Modeling CO₂ Transport and Sorption in Carbon Slit Pores
Abby Kirchofer, ‡ Mahnaz Firouzi, ‡ Peter Psarras, ‡‡ and Jennifer Wilcox*,‡

*Department of Energy Resources Engineering, Stanford University, 367 Panama Street, Stanford, California 94305, United States
‡Department of Chemical and Biological Engineering, Colorado School of Mines, 1613 Illinois Street, Golden, Colorado 80401, United States

ABSTRACT: The need to reduce carbon dioxide (CO₂) emissions is one of the most significant environmental challenges facing society. Carbon capture and storage (CCS) has the potential to mitigate gigatons of anthropogenic CO₂ emissions, and is regarded as a key method for global-scale CO₂ emissions reduction. Understanding CO₂ adsorption and transport is crucial to the development of successful carbon capture and storage technologies. This work investigates the use of an improved potential model to directly treat CO₂ electrostatic and geometric properties, thereby more accurately describing the fluid–fluid and fluid–wall interactions that determine adsorption capacity and dynamics. Nonequilibrium molecular dynamics (NEMD) simulations are conducted to investigate pore entrance effects on transport through carbon pores. CO₂ interactions with pure and hydroxyl-functionalized slit and step carbon pores are simulated to investigate pore entrance effects and trade-offs among pore size, chemistry, capacity, and transport. The relative importance of (1) CO₂ geometry and flexibility, (2) electrostatic interactions, and (3) pore surface chemistry is investigated. The transport investigations of CO₂ through carbon pores suggest that fluid density, diffusivity, and permeability are sensitive to the potential model used to describe molecular interactions, pore size, pore geometry, and surface chemistry. The differences in capacity and dynamic properties between the step and slit cases show the importance of investigating transport using models that account for different types of mass transfer resistance. The current work highlights the importance of the potential and structure models in molecular simulations of adsorption and dynamics. These fundamental studies indicate the significance of molecular-scale phenomena for carbon dioxide transport in the confined spaces for CCS applications.

1. INTRODUCTION
The need to reduce carbon dioxide (CO₂) emissions is one of the most significant environmental challenges facing society. Carbon capture and storage (CCS) has the potential to mitigate gigatons of anthropogenic CO₂ emissions, and is regarded as a key method for global-scale CO₂ emissions reduction. However, the feasibility of wide-scale deployment of CCS hinges on improving the economic and environmental viability of CCS technologies. Understanding CO₂ adsorption and transport is crucial to the tuning of adsorbent material properties to optimize capture processes, and therefore the development of cost-effective and efficient CCS technologies. More generally, developing an enhanced understanding of transport in confined spaces is necessary for the advancement of myriad technologies, including gas-solid reactions, separation processes, gas storage and heterogeneous catalysis. Transport of molecules in confined systems (i.e., in microporous materials) differs greatly from that of bulk-phase transport, as adsorption and diffusion are coupled, and diffusion may be hindered by strong adsorption or activation barriers (e.g., pore entrance effects). For systems that include charged or polarizable sorbents, or sorbents with dipole or quadrupole moments, electrostatic interactions can play an important role in sorption and transport. Previous work suggests that the type, shape and chemistry of the pore model used for molecular simulations can significantly impact adsorption results, and that such material properties could be used to enhance sorbent capacity, selectivity or uptake. However, investigations of adsorption dynamics tend to rely on simplified potential and structure models; to date, little work has investigated the transport of CO₂ on carbon materials using realistic models for fluids and solids. More so than investigations of adsorption and capacity, most of the literature regarding transport and kinetics treats CO₂ as a spherical molecule or as a rigid linear molecule.

The current work investigates CO₂ transport in porous carbon materials using more realistic potential and structural models, with the aim of developing an improved understanding of mass transfer resistance in nanopores. Previous work supports the need for additional work investigating the complex nature of mass transfer through nanoporous materials.

