Modeling CO_2 (and methane) Adsorption and Transport in Micro and Mesopores of Carbon-based Systems

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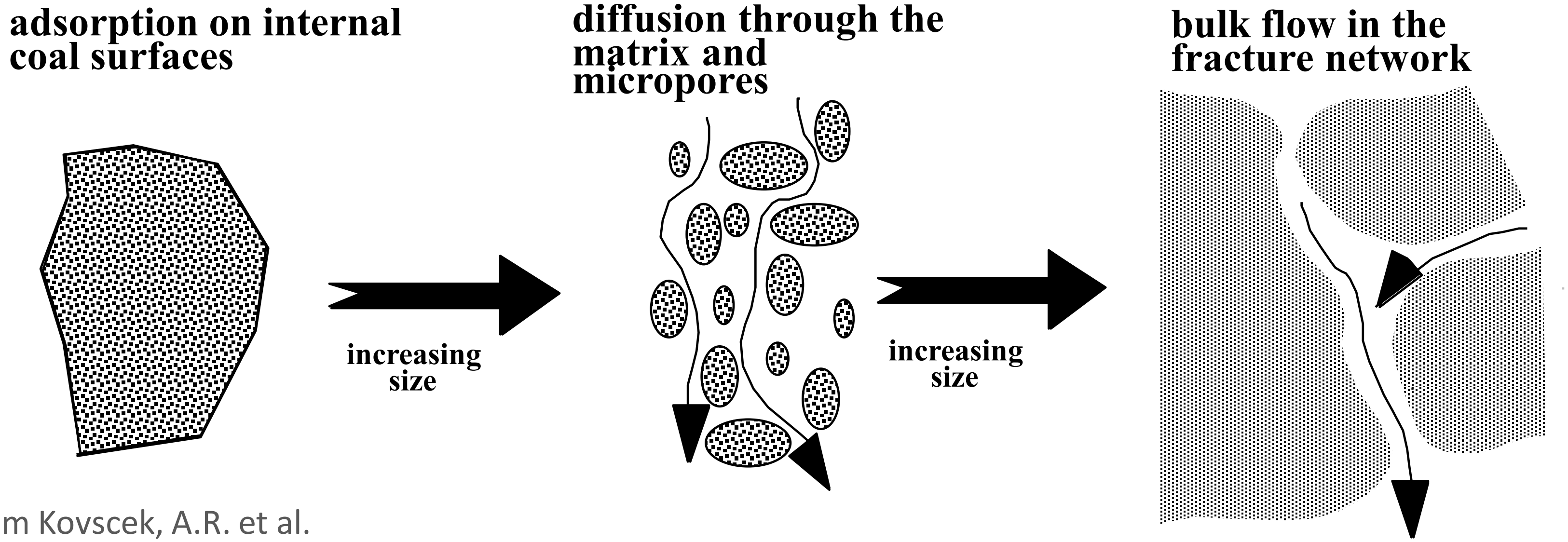
Multi-scale Approach

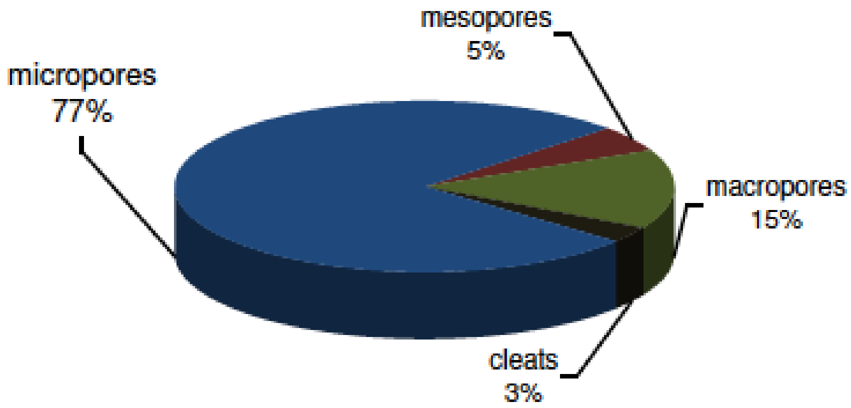
- Experimental characterization of coal and gas shale (organic-rich) samples
  - Pore size distribution, porosity, surface area, surface chemistry
- Molecular modeling to predict adsorption and transport
  - force fields → calculate energies
- Adsorption – Grand Canonical Monte Carlo (GCMC)
- Transport – Molecular Dynamics
- Pore Models → carbon-slit pores → cylindrical pores → 3-D pore networks



