Flow of Gases in Slit Shaped Organic Nanopores of Shale: A Boundary-Driven Molecular Simulation Study

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Abstract

In modeling of fluid transport in organic nanopores of shale, particular attention should be paid to the gas-wall interactions, specifically the adsorption phenomena, due to the fact that the size of pores are comparable with the mean-free-path of the gas molecules. The objective for this work is to fulfill the need for the investigation of how much the adsorbed phase contributes to the total mass flux of organic nanopores.

Molecular Dynamics (MD) is proved to be a credible technique to examine dynamics of atomic-level phenomena. In this study, transport of four different gases, Methane and Argon (adsorbing) and Helium and Neon (less-adsorbing), is studied and their transport are analyzed using dual control volume grand canonical molecular dynamics (DCV-GCMD) simulations with identical setups of graphite nano-channels. DCV-GCMD simulations are performed for different pressures, pressure gradients, and channel sizes. For each simulation, profiles of velocity, mass flux, and density across the channel height are calculated. Based on the DCV-GCMD simulation results, as the pressure of the system increases, the number of gas molecules adsorbing to the graphite walls increases to reach a state of full single-layer coverage. The absolute adsorption of a particular gas is the same for both 2 nm and 5 nm channel. However, the excess adsorption of gases in 2 nm channel are less than those in 5 nm one. Normalized velocity profiles of Argon and Methane become less concave as the pressure increase. This is in contrary to theory of slip. The normalized velocity profiles of less adsorbing gases demonstrate a plug shape type flow. As the average channel pressure increases, the contribution of the adsorbed phase to the total mass flux decreases. Furthermore, the results show that the channel length have significant impacts on transport of gases through nanochannels.

Introduction

Fundamental understanding of transport of fluids in the shale resources is of great importance due to the significance of these resources in future of energy market. Shale is different from conventional hydrocarbon resources due to presence of nanoporous organic matter embedded within an inorganic matrix. Gas flow in these nanopores usually falls into the slip or early transition flow regime. In these flow regimes, the mean free path of gas molecules are comparable to the characteristic length of the system. Therefore, the continuum-based assumptions are no longer valid. Furthermore, adsorbed molecules on the pore
surfaces significantly contribute to total mass flux (Choi et al., 2001; Skoulidas et al., 2002; Medveď and Černý, 2011). Question that arises here is that how different are the transport of gases with different adsorption properties. In other words, how much the adsorbed phase contribute to the flow. Answer to this question may bring us closer to development of predictive transport models in organic-rich reservoirs.

Flow and diffusion of gas molecules in microporous systems have been extensively studied using three different molecular dynamics 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). Transport mechanism is described by Fickian constitutive relation as,

\[ J = -D_t(c) \nabla c, \]  

where \( J \) is the molecular diffusive flux and \( \nabla c \) is the spatial concentration gradient. The transport diffusivity \( (D_t) \) is usually the transport property of interest. However, in Fick’s law ignores the cross-effects between multicomponent gases. An alternative approach to Fick’s law is the Onsager and Maxwell-Stefan (MS) formulations, which replaces Fickian fluxes of all components by a linear combination of gradients of all involved concentrations, respectively chemical potentials (Bothe, 2011). The Maxwell-Stefan formulation for single component is,

\[ J = \frac{L(c)}{k_B T} \nabla \mu, \]  

where \( L(c) \) is the single component transport coefficient, \( k_B \) is the Boltzmann constant, and \( \mu \) is the chemical potential.

The EMD method is easy to implement; however, there are some mathematical difficulties in calculation of MS transport coefficient (Arya et al., 2001). In NEMD simulation method, an external force \( (F) \) is applied to gas molecules. The external force mimics the chemical potential gradient and the transport coefficient can be calculated by substituting the \( \nabla \mu \) in Eq. 2 with the external force. The advantages of NEMD simulation method is that it is computationally efficient and easy to implement. The drawback of the method is the conversion of the external force to equivalent chemical potential gradient. The boundary driven non-equilibrium molecular dynamics method allows the gas transport between two reservoirs with fixed chemical potentials. The chemical potential of the two reservoirs are kept constant by insertion and deletion of gas molecules (usually performed through a grand canonical Monte Carlo or GCMC procedure) and the transport through the medium of interest is performed by molecular dynamics. Insertion and deletion of molecules is the significant fraction of total simulation cost in this method.

