The Impact of Pore Size on Methane and CO₂ Adsorption in Carbon
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Introduction

Abstract: Methane adsorption in coal is an important factor in determining the feasibility of CO₂ injection for enhanced coal bed methane (ECBM) recovery and sequestration or permanent storage in coal. Methane and CO₂ adsorb competitively and an understanding of the isolated behavior of each gas is important for determining a model to predict the feasibility of this as an abatement option. Coal is very heterogeneous with pores on the macro, meso, and micro-scale, and the distribution of these pore sizes will affect adsorption behavior. At some pore size the interaction of particles adsorbing to the opposite sides of the pore will begin to effect each other and the adsorption characteristics of the material. To find the size at which these effects become detectable and to determine the magnitude of this impact we have used grand canonical monte carlo simulation to separately calculate the adsorption isotherms of methane and CO₂ across a range of pore sizes and at different temperature/pressure conditions. These isotherms have been calculated on graphene and graphite surfaces as an initial model to coal and the critical pore sizes and varying levels of impact have been calculated.

Methodology

The impact of pore size on adsorption is studied through simulation of methane and CO₂ in graphite pores of different sizes and comparing the differences.

The simulation considers a box containing two walls of carbon (representing a slit pore) with the space between the walls representing the pore. A Grand Canonical Monte Carlo (GCMC) algorithm is used, which randomly considers as many as 10⁸ configurations of the gas molecules in the system, looking for the lowest energy state, which corresponds to expected natural behavior.

The energy state for the system is calculated using the Lennard-Jones parameters for the molecules in the system:

\[ \phi = 4\varepsilon \left( \frac{\sigma_i}{r} \right)^{12} - \left( \frac{\sigma_i}{r} \right)^{6} \]

Lennard-Jones equation and the mixing rules to determine forces between different types of molecules.

These parameters define the attractive force between molecules at a distance as well as the repulsive force seen when molecules are very close together.

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<th>Adsortive</th>
<th>Reactive</th>
<th>CO₂</th>
<th>CH₂</th>
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</table>

Lennard-Jones Potential vs distance for several different molecules, CO₂ has a stronger interaction than methane both with other CO₂ and with the carbon in the pore wall.

Applications

ECBM and gas separation both benefit from adsorption

For Enhanced Coal Bed Methane recovery, CO₂ is injected into unmineable coal seams, where the CO₂ drives off methane and is itself trapped in the coal.

For pressure swing separation, methane is separated from H₂S (sweetened) by forcing the mixed gas at high pressure through packing material which preferentially adsorbs methane, and then dropping the pressure over the packing material to release the pure methane. These are much lower energy processes than current cryogenic (temperature swing) separation.

Results

Benchmarking our method (left) for CO₂ and methane against published simulations shows strong agreement in both trend and quantitative results.

More CO₂ than methane will adsorb in the same sized pore, and small pores increase the adsorption of both.

Simulations confirm that CO₂ adsorbs in larger quantities than methane in the same sized pore. Furthermore, our results suggest that smaller pore sizes increase the relative amount of adsorption seen in the pore for both. Part of this is the geometry of the situation, wherein the ratio of surface area to pore volume increases, but part also appears to be the interactions of the gas molecules with each other and with the opposite wall.

Conclusions

More CO₂ than methane will adsorb in the same sized pore, and small pores increase the adsorption of both.

Future Work

Compare with experiment and include H₂O and complexity

Future goals include comparison with experiment, the study of more complex (and thus more realistic) systems, adding defect sites in the carbon pore walls, adding functional chemical groups (known to be found in coal), and adding water to the system.

Acknowledgements

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Motivation

Pore size distribution in coal and the impact it has on adsorption are currently not well understood

- Small pores allow interactions other than the gas-surface to impact adsorption (wall-wall, particle-particle, cross-wall)
- Material characterization is difficult due to the very small pores in these systems, i.e., less than 2 nm
- Characterization is lacking (ideas include BET, NMR, high res SEM)
- In need of pore size distribution data