Pressure-dependent transport characteristic of methane gas in slit nanopores

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ABSTRACT

The transport mechanism of methane gas through the nanopores is a fundamental concern in the shale gas extraction. Shale gas is mainly stored in nanopores of shale formations over a wide range of pressure which is a fundamental thermodynamic variable dominating the properties of substances, rendering that it is important to understand the pressure-dependent transport characteristic of gas molecules in nanopores. Toward this end, we performed molecular dynamics (MD) simulations to investigate the transport characteristic and its mechanism of methane gas in slit nanopores under different pressures. A modified bin method considering local gas density was proposed to reveal the mass velocity profile of methane gas in nanopores. Combining the trajectories of representative molecules, we found that the underlying mechanism of methane gas transport characteristic behaves as the competition between gas intermolecular collisions and gas-wall interactions. The transport characteristic of methane gas in slit nanopores is dependent on the pressure. Meanwhile, the pore width can significantly influence the mass flux contributions of different transport mechanisms. Under the high pressure, viscous flow is the primary transport mechanism due to the frequent gas intermolecular collisions. Under lower pressure and in larger nanopores, Knudsen diffusion becomes the dominating transport mechanism due to the enhancement of gas-wall interactions (collisions). Narrower nanopores can significantly increase the mass flux contribution of surface diffusion due to the increased proportion of absorbed gas molecules. In particular, we proposed a theoretical model coupling multiple transport mechanisms, which can accurately predict the apparent permeability of methane gas in slit nanopores. Under lower pressure and in narrower nanopores, the enhancement of surface diffusion and Knudsen diffusion can increase the apparent permeability of methane gas by as much as 50 times or more, demonstrating the sensitivity of pressure and pore size for methane gas transport.

1. Introduction

The transport mechanism of gas molecules through nanopores is a fundamental concern in many fields, such as nanofluidics, chemistry engineering, and energy engineering. In unconventional energy, because of the large amounts of reserves and wide distribution, shale gas draws more and more attentions and significantly influences the pattern of the global energy industry in past decades, leading to the worldwide "shale revolution" [1]. Shale formations, characterized by abundant nanopores, include organic kerogen pores and inorganic pores. Shale gas (methane) is mainly stored as adsorbed gas in organic nanopores under the supercritical temperature (above 273.15 K) over a wide range of pressure [2].

With the help of hydraulic fracturing techniques and the gas injection displacement [3], methane gas transports through these nanopores, eventually converging into the wellbore. Under such extreme surrounding conditions, the transport characteristic and its mechanisms of methane gas in nanopores need to be understand in detail.

The transport characteristic of gas is significant different under different pressure environments, which depends on the competition between the gas-wall interaction and the gas intermolecular interaction [4]. In the high pressure regime, gas transport is dominated by the gas intermolecular interactions due to a large number of gas molecules confined between solid walls, in which the viscous flow is the main transport mechanism. With pressure decreasing, the contribution of interaction between gas molecules and solid walls increases, resulting in that gas diffusion plays an important role in the complicated gas transport with the coexis-

tence of multiple mechanisms. Thus far, various theoretical models have been proposed to predict the transport characteristic of gas in nanopores. Research on gas flow in confined spaces has a long history. Dating back to the works of Maxwell [5] and Knudsen [6], they presented the phenomenon of gas slippage near a solid wall in the context of the gas-solid collision. After that, a series of models were proposed to consider this gas slippage (diffusion) phenomenon. Klinkenberg [7] figured out the diffusion effect and introduced the slippage factor (b_k) to explain that the actual gas transport capacity is higher than that predicted by Darcy's equation. Ertekin et al. [8] introduced the dynamic slippage into the gas apparent permeability modeled by Darcy's law. Beskok and Karniadakis [9] proposed a second-order gas permeability calculation related to the Knudsen number, which is suitable for all flow regimes. Javadpour [10] assumed that the total mass flux of shale gas through a nanoscale slit pore is the combined result of Knudsen diffusion and pressure force. In recent years, to consider the transport of adsorbed gas in nanopores of shale matrix, various models were proposed based on different assumptions. Some models [11,12] treated the adsorbed gas as immobile, however, a more general treatment [13–15] was that the adsorbed gas can be driven by the density or concentration gradient and described using surface diffusion, although differences exist in the theory and approach of describing the surface diffusion. For example, there are two distinct surface diffusion theories: hopping model for single layer adsorption assuming that the adsorbed gas hops from one adsorption site to a neighboring adsorption site on the surface [16], and hydrodynamic model for multi-layer adsorption based on the assumption that the surface diffusion is caused by viscous flow in surface liquid film [17].

