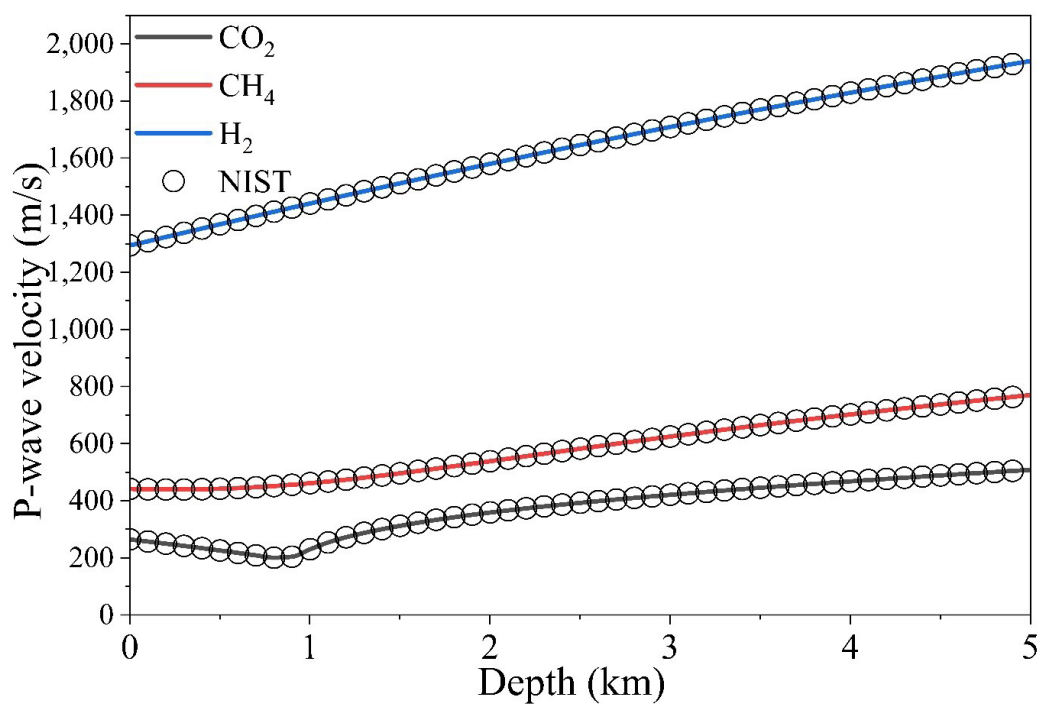


Figure 4. Graph of acoustic velocity versus depth for three gases under the modified Peng–Robinson equation of state. The solid lines represent the values calculated by the equations of state, whereas the circles indicate the reference data obtained from the NIST Chemistry WebBook for comparison. Abbreviations: CH₄: Methane; CO₂: Carbon dioxide; H₂: Hydrogen; NIST: National Institute of Standards and Technology.

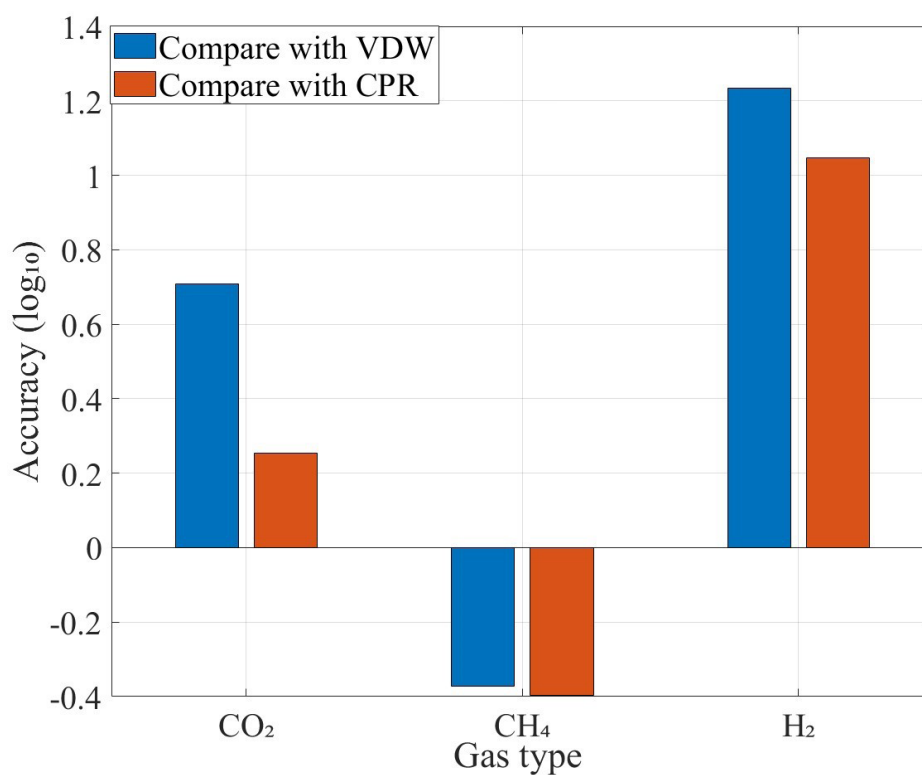


Figure 5. Accuracy of the modified Peng–Robinson algorithm compared to the other two algorithms
Abbreviations: CH₄: Methane; CO₂: Carbon dioxide; CPR: Corrected Peng–Robinson; H₂: Hydrogen; VDW: Van der Waals.

