Monte Carlo simulation of methane molecule adsorption on coal with adsorption potential

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ABSTRACT

The paper presents a Monte Carlo simulation to study the adsorption characteristics of methane molecule on coal slit pores from different aspects. Firstly, a physical model of adsorption and desorption of methane molecules on micropores was established. Secondly, a grand canonical ensemble was introduced as the Monte Carlo simulation system. Thirdly, based on the model and system, the molecule simulation program was developed with VC++6.0 to simulate the isothermal adsorption relationship between the amount of molecule absorption and the factors affecting it. Lastly, the numerically simulated results were compared with measured results of adsorption coal samples of two different coal mines with a laboratory gas absorption instrument. The results show that the molecule simulations of the adsorption constants, the adsorption quantity, and the isothermal adsorption curve at the same and different coal temperatures were in good agreement with those measured in the experiments, indicating that it is feasible to use the established model and the Monte Carlo molecule simulation to study the adsorption characteristics of methane molecules in coal.

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1. Introduction

Coal, as a natural adsorbent, has great capacity to adsorb methane (CH_4) [1–4]. Generally, there are three ways in which methane exists: the free, adsorbed and deliquescent states. In a macro view, the major factors which affect methane molecule adsorption on it are the adsorption pore volume, adsorption specific surface area, gas pressure, as well as coal's temperature, composition, and moisture, etc. In a micro view, methane adsorption on coal is mainly caused by the interaction between coal and methane molecules. Studies on the characteristics of methane adsorption on coal have been widely performed; however, few ones were reported on molecular simulation of these characteristics [1–17]. Currently, both molecular dynamics method and Monte Carlo method were used for molecular simulation. Monte Carlo method was chosen due to methane's molecular adsorption and desorption characteristics, while the grand canonical ensemble (GCE) Monte Carlo simulation was suitable for methane's status with fixed chemical potential and variable particle number [16–27].

Based on molecular thermodynamics and surface physicochemical theories, the mechanism and characteristics of coal methane molecular desorption and adsorption are simulated and analyzed at the micro level in this paper. It is of great significance for coal gas (CH_4) exploitation and mine gas control [28–30].

2. Potential energy model

Active carbon, similar to coal, also has a large number of pores and crannies in which store up a large amount of adsorbed methane. So, its slit pore model was applied to simulate that methane is adsorbed on coal pores in this study [31–40].

Fig. 1 shows the schematic of the adsorption of fluid molecules on slit pores. Here the fluid or methane molecules are considered to be confined between two infinite walls formed by slit holes or coal walls. H is the distance between two carbon atoms just outside the coal wall.

It was found that the adsorption pore specific surface area accounts for 81.1%–99.5% of the total specific surface area, which is in the main coal methane adsorption space, less than 75 nm microspore is the absorption pore, so the adsorption average pore diameter can be considered the slit pore diameter H [4].

$$H^* = \frac{V_x}{S_x} \tag{1}$$

where H^* is the adsorption average pore diameter; V_x the adsorption pore volume; and S_x the specific surface area.

The intermolecular potential among drifting molecules is represented by a truncated Lenard-Jones potential as follows [16–26]:

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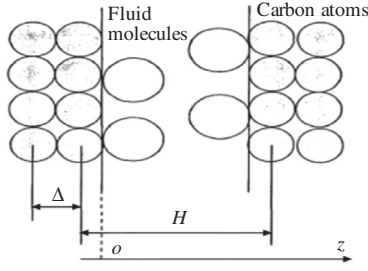 E-mail address: lxj0620@163.com (L. Xijian).

Fig. 1. Schematic of fluid molecule adsorption on slit pores.

$$\phi_{ff} = \begin{cases} \phi_{LJ}(r) - \phi_{LJ}(r_c) & r < r_c \\ 0 & r > r_c \end{cases} \tag{2}$$

where r is the intermolecular radius; r_c the truncated radius that is in the range of 2.5σ–3.5σ, and here r_c is taken as 2.5σ; and σ the methane molecular diameter. And the Lenard-Jones potential is

$$\phi_{LJ}(r) = 4\varepsilon_{ff}\left[\left(\frac{\sigma_{ff}}{r}\right)^{12} - \left(\frac{\sigma_{ff}}{r}\right)^6\right] \tag{3}$$

where ε_{ff} and σ_{ff} are the energy and dimension parameters of fluid molecules, respectively.