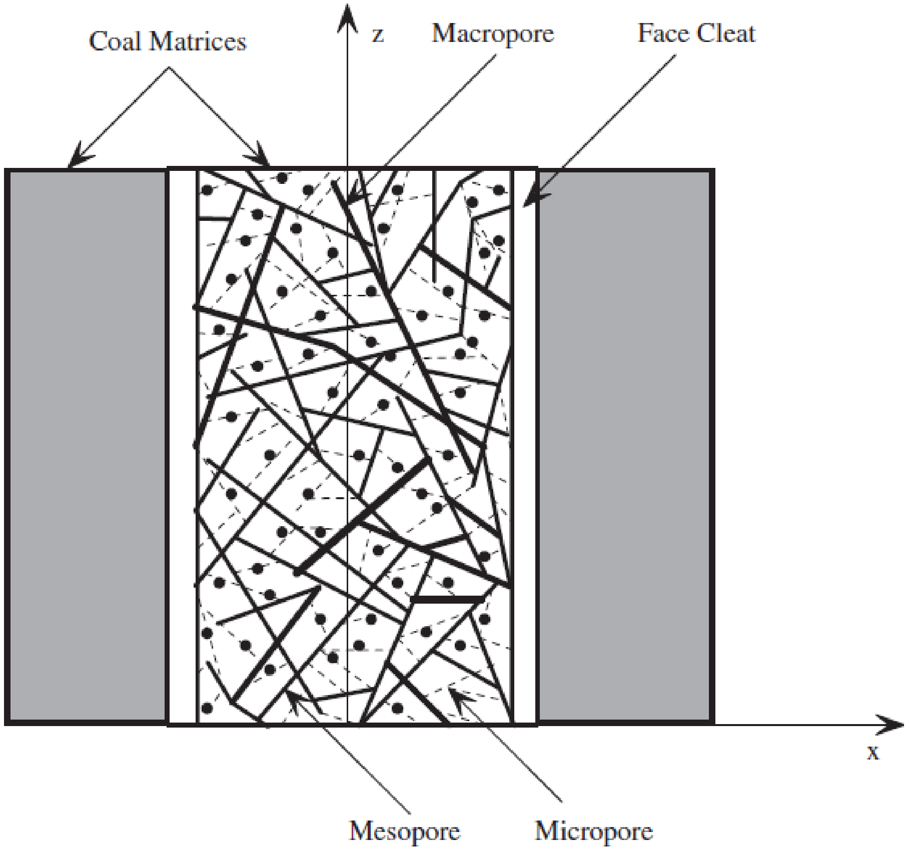
[†] Image from Kovscek, A.R. et al.

Carbon Model Geometry

- [†]Porosity in coal is comprised of:



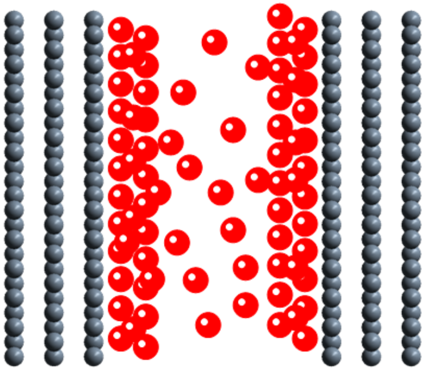
- [‡]The table below shows the specified type of pores, d [nm], based on IUPAC classification



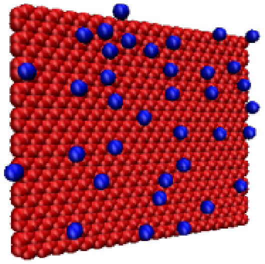
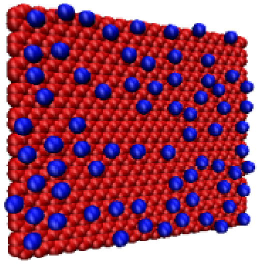
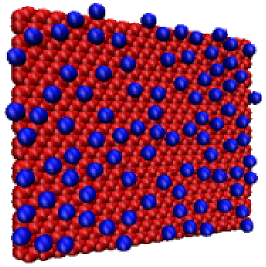
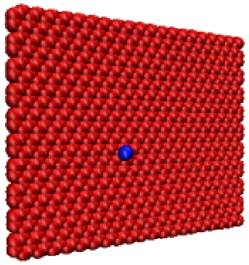
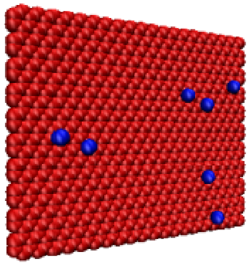
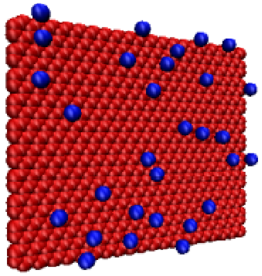
Macro-	Meso-	Micro-	Supermicro-	Ultramicro-	Submicro-
> 50	2-50	<2	0.7-2	<0.7	<0.4