Dual control volume grand canonical molecular dynamics (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). The results demonstrated that the porosity is the main factor affecting apparent permeability of these gases. Jin and Firoozabadi (2015) investigated flow of Methane in carbon nanotubes using DCV-GCMD simulations. The results demonstrated that the permeability is the significant fraction of total simulation cost in this method.

Non-Equilibrium Molecular Dynamics (NEMD) simulations have been applied to investigate the slippage of a non-adsorbing gas (Helium) (Firouzi et al., 2014) and the results were compared with experimental flow measurements of a shale core plug. The results indicated that the experimental measured permeabilities are two order of magnitude larger than NEMD results. Mobility of the adsorbed Methane in a 5 nm tube has been proven using NEMD simulations (Riewchotisakul et al., 2015). Adsorbed phase transport was concluded to be different from slippage of non-adsorbing gases. Therefore, the formulations that is used for non-adsorbing gases, may not predict the transport of adsorbing gases. Collell et al. (2015) performed molecular dynamics simulations of hydrocarbons flowing through a molecular model of kerogen type II. The results suggested that the flow inside kerogen is of diffusive
nature and that the transport properties can be calculated using equilibrium molecular dynamics. In this work, we compare the transport of adsorbing and non-adsorbing gases in nanochannels. In this article, flow of gases are considered in a graphite nanochannel.

The novelties of this work are as follows:

- This study investigates the flow of several gas types in similar simulation setups with different adsorption properties. The results of this study can be used for evaluating the models used for predicting the transport of adsorbing gases (such as Methane) and less adsorbing gases (such as Helium) through organic rich shale.
- It makes inquiries about the contribution of adsorbed phase transport comparing to gases with different adsorption capacity.
- It looks into the effect of system geometry (pore height), average pore pressure, and pressure gradient on gases transport in organic nanopores.
- It explores the sensitivity of the simulation results to the channel length.

The objective of this work are to compare the transport of gases with high adsorbing capacities (Methane and Argon) and low adsorbing gases (Helium and Neon) in graphite nanochannels. Monte Carlo simulation are performed within Grand Canonical ensemble to predict the adsorption properties (excess and absolute) of investigated gases. DCV-GCMD simulations are then carried out in 2 and 5 nm graphite nanochannels at different pressures and pressure gradients. Density, mass flux, and velocity profiles of the gases are compared.

Assumptions of this study are as follows:

- To represent organic nanopores in shale, graphite nanochannels are used.
- Methane molecule modeled with TraPPE model and the charges of carbon and hydrogen atoms are not considered.

**Computational Methodology**

**Problem Setup**

A single graphite nanochannel is created using Moltemplate molecular builder software (Jewett et al., 2013). Each side of nanochannel is consisted of three graphite layers with a distance of 0.335 nm. The distance between two adjacent carbon atoms in the same graphite layer is 0.142. In order to investigate the effect of nanochannel length on flow of gases, different channel lengths are considered. The lengths considered are 10, 20, and 40 nm for flow inside a 2nm-height channel and 16 and 130 nm for flow inside channel for 5nm-height channel.

The nanochannel is placed between two cubic bulk reservoirs at different pressures and at 300 K to perform DCV-GCMD simulations, Fig. 1. Since a periodic boundary condition is considered in flow direction, connecting the low and high reservoirs could cause high fluctuations in the pressures in the reservoirs. Therefore, two graphite walls are placed at the end of each reservoir to avoid their direct contact. The length of the left (H) (downstream) and right (L) reservoirs (upstream) are chosen to be 2 nm and 10 nm for simulation with channel heights 2 nm and 5 nm, respectively.