The potential between fluid molecules and single slit pore is described as the potential in average field theory [16–26]. Let the direction perpendicular to the slit pore wall be the Z axis, and the potential can be expressed as:

$$\phi_{fw}(z) = 2\pi\rho_w\varepsilon_{fw}\sigma_{fw}^2\Delta\left[0.4\left(\frac{\sigma_{fw}}{z}\right)^{10} - \left(\frac{\sigma_{fw}}{z}\right)^4 - \left(\frac{\sigma_{fw}^4}{3\Delta(0.61\Delta + z)^3}\right)\right] \tag{4}$$

where ρ_w is the number density of the carbon pore wall, here $114\,\text{nm}^{-3}$; $\Delta = 0.335\,\text{nm}$; z the distance between fluid molecules and coal pore wall; and ε_{fw} and σ_{fw} the interaction parameters, respectively. The Lenard-Jones interaction constant among different atoms is usually determined by Eq. (5):

$$\begin{cases} \sigma_{fw} = (\sigma_{ff} + \sigma_{ww})/2 \\ \varepsilon_{fw} = (\varepsilon_{ff} \bullet \varepsilon_{ww})^{1/2} \end{cases} \tag{5}$$

For the given pore diameter H, the total potential of fluid molecules in coal pores is the intermolecular potential plus the potential between fluid and coal pore wall.

$$\phi_T = \phi_{ff} + \phi_{fw}(z) + \phi_{fw}(H - z) \tag{6}$$

where ϕ_T is the total potential of fluid molecules in coal pores.

3. GCE simulation process

For a grand canonical ensemble (GCE) denoted by (μVT), its chemical potential (μ), volume (V), and temperature (T) keep constant in simulation. As the slit aperture H is fixed, the periodic boundary conditions are used in the x-and y-axis directions.

The simulation is a stochastic process determined by the ensemble's constants μ, V, and T, namely, the fixed chemical potential (μ), volume (V) and temperature (T) decide the maximum molecular number in each primitive cell, and hence determine the maximum adsorption capacity in the cell. Every step of the circle contains the following three tests [18]: (1) to insert a molecule into the simulation box; (2) to delete a molecule from the simulation box; (3) to move a molecule from one position to another in the simulation box. In molecule selection, the equal weight algorithm is adopted to make the possibility of three tests, insert, delete,
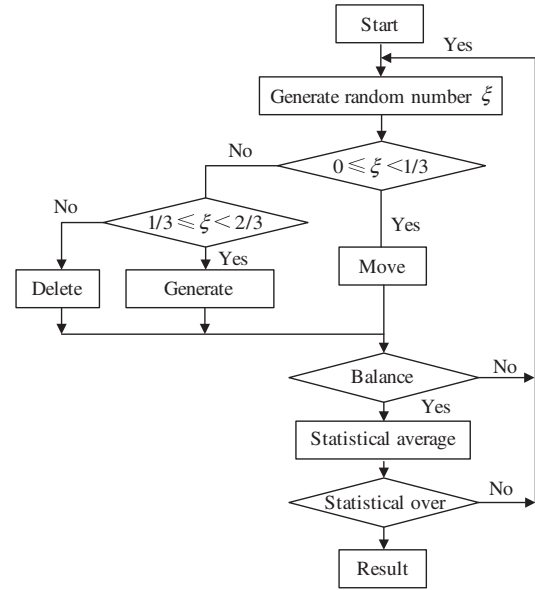

Fig. 2. Flow chart of GCE MC simulation.

and move the molecule equal 1/3 [15]. During simulation, each variable is converted to the dimensionless one:

$$\begin{aligned} \mu^* &= \mu/\varepsilon_{ff} \\ V^* &= V/\sigma_{ff}^3 \\ T^* &= k_B T/\varepsilon_{ff} \\ P^* &= P\sigma_{ff}^3/\varepsilon_{ff} \\ H^* &= H/\sigma_{ff} \\ \rho^* &= \rho\sigma_{ff}^3 \end{aligned} \tag{7}$$

where ρ is the number density; H the slit wide; P the pressure; and $*$ the contrast quantity of its corresponding physic quantity.

During simulation, fluid molecules adsorbed by each slit aperture, under certain temperature and pressure, often experience multiple configurations before reaching their equilibrium. General configurations of equilibrium are selected to be 10^5–10^{-7}. Those seen as pre-equilibrium configurations are rejected; while those as post-equilibrium ones are averaged. In this simulation, the total 2×10^5 steps are set, among which the first 1×10^5 steps are used to simulate equilibrium, while the remaining 1×10^5 steps are used to conduct adsorption quantity statistics. In order to make sure that the program can be operated in a personal computer, the number of simulations must be limited. The times of modeling MC configurations per second are 50 in this study, so the modeling time for 200,000 simulations is $t = 2 \times 10^5/(50 \times 3600) \approx 1.11\,\text{h}$, there are 7 equilibrium points, so the total simulation time is 7.77 h. Fig. 2 shows the flow chart of the simulation.

4. Discussion on influencing factors of adsorption

In a macro view, there are many influential factors of coal on the adsorption and desorption of methane gas, such as the gas pressure in coal seam, coal temperature, the proximate analysis of coal (including moisture content and ash content), coal porosity, specific surface area, different types of coal (metamorphic grade), etc. The key of the simulation is to connect these macroscopic influencing factors with the microcosmic molecules in simulation.

From the definition of adsorption quantity $\Gamma = \rho_T/(N_A \cdot \sigma_{ff}^3 \cdot \rho_c)$ (mmol/g), it is clear that the adsorption quantity of a unit mass of coal, as the macroscopic physic quantity, is closely related to the