[†]F.Y. Wang, *et. al.,* Chemical Engineering Science 62(2007), pp. 3268-3275; P.L. Walker, Philosophical Transactions of the Royal Society of London A 300(1981), pp. 65-81; [‡]B.D. Zdravkov, *et. al.,* Central European Journal of Chemistry 5(2), (2007), pp. 385-395.

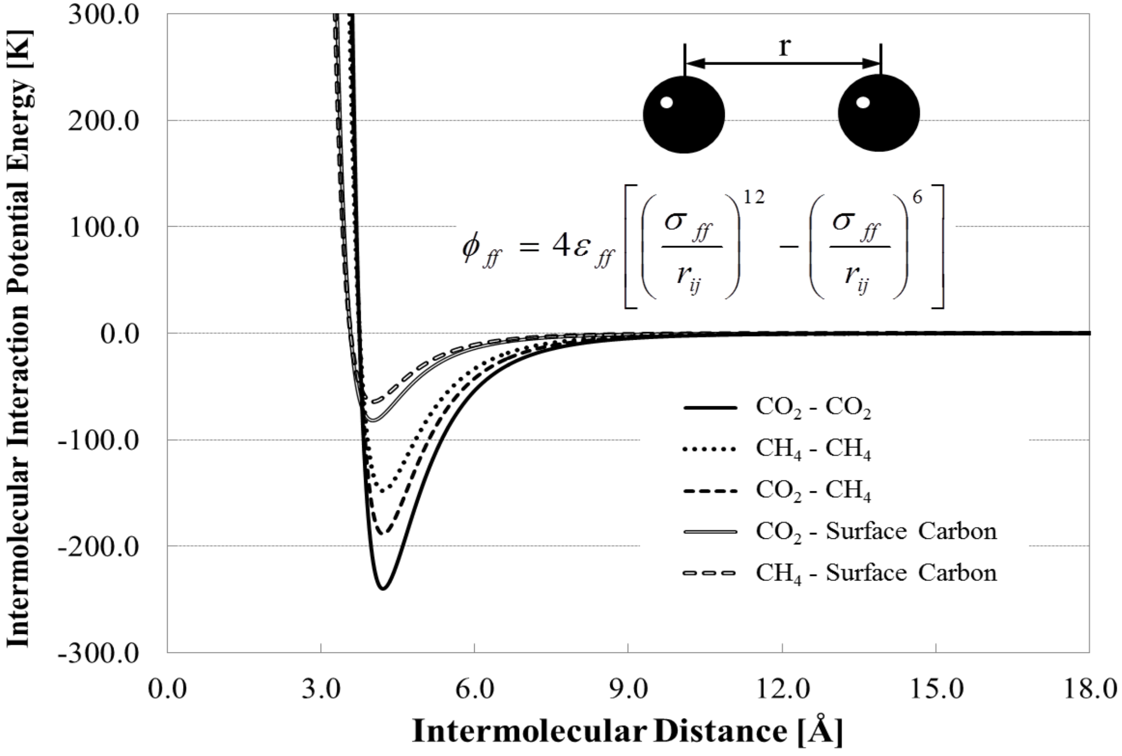
Defining Adsorption



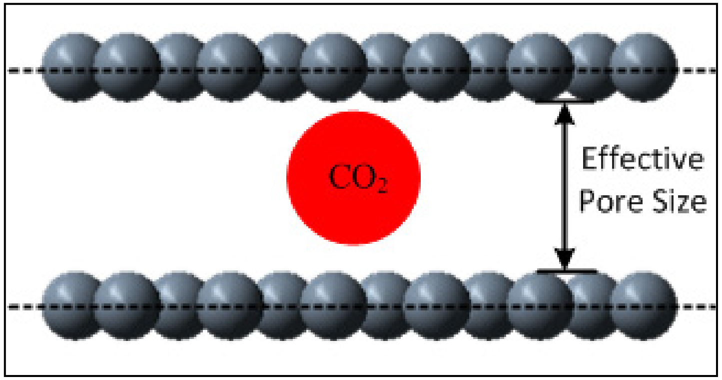
- **Total Adsorption**
  Direct results from GCMC Modeling
- **Excess Adsorption**
  Direct results from Lab Measurements
- Convert from **Total** to **Excess** Adsorption
  Total Adsorbed – Bulk = Excess