Figure 1—Simulation setup for the 2nm channel. The channel length is 40 nm. “H” and “L” represent the high and low pressure reservoirs, respectively.
The TraPPE model (Martin et al., 1998) is used to simulate the gases (Methane, Argon, Helium, and Neon). Lennard-Jones (LJ) pairwise additive potential field was employed to represent the gas molecules interaction as,

\[
U_{ij}(r_{ij}) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right],
\]

where \(r_{ij}, \varepsilon_{ij}\), and \(\sigma_{ij}\) are separation distance, strength of interaction, and LJ well depth, respectively. Unlike interactions were determined using the Lorentz-Berthelot combining rules,

\[
\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2},
\]

\[
\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}.
\]

The separation distance (\(\sigma\)) and strength (\(\varepsilon\)) parameters for all gases are shown in Table. A cut-off distance of 10 Å is considered for all simulations.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>(\varepsilon/\kappa B) (K)</th>
<th>(\Sigma(\AA))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)-CH(_4)</td>
<td>148</td>
<td>3.73</td>
<td>Müser and Berne (1996)</td>
</tr>
<tr>
<td>C-C</td>
<td>34.45</td>
<td>3.407</td>
<td>Saito et al. (2001)</td>
</tr>
<tr>
<td>Ne-Ne</td>
<td>36.83</td>
<td>2.789</td>
<td>Nagy et al. (1995)</td>
</tr>
<tr>
<td>Ar-Ar</td>
<td>119.8</td>
<td>3.405</td>
<td>Barker et al. (1971)</td>
</tr>
</tbody>
</table>

Simulation Method

In order to simulate flow of gases in graphite nanochannel, DCV-GCMD method (Wang and Li, 2004; Heffelfinger and van Swol, 1994; Xu et al., 1998), which have been extensively used in other studies (Firouzi and Wilcox, 2013; Cracknell et al., 1995), is employed. In DCV-GCMD simulations, molecular dynamics (MD) moves are combined with GCMC insertion and deletion of molecules in two control volumes. The MD simulation time integration of equation of motion are performed using Verlet velocity algorithm with a time step of 3 fs (femtoseconds). The pressure inside the control volumes is kept constant using adequate number of GCMC insertion and deletion. The probability of inserting a molecule is determined as,

\[
p^+ = \min \left\{ \frac{Z_{NCV}}{N_{CV} + 1} \exp \left( \frac{-\Delta U}{\kappa B T} \right), 1 \right\},
\]

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

\[
p^- = \min \left\{ \frac{N_{CV}}{Z_{NCV}} \exp \left( \frac{\Delta U}{\kappa B T} \right), 1 \right\}.
\]

The inserted molecules are assigned based on specified reservoir temperature (300 K). The driving force for gas molecules movement were the pressure or chemical potential difference between the two control volumes (L and H). The wall and fluid temperatures were kept constant at 300 K in NVT (constant number of molecules, constant volume and constant temperature) ensemble. The unbounded Knudsen number is found by counting the number of molecules in nanochannel and substituting in,
where \( n_v \) is the number density, \( H \) is the height of channel, and \( d_i \) is the diameter of molecule \( i \).

All the simulations are performed using Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) (Plimpton, 1995). Visual Molecular Dynamics (VMD) (Humphrey et al., 1996) is used for visualization. A raw flowchart of performing DCV-GCMD simulations are shown in Fig. 2. All the simulations are performed using Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) (Plimpton, 1995) and Visual Molecular Dynamics (VMD) (Humphrey et al., 1996) is used for visualization.

![Figure 2—Flowchart of DCV-GCMD simulations.](image)

**Results and Discussion**

Adsorption Isotherms As discussed in previous section, GCMC simulations are performed to determine the adsorption isotherms of Neon, Argon, and Methane. GCMC simulations were performed in a pressure range of 10 to 330 atmosphere and a constant temperature of 300 K. In order to study adsorption behavior of gases under confinements, two quantities are usually defined as follows. *Absolute* adsorption is the quantity of the gas in the adsorbed state. *Excess* adsorption is the subtraction of adsorbed gas density at the wall and gas density in bulk phase. These quantities are usually represented in mmol/cm³.
Adsorption isotherms of the gases in a 2 and 5 nm channel are shown in Fig. 3 and 4. The absolute adsorption of all three gases increases as the pressure increases and tend to saturate at high pressures for both channel heights. The absolute adsorptions of Argon and Methane are similar. The absolute loadings for Argon and Methane at 330 atm for a 5nm channel height are 23 and 22.2 mmol/cm³, respectively. The absolute loadings of Neon are smaller, ranging from 11 to 14.5 mmol/cm³ in 2 and 5 nm channels, respectively. For both Argon and Methane, the absolute adsorption increases in a 2 nm channel height compared to 5 nm. The absolute adsorption of Neon is slightly higher for 5 nm channel compared to the 2 nm. The results show that Helium has the lowest adsorption capacity among gases tested. The absolute adsorption isotherms overlap each other for channel heights of 2 and 5 nm except for Neon.