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Depending on the system investigated, the mass transfer mechanisms and dominating mass transfer resistances can vary widely. Such a range is promising, in that it suggests that material and molecular properties could be tuned to enhance mass transfer for a given process; however, to take advantage of such properties will require an improved mechanistic understand of adsorption dynamics at the nanopore scale. As Zimmermann et al.\textsuperscript{13} point out for zeolites, confusion remains about the basic processes of adsorption and transport in micropores, despite the great number of studies investigating adsorption and transport in zeolites. For porous carbon materials, a similar state of confusion exists, and further work is required to determine the influence of various material properties and conditions on transport and mass transfer resistances. The accuracy of MD simulations hinges on the accuracy of the potential models used to describe the system under investigation. Numerous studies have shown that predicted adsorption behavior could depend strongly on whether chemical heterogeneity, molecular geometry, or electrostatic interactions are accounted for. The potential model EPM2 developed by Harris and Yung\textsuperscript{14} successfully reproduces the vapor-liquid coexistence curve, and has been modified previously to include bond angle flexibility.\textsuperscript{15,16} Babaeaei and Jiang\textsuperscript{17} investigated diffusion and separation of CO\textsubscript{2} and CH\textsubscript{4} in carbon (C\textsubscript{168} schwarzite) and non-carbon (silicalite and IRMOF-1) sorbents using EMD. CO\textsubscript{2} was modeled using the 3-site model, fitted to experimental data by Hriotani et al.\textsuperscript{18} with point charges, rigid C-O bonds, and, for the non-carbon sorbents only, flexibility. The authors do not discuss the impact of accounting for molecular flexibility on adsorption dynamics. Skoulidas et al.\textsuperscript{10} investigated CO\textsubscript{2} diffusion in carbon nanotubes with diameters from 1.1 to 5.4 nm using equilibrium MD (EMD), and compared results based on spherical (1C-LJ) and linear (EPM2) models for CO\textsubscript{2}. However, the investigation did not account for CO\textsubscript{2} flexibility, possible defects or surface functionality on the carbon surface, or pore entrance and exit effects. Lim et al.\textsuperscript{12} investigated CO\textsubscript{2} permeability in carbon slit pores, using EMD and GC/MS to predict diffusivity and permeability. The authors compare results for spherical (1C-LJ) and linear (3-site LJ with point charges) models of CO\textsubscript{2}, and report that diffusion of CO\textsubscript{2} in small pores is underestimated by the spherical model, because such a model does not fit in small pores as well as the linear model. Additionally, Lim et al.\textsuperscript{12} report permeabilities that are three times greater than those reported based on macroscopic measurement, and suggest that the discrepancy between simulation and experimental results exists because the simulations do not account for the rate-limiting step of mass transport through the pore mouth, or for pore connectivity and tortuosity, which can play an important role in limiting mass transfer in real porous systems. The authors state that diffusion in CMS adsorbents is limited by pore-mouth resistance and estimate that pore mouth resistance is roughly 2 orders of magnitude greater than pore intracrystalline resistance, so theoretical simulations that do not take into account entrance effects would predict increased permeability and diffusivity compared to experimentality. As Lim et al.\textsuperscript{12} note, both adsorption and diffusion impact flux and permeability in microporous systems; therefore, flux and permeability do not increase monotonically with pore width. The current work investigates the use of the flexible quadrupole (FQ) model for CO\textsubscript{2}, an improved potential model to more accurately describe fluid-fluid and fluid-wall interactions by directly treating CO\textsubscript{2} electrostatic and geometric properties. The FQ model is based on the EPM2 model developed by Harris and Yung,\textsuperscript{14} but modified to include bond angle flexibility. To the author’s knowledge, potential models incorporating CO\textsubscript{2} bond flexibility have only been used to investigate transport in non-carbon systems such as silicates or clays.\textsuperscript{15,17}

Previous work also highlights the need to account for structural heterogeneity and pore connectivity to accurately predict transport properties of porous materials.\textsuperscript{3,19} Newsome and Sholl\textsuperscript{20} investigated mass transfer resistances for gas transport through carbon nanotube membranes, and estimate the relative importance of surface resistance (i.e., interfacial resistance to diffusion through the pore entrance or exit) in comparison to intracrystalline resistance (i.e., resistance to diffusion inside the pore). Previous work by Newsome and Sholl\textsuperscript{21} suggests that surface resistances for a permeating species will increases with increasing adsorption strength of that species, or with decreasing temperature. Cai et al.\textsuperscript{22} investigated the effect of the pore wall model on equilibrium and nonequilibrium MD investigations of transport in graphitic slit pores, and found that the results can vary significantly depending on which pore wall model (e.g., smooth or structured) is used to describe a given pore. Firouzi et al.\textsuperscript{19} investigated transport and separation of supercritical CO\textsubscript{2}–alkane mixtures in carbon molecular sieve (CMS) membranes using a composite pore model which included three connected graphitic slit pores with heights of 10, 23, and 77 Å. The pore wall C atoms and CO\textsubscript{2} and CH\textsubscript{4} molecules are treated as 1C-LJ spheres, while the larger alkanes are treated as flexible chains of CH\textsubscript{3} and CH\textsubscript{3} united-atom (UA) centers. Additionally, Firouzi and Wilcox\textsuperscript{23} investigated the transport of CO\textsubscript{2} in a carbon-based 3-D pore-network model, and show that morphological characteristics such as porosity play a significant role in determining the flow and transport properties of fluids. The authors conclude that transport properties can be dependent on pressure gradient and direction, depending on the porous material under consideration, and discussed the mass transfer mechanisms and resistances that can vary with pore size. Zimmermann et al.\textsuperscript{13} studied surface effects on equilibrium transport of hydrocarbon gases in zeolite pores. Depending on the conditions, material, and gases, the importance of surface effects ranges from negligible to dominating in terms of limiting mass transfer.