	1 MPa	6.2 MPa	18 MPa
Adsorbed			
Bulk			

Potential Models (L-J and TraPPE)



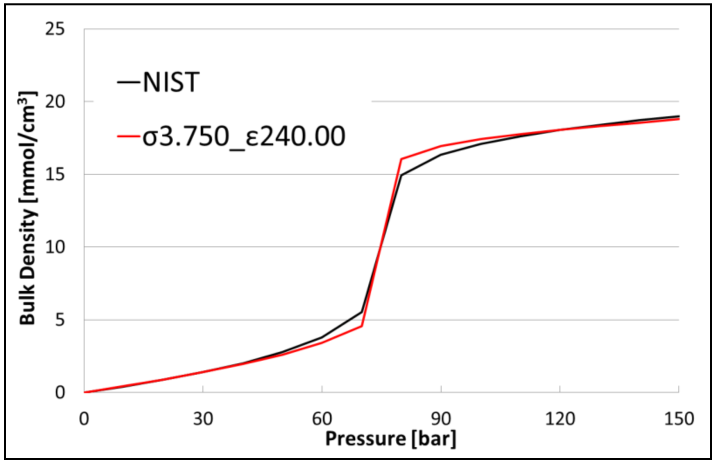
$$\phi_{ff} = 4\varepsilon_{ff}\left[\left(\frac{\sigma_{ff}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ff}}{r_{ij}}\right)^{6}\right]$$



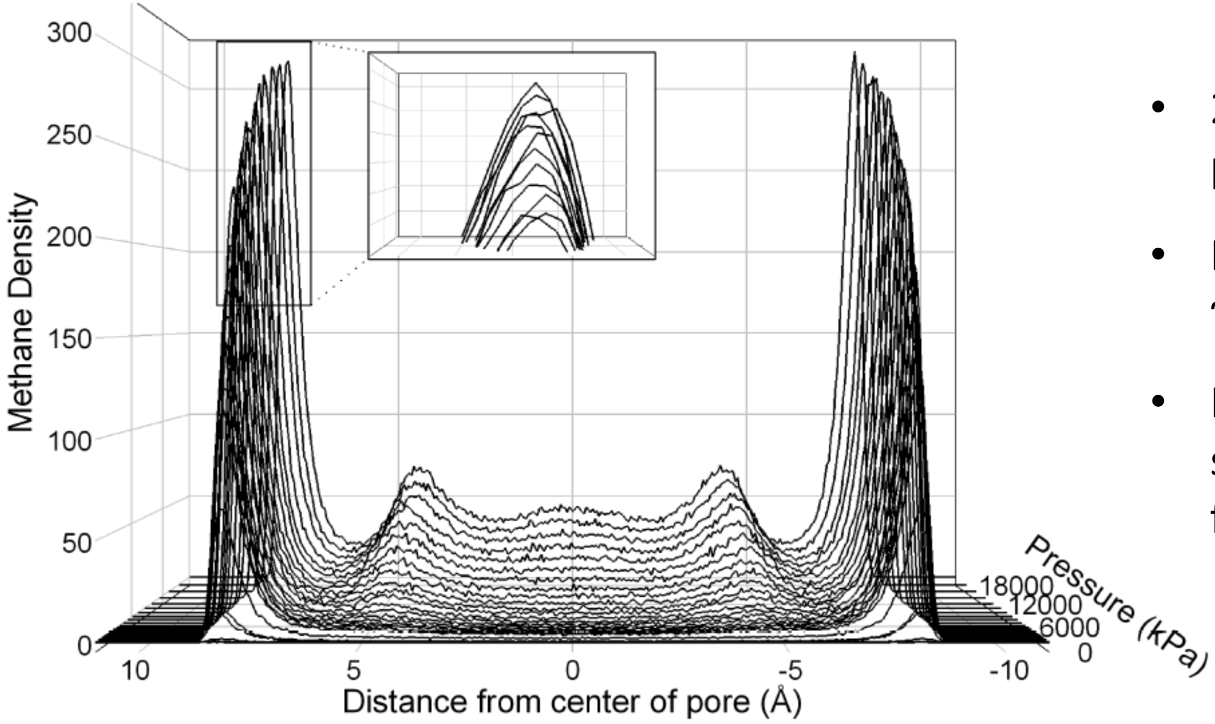
Schematic plot of one-center Lennard-Jones potential model of CO$_2$ in slit-pore

$$\sigma^{CO_2} = 3.75\,\mathring{A} \qquad \sigma^{C} = 3.40\,\mathring{A} \qquad \Rightarrow \qquad \sigma^{CO_2-C} = 3.571\,\mathring{A}$$

