Modeling of gases flow in organic nanopores of shale is associated with complexities due to ultratight pores and adsorption capacity of the kerogen. The pore sizes in organic nanopores are small such that the mean free path of gas molecules become comparable to the characteristic length of the system. The objective of this work is to fulfill the need for the investigation of flow of different gases with unlike adsorption characteristics and examining the contribution of the adsorbed phase to total mass flux. In this study, adsorption and transport of three different gases, argon, methane, and neon, are investigated by performing the dual control volume grand canonical molecular dynamics (DCV-GCMD) simulation in identical setups of carbon nanocapillaries. The simulations are performed for two capillaries of of 2 and 4 nm in diameter for a wide range of pressures and pressure gradients. The velocity, density, and molecular fluxes of these gases are computed and compared with each other. Based on the MD simulation results, as the pressure of the system increases, the number of gas molecules adsorbing to the nanocapillary walls increases to reach a state of full single-layer coverage. Normalized velocity profiles with average gas velocities show that for all gases in both nanocapillary diameters, flow profiles are plug shaped. Furthermore, it is found that the Knudsen diffusion model underestimates the molecular fluxes in carbon nanocapillaries by one order of magnitude. This underestimation is shown to be a function of excess adsorption amount and it is not a strong function of the pore size or the pore pressure.

Introduction

Gas flow in organic nanopores of shale is complex due to heterogeneous fluid distributions and surface functionality caused by strong fluid-sloid interactions. In these pores, the mean free path of the gas molecules is comparable to the characteristic length scale of the system, which causes the flow regime to fall into the slip or early transition regime (Kang et al., 2011). Adsorbed gas molecules are not immobile on pore surface and they have a significant contribution to the total mass flux of the system (Firouzi and Wilcox, 2012; Jin and Firooz- abadi, 2015; Skoulidas et al., 2002; Medved and Černy, 2011). In this article, we try to develop a fundamental understanding of the transport phenomena in shale resources by addressing the following questions:
How significant is the contribution of the adsorbed molecules to the total mass flux?
How different is the flow of adsorbing gases (argon and methane) from the less-adsorbing gases (neon)?
How precise are the predictions made by the current models, e.g., Knudsen diffusion model?

These questions shall be answered here by performing dual control volume grand canonical molecular dynamics (DCV-GCMD) simulations.

Fickian constitutive relation describes the transport of single-component gases as,

$$J = -D_t(c) \nabla c,$$

(1)

where $D_t$ is the transport diffusivity, $\nabla c$ is the spatial concentration gradient, and $J$ is the molecular diffusive flux. This equation can be written in the terms of pressure gradient as Roy et al. (2003),

$$J_{Kn} = \frac{MD_k}{RT} \nabla p,$$

(2)

where $M$ is the molar mass, $D_k$ is the Knudsen diffusion coefficient at temperature (T).

$$D_k = \frac{d_{pore}}{3} \sqrt{\frac{8RT}{\pi M}}$$

(3)

where $d_{pore}$ is the pore diameter. For a system with multicomponent gases, the Onsager and Maxwell-Stefan (MS) formulations are usually used.

$$-\frac{c_i}{RT} \nabla \mu_i = \sum_{j=1}^{n} B_{ij} N_j,$$

(4)

where $N$ is the number of possible driving forces, $\mu$ is the chemical potential, and $B_{ij}$ are elements of the matrix of Maxwell-Stefan diffusivities,

$$B_{ij} = \frac{-x_i}{D_{ij}}$$

(5)

$$B_{ij} = \frac{1}{D_i} + \sum_{j \neq i}^{n} \frac{-x_j}{D_{ij}},$$

(6)

where $D_{ij}$ are Maxwell-Stefan cross diffusivities, $D_i$ are Maxwell-Stefan diffusivities, and $x_i$ is the molar fraction of component $i$.