Given the importance of porous structure properties in influencing kinetics, there is need to develop an improved understanding of pore entrance effects\textsuperscript{9,10,12,19} and the effect of pore surface chemistry on transport. In order to develop optimal sorbents, more accurate models are required to explore and develop understanding of adsorption and transport, especially in regards to tradeoffs associated with key material properties such as surface chemistry and/or pore size. For instance, functional groups may be used to increase (or optimize) the adsorption energy, but functional groups also act to physically narrow the pore by occupying a certain volume of pore space. In confined space adsorption and diffusion are coupled, and transport may be controlled by activated diffusion or molecular sieve-like mechanisms, dependent on sorption behavior, sorbent pore morphology, and sorbate molecular geometry.\textsuperscript{24} This work attempts to develop an improved understanding of the tradeoff between capacity and kinetics, and to highlight the importance of kinetics in optimizing sorbents for CCS.
In the current work, the relationship between surface resistance, adsorption effects, and temperature will be investigated by considering the effect of temperature, fluid-fluid and gas-fluid potentials, surface chemistry, and pore structure on CO₂ transport in carbon slit pores. Non-equilibrium molecular dynamics (NEMD) simulations were conducted to investigate pore entrance effects on transport through carbon pores. CO₂ transport in various graphitic pores was simulated using the dual control-volume grand canonical molecular dynamics (DCV-GCMD) method to apply an external pressure gradient. The DCV-GCMD simulation was combined with configurational-bias Monte Carlo method, an approach first implemented by Firouzi et al. to investigate the transport of CO₂ molecules treated with the FQ model. To determine the significance of electrostatic interactions on CO₂ transport through pore entrances, simulations were conducted using potential models of varying levels of sophistication. Additionally, we consider pure and hydroxyl-functionalized slit and step pores in the micro- to mesopore range, to investigate pore entrance effects and tradeoffs between pore size, chemistry, capacity, and transport. The relative importance of 1) CO₂ geometry and flexibility, 2) electrostatic interactions, and 3) pore surface chemistry is investigated.

Figure 1. Schematic of the carbon pore model used in the simulations. P₁ and P₂ represent the high pressure and low pressure in the control volumes, respectively.

Figure 2. Location of hydroxyl functional groups in the pore model.

To the authors’ knowledge, the current work is novel and contributes to the literature in the following ways: First, previous investigations of CO₂ transport through carbon nanopores have not included such a realistic potential model, which directly treats the geometry, flexibility, and quadrupole moment of CO₂. Second, the investigation of entrance effects including a direct treatment of fluid-fluid and fluid-wall electrostatic interactions is novel. Third, the impact of surface functional groups on CO₂ transport through carbon nanopores has not been investigated previously. After describing the pore models in Section 2 and CO₂ molecular models and interaction potentials in Section 3, we provide the molecular dynamics simulation details in Section 4. The results are presented and analyzed in Section 5, and the study is summarized in Section 6.

2. PORE MODELS

Porous carbon materials have been modeled extensively as idealized independent slit pores with smooth graphitic walls and infinite connectivity. Everett and Powl described carbon pores as the absence of one, two, or three graphene layers from bulk graphite (corresponding to pore sizes of 7, 11, and 14 Å), and theorized that the microporosity of carbon materials is accurately described by slit-pore models. Although numerous molecular simulations of CO₂ adsorption and transport in
porous carbons have been conducted, to date accurate prediction of adsorption dynamics remains challenging.