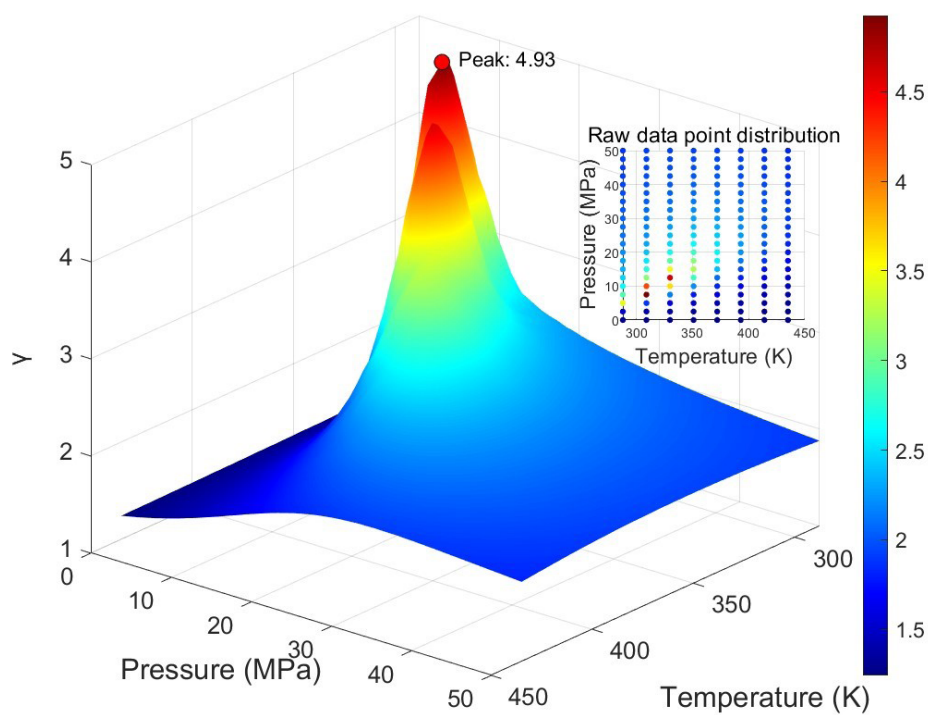


Figure 6. Surface plot of the specific heat ratio distribution for carbon dioxide

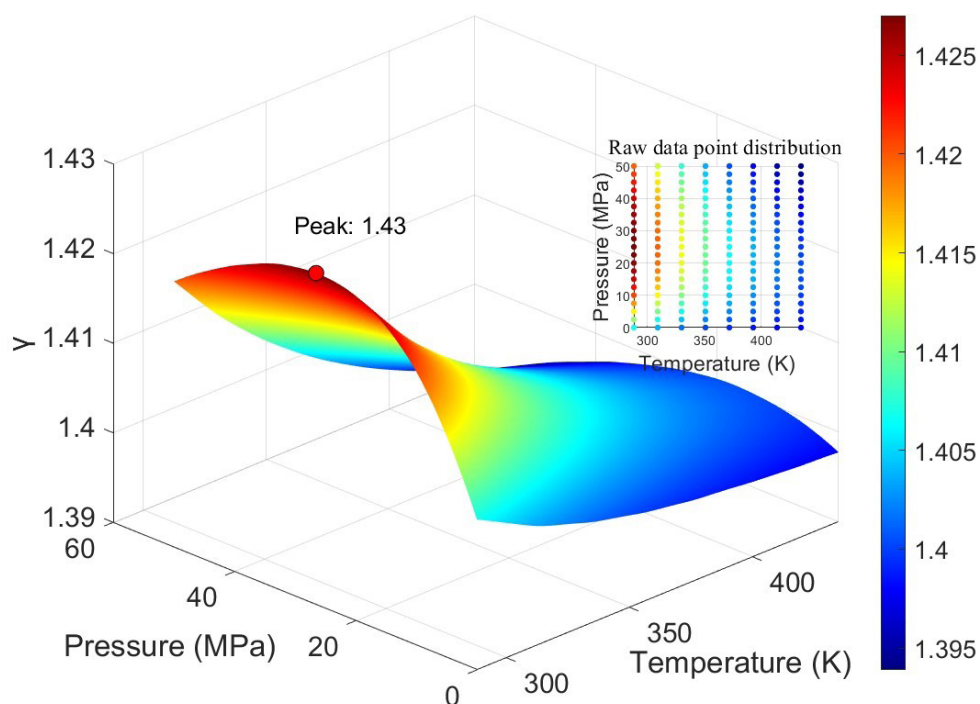


Figure 7. Surface plot of the specific heat ratio distribution for methane

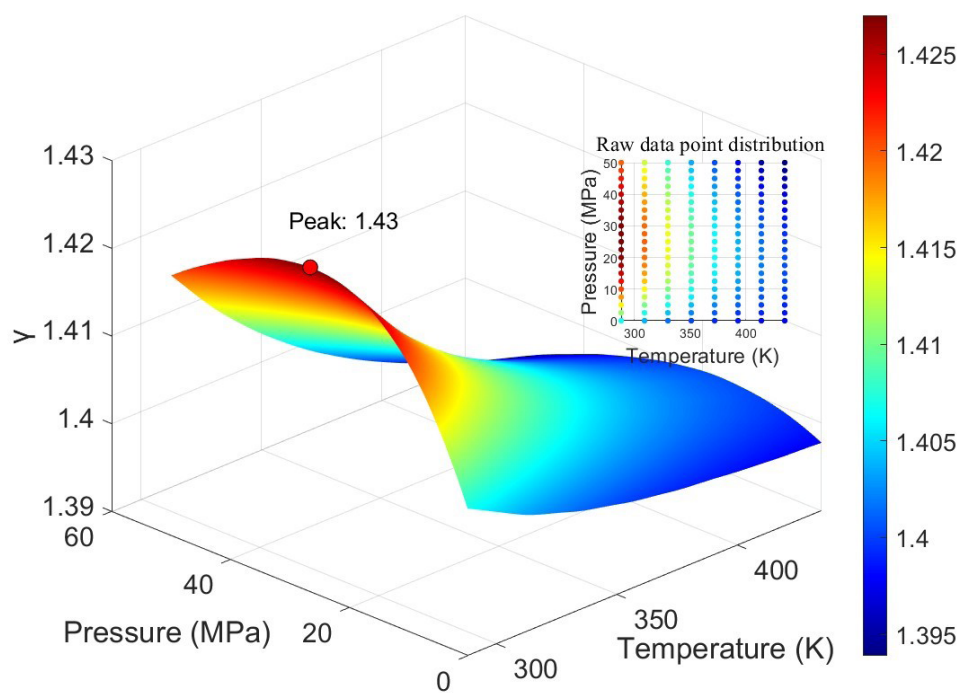


Figure 8. Surface plot of the specific heat ratio distribution for hydrogen

In comparison, CH_4 and H_2 show slower viscosity growth. At a depth of 5 km, the viscosity values of the three gases, ranked from highest to lowest, are: CO_2 , CH_4 , and H_2 .