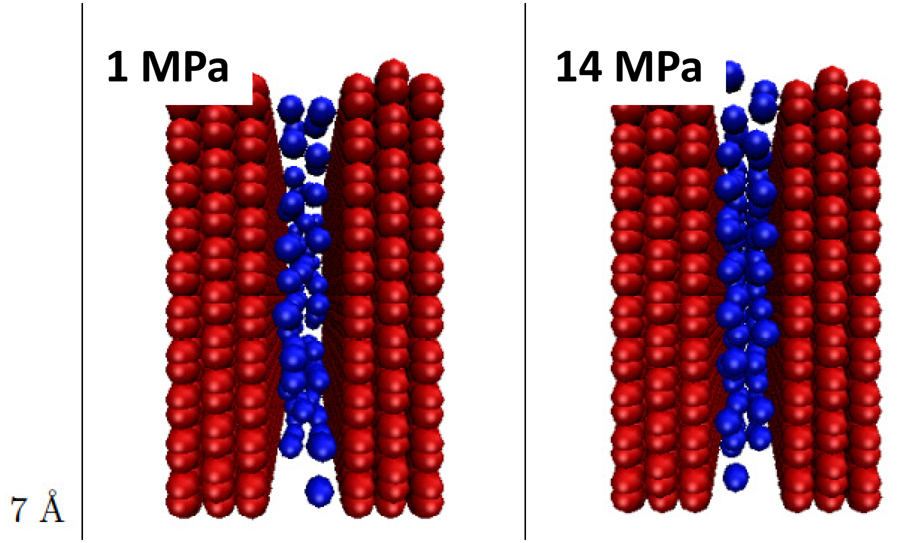
$$\frac{\varepsilon^{CO_2}}{k} = 240.00\text{K} \qquad \frac{\varepsilon^{C}}{k} = 28.00\text{K} \qquad \frac{\varepsilon^{CO_2-C}}{k} = 81.9756\text{K}$$