In this paper, we focus on pore entrance effects on transport through carbon pores. Investigations were carried out for graphitic step pores, which consist of slit pores in series with inner (small) pore heights of 10, 15, 20, 25, and 50 Å. Figure 1 provides a schematic of the step pore model, and shows the location and relative size of the control volumes for two example structures with varying pore heights. In the current work, periodic boundary conditions are applied in the y direction (i.e., perpendicular to the plane of this page). The pore wall consists of three graphene layers throughout the system, and an additional three graphene layers create the step and form the inner pore walls. In such a model, the outer pore height $z_1$ varies as a function of the inner pore height $z_2$, such that $z_1 = z_2 + 20.1$ Å, as depicted in Figure 1. For most cases, the inner pore is centered in the transport region, and the inner pore length is two-thirds the length of the transport region. For select cases, variations of inner pore location or length were considered, to investigate the effect of the small pore length and position on CO$_2$ transport properties.

To investigate the effect of surface chemistry, pure and hydroxyl-functionalized graphene layers were tested. The structures are based on DFT-relaxed structures by Liu and Wilcox multiplied to generate the overall step pore. For the hydroxyl-functionalized structures, only the inner graphene layers of the small pore are functionalized with OH-groups on the basal plane of the graphene layer, as detailed in Figure 2. Traditional slit pore structures were investigated to determine the relative importance of entrance versus intra micropore resistance. Figure 3 shows the 20 Å slit pore structure in comparison to the 20 Å step pore structure; as the figure shows, the entire slit pore structure is similar to the small pore of the step pore structure, and the total system dimensions are equal.

3. CO$_2$ MOLECULAR MODELS AND INTERACTION POTENTIALS

To accurately model fluid behavior and transport, it is imperative that realistic potential models are used to describe molecular interactions. In this work, CO$_2$ molecules are represented using the either the simple one-site Lennard-Jones potential model or the Flexible Quadrupole potential model.

Whereas the effective molecular parameters attempt to account for electrostatic interactions, the single-site per molecule limits the ability of the 1C-LJ model to accurately describe electrostatic interactions of molecules with dipole or quadrupole moments, such as CO$_2$. In comparison to the 1C-LJ model, the flexible quadrupole (FQ) model accounts for the geometry, flexibility, and intrinsic quadrupole moment of CO$_2$. The FQ model is more computationally expensive, but will allow a more realistic model of CO$_2$ transferring in confined spaces. The details for the one-site Lennard-Jones (1C-LJ) and FQ models are provided in the Supporting Information. Table 1 provides the potential parameters and charges for the materials investigated in the current work.

<table>
<thead>
<tr>
<th>atom or molecule</th>
<th>$\epsilon$ (kJ)</th>
<th>$\sigma$ (Å)</th>
<th>$Q$ (E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>240</td>
<td>3.75</td>
<td></td>
</tr>
<tr>
<td>He</td>
<td>10.9</td>
<td>2.64</td>
<td></td>
</tr>
<tr>
<td>C (pore wall)</td>
<td>28</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>OH (pore wall)</td>
<td>85.27</td>
<td>3.034</td>
<td></td>
</tr>
<tr>
<td>C (CO$_2$)</td>
<td>28.999</td>
<td>2.785</td>
<td>0.6645</td>
</tr>
<tr>
<td>O (CO$_2$)</td>
<td>82.997</td>
<td>3.064</td>
<td>−0.33225</td>
</tr>
<tr>
<td>C (pore wall)</td>
<td>28</td>
<td>3.4</td>
<td>±0.0498</td>
</tr>
<tr>
<td>O (pore wall)</td>
<td>85.27</td>
<td>3.034</td>
<td>−0.3</td>
</tr>
</tbody>
</table>

In the previous works, authors modeled smooth homogeneous graphene surface using the Steele 10−4−3 potential to predict CO$_2$ transport properties in carbon pores. In the current work, the atoms comprising the graphitic pore walls are treated explicitly as 1C-LJ sites to address the problem of representing the morphology of a carbon surface by a realistic model including discrete carbon atoms. We used the LJ potential for the interactions between CO$_2$ and the individual carbon atoms on the walls, arranged as in graphite with a cutoff distance of 3.9 $\sigma_C$.