3. The properties of brine

The calculation of brine properties is also related to temperature and pressure. Following the Batzle–Wang⁶ model and considering the compressional wave velocity, density, and viscosity of brine under different temperature–pressure conditions, the brine density formula can be expressed as:

$$\rho_b = \rho_w + S\{0.668 + 0.445 + 10^{-6}[300p - 2400pS + T_c(80 + 3T_c - 3300S - 13p + 47pS)]\} \quad (22)$$

where,

$$\rho_w = 1 + 10^{-6}(-80T_c - 3.3T_c^2 + 0.00175T_c^3 + 489p - 2T_cp + 0.016T_c^2p - 1.3 \times 10^{-5}T_c^3p - 0.333p^2 - 0.002T_cp^2) \quad (23)$$

where S is the mass fraction of sodium chloride (ppm/1,000,000). In this study, $S = 50,000$ ppm.

The brine velocity is given by:

$$V_b = V_w + S(1170 - 9.6T_c + 0.055T_c^2 - 8.5 \times 10^{-5}T_c^3 + 2.6p - 0.0029T_cp - 0.0476p^2) + S^{1.5}(780 - 10p + 0.16p^2) - 1820S^2 \quad (24)$$

where V_w is the velocity of pure water, calculated as:

$$V_w = \sum_{i=0}^4 \sum_{j=0}^3 w_{ij} T_c^i p^j \quad (25)$$

and w_{ij} are provided in Table 2.

The bulk modulus of brine is:

$$K_b = \rho_b V_b^2 \quad (26)$$

and the viscosity of brine is:

$$\eta_g = 0.1 + 0.333S + (1.65 + 91.9S^3) \exp\left\{-\left[0.42(S^{0.8} - 0.17)^2 + 0.045\right]T_c^{0.8}\right\} \quad (27)$$

Figure 10 shows the density and P-wave velocity of brine. The figure illustrates that the P-wave velocity curve exhibits a characteristic, non-monotonic, and complex trend, which can be divided into three distinct segments:

- (i) Shallow rapid-increase segment (0–1,000 m): Within this interval, as depth increases, the effect of lithostatic pressure dominates. The rising pressure reduces the

volume of the brine and significantly increases its bulk modulus, leading to a rapid rise in acoustic velocity. Although temperature also increases with depth—which would typically reduce velocity in the shallow section—the rate of increase from pressure effects far exceeds that from temperature effects.

- (ii) Mid-depth transitional-decline segment (1,000–3,000 m): The curve peaks at approximately 1,000 m depth, then turns and begins a gradual decline. This indicates that as depth continues to increase, the velocity-reducing effect of rising temperature strengthens and gradually counteracts—even surpasses—the velocity-enhancing effect of pressure.
- (iii) Deep gradual-recovery segment (3,000–5,000 m): Beyond about 3,000 m depth, the curve slowly rises again. This occurs because, under high-temperature and high-pressure conditions, the physical properties of the brine change. At such extreme pressures, the compressibility of water becomes low, and the enhancing effect of pressure reasserts itself significantly, driving a slow recovery in velocity despite the high temperatures.

Table 2. Coefficients for brine property calculation

$w_{00} = 1,402.85$	$w_{02} = 3.437 \times 10^{-3}$
$w_{10} = 4.871$	$w_{12} = 1.739 \times 10^{-4}$
$w_{20} = -0.04783$	$w_{22} = -2.135 \times 10^{-6}$
$w_{30} = 1.487 \times 10^{-4}$	$w_{32} = -1.455 \times 10^{-8}$
$w_{40} = 2.197 \times 10^{-7}$	$w_{42} = 5.230 \times 10^{-11}$
$w_{01} = 1.524$	$w_{03} = -1.197 \times 10^{-5}$
$w_{11} = -0.0111$	$w_{13} = -1.628 \times 10^{-6}$
$w_{21} = 2.747 \times 10^{-4}$	$w_{23} = 1.237 \times 10^{-8}$
$w_{31} = -6.503 \times 10^{-7}$	$w_{33} = 1.327 \times 10^{-10}$
$w_{41} = 7.987 \times 10^{-10}$	$w_{43} = 4.614 \times 10^{-13}$

Meanwhile, the blue density ρ_b curve shows a continuous yet gradually slowing decline. As depth increases, the sustained rise in temperature causes the brine to expand thermally, increasing its volume and thus decreasing its bulk density. Although increasing pressure compresses the water and would act to increase density, over the entire 0–5,000 m interval, the effect of the rising geothermal gradient leads to a monotonic decrease in

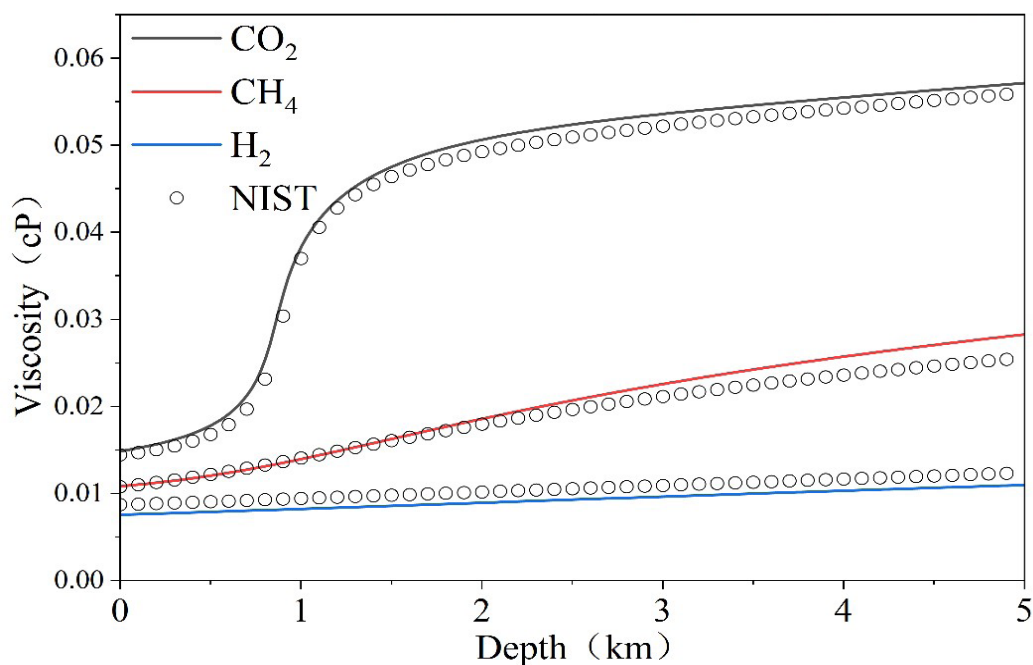


Figure 9. Plot of viscosity variation with depth for the three gases under the Lohrenz–Bray–Clark equation. Black circles denote the reference data obtained from the NIST Chemistry WebBook.

