



Molecular simulation of methane adsorption in shale based on grand canonical Monte Carlo method and pore size distribution



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ABSTRACT

To explore the influence of the pore size distribution on the methane adsorption capacity of shale, methane adsorption amount for different pore sizes has been calculated by using the simulation results and pore size distribution data. In the study, excess adsorption per unit area of different pore sizes has been simulated by the grand canonical Monte Carlo (GCMC) method. And the pore size distribution of Longmaxi Formation shale samples was characterized by high pressure mercury injection (HPMI) experiment, low pressure nitrogen adsorption (LP-N₂-GA) experiment, and low pressure CO₂ adsorption (LP-CO₂-GA) experiment. The results indicate that in the range of 0.5–1.5 nm, the excess adsorption per unit area shows a stepped increase with the pore size increasing. When the pore size is larger than 1.5 nm, the excess adsorption per unit area keep unchanged with the increase in pore size. According to the methane adsorption capacity and pore surface area, pores in the shale samples can be divided to three parts: <1 nm, 1–4 nm, >4 nm. Pores in the first part (width <1 nm) have a large specific surface area, but the excess adsorption per unit area is much smaller than other pores. They account for about 65% of the total specific surface area, while accounting for only 48% of the total adsorption amount. Pores in the second part (1–4 nm) have a large specific pore area and large methane adsorption capacity. They provide 30% of the total specific surface area, while providing 44% of the total adsorption amount. Pores in the third part (width >4 nm) contribute only 8% of total adsorption amount as the specific surface area of these pores is notably small.

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1. Introduction

Shale gas has attracted increasing attentions in recent years because of the huge environmental benefits and energy benefits (Curtis, 2002). Shale gas is composed primarily of adsorbed gas and free gas (Pan and Connell, 2015; Curtis, 2002), and the study of adsorbed gas is highly important in the prediction of gas-in-place, which is the key to shale-gas resource assessment (McGlade et al., 2013; Pan and Connell, 2015). The pore system in shale is highly complex as it has a large range of pore sizes (from nanometer to

micrometer) and different pore types. This makes the study of adsorbed gas in shale notably difficult (Loucks et al., 2009; Ross and Marc Bustin, 2009; Tian et al., 2013; Wang et al., 2014).

There are a large number of experimental and theoretical studies in the field of adsorbed gas on shale (Ross and Marc Bustin, 2009; Chareonsuppanimit et al., 2012; Heller and Zoback, 2014; Hu et al., 2015; Li et al., 2014; Ross and Marc Bustin, 2007; Tan et al., 2014; Zhang et al., 2012), and previous studies have indicated that the methane sorption capacity of the shale reservoir has a strong correlation with the total organic carbon (TOC) content (Ross and Marc Bustin, 2009; Zhang et al., 2012). That is because the nanoscale pores that are mainly in the organic matter (OM) of the shale (Loucks et al., 2009), and the total pore surface area of the shale mainly contributed by pores smaller than 8 nm (Cao et al., 2015). Methane adsorption in organic matter of shale has a

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similarity to that in coal. Thus research methods of methane adsorption in coal and active carbon could be applied to the relevant researches in shale gas adsorption (Mosher et al., 2013; Charoensuppanimit et al., 2015).

The heterogeneity of the material composition, pore structure and pore morphology in the shale and coal reservoirs makes it difficult to explain the methane adsorption mechanism only using the experimental methods (Ross and Marc Bustin, 2009). To solve this problem, molecular simulation methods have been introduced, in which the grand canonical Monte Carlo (GCMC) method is one of the most common methods (Do and Do, 2005; Do et al., 2009; Mosher et al., 2013; Peng et al., 2007; Zhang et al., 2014; Ziming Tan, 1990).

GCMC method in sorption is based on the physical interaction of gas molecular with the solid surface. In the Monte Carlo method of sorption, a chain of configurations would be generated. These configurations change randomly, and rules for the acceptance of the random changes are applied that cause the system to approach the statistical mechanical ensemble proposed by J. Willard Gibbs (Steele, 2002). In the GCMC simulation, tens of millions of steps were performed to be equipped. The data of adsorbates in the equilibrium state could be achieved. Details of the GCMC method could be found elsewhere (Frenkel and Smit, 2001). GCMC method is commonly used on the adsorption in the porous material such as active carbon and zeolite (He et al., 2012; Liu et al., 2011; Mahdizadeh and Goharshadi, 2013; Mohammadhosseini et al., 2013; Pizio et al., 2009; Steele, 2002; Suzuki et al., 1996). Previous studies showed the GCMC simulation results had a good agreement with the experiment results (Steele, 2002).