As pressure increases, the excess loadings increase to reach a maximum value at an optimum pressure and then decrease. For each channel size, Methane has a smaller value for optimum pressure than Argon. The maximum excess adsorption of both Argon and Methane is found to be 12 mmol/cm³ for 5 nm channel. This value decreases to 10.8 and 11.5 mmol/cm³ for Argon and Methane in a 2 nm channel,
respectively. The excess adsorption for Neon continuously increase from 0.5 mmol/cm$^3$ in 2 nm channel to 4 mmol/cm$^3$ in 5 nm for the pressure range studied. Although the absolute adsorption of gases for channel heights 2 and 5 nm lie on top of each other, the excess adsorption of these gases are different at channel height 2 nm compared with 5 nm. As the pressure increases, the adsorption surface coverage increases until it reaches to its maximum, i.e., 1. Further pressure increase causes a second layer to form and therefore, the average bulk density increases while the gas density at the wall is approximately constant. This would reduce the excess adsorption more significantly for a 2 nm channel height compared with the 5 nm one.

**Chemical Potential Driven Flow**

In this section, the velocity and density profiles of Methane, Argon, Neon, and Helium at 2 and 5 nm channels are presented. Simulations are performed at different gas pressures and pressure drops across the nanochannels.

The computed velocity profiles are normalized with the average velocity values across the channel height. The normalized velocities at the same average pressure should be the same for different pressure drops as long as the flow regime lies on the linear response regime (Arya et al., 2001) (Fig. 5a). The normalized velocity profiles at pressure gradient of 0.6, 1.2, and 1.75 atm/nm line on top of each other. Average velocities across the channel height are plotted against pressure gradient in Fig. 5b. The results confirm that the simulations are in linear response regime.

**A. 2 nm channel height**

Simulations are performed at three different average pressures of 20, 50, and 90 atmospheres. These pressures are the average pressure of the low and high pressure reservoirs.

The normalized velocity profiles of Argon along with the corresponding density profiles at 20, 50, 90 atm are presented in Fig. 6a. The density of adsorbed Argon molecules increases from 212 to 586 kg/m$^3$ as pressure increases from 20 to 90 atm. The adsorbed density of Methane increases from 141 to 279 kg/m$^3$ as pressure increases from 20 to 90 atm. The normalized velocity profiles become less concave as the pressure increases. In other words, the ratio of the velocity at the center of the channel (maximum velocity) and velocity at the vicinity of the channel wall (slip velocity) becomes smaller. This is contrary to the published results on the theory of the slip in nanochannels (Beskok and Karniadakis, 1999; Kazemi and Takhir-Borujeni, 2015a,b). According to these theories, the contribution of the molecules that lie in the vicinity of the channel wall to flow becomes less significant as pressure increases (i.e., lower
unbounded Knudsen number). Similar results are also seen for flow of Methane in graphite nanochannel (Fig. 6b) (Jin and Firoozabadi, 2015; Firouzi and Wilcox, 2013).

The normalized velocity profiles ranges from 0.8 –1.15 for Argon and 0.75–1.2 for Methane. Although the adsorption of Neon is (Figs. 3 and 4) less than Argon and Methane, the normalized velocity at the channel wall increases as the average pore pressure increases (Fig. 7). However, the normalized velocity profile ranges from 0.94 to 1.05, which represents a plug regime flow profile. The same results are obtained for flow of Helium. Helium has smaller adsorption loading quantities than Neon. The normalized velocity profile of Helium ranges from 0.98 –1.02. Therefore, the less the adsorption, the less the concavity of normalized velocity profile inside organic nanochannel for the gases studies in this work.