Abbreviations: CH₄: Methane; CO₂: Carbon dioxide; H₂: Hydrogen; NIST: National Institute of Standards and Technology.

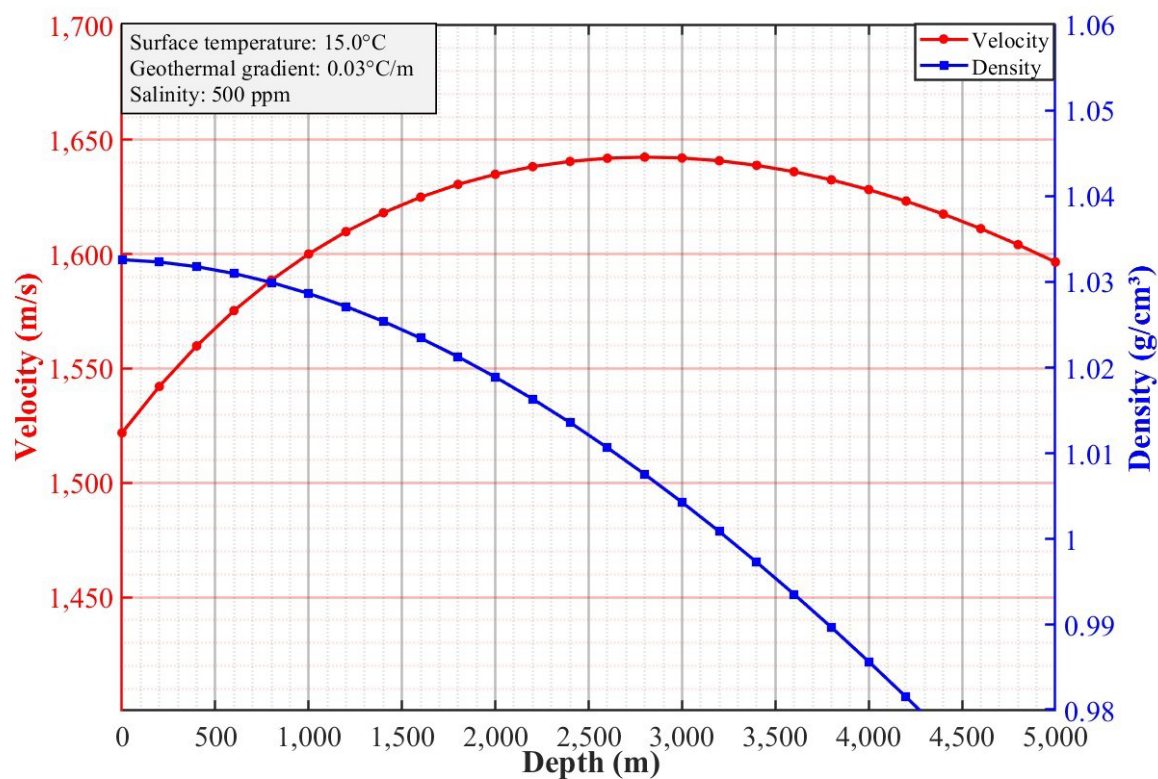


Figure 10. Density and P-wave velocity of brine as functions of depth

density. The slowing rate of decline with depth is due to the partially offsetting influence of pressure on density.

In summary, the two curves clearly demonstrate that with increasing depth, the P-wave velocity of the brine shows an overall rising trend while its density exhibits a falling trend—the two parameters vary inversely.

4. Effective fluid model

By considering the mineral composition of reservoir rocks and the characteristics of their pore microstructure, and based on the effective medium assumption, seismic rock physics modeling methods can be effectively applied to calculate their elastic parameters.³³ Through the calculations and analyses presented above, the modeled characteristics and systems for gases and brine have been established. These properties now need to be integrated with the rock matrix to obtain the elastic characteristics of the fluid-bearing rock model. Currently, various theories exist to describe the frequency-dependent dispersion and attenuation of seismic waves in fluid-saturated rocks.

For an effective fluid model, the key parameters are the respective bulk moduli and saturations, namely S_g (gas saturation) and S_b (brine saturation), which satisfy the following equation:

$$S_g + S_b = 1, \quad (28)$$

and the density of the gas–liquid mixture can be calculated as:

$$\rho_f = S_g \rho_g + S_b \rho_b \quad (29)$$

Next, the relationship of the bulk modulus for the gas–brine mixture can be determined using Wood's⁸ equation:

$$K_w = (S_g K_g^{-1} + S_b K_b^{-1})^{-1} \quad (30)$$

where K_g and K_b represent the bulk moduli of the gas and the brine, respectively.

Due to the influence of pore fluids, the propagation velocities of compressional waves in the same rock can differ significantly across frequency bands, which is manifested as velocity dispersion in multiscale seismic data.³⁴ In fluid-bearing rocks where gas, water, or mixed fluids coexist without mutual mixing, pressure differences near the gas–water interfaces become pronounced under wave excitation, inducing vigorous fluid motion. Such motion occurs extensively inside the rock; consequently, the superposition of local fluid flow across numerous

discontinuous interfaces within a unit volume of rock can lead to substantial attenuation.

To simulate the inelastic behavior of rocks, this study adopts the patchy saturation model proposed by the Johnson model as the primary framework for analyzing the waveresponse characteristics of the rock-physics model. The results obtained from this model will be compared with those from the White model to discuss their differences and provide recommendations for model selection. Secondly, regarding the frequency-dependent characteristics of this study, since the dominant frequency range for seismic exploration is 10–60 Hz, with the advantageous band being 20–40 Hz, the frequency is set to $f = 30$ Hz for the analysis. The model developed in this work allows for obtaining responses at various frequencies by simply changing the value of f . Using 30 Hz here is solely intended to clearly illustrate and highlight the computational differences between the Johnson and White models at a specific frequency, thereby enabling a better understanding and analysis of the proposed rock-physics modeling.

The analysis was conducted at a frequency of $f = 30$ Hz, focusing on how compressional-wave velocity and attenuation factors vary under two distinct patch geometries: concentric-circle patches and fractal patches. In the concentric-circle configuration—which can be visualized as “brinecoated gas patches,” where an outer layer of brine encloses an inner gas core—the outer brine radius is set to $R = 30$ cm. The saturations of the liquid (brine) and gas are denoted as S_g and S_b , respectively. When fluids are not fully mixed within the pore volume but instead distributed in patchy form, the high-frequency effective bulk modulus tends to be higher than the value predicted by the Wood model.

