



Non-equilibrium molecular dynamics simulation of gas flow in organic nanochannels



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ABSTRACT

The objective for this work is to investigate the contribution of the adsorbed phase to the mass flux and comparing transport of gases with different adsorption affinities in organic nano-scale channels. In this work, force-driven Non-Equilibrium molecular dynamics (NEMD) simulations are used to compare the transport of gases with high adsorption affinity (Methane and Argon) with the ones with low adsorption affinity (Helium), for channel heights of 2, 4, 6, and 8 nm at two Knudsen numbers of 0.1 and 0.2. Velocity and mass flux profiles across the channel for Argon, Methane, and Helium are compared. Transport diffusion coefficients and molecular flux of these gas are also calculated. Furthermore, adsorption properties are analysed using Grand Canonical Monte Carlo simulations.

For all the gases studied, plug-shaped velocity profiles are observed irrespective of the channel size and Knudsen number. Mass flux profiles of Argon and Methane across the channels demonstrate a significant contribution of adsorbed molecules to the total mass flux. Furthermore, as Knudsen number increases, the contribution of the adsorbed phase to the total mass flux becomes higher. Molecular flux of Helium is smaller than that of Argon and Methane for all channel sizes. The calculated diffusion coefficients of Methane are higher than those for Argon for all the channel sizes and they decrease as the channel size increases. For Argon and Methane, the diffusion coefficients become smaller as Knudsen number increases. For Helium, the diffusion coefficients are weak functions of the channel size and Knudsen number. Based on the results, contribution of the adsorbed molecules can be more than 50% of the total mass flux of the channel. For the pressure ranges studies, transport diffusivity of Helium is less sensitive to pressure and Knudsen number compared to Argon and Methane.

This study shows that the transport through organic nano-scale conduits is essentially diffusive. Therefore, to have a realistic model for predicting the recovery of fluids from unconventional resources, the transport equations in organic nanopores should be replaced by the diffusive transport equations.

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1. Introduction

Gas recovery mechanisms from shale resources are different from those of conventional resources due to presence of organic nanopores. In one hand, the gas molecules have a tendency to be adsorbed to the surfaces of the organic pores that results in heterogeneous fluid distributions within the pores. Adsorption of gas molecules to the pore surfaces causes molecular level transport effects, such as surface-diffusion. On the other hand, the pore sizes are comparable to the mean free path of the molecules, which causes non-continuum flow regimes. The transport of fluids in this

systems cannot be described by classical continuum-based hydrodynamic equations. A question then arises as to how different is the transport of gases with low adsorption affinity, e.g., Helium, compared to the ones with high adsorption affinities, e.g., Methane and Argon, in organic nano-scale conduits? Answer to this question can enhance our understanding of the fluid transport mechanisms in shale resources.

Molecular dynamics is an effective tool to study the details of fluid-fluid and fluid-solid interactions in nano-scale conduits. Transport of gas molecules in microporous systems have been extensively studied using three different MD simulation methods: equilibrium molecular dynamics (EMD), external field Non-Equilibrium Molecular Dynamics (NEMD), and boundary driven non-equilibrium molecular dynamics (dual control volume grand canonical molecular dynamics or DCV-GCMD) (Arya et al., 2001).

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DCV-GCMD simulations have been used to investigate the sensitivity of transport properties of methane, carbon dioxide, and nitrogen to pore size, porosity, and pressure gradient (Firouzi and Wilcox, 2012). Jin and Firoozabadi (2015) investigated flow of Methane in carbon nanotubes using DCV-GCMD simulations and the mobility of adsorbed phase in high and low pressures were demonstrated. They found that the Knudsen diffusion and Hagen-Poiseuille equations can underestimate the Methane flow by one order of magnitude. Kazemi and Takbiri-Borujeni (2016b) studied the transport of four different gases, Methane and Argon (adsorbing) and Helium and Neon (less-adsorbing). They showed that as the average channel pressure increases, the contribution of the adsorbed phase to the total mass flux decreases. For organic nanocapillaries, DCV-GCMD simulations have shown that the Knudsen diffusion model underestimates the molecular flux Kazemi and Takbiri-Borujeni (2016a). This underestimation was not a strong function of the pore size or the pore pressure.

NEMD simulations are easy to implement and computationally efficient for simulating the transport phenomena; however, the equivalence of external forcing function that drives diffusion and the actual chemical potential gradient has not been formally demonstrated (Arya et al., 2001). NEMD simulations have been applied to investigate the slippage of a non-adsorbing gas (Helium) in microporous media (Firouzi et al., 2014). Collell et al. (2015) performed MD simulations of hydrocarbons flowing through a molecular model of kerogen type II. The results suggested that the flow inside kerogen is of diffusive nature. Feng et al. (2015) carried out NEMD and DCV-GCMD to study the flow of Methane in nanocapillaries. They showed that the surface transport of adsorbed Methane have a significant contribution to total mass flux in nanocapillaries.