By GCMC simulation, the adsorption behavior of methane molecules in the pores of a specific pore size has been recognized, and the effects of temperature and pressure on the adsorption have been studied (Mosher et al., 2013; Ziming Tan, 1990). It was indicated that pore size would strongly affect the adsorption behavior (Mosher et al., 2013). In adsorption models, the slit pore is commonly used to study the methane adsorption in organic matter (Mosher et al., 2013; Ziming Tan, 1990). Additionally, the effects of oxygen functional groups on methane adsorption have been investigated (Gotzias et al., 2012). In recent studies, the macromolecular models of organic matter (OM) have been applied to the methane adsorption simulation, and the accuracy of the simulation has been improved (Hu et al., 2010; Zhang et al., 2014). Besides Zhang et al. (2014) studied the gas adsorption-induced swelling by using GCMC simulation method.

Simulation methods would help understand methane adsorption characteristics in shale. At present, the molecular simulation research works for the methane adsorption in shale are relatively rare. In this study, methane adsorption amount for different pore sizes of the shale samples has been calculated based on the simulation results and pore size distribution data. GCMC method was used to simulate the methane adsorption capacity per unit area of different pore sizes. Pore size distribution of the Longmaxi formation shale samples was characterized by high pressure mercury injection experiment (HPMI), low pressure nitrogen adsorption experiment (LP-N₂-GA), and low pressure CO₂ adsorption experiment (LP-CO₂-GA). Besides, the simulated adsorption isothermal curve has been compared with the experimental results.

2. Simulation theory and methods

2.1. Pore model

We used the Sorption module in the Materials Studio of Accelrys Company to simulate methane adsorption. The simulation program is performed in Taiyuan University of Technology.

In the adsorption simulation, slit pore is used as a simplified pore model. The slit pore is slitlike geometry with parallel wall of infinite extent separated by a pore width H (Fig. 1), and the walls are assumed to be represented by the basal plane of graphite (Ziming Tan, 1990; Zhou and Wang, 2000). The available pore width H' (Fig. 1) is defined as the width of the space available for the methane molecule. As the carbon atoms would occupy a certain space in the slit pore defined (Fig. 1), the available pore width H' could be calculated by Eq. (1):

$$H' = H - \sigma_c \quad (1)$$

H is the distance between centers of the carbon atoms on the surface; σ_c is the Lennard-Jones diameter of a carbon atom in graphite.

2.2. Simulation theory

In pores, the adsorption is governed by combined gas-surface and gas-gas interactions, which are all vander Waals forces (Mosher et al., 2013). The simulation method used in this study is the grand canonical Monte Carlo method. The force field we used is Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) (Hu et al., 2010). In the COMPASS force field, the vander Waals force is calculated by the Lennard-Jones-9-6 function (Peng et al., 1997) (Eq. (2)).

$$E_{ij} = \sum_{ij} \varepsilon_{ij} \left[2 \left(\frac{r_{ij}^0}{r_{ij}} \right)^9 - 3 \left(\frac{r_{ij}^0}{r_{ij}} \right)^6 \right] \quad (2)$$

where r_{ij}^0 , ε_{ij} are the corresponding vander Waals parameters for the i, j atom pair, and r_{ij} is the distance between atom i and j .

For the r_{ij}^0 and ε_{ij} between different atoms, we can use the method of Eqs. (3) and (4) to calculate on the basis of the parameter r^0 and ε for the same atom.

$$r_{i,j}^0 = \left(\frac{(r_i^0)^6 - (r_j^0)^6}{2} \right)^{1/6} \quad (3)$$

$$\varepsilon_{ij} = 2\sqrt{\varepsilon_i \varepsilon_j} \left(\frac{(r_i^0)^3 \cdot (r_j^0)^3}{(r_i^0)^6 \cdot (r_j^0)^6} \right) \quad (4)$$

It is necessary to define the total gas, bulk phase gas and excess adsorption in this study.

The total gas is defined as all of the methane molecular in the slit pore, containing both the methane in the center of pore (free gas) and the methane adsorbed to the pore surface.

The bulk phase gas is defined as the gas in a given volume at a given temperature and pressure at the absence of pore walls. In a

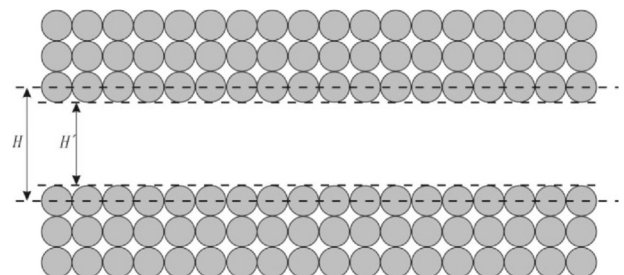


Fig. 1. Pore slit model.

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