Following the approach of Picotti *et al.*,³⁵ two key parameters describe these patchy systems: the size factor T and the surfacetovolume ratio (S/V). In this study, the same size factor T was used for both fractal and concentric-circle patches. By increasing the S/V parameter by a factor of 10, the originally regular spherical patches are transformed into rough, irregular geometries. This modification allows the mixed fluid to be incorporated into the rock pores, enabling subsequent calculations of wave velocity and attenuation.

According to the Johnson model, the equivalent bulk modulus of rocks is calculated at the low- and high-frequency limits. For intermediate frequencies between these limits, a closed-form analytical expression is provided for approximation.

The bulk modulus of the saturated rock at low frequencies

can be computed using the Gassmann equations,³⁶ which are expressed as:

$$K_g(K_f) = K_m + a^2 M(K_f) \quad (31)$$

$$\alpha = 1 - \frac{K_m}{K_s} \quad (32)$$

$$M(K_f) = \left(\frac{\alpha - \phi}{K_s} + \frac{\phi}{K_f} \right)^{-1} \quad (33)$$

where K_f represents the bulk modulus of the fluid within the pores.

For a gas-brine mixture, the shear modulus K_f can take the value of either K_w or K_b , depending on the distribution of the two-phase fluid in the pore space. K_m is the bulk modulus of the dry rock matrix, ϕ denotes the rock porosity, and K_s stands for the bulk modulus of the rock mineral grains. Substituting these parameters into the Johnson model yields the bulk modulus under low-frequency conditions as:

$$K_{gw} = K_g(K_w) \quad (34)$$

In this case, the computed value corresponds to substituting the bulk modulus of the mixed fluid calculated using the Wood model into **Equation 30**. Dutta and Ode³⁷ derived and validated this approach based on classical Biot theory. The predicted bulk modulus corresponds to the scenario in which the two-phase fluid in the rock is in a fully relaxed state, resulting in the softest effective state of the rock and the lowest seismic-wave propagation velocity. Hence, this value is regarded as the lower bound for seismic-wave velocities in partially saturated rocks.

Under high-frequency conditions, pore pressure is nonuniform across the whole medium but can be considered constant within each fluid phase. In this case, the effective bulk modulus can be calculated using the Hill equation³⁸ for bulk modulus, expressed as:

$$K_{gh} = \left(\frac{S_g}{K_g(K_g) + 4/3\mu_m} + \frac{S_b}{K_g(K_b) + 4/3\mu_m} \right)^{-1} - 4/3\mu_m \quad (35)$$

where, μ_m denotes the shear modulus of the dry rock. For practical purposes, the shear modulus of the fluid-saturated rock can be taken as equal to that of the dry rock. $K_g(K_g)$

and $K_g(K_b)$ represent the results obtained from **Equation 30** by substituting the bulk modulus of the pore fluid with that of the gas and the brine, respectively. Substituting the calculated K_{gw} and K_{gh} into the expression for the bulk modulus at intermediate frequencies, the equation based on Pride's³⁹ simple branch function is given as:

$$K(\omega) = K_{gh} - \frac{K_{gh} - K_{gw}}{1 - \xi + \xi \sqrt{1 - i\omega\tau / \xi^2}} \quad (36)$$

where i denotes the imaginary unit, ξ represents the shape parameter (a broader transition region corresponds to $\xi < 1$, while a narrower one corresponds to $\xi > 1$), and τ is the frequency-scale parameter. Both ξ and τ can be calculated with S/V and T . For S/V , the calculation method is as follows:

$$\frac{S}{V} = 3 \times \frac{a^2}{b^3} \quad (37)$$

$$a = b \times S_g^{1/3} \quad (38)$$

where b is the outer brine layer radius of 30 cm. The formula for calculating T is:

$$T = \frac{K_{gw}\phi^2}{30\kappa b^3} \{ [3\eta_2 g_2^2 + 5(\eta_1 - \eta_2)g_1 g_2 - 3\eta_1 g_1^2] a^5 - 15\eta_2 g_2 (g_2 - g_1) a^3 b^2 + 5g_2 [3\eta_2 g_2 - (2\eta_1 - \eta_2)g_1] a^2 b^3 - 3\eta_2 g_2^2 b^5 \} \quad (39)$$

where

$$g_j = \frac{(1 - K_m/K_s)(1/K_w - 1/K_{f_j})}{1 - K_m/K_s - \phi K_m/K_s + \phi K_m/K_w}, j = 1, 2 \quad (40)$$

Subsequently, the P-wave modulus is:

$$E(\omega) = K(\omega) + 4/3\mu_m \quad (41)$$

the P-wave velocity is:

$$V_c = \sqrt{\frac{K(\omega) + 4/3\mu_m}{\rho}} \quad (42)$$

the final phase velocity is:

$$V_p = \left[\text{Re} \left(\frac{1}{V_c} \right) \right]^{-1} \quad (43)$$

and the attenuation factor is calculated as:

$$Q = \frac{\text{Re}(V_c^2)}{\text{Im}(V_c^2)} \quad (44)$$

where Re and Im represent the real and imaginary parts, respectively, of the result calculated from **Equation 41**. Based on the data provided by Gei *et al.*,⁴⁰ this study employs parameters of Utsira-type sand at depths of 800 m and 3,000 m for simulation calculations, with the relevant properties of the gases and rocks provided in **Table 3**. The resulting plots of V_p and Q are shown in **Figure 11**.