**B. 5 nm channel height**  Flow of Argon, Methane, and Neon are investigated in a graphite nanochannel of 5 nm height and 130 nm length.

Similar to 2nm channel, as the pore pressure increases, the contribution of the molecules that lie on the channel walls to the total flow rate becomes more significant for Argon (Fig. 8a), Methane (Fig. 8b), and Neon (Fig. 9). However, comparing to 2 nm channel, higher ratios of adsorbed phase velocity to the maximum velocity at the channel are obtained.
Flow of Neon in a 5 nm channel height also demonstrates a plug like flow profile. The range of normalized velocity for Neon is between 0.93 and 1.02. The profile becomes less concave as the pressure increases.

As shown Figs. 6, 7, 8, and 9, the velocity profiles of both highly adsorbing (Argon and Methane) and low adsorbing gases (Helium and Neon) are different from the prediction made by the current models (Kazemi and Takbiri-Borujeni, 2015a,b; Beskok and Karniadakis, 1999) in the sense that contribution of the molecules lying on the channel walls to the flow becomes smaller.

**Mass Flux Profiles**

The channel height is divided to equally-sized bins, each with a height of 2.5 and 5 angstroms for channel heights 2 and 5 nm, respectively. At each bin, the average velocity is multiplied with average density of that particular bin and divided by product of the average velocity and density of the channel to determine the dimensionless mass flux of the bin. The dimensionless mass fluxes of Methane flow in 2 and 5 nm channels are plotted in Fig. 10. As expected, the highest mass flux is observed at bins near the graphite walls. This is due to the fact that the density of Methane is higher than its density at bulk phase. Additionally, the adsorbed Methane molecules are not stationary at the graphite surface and they contribute to total mass flux. As the average pore pressure increases (Knudsen number decreases), the contribution of the adsorbed phase to the total mass flux decreases. This contribution is the approximately
the same at pressures 20 and 50 atm and is equal 32% for each wall (totally 64%). However, for 90 atm pressure, the contribution is slightly smaller and is equal to 28% for each wall (totally 56%).

Similarly, for the 5 nm channel, as the pore pressure decreases, the contribution of adsorbed phase to the total mass flux increases.

These contributions are 54, 48, and 42% of total mass flux for average pore pressures 15, 36, and 60 atm.

**Effect of Channel Length**

Distance between high and low pressure reservoirs were reported to impact the gas flow (Jin et al., 2015). In order to investigate this effect, DCV-GCMD simulations are performed at different lengths for both 2 and 5 nm channels using Methane and Argon as flowing gases. For the channel with 2 nm height, simulations are performed with length 10, 20, and 40 nm. Velocity profiles of Methane flow are presented at two different pressures at the same pressure drop of 60 atm in Fig. 11. Velocity profiles demonstrate that the 20nm-long channel has the highest and 40nm-long channel has the lowest velocities in both pressures. Furthermore, the velocity of the adsorbed gas molecules approaches the bulk phase velocity as the length of the channel increases.
Similar results are obtained for simulations of flow of Argon inside a channel with 5 nm height. The simulations were performed for two different lengths of 16 and 130 nm and three different pressures of 20 atm (L), 50 atm (M), and 90 atm (H). The pressure drops of simulations were chosen to be 25, 60, and 98 atm for pressures 20, 50, and 90, respectively. For all pressures, increasing the channel length causes the reduction of average velocity in that particular pressure. Similar to 2 nm channel height, the velocity profiles become flat for higher lengths.

Conclusions

- As the pressure increases, the amount of adsorbed gas molecules increases and tend to saturate at high pressures.
- The absolute adsorption of a particular gas is the same for both 2 and 5 nm channel heights; however, the excess adsorption of 2 nm channel is smaller than that of 5 nm.
- In contrary to slip theory of gases, as the pressure increases, the velocity profiles of adsorbing gases become less concave.
- The normalized velocity profiles of less adsorbing gases (Helium and Neon) demonstrate a plug flow type profile.
- The contribution of adsorbed phase to total mass flux is smaller at higher pressures.
- Channel length could have a significant impact on DCV-GCMD results.

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