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Perspective

Gas adsorption behavior in shale reservoirs: Insights from molecular scale

Xuanzhe Xia[1], Xinghe Jiao[1], Junqian Li[2], Weijun Shen[3], Yuxuan Xia[1], Han Wang[1]*

[1]*State Key Laboratory of Petroleum Resources and Engineering, China University of Petroleum, Beijing 102249, P. R. China*

[2]*State Key Laboratory of Deep Oil and Gas, China University of Petroleum (East China), Qingdao 266580, P. R. China*

[3]*Key Laboratory for Mechanics in Fluid Solid Coupling Systems, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, P. R. China*

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Abstract:
Adsorbed gas confined in nanopores is a significant component of shale gas, and understanding the mechanisms of gas adsorption in shale nanopores is crucial for enhancing shale gas recovery and carbon dioxide geological sequestration. Due to the nanoscale pore sizes, complex pore structures, and diverse mineral types, adsorption experiments have a limited capacity to elucidate the microscopic mechanisms of gas adsorption. Compared to expensive adsorption experiments, molecular simulation methods can not only simulate reservoir in-situ conditions but also reveal the adsorption mechanisms from the molecular scale perspective. This work provides a brief review for the characteristics of methane adsorption in shale inorganic minerals and organic matter. Additionally, the competitive adsorption behavior of methane and carbon dioxide in shale is introduced to clarify the potential of shale reservoirs for carbon dioxide geological storage. Finally, the challenges faced by molecular simulation methods in gas adsorption research are discussed.

1. Introduction

Shale gas has abundant recoverable reserves globally, which can meet the future energy supply needs of human society and support the development of a low-carbon economy (Zou et al., 2010; Cai et al., 2021). The Sichuan Basin in China has trillions of cubic meters of shale gas resources, the main component of which is methane. Shale gas mainly exists in the three forms of adsorbed, free, and dissolved gas within the shale matrix pores, and reservoir water. Adsorbed gas is a significant component of shale gas, accounting for 20% to 85% of the total shale gas content. The adsorption mechanisms of shale gas are complex and are typically influenced by factors such as temperature, maturity, mineral composition, water content, and pore structure (Li et al., 2020; Tian et al., 2021; Qi et al., 2022). Therefore, understanding the adsorption mechanisms of shale gas and the complex fluid occurrence states within the reservoir is essential for the efficient development of shale gas resources.

However, the extremely low porosity and permeability of shale reservoirs make it challenging to conduct adsorption experiments (Memon et al., 2020). Even though current experimental equipment can provide pressures up to 60 MPa, the inherent tightness of shale reservoirs makes gas injection difficult. As a result, it is essential to grind the samples into a powder for adsorption experiments. Additionally, replicating the high-temperature and high-pressure conditions of shale reservoirs in these experiments presents significant challenges. Therefore, researchers have introduced molecular

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*Corresponding author.
E-mail address: xxz1209@163.com (X. Xia); jiaoxinh1@163.com (X. Jiao); lijunqian@upc.edu.cn (J. Li); wjshen763@imech.ac.cn (W. Shen); xiayx@cup.edu.cn (Y. Xia); hanwang@cup.edu.cn (H. Wang).