Table 3. Properties of the three gases, the rock, and brine

Properties	Depth	
	800 m	3,000 m
Physical conditions	P = 8.1 MPa P _c = 18.2 MPa T _c = 39 °C	P = 30.1 MPa P _c = 67.8 MPa T _c = 105 °C
Sediment	$\phi = 0.29$ K _m = 1.39 GPa $\mu_m = 0.83$ GPa $\kappa = 0.41$ d	$\phi = 0.17$ K _m = 8.75 GPa $\mu_m = 5.23$ GPa $\kappa = 0.06$ d
Brine	K _b = 2.6 GPa $\rho_b = 1,030$ kg/m ³ $\eta_b = 0.8$ mPa·s	K _b = 2.7 GPa $\rho_b = 1,004$ kg/m ³ $\eta_b = 0.35$ mPa·s
CO ₂	K _g = 9.97 MPa $\rho_g = 310$ kg/m ³ $\eta_g = 25.25$ μ Pa·s	K _g = 115.7 MPa $\rho_g = 644$ kg/m ³ $\eta_g = 53.72$ μ Pa·s
CH ₄	K _g = 11.37 MPa $\rho_g = 56$ kg/m ³ $\eta_g = 13.13$ μ Pa·s	K _g = 59.17 MPa $\rho_g = 152$ kg/m ³ $\eta_g = 21.67$ μ Pa·s
H ₂	K _g = 11.98 MPa $\rho_g = 6$ kg/m ³ $\eta_g = 8.08$ μ Pa·s	K _g = 48.9 MPa $\rho_g = 17$ kg/m ³ $\eta_g = 9.62$ μ Pa·s

Abbreviations: CH₄: Methane; CO₂: Carbon dioxide; H₂: Hydrogen.

In **Figure 11A** and **11C**, the P-wave velocity exhibits an increasing trend with rising brine saturation. This occurs because the compressibility of the liquid brine phase is significantly lower than that of the gaseous phase. As brine saturation increases, the effective bulk modulus of the rock increases, leading to higher Pwave velocity. In contrast, the presence of gas tends to “soften” the rock and reduce wave velocity.

Specifically, regarding different gases, it can be

observed that the P-wave velocity of brine containing CO₂ is higher than that of brines containing the other two gases. Its “hookshaped” curve also approaches a more linear, gradual variation. Furthermore, from the perspective of patch geometry, the P-wave velocity for spherical patches is generally higher than that for fractal patches. At a depth of 3,000 m, the Pwave velocities of rocks containing the three gases with the same brine follow the order CO₂ > CH₄ > H₂. This difference is even more pronounced for fractal patches.

Under higher confining pressure at 3,000 m depth, the rock frame becomes denser, resulting in an overall higher P-wave velocity compared to the 800 m depth. However, the relative amplitude of fluidsubstitution effects may be reduced, likely due to decreased pore compressibility under high pressure.

Figure 11B and **11D** illustrate the variation of attenuation factors with brine saturation. Attenuation peaks typically occur within the partial-saturation range, which is dominated by wave-induced fluid flow mechanisms. In the figure, the spherical gas bubbles of CO₂ and H₂ may lead to relatively narrow attenuation peaks at moderate saturations, as uniform bubble geometries promote local fluid flow. In contrast, the fractal geometry of CH₄ may broaden the attenuation peak or shift its position, because the fractal structure enhances pore-scale heterogeneity, triggering more complex fluid motion.

A comparison of depths shows that the attenuation values at 3,000 m are lower than those at 800 m. This is because the high-pressure environment suppresses the relative motion of pore fluids, thereby reducing energy dissipation. The frequency is fixed at 30 Hz (within the seismic frequency band), which ensures that the attenuation mechanism is dominated by macroscopic fluid flow rather than highfrequency scattering.

This analysis reveals how gas morphology (geometry) and depth jointly regulate acoustic parameters, providing insights for interpreting seismic responses in partially saturated reservoirs under varying burial conditions.

5. Model validation and comparative analysis: Johnson and White model prediction differences

To more intuitively characterize fluid behavior in deep geological environments and highlight the differences between modeling approaches, we further calculated the compressional wave velocity and attenuation factor using the improved White model by Dutta and Ode.³⁴ A comparison with the Johnson model is shown in **Figure 12**.

As shown in **Figure 12**, a more intuitive comparison

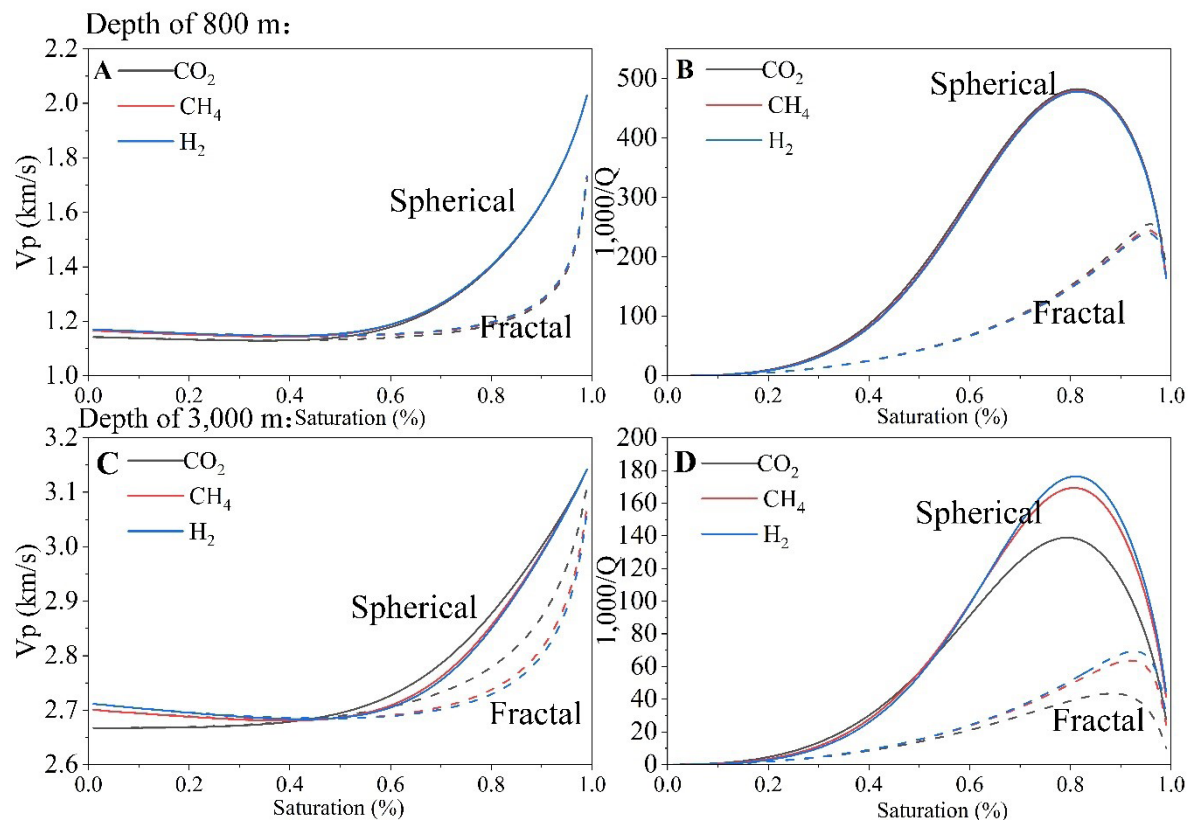


Figure 11. Variation of Vp and attenuation factor of wet rock versus saturation at depths of 800 m and 3,000 m. (A) Vp and (B) attenuation factor at 800 m; (C) Vp and (D) attenuation factor at 3,000 m.