In simulations where CO$_2$ is treated using the FQ model, the charges of the individual wall atoms are included to describe the electrostatic interactions between CO$_2$ and the pore wall.
4. MOLECULAR DYNAMICS SIMULATION

The dual control-volume GCMD technique (DCV-GCMD), which has been used extensively in the past by several research groups and described in detail in the previous works by Firouzi et al., was employed to investigate the transport properties of CO$_2$ molecules. In the MD simulations, the Verlet velocity algorithm was used to integrate the equations of motion with a dimensionless time step, $\Delta t^*=5 \times 10^{-3}$ (i.e., $\Delta t = 0.00685$ ps). The equations of motion were integrated with up to $1 \times 10^7$ time steps to ensure that steady state had been reached, after which the properties, such as concentration and velocity profiles, fluxes, etc., were calculated and averaged over the last one million time steps. More details for MD simulations are provided in the Supporting Information. In this work the walls are rigid. We computed several quantities of interest, including the density profiles of the component $i$ along the $x$- and $z$-directions, $p_i^x(x)$ and $p_i^z(z)$, respectively. As discussed next in greater detail, these quantities are important in understanding the gas transport properties in nanoconfined pore systems. In addition, for each component $i$ the flux, $J_i$, in the direction of the applied pressure gradient was calculated by measuring the net number of gas molecules crossing a given $yz$ plane. The permeability, $K_i$, of component $i$ was then calculated using

$$K_i = \frac{J_i}{\Delta P_i/nL} = \frac{nLJ_i}{\Delta P_i}$$

where $\Delta P_i = x_i \Delta P$ is the partial pressure drop for component $i$ along the pore, with $x_i$ being the mole fraction of component $i$, $\Delta P$ the total pressure drop imposed along the pore, and $nL$ the
pore length in the transport direction. In the current work, the pore length is defined as the distance from the upstream CV to the downstream CV, which includes both the large and small pore segments of the transport region, and equals 148 Å. Time-

Figure 6. Z density profiles for 25 Å cases at 25 or 75 °C and 50–10 atm.

Figure 7. Projections of CO₂ in 25 °C and 50–10 atm in the y direction for (a) pure-FQ, (b) OH-FQ, (c) pure-LJ, and (d) OH-LJ 20 Å step pores; the projection depth equals 85.4 Å.
averaged density profiles for a given case are computed using the bin method for the $x$ and $z$ directions, in which the simulation cell is divided into bins along a given axis, and the number of molecules in each bin is recorded. The transport diffusivity $D$ is calculated as a function of flux and the concentration gradient across the transport region

$$J = -D \frac{\Delta \rho}{x_{\text{transport}}}$$

where $x_{\text{transport}}$ is the length of the transport region and $\Delta \rho$ is the change in density across the transport region (no./cm$^3$), defined as the density difference between the upstream and downstream control volumes. In what follows, we present and discuss the results of our simulation.

5. RESULTS AND DISCUSSION

Impact of Different Potential Models. For the LJ simulations, flux data were collected at different locations along the transport pore to ensure that the fluxes are equal for a given pore height at different locations. More details are provided in the Supporting Information. Snapshots of CO$_2$ in corresponding LJ and FQ cases are shown in Figure 4 as projections in the $y$-direction (perpendicular to the transport direction), to provide a visual comparison of the distribution of fluid particles inside pores simulated using the LJ and the FQ model. The depth of the snapshots equals the length of the simulation cell in the $y$ direction, 85.4 Å. The snapshots show higher density in the upstream CV (where $P = 50$ atm) than the downstream CV (where $P = 10$ atm). As the snapshots highlight, for both FQ and LJ cases the CO$_2$ density is highest near the pore walls. To gain further insight into the differences between LJ versus FQ cases, density profiles along the $z$ direction were considered at various positions along the $x$ (transport) direction, since such profiles depict how the density changes as the fluid progresses through the pore. Figure 5 provides density profiles along the $z$ direction for LJ and FQ 10 and 20 Å cases at 75 °C. Figure 6 provides select profiles for 25 Å FQ and LJ cases at 25 and 75 °C. As expected, for both the LJ and FQ cases, the density profiles reflect the higher density in the lower temperature (25 °C) cases. In all cases, the density profiles reflect the higher density in the LJ cases than the FQ cases of corresponding pore size and conditions. The CO$_2$ molecules are primarily located in layers adjacent to the pore wall, and the CO$_2$ molecules must shift closer to the pore center in the $z$ direction in order to transition into the inner pore. In all cases, the density increases just before the inner pore entrance; however, this increase is more dramatic for LJ cases. Furthermore, the density profiles in the inner pore entrance for the LJ cases show very small density, while for the FQ cases the density throughout the inner pore height is significant. The differences in the LJ and FQ profiles suggest that the FQ fluid is able to transition through the pore entrance more readily than the LJ fluid.

