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Investigation of methane adsorption and its effect on gas transport in shale matrix through microscale and mesoscale simulations

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ABSTRACT

Methane adsorption and its effect on fluid flow in shale matrix are investigated through multi-scale simulation scheme by using molecular dynamics (MD) and lattice Boltzmann (LB) methods. Equilibrium MD simulations are conducted to study methane adsorption on the organic and inorganic walls of nanopores in shale matrix with different pore sizes and pressures. Density and pressure distributions within the adsorbed layer and the free gas region are discussed. The illumination of the MD results on larger scale LB simulations is presented. Pressure-dependent thickness of adsorbed layer should be adopted and the transport of adsorbed layer should be properly considered in LB simulations. LB simulations, which are based on a generalized Navier–Stokes equation for flow through low-permeability porous media with slippage, are conducted by taking into consideration the effects of adsorbed layer. It is found that competitive effects of slippage and adsorbed layer exist on the permeability of shale matrix, leading to different changing trends of the apparent permeability.

1. Introduction

Shale gas refers to natural gas trapped in fine grained sedimentary rocks called mudstone or shale that are rich of oil/gas. Over the past decades, advanced techniques such as horizontal drilling and multi-stage hydraulic fracturing have greatly promoted the exploitation of shale gas from shale matrix with low permeability. With hydraulic fracturing, it is now generally agreed that the fabric of shale systems comprises primarily organic matter, inorganic matter, natural fractures and hydraulic fractures [1,2]. Such structure characteristics lead to multiscale pore systems in shale gas reservoir and different transport mechanisms at different scales including viscous flow, slip flow, Knudsen diffusion, and adsorption/desorption [1].

Advanced direct measurement techniques, such as scanning electron microscopy (SEM) combined with focused ion beam (FIB) milling, allow visualization of the nanoscale structures of shales on high quality flat surfaces, and provide new insights in the micro/nano-scale structures of shale matrix [1,2]. Interparticle pores, intraparticle pores and organic matter pores have been observed in shale matrix, with diameter from a few nanometers to a few micrometers [2]. The organic matter, widely known as kerogen, usually presents as discrete grains randomly imbedded within the inorganic matrix. The weight percentage of the organic matter in shale matrix is called total organic content (TOC), which is an important indicator of shale gas reserve. Shale gas is stored in shale matrix as free gas in the void space as well as adsorbed gas on the solid surface of pores. It is found that the amount of both adsorbed gas and free gas increases as the TOC increases. In some shales, most of the porosity can be contributed by nanosize pores in the organic matter. These nanosize pores have significant internal surface areas, resulting in substantial adsorption of high-density shale gas on the pore walls [1,2]. It was estimated that between 20% and 85% of natural gas in shale gas reservoir can be stored in the form of adsorbed gas [3]. Adsorption is usually described through adsorption isotherms. Langmuir isotherm is widely adopted to fit the experimental data of adsorption in shale samples. It has been reported that Langmuir isotherm can well describe methane adsorption isotherms in shale samples from different plays in several experimental studies [4,5]. The adsorption isotherm is influenced by several factors including pore size distribution, solid constituents and gas components [4,5].

Permeability is a key variable to describe the transport capacity of a porous medium. Merely structure-dependent permeability is called intrinsic permeability where there is no slippage. For shale matrix with typical pore size of nanometers to microns, *Kn* number, defined as the ratio of mean free path to pore size, is relatively

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Nomenclature

$\mathbf{a}$	acceleration
b	slip coefficient
E	potential energy
$\mathbf{F}$	force
f_c	correction factor
$\mathbf{G}$	external force
J	viscosity ratio
k_a	apparent permeability
k_d	intrinsic permeability
Kn	Knudsen number
m	mass
M	molecular weight
N_A	Avogadro constant
P	pressure
q	partial charge
R	gas constant
$\mathbf{r}$	position vector
r	pore radius of the porous medium
S	stress tensor
t	time
T	temperature
$\mathbf{u}$	superficial velocity
V	volume
α	rarefaction coefficient
ρ	density
λ	mean free path
υ	viscosity
υ_e	effective viscosity
σ	distance parameters of LJ potential
ε	energy parameters of LJ potential or porosity
ε_0	dielectric permittivity of vacuum
δ	thickness of the adsorption layer
τ	relaxation time