The quantity of interest in the above equations are the diffusivity coefficients. MD simulations based on realistic interactions forces between fluid-fluid and fluid-solid molecules are credible alternatives to the experimental methods for simulating transport of fluids in confined systems. Equilibrium Molecular Dynamics (EMD), external field Non-Equilibrium Molecular Dynamics (NEMD), and DCV-GCMD simulations are among the MD techniques to investigate transport mechanism of gases. Implementing the EMD method is not complicated; however, complexities exist in calculating the transport coefficients. NEMD simulation can be carried out by applying an external force to the gas molecules. The external force mimic the chemical potential gradient and the transport diffusivities can be determined by substituting the chemical potential gradient with the external force in Eq. 4. Although this method is computationally efficient and easy to implement, the conversion of the external force to equivalent chemical potential gradient is not straightforward in this method. In DCV-GCMD simulations, the transport medium is confined between two high and low pressure reservoirs. The pressure (or chemical potential) of these reservoirs are kept constant by insertion and deletion of molecules. The drawback of this method is the significant simulation cost due to insertion and deletion of molecules (Arya et al., 2001).
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). Firouzi et al. (2014) performed NEMD simulations to investigate the slippage of a non-adsorbing gas (Helium). They compared the NEMD simulation results with experimental flow measurements of a shale core plug and found that the experimental measured permeabilities are two order of magnitude larger than NEMD results. Feng et al. (2015) carried out NEMD and DCV-GCMD to study the flow of methane in nano-capillaries. They showed that the surface transport of adsorbed methane have significant contribution to total mass flux. The simulations were performed in tubes of 3 to 9 nm diameter while the length of the tubes were 15 nm. The small nanocapillary length has been shown to have a significant influence on the simulation results (Kazemi and Takbiri-Borujeni, 2016). Same issue exists in NEMD simulations of Riewchotsakul et al. (2015), where flow of methane in a 5 nm tube with 10 nm length were investigated. They concluded that the adsorbed phase is mobile and concluded that the adsorbed phase transport is different from the slippage of non-adsorbing gases. Therefore, the formulations that is used for non-adsorbing gases, may not predict the transport of adsorbing gases. Jin and Firoozabadi (2015) used DCV-GCMD simulations to study flow of methane in slit pores at high and low pressures. They found that the Knudsen diffusion and Hagen-Poiseuille equations can underestimate the methane flow by one order of magnitude. 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 and that the transport properties can be calculated using EMD.

In this work, we compare the transport of gases with high adsorbing capacity (methane and argon) with the ones with low adsorbing capacity (neon) in carbon nanocapillaries. 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 capillaries with 2 and 4 nm diameter at different pressures and pressure gradients. Furthermore, density, mass flux, and velocity profiles of the gases are compared. The predictions made by the Knudsen diffusion model are compared with DCV-GCMD results. The novelties of this work are as follows:

- Flow of several gas types in similar simulation setups with different adsorption properties are investigated. 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 neon) through organic nanopores.
- Contribution of adsorbed phase transport is investigated by the transport of gases with different adsorption capacities.
- Effect of system geometry (pore height), average pore pressure, and pressure gradient on gases transport in organic nanopores is studied.
- Predictions made by the Knudsen diffusion model is compared with DCV-GCMD results.

Assumptions of this study are as follows:

- To represent organic nanopores in shale, carbon nanocapillaries 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 multiwall carbon nanocapillary was created using Moltemplate molecular builder software (Jewett et al., 2013). The distance between concentric carbon nanocapillaries are 0.335 nm. The distance between two adjacent carbon atoms in the same carbon nanocapillary is 0.142. Simulations are performed for two different nanocapillary diameters of 2 and 4 nm. The length for these carbon nanocapillaries are...
chosen to be 40 and 80 nm \((L/D = 20)\), respectively. Furthermore, the lengths of bulk reservoirs are selected to be 2 and 4 nm, respectively. The nanocapillaries are placed between two bulk reservoirs with high (H) and low (L) pressures. The pressures of the bulk reservoirs are kept constant by insertion and deletion of molecules. The temperature of system is set to 300 \(K\) using the Nose-Hoover thermostat. Two walls are created at both ends of the bulk reservoirs to avoid their direct contact because of the periodic boundary conditions that are applied in \(z\) direction. Additionally, two hollowed walls are placed at both ends of nanocapillary to guide all the gas molecules.

![Figure 1—Simulation setup for the 2 nm nanocapillary. The nanocapillary length is 40 nm. “H” and “L” represent the high and low pressure reservoirs, respectively.](image)

The TraPPE model (Martins et al., 1990) is used to for force field of gases (methane, argon, and neon). Lennard-Jones (LJ) pairwise additive potential field is 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 are 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 following Table. A cut-off distance of 10 \(\text{Å}\) is considered for all simulations.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>(\varepsilon/k_b(K))</th>
<th>(\sigma(\text{Å}))</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 nanocapillary, DCV-GCMD method (Wang and Li, 2004; Heffelfinger and van Swol, 1994; Xu et al., 1998) 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,

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

where $Z = \exp \left( \frac{\mu}{k_B T} \right)$ is the absolute activity at temperature $T$, $\Lambda$ is the de Broglie wavelength, $\mu$ is the chemical potential, and $k_B$ is the Boltzmann constant. Potential energy change resulting from insertion and deletion of molecules is represented by $\Delta U$, volume of control volume is $V_{CV}$, 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,

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

The inserted molecules are assigned based on specified reservoir temperature (300 K). The driving force for gas molecules movement are the pressure or chemical potential difference between the two control volumes (L and H). Temperature of the wall and fluid are kept constant at 300 K in NVT (constant number of molecules, constant volume and constant temperature) ensemble. 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.