Pore Model Chemistry and Structure Effects. Transport through slit pores was investigated to provide context for the step pore results. The results from a given slit case can be considered a baseline for the corresponding step case results, and the differences in density, flux, and diffusivity are a measure of the significance of pore entrance effects. Furthermore, by contrasting the slit pore LJ and FQ cases we gain insight into the importance of using a more realistic potential model to accurately predict transport properties. Figure 7 provides snapshots of CO$_2$ in LJ and FQ pure and OH 20 Å cases, shown as projections in the $y$ direction (perpendicular to the transport direction). The depth of the snapshots equals the length of the simulation cell in the $y$ direction, 85.4 Å. The snapshots show the higher density in the upstream CV (where $P = 50$ atm) than the downstream CV (where $P = 10$ atm). As the snapshots highlight, the density in the inner pores of the OH cases fluctuates due to the location of OH groups. Figure 8 provides density profiles along the $z$ direction for pure and OH 20 Å cases at 75 °C. The profiles for the pure and OH cases are similar, although the density peaks for each position in the pore are slightly lower for the OH case than the pure case. Additionally, there is slight asymmetry in the OH entrance and inner pore profiles, due to the asymmetry in the position of OH groups on opposing pore walls. Future work should include the investigation of different functional groups and different surface coverage. It is important to note that the densities in the upstream CV’s are higher in the step cases than the corresponding slit cases, despite the equal dimensions of the CV for corresponding step and slit cases; this effect is likely because the CV in the step cases is influenced by the inner pore, and the density is higher because of pressure buildup at the pore entrance. This effect decreases with increasing pore height, likely because the significance of the entrance effects decreases with increasing pore height.

Transport Properties. The flux, diffusivity, and permeability for each case were determined based on the simulation results. The direct output from the simulations includes the number of passing molecules at the transport region entrance and exit at a given time step. Figure 9 provides the number of
passing CO$_2$ molecules for FQ and LJ step pores at 25 or 75 °C and 50–10 atm.

**Figure 9.** Number of passing CO$_2$ molecules in step pores at 25 or 75 °C and 50–10 atm.

As expected, the number of passing CO$_2$ molecules is greater at 25 °C than 75 °C for a given pore height and potential model. It is interesting to note that the difference between the low and high temperature cases decreases with increasing pore height, presumably because temperature effects are greater for the adsorbed phase (i.e., molecules forming a higher density layer adjacent to the pore wall) than the bulk phase molecules in the pore center, and the ratio of adsorbed to bulk phase decreases with increasing pore height. Additionally, for a given pore height, the LJ cases have lower passing numbers than the corresponding FQ cases, and this difference increases with increasing pore height. Likely this is because for pure graphene pores the difference between the LJ versus FQ fluid–wall interactions is less significant than the difference between the LJ versus FQ fluid–fluid interactions, and the importance of fluid–fluid interactions increases with increasing pore height. From the flux and density results, diffusivity and permeability for each case was determined. Table 2 summarizes diffusivities for 20 and 50 Å cases. In general, diffusivity increases with increasing temperature; however, this effect is more significant for FQ cases than for LJ cases. This effect may be due to the relationship between density and temperature: at higher temperature, the density is lower and there is less resistance to motion because the pore is less packed. Permeability, on the other hand, tends to decrease with increasing temperature, largely due to the decrease in density with increasing temperature.

Previous results predict collective diffusivities for CO$_2$ in carbon slit pores of 5.96 × 10$^{-5}$ to 1.29 × 10$^{-4}$ cm$^2$/s at 25 °C and 5 atm, and 6.27 × 10$^{-5}$ to 1.38 × 10$^{-4}$ cm$^2$/s in slit pores at 45 °C and 5 atm. The results are in agreement with previous investigations of transport using molecular simulation, which predict permeabilities for CO$_2$ in carbon step pores at 55 °C and 45 atm of 6.1 × 10$^{-7}$ to 5.5 × 10$^{-6}$ mol-cm/min-cm$^2$-atm$^9,19$ and in carbon slit pores at 35 °C and 5 atm of 4.0 × 10$^{-5}$ to 6.5 × 10$^{-5}$ mol-cm/min-cm$^2$-atm$^{12}$. A more detailed comparison is not possible because of the differences in potential model, structure model, and thermodynamic conditions simulated in the current work and previous investigations from the literature. For more explicit and detailed comparison, future work should include combined experimental and theoretical investigations. This would enable benchmarking simulation results, for instance to confirm that the computationally expensive FQ model (in comparison to the LJ model) provides a more realistic depiction of CO$_2$ adsorption dynamics.

