



Methane and CO₂ Adsorption and Transport in Carbon-based Systems from Experiments and Molecular Simulation

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Carbon capture and sequestration is one strategy that could potentially mitigate gigatons of CO₂ emissions per year; however, technical obstacles have thus far hindered wide-scale deployment of this strategy. To design efficient and reliable strategies for either carbon capture or sequestration at the full-scale, one needs to understand the chemical and physical properties of CO₂ and its interaction with its local surroundings at the molecular-scale. To investigate the chemical and physical properties of CO₂ and its local surroundings at the molecular-scale, surface characterization studies are carried out alongside theoretical model efforts. Experimental investigation of CO₂ interactions with organic-based porous materials ranging in complexity from functionalized graphene and activated carbon to various-rank coal and gas shale samples to create a set of realistic models that take into account both surface and pore heterogeneity. Integration of theory and experiments takes place to allow for the relevant physics at the molecular-level to be revealed. Determining adsorption and transport phenomena of CO₂ (and mixtures, including H₂O, and CH₄) within the model pore systems can be used to understand the complex pore matrices of carbon-based sorbents, coal, and the organic components of gas shale that are crucial to determining their carbon capture or sequestration potential.

Non-equilibrium molecular dynamics (NEMD) simulations of pure carbon dioxide, methane, helium and their mixtures have been carried out in carbon slit pores to investigate gas slippage and Klinkenberg effects in the organic matrices of coal and gas shale rocks. NEMD techniques are ideally suited for the experimental situation in which an external driving force, such as a chemical potential or pressure gradient, are applied on the system. Simulations have been conducted to determine the effect of pore size and exposure to an external potential on the velocity profile and slip-stick boundary conditions. The simulations indicate that molecule-wall collisions influence the velocity profile, which deviates significantly from the Navier-Stokes hydrodynamic prediction for micro and mesopores. Also, the shape of the velocity profile is found to be independent of the applied pressure gradient in micropores. The results indicate that the velocity profile is uniform for pore sizes less than 2 nm (micropores). As pore sizes increase to 10 nm, parabolic profiles are observed due to the reduced interaction of gas molecules with the pore walls. Interestingly, in small pores unlike in large pores, the gas velocity at the walls is non-zero and predicted gas transport is somewhat enhanced as the gas flow transitions from a parabolic velocity profile to plug-flow.

In addition, a 3-D pore network, representative of porous carbon-based materials, has been generated atomistically using the Voronoi tessellation method. Simulations have been carried out to determine the effect of the pore structure and modeled viscosity on permeability and Klinkenberg parameters. The use of the bulk-phase viscosity for estimating the permeability of CO₂ in units of Darcy in a 3-D micropore network is not an appropriate assumption as it significantly underestimates the CO₂ permeability given that CO₂ is an adsorbing gas with strong pore wall interactions. On the other hand, since the transport properties of CH₄ are less influenced by the pore walls compared with CO₂, the use of the bulk-phase CH₄ viscosity estimates are a reasonable assumption.

The application of this work is to advance our understanding of gas transport and to provide insight into mechanisms of gas-surface interactions in the complex natural systems such as gas shale so that we can make accurate capacity estimates in addition to assisting in enhancing natural gas recovery from these systems. These results will potentially have important implications on CO₂ adsorption and transport in carbon-based materials and geologic formations and may provide an understanding of the limitations of the use of bulk-phase fluid viscosities to model transport properties for nanoconfined fluids.