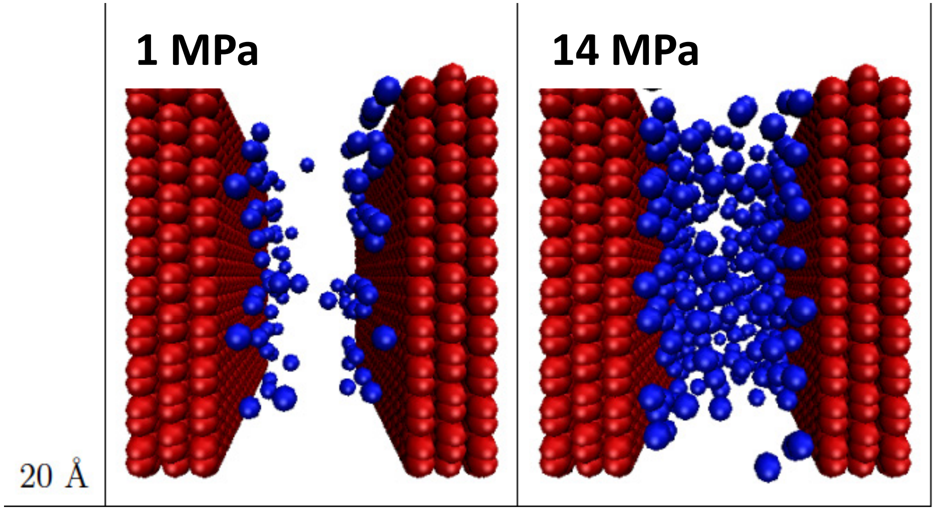


Methane Density Changes in Pores

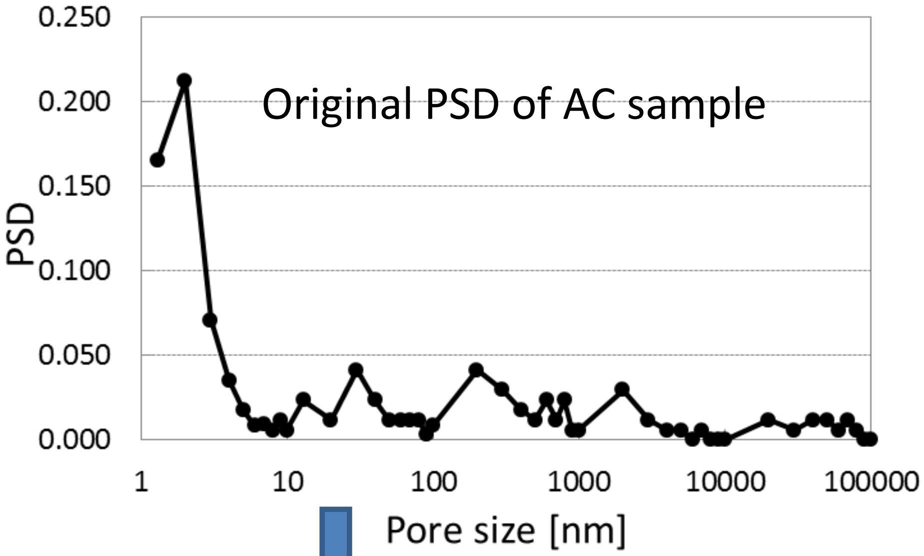


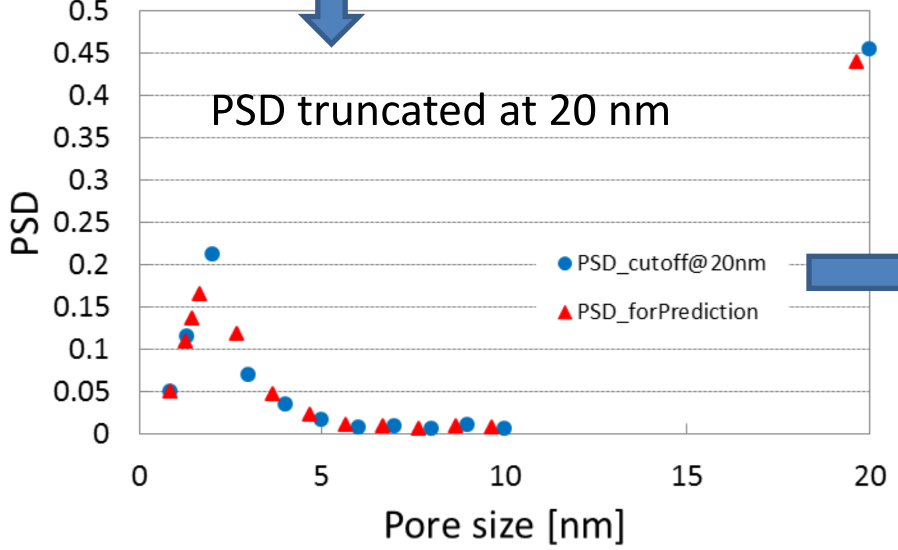
- 2 nm pores at 298K and varying pressure
- Density at the wall plateaus at ~ 14MPa
- Density in the core increases steadily with second layer formation clear with ↑P





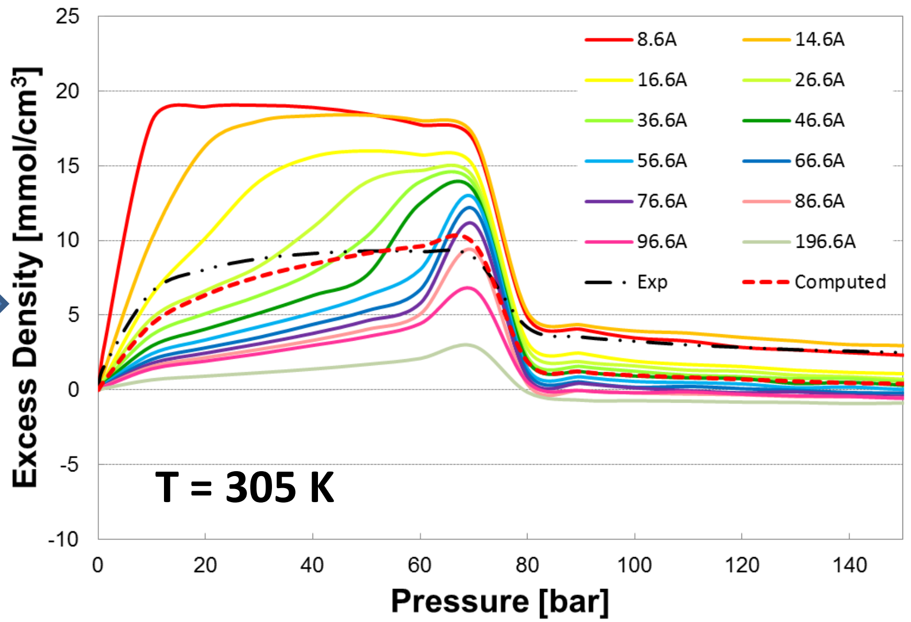
Adsorption Isotherm Prediction Based on PSD





