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Molecular simulation of natural gas transport and storage in shale rocks with heterogeneous nano-pore structures

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ABSTRACT

Although natural gas is widely produced from shale, the mechanisms of natural gas transport in shale matrices remain poorly understood due to the complex chemical compounds of the matrices and the nanoscale pore size distribution. Using molecular simulations, we investigate natural gas transport and storage in nano-pore networks. Carbon-based 3-D pore networks are generated from 2-D scanning electron microscopy (SEM) images of a shale rock using the Markov Chain Monte Carlo simulation method. We employ a grand canonical Monte Carlo (GCMC) simulation to calculate adsorption isotherms of natural gas in carbon-based 3-D pore networks, which can be fit by a Langmuir isotherm model. To investigate gas transport in the same structures, we insert an external driving force into non-equilibrium molecular dynamics (NEMD) simulations and find that Knudsen diffusion is the dominant transport mechanism in the pore networks. Although porosity and pore connectivity affect the natural gas diffusion in the pore networks, we typically observe a linear relationship between average molar flow rate through a cross-sectional area and the external driving force.

1. Introduction

As conventional hydrocarbon resources are rapidly being depleted, shale gas has become increasingly important as a strategic energy supply for US energy independence and security (Ambrose et al., 2010; Civan, 2010; Collell et al., 2014; Darabi et al., 2012; Fathi et al., 2013; Javadpour, 2009; Mosher et al., 2013; Swami and Settari, 2012; Yiannourakou et al., 2013; Yuan et al., 2014). Shale gas is natural gas trapped in fine-grained sedimentary rock formations, which are usually characterized as anisotropic and heterogeneous porous media with very small pores. Consequently, the permeability of shale formations is extremely low and is typically of the order of magnitude of one hundred nanodarcies (Sakhaee-Pour and Bryant, 2012). The ultra-low permeability of shale formations presents a significant challenge in the production of shale gas in an economically viable fashion. Although horizontal drilling and multi-stage hydraulic fracturing stimulation make commercial shale gas production possible, the underlying mechanisms of gas transport in these highly confined media remain unclear and need to be fully understood for optimal production performance and reserve estimation (Collell et al., 2014). Several limitations about the current shale gas reservoir simulator and further research and development efforts have been reviewed in Andrade's work (Andrade et al., 2011).

There are two main challenges in identifying the underlying mechanisms of gas transport in shale reservoirs. First, petrophysical studies indicate that more than 60% of the pores in shale formations are micropores with a characteristic length scale of less than 30 nm (Darabi et al., 2012; Mosher et al., 2013). At this scale, the mean free path λ of fluid molecules becomes comparable to the characteristic length L of the flow channel. As one consequence, Darcy's equation ($v = -(k/\mu)\nabla P$, where v is the mean fluid velocity, ∇P is the gradient of the pressure, k is the permeability, and μ is the viscosity) cannot accurately describe transport at this scale because the continuum theory breaks down when the Knudsen number $Kn = \lambda/L$ exceeds 0.1 (Roy et al., 2003). Therefore, accurate descriptions of gas transport through nanoscale pores require experimental and/or numerical studies at these length scales. Second, besides the nanoscale pore size, shale matrices consist of various types of kerogen, clays, and other minerals that exhibit differences in porosity, tortuosity, and pore size distribution. Describing the intermolecular interaction between gas and boundary molecules in these heterogeneous pores, which heavily influences gas storage and transport behaviors, remains a significant challenge both experimentally and computationally. Methods to generate understanding of gas flow and storage mechanisms at the molecular level must address these challenges and are required to enhance shale gas production performance.

Towards this end, several recent studies have investigated gas storage and transport mechanisms in micropores using simple

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geometries and microporous model materials. Experimental measurements of high-pressure methane adsorption isotherms in porous media have been widely reported (Heller and Zoback, 2014; Ji et al., 2012; Rexer et al., 2014; Zhang et al., 2012). Numerically, sophisticated molecule structures (Katti et al., 2014; Zheng et al., 2014) and simple organic carbon molecule structures (Ambrose et al., 2010; Mosher et al., 2013) have been developed to replace kerogen molecules to investigate gas adsorption. Both experiments and simulations show that the adsorption obeys the Langmuir isotherm and that the adsorption capacity is associated with total organic carbon (TOC), organic matter type, thermal maturity, and clay minerals content (Heller and Zoback, 2014; Rexer et al., 2014; Zhang et al., 2012).

A variety of studies show that transport in nanoporous media exhibits a variety of non-continuum features. Experiments demonstrate that fluid flow in carbon nanotubes differs from that predicted based on continuum hydrodynamics models, such as the Hagen–Poiseuille equation (Majumder et al., 2005). Similarly, the experimentally measured flow rate of water and air through nanoscale pores is measured to be several orders of magnitude faster than that predicted using continuum theory (Holt et al., 2006). Furthermore, slip boundary conditions in nanotube and planar flow have been widely reported (Chen et al., 2008; Kannam et al., 2011; Thomas and McGaughey, 2009). Finally, Knudsen diffusion and free molecular diffusion dominate flow mechanisms in nanochannels and nanotubes (Roy et al., 2003). As a complement to experimental studies, molecular simulation techniques, including dual control volume grand canonical molecular dynamics (DCV-GCMD) simulations (Boţan et al., 2013) and non-equilibrium molecular dynamics (NEMD) simulations (Wang et al., 2013, 2012), are widely employed to simulate permeation experiments. As one example, a computational study of gas transport in models of graphite-like 3-D porous materials shows that the porosity (ϕ), the ratio of the pore volume to the total volume of the rock, strongly affects permeability, with the lack of pore connectivity hindering gas transport at porosities of less than 0.2 (Firouzi and Wilcox, 2012).