**Results and Discussion**

**Adsorption isotherms**

GCMC simulations are performed at 10 to 330 atm pressure range to investigate the adsorption of argon, methane, and neon to carbon nanocapillaries. The diameter of the nanocapillaries is divided into bins with 3.33 Å thickness and the density of gases at each bin are determined. Absolute and excess adsorption of the gases are studied. **Absolute** adsorption is the quantity of the gas in adsorbed state per unit volume and is directly related to the gas density at the wall. Gas molecules in the nearest bin to the wall are considered adsorbed gases. This might not be precise because as pressure increases, a second adsorption layer can be formed. However, to compare the adsorption properties of these gases, a single layer adsorption is assumed. **Excess** adsorption is the subtraction of amount of gases in bulk phase from that of adsorbed phase per unit volume. The amount of gas in bulk phase is defined as the amount of gas in the absence of pore walls at specified temperature and pressure. These quantities are usually represented in mmol/cm³.

Absolute adsorption plots of argon, methane, and neon for two nanocapillaries with of 2 and 4 nm diameters is shown in **Fig. 2**. The adsorbed amount of gases increases as the pressure increases and tend to saturate at higher pressures especially for argon and methane. At lower pressures, methane has higher adsorption capacity than argon and neon. At higher pressures, the absolute adsorption of argon and methane are similar for both nanocapillary diameters. Interpretation of absolute adsorption values are challenging because it is difficult to identify the actual adsorbed molecules and separating them from free gas molecules in bulk phase (Mosher et al., 2011).
The excess adsorption isotherms are plotted in Fig. 3. Excess loading of methane is higher at lower pressure. At high pressures, the density of the adsorbed phase is lower than the bulk phase density (density of the gas without confinements). The excess adsorption reaches to its highest values at a pressure of 50 atm for both argon and methane. neon excess adsorption is less than the other two gases and is in the range of 0.2 to 1.8 mmol/cm$^3$ for 2 nm nanocapillary and −1.5 to 0.65 for 5 nm nanocapillary. Therefore, the neon density under confinement is similar to its density without confinement. Density of argon and methane molecules at the wall is higher than the bulk phase density up to a pressure of roughly 140 atm (2057 psi).

**Chemical Potential Driven Flow**

In this section, the normalized velocity (velocity divided by the average velocity across the nanocapillary) of the gases are plotted along with the densities across the nanocapillary. The normalized velocity profiles at the same pressure and different pressure gradients are the same, which shows that the flow regime falls in the linear response regime (Arya et al., 2001). As mentioned earlier the simulations are performed for four different nanocapillary diameters of 2 and 4 nm. The mass flux profiles are also analyzed for these gases at different nanocapillary diameters.
**2 nm nanocapillary** DCV-GCMD simulations are performed at three mean pressures of 20, 50, and 90 atm. The mean pressure is the average pressure of the two reservoirs. The length of the nanocapillary is selected to be 40 nm in order to avoid the correlations between the two reservoirs. A variety of pressure gradients are applied at each mean pressure. The normalized gas velocity profiles at different pressures are plotted in Figs. 4a, 5a, and 6a.

**Figure 4**—DCV-GCMD simulations of argon in a 2 nm carbon nanocapillary. (a) Density and normalized velocity profiles (b) A comparison of calculated mass flux with the ones predicted by Knudsen diffusion.

**Figure 5**—DCV-GCMD simulations of methane in a 2 nm carbon nanocapillary. (a) Density and normalized velocity profiles (b) A comparison of Knudsen diffusion and simulations molecular fluxes of methane.

**Figure 6**—DCV-GCMD simulations of neon flow in a 2 nm carbon nanocapillary. (a) Density and normalized velocity profiles (b) A comparison of Knudsen diffusion and simulations molecular fluxes of neon.
For argon, the gas density at the wall increases from 134 to 263 kg/m$^3$ as pressure increases from 20 to 100 atm. The excess adsorption reduces from 1.07 to 0.825 mmol/cm$^3$. This means that for pressures above 20 atm, a full adsorption surface coverage is achieved (Fig. 2). The normalized velocity values range from 0.95 to 1.05, which shows that a plug-shaped flow profile exists for argon in the carbon nanocapillary. Gas molecules in both bulk phase and adsorbed phase have approximately equal velocities for all the examined pressure gradients. Therefore, the mathematical models of flow in organic nanopores, such as R13 (Kazemi and Takbiri-Borujeni, 2015a,b), may need to be modified in order to predict transport properties accurately. Fig. 4b demonstrates the molecular fluxes of argon at different pressure gradients and mean pressures along with the molecular fluxes calculated by Knudsen diffusion (Eq. 2). The molecular fluxes determined from DCV-GCMD simulations are at least one order of magnitude higher than those estimated by the Knudsen diffusion. This is due to the contribution of adsorbed phase to the flow. These results are consistent with the results published by Holt et al. (2006). The simulation results also show that at lower pressures, the molecular fluxes are slightly higher than high pressures at the same pressure gradients. This reveals that the contribution of the adsorbed phase to total mass flux reduces as the pressure increases.