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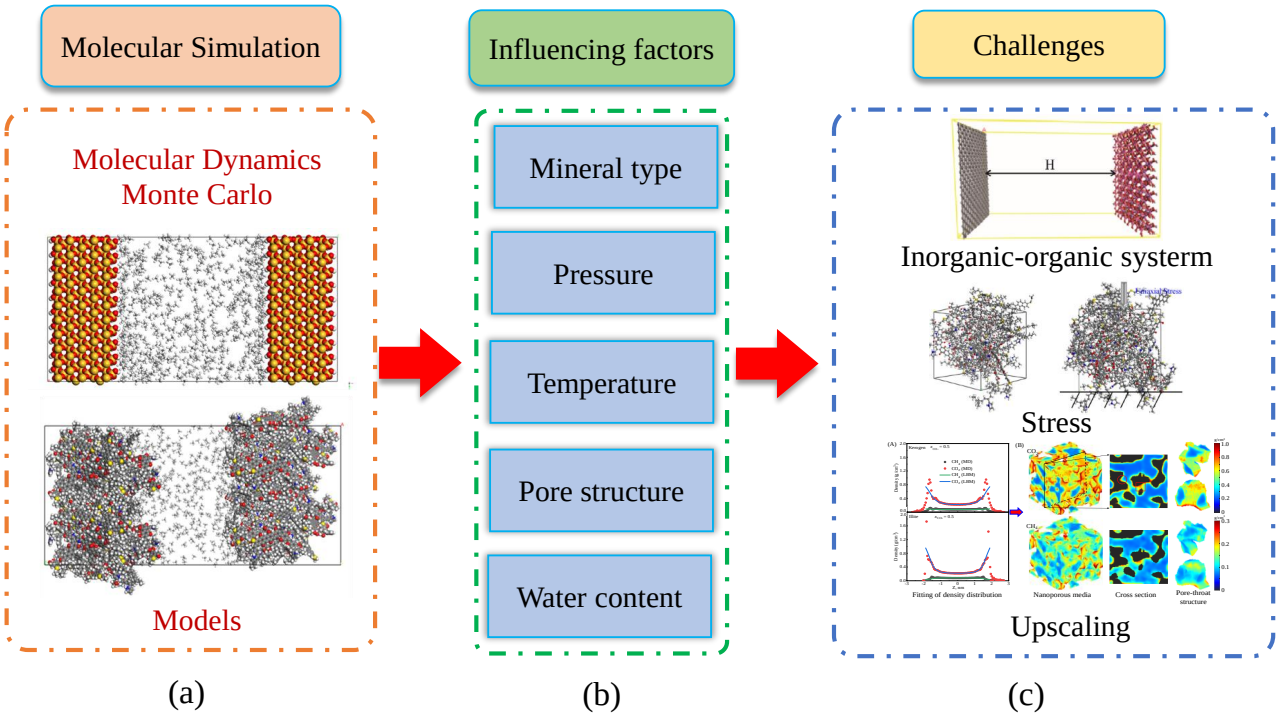

Fig. 1. Gas adsorption characteristic in shale based on molecular simulation. (a) Molecular method, (b) influencing factors for gas adsorption and (c) challenges faced by molecular simulation (Chen et al., 2023; Cui et al., 2024; Wang et al., 2024b).

simulation (MS) to assist in analyzing gas adsorption behaviors (Bekeshov et al., 2023; Cai et al., 2024; Pan et al., 2024). By establishing nanoscale pores models with various shapes and mineral, the MS replicates the micro-scale pore characteristics of shale reservoirs and explores the mechanisms of gas occurrence at the microscopic scale. This work systematically discusses the adsorption mechanisms of gas within shale (Fig. 1). First, the principle of MS is introduced (Fig. 1(a)). Next, the adsorption patterns and mechanisms of gas within the shale pores are described in detail (Fig. 1(b)). Then, the competitive adsorption mechanisms of CO_2 and CH_4 in shale reservoirs and their implications for enhancing CH_4 recovery are presented. Finally, the challenges and suggestions for the development of molecular dynamics simulations are proposed (Fig. 1(c)).

2. Molecular simulation method

Molecular simulation methods, utilizing computational techniques and incorporating principles from physics, chemistry, and statistical mechanics, investigate the dynamic evolution of molecular systems at the microscopic scale for revealing details that are not directly accessible through experiments. Molecular simulations can be typically categorized into two types: molecular dynamics (MD) and Monte Carlo (MC). Based on the principles of classical mechanics, MD simulation takes into account the interatomic forces within the system and uses Newton's equations of motion to calculate the position and velocity of atoms at different time. Therefore, MD method could determine the molecular trajectories and simulate the dynamic behavior of the system. MC simulation doesn't focus on the time evolution of molecules, but instead constructs different molecular states and samples them according to specific probabilistic rules. The MC method is particularly suited for studying thermodynamic equilibrium states.