In order to obtain the detailed transport characteristic (e.g., transport velocity distribution and particle behavior), some particle-based numerical simulation methods, such as direct simulation Monte Carol (DSMC), lattice Boltzmann method (LBM), and molecular dynamics (MD) simulation, have been proved to be the appropriate and powerful approaches. DSMC method has been widely employed in the investigations of high speed rarefied gas in outer space. But the flow speed of shale gas in nanopores is extremely slow, which will result in a high nose in DSMC simulations. LBM is virtually equivalent to Navier-Stokes (N-S) equation at macroscale [18]. By introducing microscale boundary conditions, LBM can be used to solve the microscale flow [19]. Nevertheless, LBM is an approximate algorithm at microscale, in which the determination of microscale boundary conditions depends on molecular simulations [20]. In some cases, nanoscale mechanism of gas transport might not be easily figured out through LBM [18]. MD simulation is based on the Newton mechanics, which can accurately describe the mechanical and dynamical behavior of each particle. MD simulations have been extensively carried out to investigate the transport characteristic of gas in nanopores, especially the hydrocarbon transport in different nanopores (organic and inorganic). The organic matter is known as kerogen, which is the source and reservoir of hydrocarbons. Falk et al. [21] simulated hydrocarbon transport in kerogen nanoporous media based on a realistic molecular kerogen model [22], suggesting that the Darcy's law fails to predict the transport in shale matrix (kerogen). Collell et al. [23] performed MD simulations of hydrocarbons permeating through a molecular model representing oil-prone type II kerogen and demonstrated that the permeation mechanisms through this type of material is purely diffusive. Differing from simulating the hydrocarbon transport in complete kerogen directly, some literatures focused on single organic nanochannel or nanocapillary [24,25]. A pore-width dependent flow characteristic of methane in carbon nanochannel were revealed by Chen et al. [25]. In relatively large nanochannels (6–10 nm), the velocity profile is parabolic with typical slip boundaries, whereas, in smaller nanochannels (<2 nm), the velocity profile tends to be uniform (plug flow) in the pore central region and exhibits a linear increase towards to the walls. The constituents of inorganic matter includes carbonates, quartz and clays. The transport and adsorption behaviors of methane confined in graphene, quartz and calcite nanopores were compared by Wang et al. [26], respectively, suggesting that the transport behaviors of methane were influenced by attractive potential and surface roughness of substance in different nanopores. Wu et al. [27] employed MD simulations to investigate the shale gas flow in nanoscale channels modeled by the illite and graphene, indicating that the velocity oscillation exists along the cross section of the nano-channel.

Although some qualitative and suggestive conclusions on shale gas transport have been obtained from previous studies (gas transport model and MD simulations) [5–17,21–27], to our knowledge, a comprehensive study on the combination of MD simulations and gas transport mechanism for methane gas transport in slit nanopores is still lacking. Most recently, Akkutlu and his co-workers [24,28] performed MD simulations to investigate the gas transport mechanism in kerogen at multiscale. It was found that the adsorbed methane molecules are mobile and contribute a significant portion to the total mass flux in nanocapillaries with the diameter less than 10 nm. Based on the results from MD simulations, they proposed a modified Hagen-Poiseuille equation combining a simple network of interconnected nanocapillaries representing kerogen to describe the gas transport in kerogen at multiscale.

In this study, as an effort to investigate the pressure-dependent transport characteristic of methane gas in slit nanopores, we carried out extensive MD simulations and combined the theoretical model coupling multiple transport mechanisms to predict the apparent permeability accurately. Firstly, the simulated isotherm density profile of methane gas was compared with an experimental one to verify the accuracy of our MD simulations. Then, considering different pressure conditions, the mass transport and density profiles of methane gas in nanopores, as well as the trajectories of representative particles, were discussed to understand the transport characteristic with the corresponding mechanism. For methane gas transport in nanopores with different channel widths, the mass flux contributions of different mechanisms, including viscous flow, Knudsen diffusion, and surface diffusion, were compared and quantitatively analyzed. In particular, based on the results of our MD simulations, we proposed a theoretical model coupling multiple transport mechanisms, which can accurately predict the apparent permeability of methane gas transport in nanopores.

2. Model and methods

The constituents of shale matrix include organic matter (kerogen) and inorganic substances. The structure of kerogen is very complex and the simplified model lacks the essential elements (e.g., hydrogen, oxygen and nitrogen) [29]. Here, based on our literature review, we employ the inorganic minerals as the substance of nanopores to investigate the methane gas transport. As shown in Fig. S1, it is clear that the calcite is the main composition among these inorganic substances. As a particularly amazing mineral, carbonate rocks constituted of calcite serve as the host for more than 60% of the world petroleum reserves and most aquifers [26]. An abundance of nanoscale slit pores is found in the samples of shale formations [30], thus, our simulation system [Fig. 1(a)] of methane within a nanometer-sized slit pore is ideally modeled as two calcite slabs (10 Å × 200 Å × 40 Å) and a certain amount of methane molecules. Fig. 1(b–d) and (e) illustrate the calcite lattice and the methane molecule, respectively. The exposed calcite surfaces were