Abbreviations: CH₄: Methane; CO₂: Carbon dioxide; H₂: Hydrogen; Vp: P-wave velocity.

reveals that both the Johnson and White models predict essentially the same trend for P-wave velocity—monotonically increasing with rising brine saturation. This indicates that, for elastic properties such as seismic velocity, the macroscopic averaging effects of the two models are similar. For P-wave velocity, regardless of whether the geometry is spherical or fractal patches, an inflection point occurs at approximately 50% brine saturation, beyond which the velocity increases markedly. Among the three gases, CO₂ exhibits the highest velocity, followed by CH₄ and H₂. This difference is primarily governed by the mass of the gas, with heavier gases generally producing higher velocities than lighter ones.

In terms of the attenuation factor, which characterizes energy dissipation, the attenuation peak predicted by the White model is lower than that of the Johnson model. Furthermore, the White model yields a broader, more symmetric attenuation peak in fractal patches, centered around 50% saturation. In contrast, the Johnson model produces a sharper, narrower attenuation peak whose

position is shifted. To clarify the distinctions between the two models more explicitly, CO₂—which exhibits the most pronounced differences—was selected for separate plotting and further analysis.

The critical point of CO₂ (304.12 K, 7.38 MPa) lies within the depth range of this study. At a depth of 800 m, it exists in a gaseous or near-critical state, while at 3,000 m, it is in a supercritical state. This significant phase change leads to drastic variations in its acoustic properties, with clear differences observed in compressional wave velocity and attenuation factor.

The differences between the two models are more clearly illustrated in Figure 13. The White model predicts a broad, symmetric attenuation peak located approximately near 50% saturation. In contrast, the attenuation peak predicted by the Johnson model is sharper and narrower. This is because, in the Johnson model, the mechanism is primarily wave-field-induced squirt flow, where fluid is injected from soft pores into adjacent stiff pores due to wave compression.⁴¹ Furthermore, the peak position is shifted—

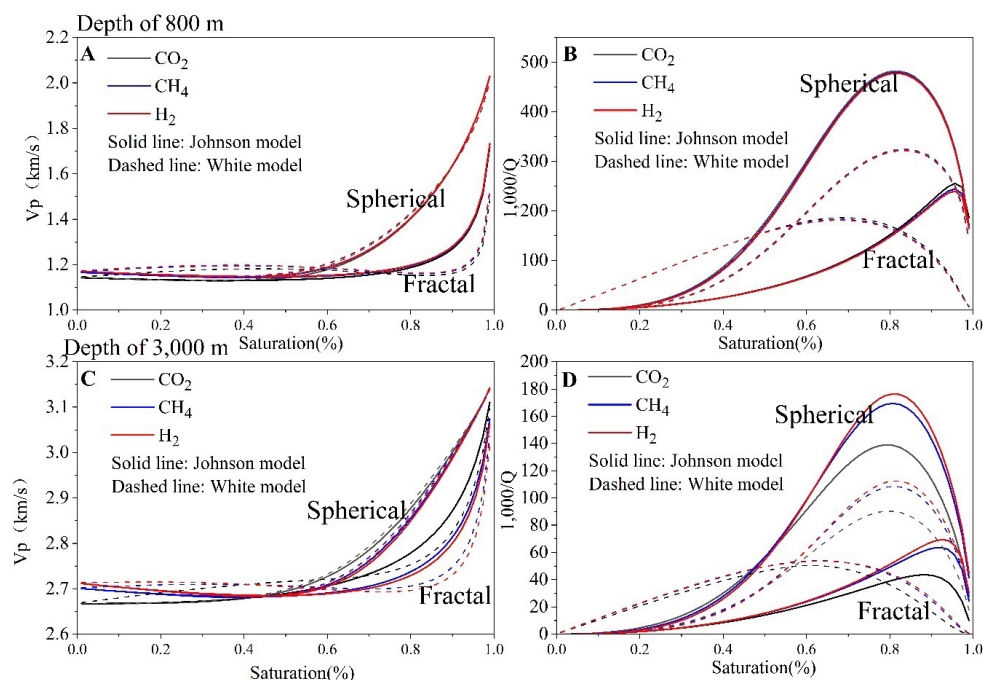


Figure 12. Variations of V_p and the attenuation factor with saturation for gas-brine mixtures of the three gases under the Johnson and White models at depths of 800 m and 3,000 m. (A) V_p and (B) attenuation factor at 800 m. (C) V_p and (D) attenuation factor at 3,000 m.

Abbreviations: CH_4 : Methane; CO_2 : Carbon dioxide; H_2 : Hydrogen; V_p : P-wave velocity.