**Table 2.** Diffusivity and Permeability for Select Cases at 50–10 atm

<table>
<thead>
<tr>
<th>case</th>
<th>diffusivity (cm$^2$/s)</th>
<th>permeability × 10$^5$ (mol-cm/min-cm$^2$-atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LJ</td>
<td>FQ</td>
</tr>
<tr>
<td>step–20 (25 °C)</td>
<td>0.0027</td>
<td>0.0050</td>
</tr>
<tr>
<td>step–20 (75 °C)</td>
<td>0.0030</td>
<td>0.0063</td>
</tr>
<tr>
<td>OH–step–20 (25 °C)</td>
<td>0.0010</td>
<td>0.0014</td>
</tr>
<tr>
<td>OH–step–20 (75 °C)</td>
<td>0.0011</td>
<td>0.0011</td>
</tr>
<tr>
<td>slit–20 (25 °C)</td>
<td>0.0217</td>
<td>0.0294</td>
</tr>
<tr>
<td>step–50 (25 °C)</td>
<td>0.0036</td>
<td>0.0075</td>
</tr>
<tr>
<td>step–50 (75 °C)</td>
<td>0.0046</td>
<td>0.0110</td>
</tr>
<tr>
<td>OH–step–50 (25 °C)</td>
<td>0.0021</td>
<td>0.0035</td>
</tr>
<tr>
<td>OH–step–50 (75 °C)</td>
<td>0.0030</td>
<td>0.0037</td>
</tr>
<tr>
<td>slit–50 (25 °C)</td>
<td>0.0157</td>
<td>0.0155</td>
</tr>
</tbody>
</table>

for 20 and 50 Å cases. As expected, the number of passing CO$_2$ molecules is greater at 25 °C than 75 °C for a given pore height and potential model. It is interesting to note that the difference between the low and high temperature cases decreases with increasing pore height, presumably because temperature effects are greater for the adsorbed phase (i.e., molecules forming a higher density layer adjacent to the pore wall) than the bulk phase molecules in the pore center, and the ratio of adsorbed to bulk phase decreases with increasing pore height. Additionally, for a given pore height, the LJ cases have lower passing numbers than the corresponding FQ cases, and this difference increases with increasing pore height. Likely this is because for pure graphene pores the difference between the LJ versus FQ fluid–wall interactions is less significant than the difference between the LJ versus FQ fluid–fluid interactions, and the importance of fluid–fluid interactions increases with increasing pore height. From the flux and density results, diffusivity and permeability for each case was determined. Table 2 summarizes diffusivities for 20 and 50 Å cases. In general, diffusivity increases with increasing temperature; however, this effect is more significant for FQ cases than for LJ cases. This effect may be due to the relationship between density and temperature: at higher temperature, the density is lower and there is less resistance to motion because the pore is less packed. Permeability, on the other hand, tends to decrease with increasing temperature, largely due to the decrease in density with increasing temperature.

Previous results predict collective diffusivities for CO$_2$ in carbon slit pores of 5.96 × 10$^{-5}$ to 1.29 × 10$^{-4}$ cm$^2$/s at 25 °C and 5 atm, and 6.27 × 10$^{-5}$ to 1.38 × 10$^{-4}$ cm$^2$/s in slit pores at 45 °C and 5 atm. The results are in agreement with previous investigations of transport using molecular simulation, which predict permeabilities for CO$_2$ in carbon step pores at 55 °C and 45 atm of 6.1 × 10$^{-7}$ to 5.5 × 10$^{-6}$ mol-cm/min-cm$^2$-atm$^9,19$ and in carbon slit pores at 35 °C and 5 atm of 4.0 × 10$^{-5}$ to 6.5 × 10$^{-5}$ mol-cm/min-cm$^2$-atm$^{12}$. A more detailed comparison is not possible because of the differences in potential model, structure model, and thermodynamic conditions simulated in the current work and previous investigations from the literature. For more explicit and detailed comparison, future work should include combined experimental and theoretical investigations. This would enable benchmarking simulation results, for instance to confirm that the computationally expensive FQ model (in comparison to the LJ model) provides a more realistic depiction of CO$_2$ adsorption dynamics.

**Figure 10.** Permeabilities for LJ and FQ pure 50–10 atm cases.

Permeabilities for slit pore cases are drastically higher than permeabilities for the corresponding step pore cases, because the slit pore cases do not involve transfer through a pore entrance. In other words, the slit cases do not include the resistance to mass transfer due to the step through the pore entrance; therefore, permeability through the step cases would only approach permeability through the slit cases if there was no barrier or resistance to mass transfer through the pore entrance. Given the difference in predicted permeabilities and diffusivities for slit and step cases, the results highlight the importance of pore entrance effects in limiting CO$_2$ transport through carbon nanopores. Figure 11 provides the permeabilities for pure LJ and FQ step pores at 25 or 75 °C and 50–10 atm or 10–5 atm. The FQ cases appear more sensitive to temperature and pressure conditions than the corresponding LJ cases.

