Microporous and Mesoporous Materials 249 (2017) 88–96

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

A non-equilibrium molecular dynamics study of methane transport in clay nano-pores

Shuai He [a], Jeremy C. Palmer [b, **], Guan Qin [a, *]

[a] Department of Petroleum Engineering, University of Houston, Houston, TX 77204, USA
[b] Department of Chemical and Biomolecular Engineering, University of Houston, Houston, TX 77204, USA

ARTICLE INFO

Article history:
Received 5 February 2017
Received in revised form
18 April 2017
Accepted 20 April 2017
Available online 22 April 2017

Keywords:
Non-equilibrium molecular dynamics
Transport diffusivity
Temperature control
Knudsen diffusion

ABSTRACT

Accurate characterization of shale reservoir properties is vitally important for reliable gas production forecasting and reserve estimation. In this work, we use boundary-driven non-equilibrium molecular dynamics (BD-NEMD) to investigate methane transport in porous clays, which are one of the major mineral components of shale. One of the critical issues in BD-NEMD simulations is robust temperature control schemes to maintain isothermal conditions when the external force is applied to drive fluid flow. To this end, we scrutinize the performance of six temperature control schemes for BD-NEMD. We identify a number of effective temperature control schemes, and we show that careful algorithm selection can considerably reduce the number of simulations required to estimate transport diffusion coefficients. Using a robust temperature control scheme identified in our study, we examine the validity of the Knudsen model for predicting methane diffusivities in clay nano-pores. Although the Knudsen model is one of the most widely used theoretical approaches for predicting reservoir properties, we find that it fails to accurately predict methane transport diffusivities in small clay nano-pores. Our findings therefore suggest that reservoir models based on Knudsen theory may result in significant over- or under-prediction of gas production, depending on reservoir conditions. These findings are consistent with other studies, which posit that the Knudsen diffusion model breaks down in nano-confined systems because it neglects to account for the effects of adsorption on gas transport.

1. Introduction

Shale gas has become an important energy supply for US energy independence and security [1]. One of the distinctive characteristics of shale rock formations is that typically more than 60% of their porosity can be attributed to small nano-pores less than 30 nm in diameter [1–10]. As a result, these formations have extremely low permeability, typically of the order of magnitude of one hundred nanodarcies [11]. This low permeability poses a significant challenge in extracting shale gas in an economically viable fashion. Although new drilling and fracturing technologies have made commercial shale gas production possible, improved methods for characterizing reservoir rock and confined fluid properties are needed for production forecasting and reliable reserve estimation for shale gas [12].

Experimental and numerical studies have demonstrated that natural gas adsorption in the nano-porous features of shale rocks is well-described by Langmuir-type models and that the total adsorption capacity varies with organic matter type and clay mineral content of the formation [13–19]. Characterizing gas transport properties remains challenging, however, due to the presence of multi-scale porous features and compositional heterogeneity of the rocks found in unconventional reservoirs [6,7,20]. In small nano-pores, for example, the mean free path of fluid molecules becomes comparable to the characteristic pore size [21]. Consequently, conventional theoretical approaches such as Darcy's law cannot accurately describe transport at this scale because the continuum theory breaks down [22].

Molecular dynamics (MD) has become a valuable tool for investigating the effects of confinement on fluid properties and calculating phenomenological transport coefficients (*e.g.*, diffusivities) for use in multi-scale models of fluid flow [4,14,23–28]. Both equilibrium and non-equilibrium MD methods have been successfully applied to estimate transport diffusivities for confined fluids. In equilibrium MD (EMD) methods, the collective diffusion

* Corresponding author.
** Corresponding author.
E-mail addresses: jcpalmer@uh.edu (J.C. Palmer), gqin@uh.edu (G. Qin).

http://dx.doi.org/10.1016/j.micromeso.2017.04.044
1387-1811/

coefficient computed using a generalized Green-Kubo relation is corrected by a thermodynamic factor to obtain the transport diffusivity [28–30]. Because the collective diffusivity is a slowly converging property, accurate estimation of this quantity typically requires averaging results from multiple EMD simulations [29,31]. Determination of the thermodynamic correction factor also requires computing the fluid's adsorption isotherm using methods such as grand canonical Monte Carlo [32,33]. Estimation of transport diffusivities with EMD methods is therefore often computationally expensive, requiring multiple simulations to be performed at each condition of interest. Alternatively, a number of non-equilibrium MD (NEMD) approaches have been developed to calculate transport diffusivities [4,28,30,34–40]. Such methods are based on the application of an external perturbation (e.g., pressure gradient) to drive the system out of equilibrium. For sufficiently small perturbations, the system will exhibit a linear response, and the transport diffusivity can be estimated from the resulting gradient and molar flux measured during a single simulation [28,30,34,35,37].