Measured PSD → predict adsorption isotherm

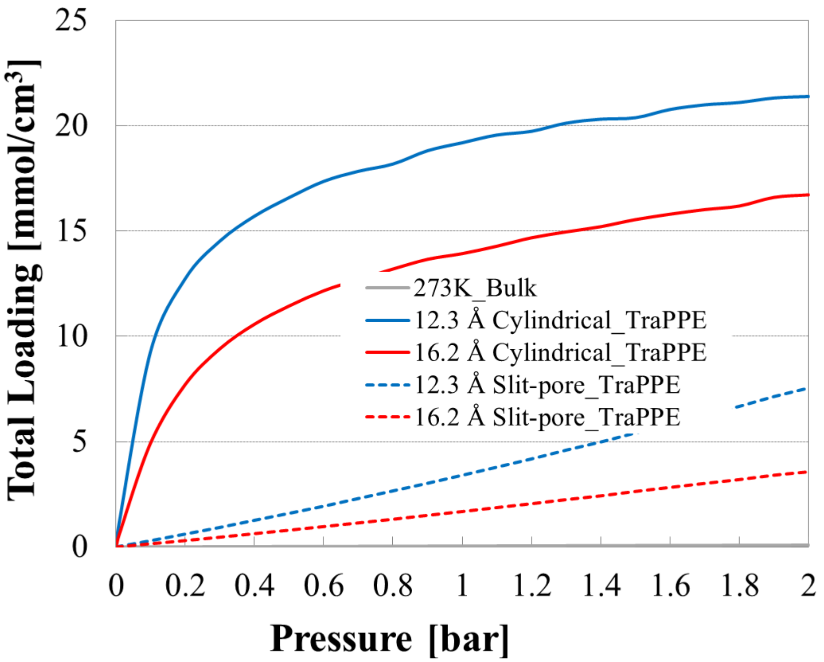
- Assume the total isotherm consists of a number of individual “single pore” isotherms multiplied by their relative distribution over a range of pore sizes.
- The set of isotherms for a given system can be obtained by GCMC simulations.



†Exp data from Ronny Pini, Stanford University (and ETH, Zurich)

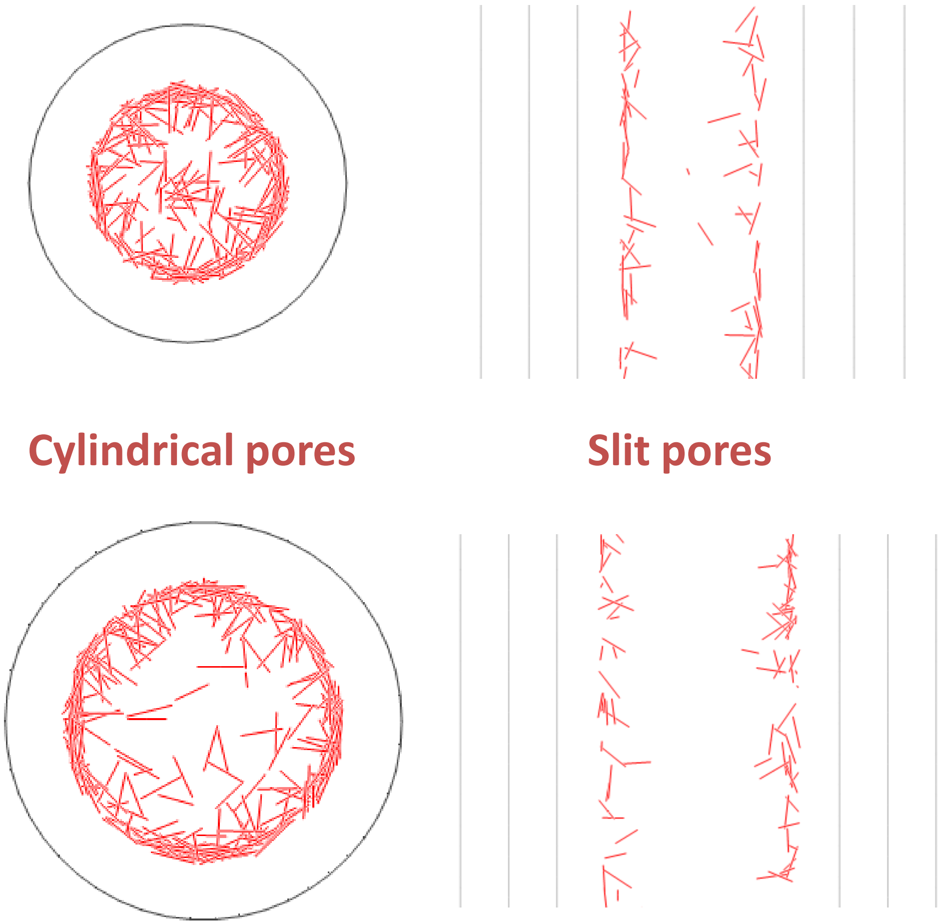
Effect of Surface Curvature - Adsorption at 273 K