**Figure 11.** Permeabilities for pure and OH LJ and FQ step pores at 25 or 75 °C and 50–10 atm. Regardless of pore height, potential model, or temperature, the OH cases have lower permeability than the corresponding pure cases. As with the pure cases, the FQ 25 °C cases gave markedly higher permeabilities than the cases investigated. Figure 13 shows the...
diffusivities for pure LJ and FQ step pores at 25 or 75 °C and 50–10 atm or 10–5 atm. For comparison, the Knudsen and molecular diffusivities, $D_K$ and $D_m$, respectively, are plotted. In general, the diffusivity is higher for the 50–10 atm cases than for the corresponding 10–5 atm cases, and higher for the 75 °C cases than the corresponding 25 °C cases. However, the effect of pressure appears greater for the LJ cases, and the effect of temperature appears greater for the FQ cases. Furthermore, as pore size decreases, the effect of temperature appears to decrease for both LJ and FQ cases.

As expected and shown in Table 2, the diffusivities for slit cases, which do not account for pore entrance effects, are higher than the diffusivities for the corresponding step cases, which include mass transfer resistance due to the step into the inner pore. It is interesting to note that the diffusivity for step cases tends to increase with increasing pore height, likely because the mass transfer resistance due to the step into the inner pore plays a less significant role as the inner pore height increases, while the diffusivity for slit cases tends to decrease with increasing pore height in the micropore range (i.e., for pore heights less than 20 Å). Recalling that diffusivity is the proportionality constant for the concentration gradient and the flux, this result is due to the relative changes in the concentration gradient and flux as pore height increases: for
the 10–20 Å cases, the ratio of the change in flux to the change in concentration gradient decreases with increasing pore height, therefore the diffusivity decreases with increasing pore height. For the micropore slit cases, the density throughout the system is greater than the critical density, and the concentration gradient throughout the system is small; there is a significant increase in concentration gradient for the 20 Å cases, and thereafter the concentration gradient decreases with increasing pore height. Given this increase in concentration gradient in the micropore cases, which outweighs the change in flux, the diffusivity decreases. The difference in trends and quantitative results between the step and slit cases highlights the importance of investigating transport using models that account for different types of mass transfer resistance.

6. CONCLUSIONS

The current work highlights the importance of the potential and structure models in molecular simulations of transport properties. The DCV-GCMD investigations of CO2 transport through carbon pores suggest that fluid density, diffusivity, and permeability are sensitive to the potential model used to describe molecular interactions, pore height, pore type, and surface chemistry. The difference in trends and quantitative results between the step and slit cases shows the importance of investigating transport using models that account for different types of mass transfer resistance. The LJ cases predict significantly higher densities than the corresponding FQ cases, and show heightened sensitivity to pore height. On the other hand, the capacity and kinetic results for FQ cases are more sensitive to changes in temperature and pressure. For both LJ and FQ cases, the pore entrance and exit effects decrease with increasing pore height, because as the pore height increases the importance of the step diminishes. Pore entrance and exit effects, specifically the density peaks, are more significant for the LJ cases. Also, the transition region for the inner pore entrance, where the density profile changes due to the inner pore entrance, is shorter for the FQ cases than the LJ cases. The results suggest that the FQ fluid transitions through the pore entrance more readily than the LJ fluid. The current work on CO2 transport provides a preliminary step forward in understanding the trade-offs between adsorption and dynamics and in providing the molecular results required for improved process modeling. For CCS, as well as other emerging technologies, there is great need for molecular simulation of adsorption and transport to link material properties to the process scale, so that material properties can be optimized for a given process. Future work at the molecular scale should consider mixtures of CO2, CH4, H2O and other gases relevant to capture processes. Future work should also include the investigation of different functional groups, different surface coverages, and pore entrance effects as a function of step height. Depending on the application of the work, functional groups could be tailored to represent chemical heterogeneity of natural carbons such as coal, or to represent synthetic materials functionalized to improve capture properties.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b06780.

Description of potential models for sorbate representation, flux data collection locations, example flux data results (PDF)

AUTHOR INFORMATION

ORCID

Peter Psarras: 0000-0002-5302-3412
Jennifer Wilcox: 0000-0001-8241-727X

Notes

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REFERENCES