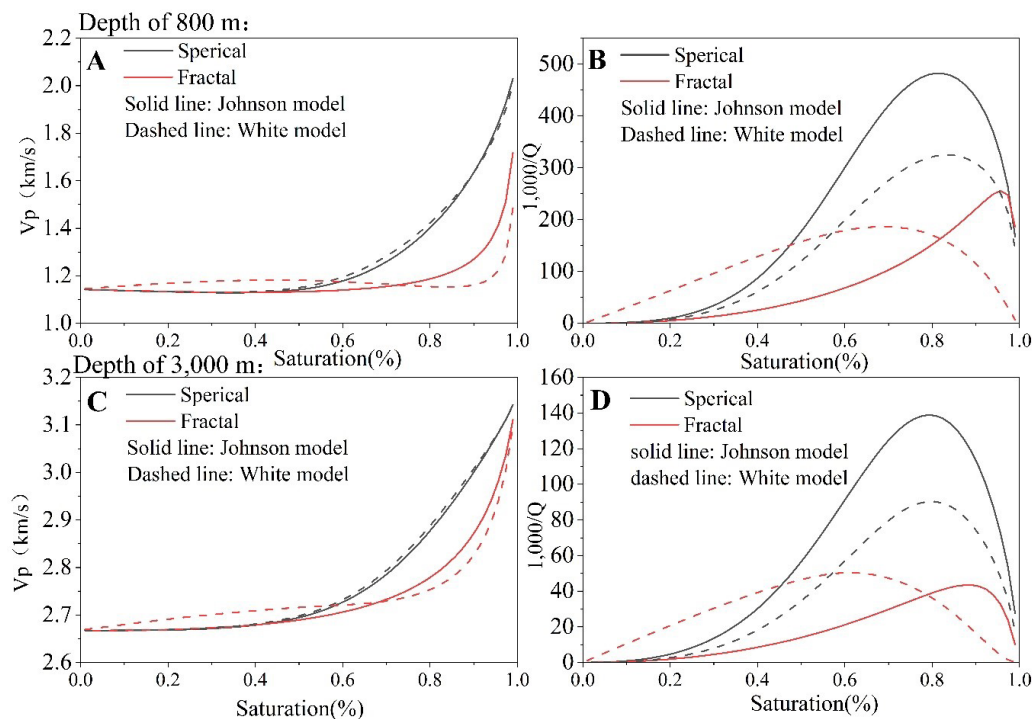


Figure 13. Comparative plots of carbon dioxide under the Johnson and White models. (A) V_p and (B) attenuation factor for rocks containing carbon dioxide-brine mixture at 800 m. (C) V_p and (D) attenuation factor at 3,000 m.

Abbreviation: V_p : P-wave velocity.

particularly evident in the fractal patch model—due to wave-induced fluid flow at the mesoscopic scale, which operates at a scale larger than pore sizes but smaller than the wavelength.⁴² In the White model, attenuation arises from macroscopic fluid flow driven by pressure gradients between differently saturated fluid patches, induced by the wave field. This flow occurs over a large scale with a broad distribution of relaxation times, resulting in a broad attenuation peak. The peak occurs at intermediate saturations because at this point, both gas and water phases are continuous, allowing for the highest efficiency of pressure diffusion.

In terms of P-wave velocity, the predicted values from the two models are generally consistent. However, in the Johnson model, the influence of heterogeneous fluid distribution on the effective bulk modulus of the rock is directly coupled into the frame elastic modulus. Its squirt-flow mechanism not only enhances attenuation but also contributes additional stiffness, leading to a higher estimated overall rock stiffness in partially saturated states and therefore relatively higher predicted wave velocities. In contrast, the macroscopic flow mechanism in the White model primarily affects wave velocity through fluid substitution and global pressure relaxation, while its description of the hardening effect on the effective modulus of the frame itself is relatively weaker. Consequently, its predictions are usually lower than those of the Johnson model, which accounts for both microscopic and macroscopic stiffening mechanisms.⁴³

A comparison of Figure 13B and 13D indicates that attenuation predicted by both models decreases markedly under high-pressure conditions. This occurs because high confining pressure compresses the soft pores in the rock, significantly suppressing microscopic squirt-flow activity, which relies on the existence of such soft pores. Consequently, the attenuation predicted by the Johnson model drops substantially under high-pressure conditions. Meanwhile, although pressure diffusion between macroscopic patches is also influenced by changes in fluid compressibility, the mechanism itself is less sensitive to pore closure than squirt flow. Therefore, under deep high-pressure conditions, the relative importance of microscopic flow mechanisms declines, while the contribution of macroscopic flow mechanisms increases, leading to a convergence of the predictions from the two models. This provides an important boundary condition for the applicability of the models in seismic interpretation of deep reservoirs.

In summary, this section systematically analyzes the differences and underlying mechanisms between the Johnson and White models in predicting compressional

wave velocity V_p and attenuation factor Q in sandstone reservoirs saturated with CO_2 -, CH_4 -, and H_2 -bearing fluids, through theoretical comparison and numerical simulation. It must be clearly noted that the specific numerical conclusions and comparative analyses presented here are primarily based on the sandstone matrix parameters and the defined patch morphology given in Table 3. The applicability of the two models is also influenced by the inherent physical mechanism differences of the models themselves, the reservoir conditions, and the fluid properties. In practical monitoring of fluids in underground reservoirs, the optimal model selection should be based on a comprehensive understanding of the target reservoir's lithology, pore structure, temperature–pressure conditions, and fluid phase state, and should be calibrated and validated using actual data (e.g., well logs, core experiments, and seismic data). This study provides a quantitative analysis framework for understanding the behavioral differences of the two models under various conditions, serving as a theoretical reference for selecting or improving rock physics models based on specific application scenarios.

6. Conclusion

This study proposes a methodology for constructing a frequency-dependent rock physics model that incorporates fluid thermodynamic parameters, aimed at investigating the behavior and state of fluids in deep geological storage and energy-storage environments. The research primarily focuses on three gases— CO_2 , CH_4 , and H_2 —taking into account not only the variations in their elastic parameters and viscosity under different temperature and pressure conditions but also the changes in brine properties with temperature and pressure. By combining these, the parameter variations of fluids when filling rock pores are obtained, allowing for a more accurate description of the physical characteristics and flow behavior of fluids in reservoirs at different depths, thereby better aligning with realistic subsurface fluid states.

Furthermore, through an in-depth analysis of patch saturation effects in this frequency-dependent rock physics model with integrated fluid thermodynamic parameters, the study demonstrates how different unsaturated-patch prediction models can be applied to analyze the inelastic properties of the investigated reservoirs. This provides a critical theoretical foundation and quantitative tools for the identification and monitoring of underground storage of CO_2 , CH_4 , and H_2 . It should be noted that the findings of this study are based on simulation calculations conducted in relatively ideal, porous sandstone reservoirs, without extensive consideration of complex pore structures or

special lithologies. Therefore, future work should be expanded to incorporate more complex rock-pore-structure models and anisotropy factors. Additionally, as this study relies on simulation results, it lacks certain conditions and factors present in real systems and can only serve as a theoretical reference. Subsequent research should aim to validate and apply the model by integrating actual well logs, core analysis, and seismic data, optimizing the study from practical perspectives to enrich the findings. Finally, the research can be extended to include more comprehensive seismic-attribute analyses, such as shear waves and anisotropy, with the goal of constructing a more comprehensive fluid identification and monitoring index system.

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Conflict of interest

Guangtan Huang is an Editorial Board Member of this journal, but was not in any way involved in the editorial and peer-review process conducted for this paper, directly or indirectly. The authors declare there is no conflict of interest.

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Availability of data

Some of the data used in this study are available from the NIST Chemistry WebBook (<https://webbook.nist.gov/chemistry>).

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