Although current NEMD methods are based on similar principles, they can differ substantially in their implementation and the approach used to apply the external perturbation. Of these methods, boundary-driven NEMD (BD-NEMD) has shown particular promise as a computationally efficient approach for accurately estimating transport diffusivities [8,30,34]. In BD-NEMD, an external force is applied to a small region of the simulation cell to establish a density gradient across the system. Once the resulting unidirectional molar flux of fluid molecules reaches steady state, the transport diffusion coefficient can be determined from Fick's law:

$$J_t = -D_t \frac{d\rho}{dx}, \tag{1}$$

where the total molar (mass) flux J_t is linearly proportional to the molar (mass) density gradient $d\rho/dx$ with the transport diffusivity coefficient D_t as the constant of proportionality. The total molar flux (J_t) consists of the diffusive flux driven by the density gradient and the convective flux driven by the pressure gradient. For a single component fluid, the density and pressure gradients are related via:

$$J_t = J_D + J_C = -D\frac{d\rho}{dx} - \kappa\frac{dP}{dx} = -\left(D + \kappa\frac{dP}{d\rho}\right)\frac{d\rho}{dx}. \tag{2}$$

Comparison of Eqs. (1) and (2) reveals that both the diffusive property D and convective property κ contribute to the transport diffusivity coefficient D_t. A comprehensive discussion of these transport coefficients and their relationship to microscopic quantities may be found in Refs. [28,30,41].

In BD-NEMD and other NEMD methods, the applied external force performs work on the fluid, thereby increasing the system's kinetic energy and temperature [42]. A number of temperature control schemes based on standard equilibrium molecular thermostats have been proposed to address this issue [8,30,36,42–45]. Although these thermostats facilitate sampling of structural and thermodynamic properties in EMD simulations, they perturb dynamical properties and do not have a rigorous theoretical foundation when applied to systems out of equilibrium [46]. Consequently, they must be applied judiciously during NEMD simulations to minimize the introduction of potential artifacts that adversely affect the estimation of transport properties. To our knowledge, however, there is no broad consensus regarding which temperature control schemes are robust and accurate for estimating transport properties in confined systems.

In this work, we critically examine six different temperature control schemes for BD-NEMD that have been employed in the literature. We identify several robust schemes that provide satisfactory temperature control and yield estimates of the transport diffusivity that are independent of the magnitude of the applied external force, thereby minimizing sensitivity to parameter choice. Using one of the robust schemes identified in our study, we investigate methane transport in model montmorillonite nanopores, which resemble the porous clay materials found in shale. Finally, we use transport diffusivities computed from simulation to scrutinize the validity of the Knudsen model of diffusion, which is commonly employed to estimate rock permeability in shale formations.

This paper is organized as follows: methodological details, including an overview of the BD-NEMD algorithm, temperature control schemes, and models, are provided in Section 2. Section 3 presents our main results and discussion of methane transport in montmorillonite clay nano-channels, the sensitivity of the results to various temperature control schemes, and correlation of modified Knudsen number with transport diffusivities in various pore sizes. Conclusions and promising avenues for future work are presented in Section 4.

2. Methods

2.1. Models and general simulation protocol

Shale matrices are structurally complex composites composed of various types of organic matter (*e.g.*, kerogens) and inorganic materials such as clays [25]. Each of these components have different porosities, tortuosities, pore size distributions, and physical interactions with adsorbed gas molecules that influence transport properties. To develop fundamental understanding of methane transport and characterize the behavior of different BD-NEMD temperature control schemes, we focus on modeling diffusion through the clay components of shale at the single-pore scale. Imaging and X-ray diffraction experiments on clays show that their pores are approximately slit-shaped [47]. Consequently, following

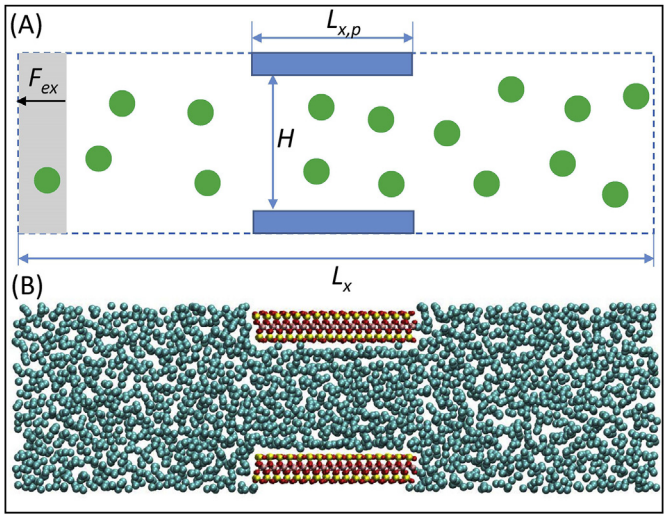

Fig. 1. (A). Schematic illustration of the simulated system. An external force field is applied to fluid molecules (green spheres) in the shaded region to drive flow through the slit-shaped nano-pore (blue rectangles). (B). Molecular rendering of the simulated model (coloring: Al = pink, O = red, Si = yellow, CH_4 = cyan). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)