3. CH_4 adsorption characteristic in shale nanopores

The adsorption of CH_4 in shale nanopores is mainly physical adsorption, and the force between fluid molecules and nanopore wall is van der Waals force. The adsorption capacity between inorganic minerals and gas have been widely carried out by MS, such as quartz, calcite, montmorillonite and kaolinite (Xiong et al., 2016a; Tian et al., 2017). MS is an effective technique to study shale gas adsorption which can reveal the adsorption mechanism by considering the density distribution, adsorption layer, pore size, temperature and pressure. Due to the strong interaction between the gas and the pore surface, the density curve of gas distribution shows a clear peak near the pore surface. For different inorganic mineral types, there are also differences in peak strength. At low pressure, methane molecules tend to preferentially adsorb at the strong adsorption sites on the nanopore walls. With the increasing pressure, the strong adsorption sites are first filled, and then methane adhere to the weak adsorption site. As the pressure continues to increase, the single layer adsorption is completed and then the multilayer adsorption begins. Monolayer/multilayer adsorption of shale nanoporous gas is determined by pore structure, mineral composition, TOC, pressure and temperature (Wu and Chen, 2016; Shen et al., 2021). Methane undergoes filling

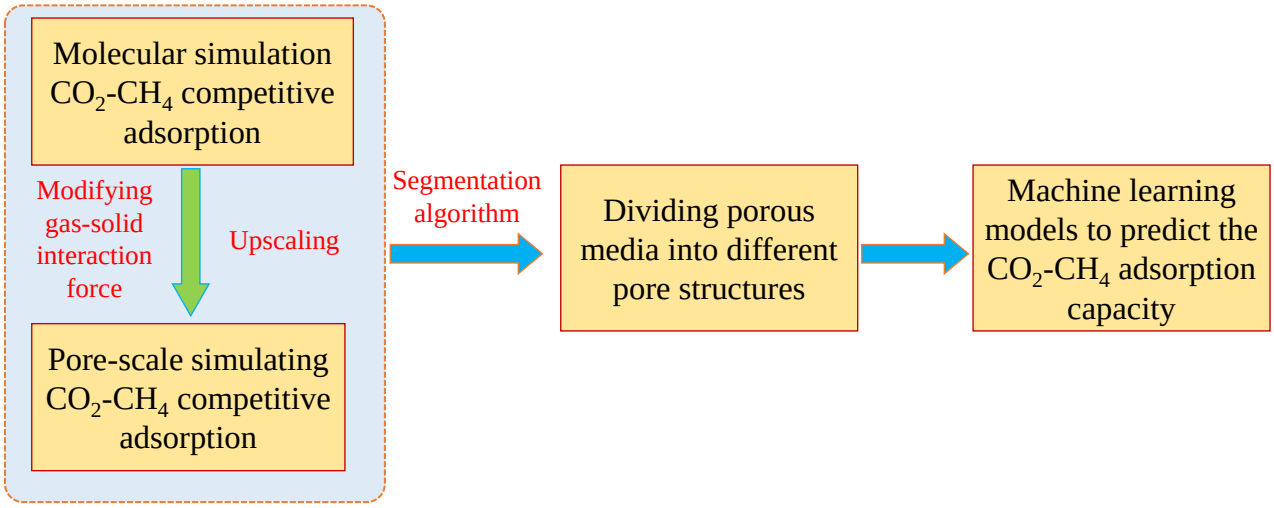

Fig. 2. Workflow of predicting the CO_2-CH_4 competitive adsorption in pore scale.

adsorption in micropores, whereas surface adsorption occurs in mesopores (Zhang et al., 2024). Under the same pressure, the adsorption ratio of methane molecules in the pore decreases with the increase of the pore size (Xiong et al., 2016b). Babaei et al. (2023) used the hybrid grand canonical monte carlo and MD simulation approach to investigate the methane adsorption characteristics in illite under varying temperatures, pressures, and water contents. They found that the presence of water reduced the methane adsorption sites on the illite surface, which leads to the complex adsorption behavior in pore space.