Comparing the transport properties of different types of gases in nano-scale conduits using NEMD is challenging because these systems have many degrees of freedom, e.g., channel size, molecule size, gas density, and therefore, finding equivalent systems is difficult. Furthermore, for systems under confinement, there is a positional dependence of density and also the state variables, pressure and temperature (Travis et al., 2000). Investigation of gas systems with respect to the Knudsen number might be a viable option. The gas flow regimes are characterized by Knudsen number (Kn), which is the ratio of mean free path of molecules to the characteristic length of the system,

$$Kn = \frac{1}{\sqrt{2}\pi n H d^2}, \quad (1)$$

where n is the number density, H is the channel height, and d is the molecular diameter. This formulation of Knudsen number incorporates molecular size, number density, and channel size and provides a means for comparing systems with different sizes and gas types.

The objective for this work is to investigate the adsorbed phase transport by comparing the velocity profiles, mass fluxes, and diffusion coefficients of different gases with different adsorption affinities (Argon, Methane, and Helium). In order to determine the adsorption affinities of different gases, Grand Canonical Monte Carlo simulations are performed for two channel heights of 2 and 4 nm. NEMD simulations of force-driven flow is carried out in graphite nanochannels with 2, 4, 6, and 8 nm height at Knudsen numbers of 0.1 and 0.2. The density, velocity profiles, mass fluxes, and diffusion coefficients of these gases are then compared.

2. Molecular dynamics methods

The Grand Canonical Monte Carlo (GCMC) simulations are

performed at different pressures for two graphite nanochannel heights of 2 and 4 nm to determine the gas adsorption isotherms of Methane, Argon, and Helium. In GCMC simulations, the pressure inside the control volume is kept constant by insertion and deletion of molecules. The probability of inserting a molecule is determined as,

$$p^+ = \min \left\{ \frac{Z V_{CV}}{N_{CV} + 1} \exp \left(- \frac{\Delta U}{k_B T} \right), 1 \right\}, \quad (2)$$

where $Z = \exp \left(\frac{\mu}{k_B T} \right) / \Lambda$ is the absolute activity at temperature T , Λ is the de Broglie wavelength, μ is the chemical potential, and k_B is the Boltzmann constant. Changes in potential energy resulting from insertion and deletion of molecules are represented by ΔU , volume of control volume is V_{CV} , and number of molecules in control volume is N_{CV} . Inserted molecules are assigned a velocity using Maxwell-Boltzmann distribution. The probability of deleting a molecule is,

$$p^- = \min \left\{ \frac{N_{CV}}{Z V_{CV}} \exp \left(- \frac{\Delta U}{k_B T} \right), 1 \right\}. \quad (3)$$

The temperature of the inserted molecules is determined based on the specified reservoir temperature (300 K).

Non-equilibrium molecular dynamics (NEMD) simulations of force-driven flow of Argon, Methane, and Helium are performed in three-dimensional graphite channels (with hexagonal lattice) of heights 2, 4, 6, 8 nanometers (nm). The width of the channel is chosen to be 4.5 nm for all the simulations; however, the channel lengths change with respect to the channel height such that the ratio of the length to height of the channels to be 20 in order to have a fully developed flow. For example, the channel lengths for simulations with 2 nm and 4 nm channel heights is selected to be 40 nm and 80 nm, respectively. The three-layered channel walls are placed in x-y plane. The simulations are performed for two Knudsen numbers of 0.1 and 0.2. The number of molecules for each specific gas and geometry is different and is determined by Eq. (1). The potential fields of Argon, Helium, and graphite are modeled by 6–12 Lennard-Jones potentials as,

$$U(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right], \quad (4)$$

where ϵ is a parameter characterizing the strength of interactions, σ is the Lennard diameter, and r_{ij} is the distance between molecules i and j . Lennard-Jones parameters used in the simulations are listed in Table 1.

The OPLS all-atom force field is used to simulate the flow of Methane molecules in nanochannel (Jorgensen et al., 1996). The charges of the Hydrogen and Carbon atoms of Methane are set to 0.06 e and 0.24 e , respectively, and the Lennard-Jones parameters are $\sigma_H = 2.5 \text{ \AA}$, $\epsilon_H = 0.03 \text{ Kcal/mol}$, $\sigma_C = 3.5 \text{ \AA}$, $\epsilon_C = 0.066 \text{ Kcal/mol}$. A cut-off distance of 9° Å is considered. The wall temperature is set to 300 K and the location of its carbon molecules is kept fixed using

Table 1
Lennard-Jones parameters of Argon, Carbon, and Helium.

	$\epsilon(\text{Kcal/mol})$	$\sigma(\text{Å})$
Ar–Ar	0.2403	3.405
C–C	0.0684	3.407
Ar–C	0.1282	3.406
He–He	0.0218	2.640
He–C	0.0387	3.023

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