high. Thus, gas flow can be beyond the continuous flow regime, leading to slip flow or even transition flow [1]. Due to slippage, the measured gas permeability (apparent permeability) is higher than that of the liquid (intrinsic permeability, without slippage), and the difference becomes increasingly important as Kn increases [6]. Gas slippage in porous media and its effects on permeability was first studied by Klinkenberg [6], who proposed a linear correlation between apparent permeability and the reciprocal of the pressure [6]. Karniadakis and Beskok [7] developed a second-order correlation based on fluid flow in micro-tubes, which was shown to be valid over the flow regimes. Recently, the authors' group developed a pore-scale LB model based on Dusty gas model to predict the apparent permeability of complex porous structures of shale. It was found that the correlation of Karniadakis and Beskok agrees the best with the pore-scale simulation results [8,9].

Several permeability models have been developed to incorporate slip effects in continuum models [10–13], and one can refer to an excellent review very recently by Singh et al. [14]. Note that most of the models are focused on the effects of slippage, while there are few studies considering the effects of adsorption [13,14]. Singh et al. proposed a permeability model where not only slippage but also adsorption are considered [13]. Shale permeability is affected by surface adsorption/desorption processes which change the volume of the void space and influence the local gas flow near the surface [13–17]. Effects of the adsorption on the fluid flow can be neglected for conventional rocks with relatively large pore size. However, it should be considered in shale matrix where nanosize pores are dominant [8,9,15–24]. Adsorption will affect the fluid flow in a nanosize pore through two mechanisms [19]. On one hand, in a nanosize pore gas slippage on the solid surface occurs. The adsorbed layer, sandwiched between the walls and the free gas region in the middle of the pores, will change the interactions between gas molecules and the wall, and thus greatly affects the slippage [16,19]. On the other hand, the adsorbed methane occupies a significant part of the void space of a nanopore [13,18]. For example, 29.4% of the void space of a cylinder with a radius of 5 nm is occupied by the adsorbed layer with a thickness of 0.7 nm based on the molecular dynamics simulation (MDS) results in Ref. [18].

In this work, multiscale simulations are performed to investigate methane adsorption and its effects on fluid flow in shale matrix by using molecular dynamics (MD) method and lattice Boltzmann (LB) method. MD simulations are conducted to investigate the methane adsorption in nanopores of shale matrix with different solid surfaces and under different pressures, the results of which are then upscaled into larger scale LB studies. The remaining part of the present study is as follows. In Section 2, equilibrium MD simulations are performed to study the adsorption phenomenon of methane on the walls of the nanosize pores in shale matrix. Effects of the pore size, pressure and solid wall characteristics are explored in detail. In Section 3, the illumination of the MD simulation results on the investigation at a larger scale is discussed, and upscaling the MD results to the LB simulations is presented. Consequently in Section 4, a generalized LB model for fluid flow through tight porous media with slippage, which is developed in our previous work [24], is further improved to incorporate the effects of the adsorbed layer. The improved LB model is then employed to investigate the competitive effects of gas slippage and adsorption layer on permeability of shale matrix. Finally, some conclusions are drawn in Section 5.

2. Molecular dynamics simulation of methane adsorption

2.1. Brief introduction of molecular dynamics simulation

MD simulations provide a methodology for detailed microscopic modeling on the molecular scale. In a MD simulation, each atom or molecule of the matter studied is treated as a point mass and Newton's second law equation is integrated to compute their motion

$$\vec{F} = m\vec{a} = m\frac{d^2\vec{r}}{dt^2} \tag{1}$$

where m is the mass of the site, $\vec{a}$ is the acceleration, $\vec{r}$ is the position vector and t is the time. The force $\vec{F}$ is derived from the potential energy

$$\vec{F} = -\nabla E \tag{2}$$

The total potential energy E contains two parts: intermolecular term and intramolecular term. The intramolecular term, E_{bond}, represents the interactions between the bonded atoms within the same molecule including the bond stretch, angle bend and torsion energy terms; whereas the intermolecular term, E_{nonbond}, is used to describe the interactions between atoms from different