Methane density increases from 73 to 105 kg/m$^3$ for a pressure range of 20 to 100 atm Fig. 5a. The normalized velocity at different pressures ranges from 0.98 to 1.02. Similar to argon, this demonstrates a plug shape flow profile. In other words, methane molecules at the wall flow with a similar velocity as the gas molecules in bulk phase. Furthermore, the DCV-GCMD molecular flux of methane is at least one order of magnitude higher than the predicted Knudsen diffusion mass flux (Fig. 5b).

The density and normalized velocity profiles of neon in the 2nm carbon tube is shown in Fig. 6. The adsorbed gas density is approximately equal to the bulk phase density for a pressure range of 20 to 100 atm. The velocities of gas molecules are similar across the tube and a plug-shaped flow profile is observed. The simulations molecular fluxes are roughly 5 times higher than those of predicted with Knudsen diffusion model.

**4 nm nanocapillary** Similar to 2 nm nanocapillary, DCV-GCMD simulations are performed at three different mean pressures of 20, 50, and 100 atm. The length of the tube is designed to be 80 nm in order to reduce the effects of inlet and outlet. The density and normalized velocity profiles of argon, methane, and neon are plotted in Figs. 7a, 8a, and 9a. The normalized velocity profiles of argon at different pressures ranges from 0.9 to 1.05, which is slightly wider than those in the 2nm tube. As the pressure increases, the velocity profile become less concave until it reaches to a plug shape flow profile. The adsorbed phase densities of 4 nm tube (ranging from 91 to 215 kg/m$^3$) are lower than those in the 2 nm tube (ranges from 133 to 260 kg/m$^3$). One reason for this difference might be the difference bin sizes chosen for plotting the density profiles for these two nanocapillaries. The absolute adsorption curves (Fig. 2), however, demonstrate the same adsorbed density for both tubes for the same pressures. The normalized velocity profiles of methane lay on top of each other for the pressure range investigated (Fig. 8a). The density profiles of neon indicate that the density of gas molecules at the wall are lower than the molecules away from the wall. The normalized velocity values range from 0.95 to 1.05 which imply a plug shape flow profile.

The molecular fluxes of argon, methane, and neon are plotted in Figs. 7b, 8b, and 9b along with the Knudsen diffusion prediction. The molecular fluxes determined from DCV-GCMD simulations are at most one order of magnitude higher than those predicted from Knudsen diffusion model for both argon and methane (Fig. 7b and 8b). This underestimation is lower for neon in comparison with argon and methane. In order to have a more quantitative comparison, an enhancement factor is defined as the ratio of DCV-GCMD simulation molecular flux to that of Knudsen diffusion prediction,
Figure 7—DCV-GCMD simulations of argon flow in a 4 nm carbon nanocapillary. (a) Density and normalized velocity profiles (b) A comparison of Knudsen diffusion and simulations molecular fluxes of argon.

Figure 8—DCV-GCMD simulations of methane flow in a 4 nm carbon nanocapillary. (a) Density and normalized velocity profiles (b) A comparison of Knudsen diffusion and simulations molecular fluxes of methane.

Figure 9—DCV-GCMD simulations of neon flow in a 4 nm carbon nanocapillary. (a) Density and normalized velocity profiles (b) A comparison of Knudsen diffusion and simulations molecular fluxes of neon.
The enhancement factor variation with respect to excess adsorption is shown in Fig. 10. The excess adsorption and Knudsen diffusion molecular flux of all three gases are plotted without distinguishing different gas types. The enhancement factors for both diameters (2 and 4 nm) are included in this figure. The points which are vertically aligned are the simulations at the same pressure but different pressure gradients. A trend line is plotted using the least square method for eye guidance. As shown, the higher the excess adsorption is, the higher the enhancement factor will be for all the gases (whether adsorbing or non-adsorbing) and all the tube diameters (2 and 4 nm) studied. The 2 nm tube generally exhibits higher enhancement factors in comparison with the 4 nm tube.

Conclusions

Based on DCV-GCMD simulations results, the following conclusions are made:

- 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 4 nm tube diameters.
- Plug shaped flow profiles is found for flow of all the gases studies in this work.
- The Knudsen diffusion model underestimates the molecular flux by at most one order of magnitude.
- The underestimation of Knudsen diffusion model for flow of low adsorbing gases is less than that of high adsorbing gases flow in carbon nanocapillaries.
- The enhancement factor of gases is demonstrated to be a strong function of excess adsorption.
- The transport models based on slip theory (such as R13 or Navier-Stokes), are not able to predict the flow gases in organic nanopores.

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References