Although these and other studies of simple geometries and microporous materials have provided fundamental insights into the mechanisms of fluid storage and transport in microscopic systems, they do not adequately capture the complexity or heterogeneity of shale gas matrices. These simplified models recreate neither the complex chemical composition (kerogen, clay, quartz, etc.) nor the complex pore connectivity found in shale. To generate more realistic models of natural shale, digital rock reconstruction (Wang and Pan, 2008), widely used in conventional reservoir modeling, can be used to recreate the detailed pore structure.

Generally, pore reconstruction techniques are necessary when 3D images with the required resolution are not easily acquired. Commonly used reconstruction methods can be divided into two classes. The first is the apparent-similarity method, which neglects the details of particle geometry and instead considers macroscopic properties (Li et al., 2005; Wang and Pan, 2008; Yang et al., 1996). An alternative method, digital rock reconstruction, focuses on the geometric details and aims to build more realistic structures by exploiting improvements in microscope instrumentation and in image mapping technology. In this technique, rock sections obtained by scanning microscopy methods, such as computed tomography (CT) or scanning electron microscopy (SEM), are digitally reconstructed. The detailed pore structure (porosity and connectivity) is recreated in the computational model. One algorithm commonly used in petroleum engineering and earth science research is the Markov Chain Monte Carlo (Wu et al., 2006, 2004) (MCMC) simulation, which recreates the 3-D microstructure based on thin 2-D images of rock samples obtained using SEM. Continuum fluid transport mechanisms have been widely studied in digital rock reconstructions (Boek and Venturoli, 2010; Manwart et al., 2002). By contrast, only few studies have investigated transport mechanisms in the non-continuum flow regime in digital rock reconstructions, despite the increased complexity and verisimilitude of these models (Boţan et al., 2015). Studies of non-continuum transport in digital rock reconstructions are therefore expected to generate new insight into the transport mechanisms operating in nanoporous natural shale.

In this paper, we combine digital rock reconstruction and molecular simulation to investigate gas transport and storage and fluid–boundary molecular interactions in models of nanoporous shale matrices. In Section 2, we describe digital rock sample and simulation methods. We use an established method for 3-D pore network reconstruction, the Markov Chain Monte Carlo (MCMC) algorithm, to generate digital rock samples from 2-D SEM images of shale samples taken from the low Silurian Marine formation. To elucidate storage mechanisms, we use grand canonical Monte Carlo (GCMC) simulations to predict adsorption isotherms in carbon-based nanopore networks. To study gas transport, we perform NEMD simulations by inserting different external body force values in the system and subsequently correlate the average molar flow rate through the cross-sectional area to the external driving force. In Section 3, we discuss results for the adsorption isotherms and for gas transport. We find that the adsorption data can be fit by the Langmuir isotherm model and that Knudsen diffusion is the dominant transport mechanism. Conclusions and future work are discussed in Section 4.

2. Simulation methods

2.1. Pore structure construction method: MCMC algorithm

The MCMC method is used to model the spatially anisotropic and heterogeneous structure of multi-phase media (matrix, pore, etc.) based on 2-D thin section information (Wu et al., 2004). As shown in Fig. 1, the state of each particular voxel (x_{ijk}) is assigned a value of 0 or 1, corresponding to pore or rock, respectively, and is

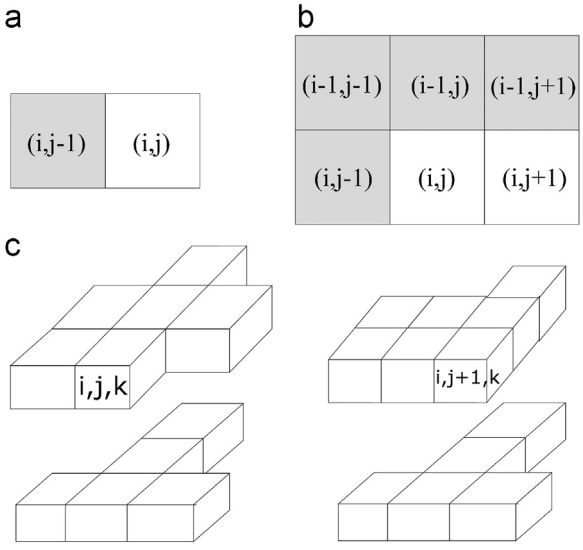

Fig. 1. Schematic illustration of the MCMC neighborhoods algorithm. (a) The 1-D 2-neighbor condition for updating voxel (i, j) based on (i, $j-1$). (b) The 2-D 5- and 6- neighbor conditions for updating two voxels (i, j) and (i, $j+1$) simultaneously. (c) The 3-D 11- and 12- neighbor conditions for updating two voxels (i, j, k) and (i, $j+1$, k) simultaneously. From the initial point ($i=1$, $j=1$, $k=1$), the voxels in the first row are conditionally determined by the 1-D neighbors. Next, voxels in the same plane (i, j, $k=1$) are conditionally determined by the 2-D neighbors, and the remaining voxels are determined by the 3-D neighbors.