The primary component of organic matter in shale is kerogen, which contains considerable nanopores (2-50 nm). The relative content of inorganic minerals is much higher than that of organic matter in shale, but the adsorption performance of organic matter is much higher than that of inorganic minerals (Guo et al., 2023). Kerogen is a key component in the formation of hydrocarbons and can be divided into four main types based on their origin and chemical composition. The adsorption behavior of methane in different types of kerogens is also different. Araujo et al. (2023) used grand canonical monte carlo simulations to investigate the methane adsorption behavior in different types of kerogens. They found that in type II kerogen, the methane adsorption increased with increasing thermal maturity from IIA to IID under low pressure and 300 K. Currently, the shale models used in MS are still relatively simplistic and fail to fully account for the heterogeneity of real structures. For inorganic minerals, the commonly used idealized slit pore model presents smooth surfaces, whereas the irregularity of actual mineral surfaces should be considered. Furthermore, due to the limitations in the size of kerogen models, simulating methane adsorption with a multiscale pore structure that includes kerogen remains challenging. Additionally, the potential mechanical deformation of the pore structure during the methane adsorption process should be considered in future studies.

4. CO_2 enhanced CH_4 recovery

Carbon capture, utilization, and storage technology aims to reduce carbon emissions in the industry and is regarded as a crucial strategy for achieving global carbon neutrality. Injecting CO_2 into shale gas reservoirs not only facilitates the desorption of CH_4 and increases shale gas production but also enables CO_2 sequestration. The CO_2 adsorption capacity of different shales is 2.68 to 19.41 times larger than that of CH_4 (Klewiah et al., 2020). MS has been widely used to study the competitive adsorption of CO_2/CH_4. Compared with CH_4, CO_2 has a stronger retention capacity in kerogen matrix, and its self-diffusion coefficient is one order of magnitude smaller (Pathak et al., 2018). The adsorption capacity of CO_2 in shale kerogen is greater than that of CH_4 (Wang et al., 2018). For the binary mixture of CO_2 and methane in shale kerogen, the adsorbed hydrocarbons in kerogen can be efficiently extracted, while CO_2 can enter into kerogen and be stored in kerogen (Li et al., 2024). Under reservoir conditions, the interaction between CO_2 and shale is a complex process that involves changes in pore structure, wettability, mineral composition, mechanical properties, and adsorption characteristics (Zhou et al., 2022). Most studies focus on the effect of pure water on the competitive adsorption in shale. However, the formation water in shale reservoirs contains a certain degree of salinity, and the impact of salinity on the competitive adsorption of CO_2/CH_4 is worth considering. Organic matter is dispersed within the inorganic minerals in shale, and therefore, it is necessary to consider the CO_2/CH_4 competitive adsorption within the inorganic-organic system to simulate the real conditions in shale. Considering the complexity of shale structure and properties, elucidating the CO_2/CH_4 competitive adsorption mechanism at the molecular scale is crucial for enhancing CH_4 recovery rates and CO_2 geological storage.

5. Conclusion and prospect

Molecular simulation provides valuable insights into gas adsorption mechanisms and behaviors at the microscopic scale,

their limitations must be acknowledged. Improving force field accuracy, enhancing computational efficiency, and integrating more detailed models are essential for advancing the utility of MS in gas adsorption research. Additionally, close collaboration with adsorption experiments studies is necessary to validate and refine MS methodologies, ensuring their relevance and reliability in real applications.

Since MS can only simulate a limited scale (nanoscale), it is a challenge to use microscopic adsorption phenomena to explain the gas adsorption characteristics at a larger scale. As shown in Fig. 2, Lattice Boltzmann Method (mesoscopic simulation) determines the microscopic force parameters by coupling the gas density distribution curve obtained by MS, and then conducts gas adsorption research at the pore scale (Wang et al., 2024a). By using machine learning methods to train pore-scale gas adsorption data, the artificial intelligence model can predict the adsorption characteristics within any large-scale porous media model (Wang et al., 2024b). This can provide a basis for studying gas adsorption behavior on a large scale.

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Conflict of interest

The authors declare no competing interest.

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