- TraPPE† force field is 3-charge and captures the CO_2 quadrupole moment more effectively



- Enhanced wall-wall interactions of cylindrical pore → higher loading in smaller pores
- Higher packing efficiency of linear CO_2 in cylindrical pore at low pressure

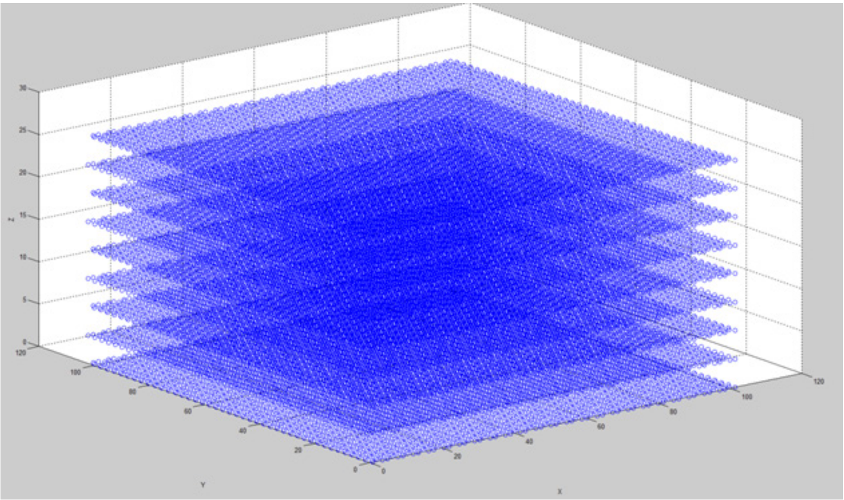
Effective pore width = 1.2 nm @ 2 bar



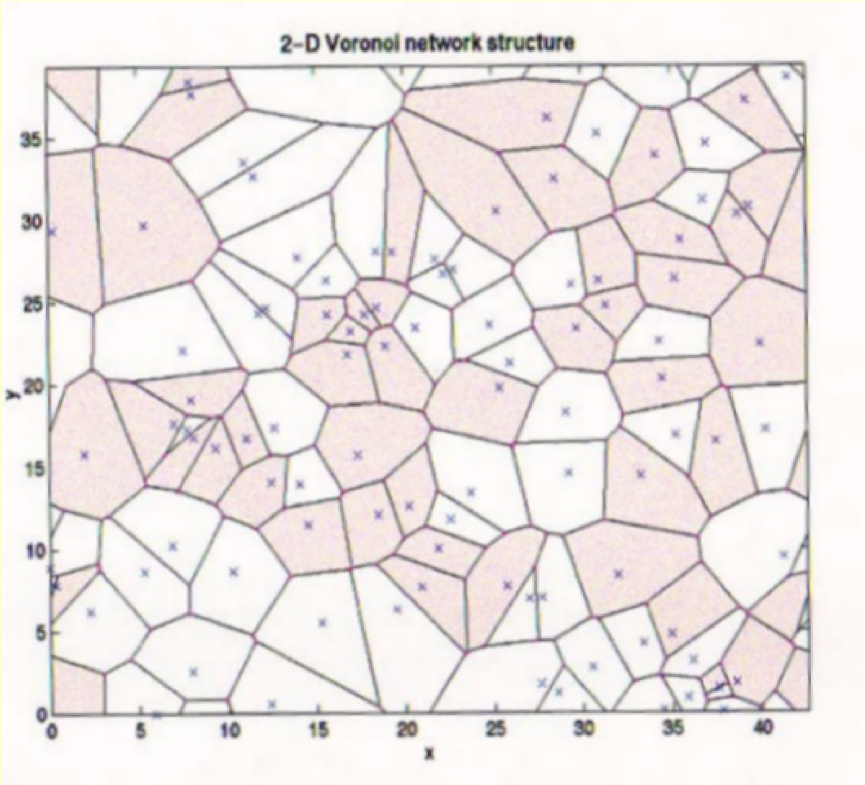
Effective pore width = 1.6 nm @ 2 bar

† Potoff, J.J., Siepmann, J.I., AIChE Journal 2000, Vol. 47, No. 7

3-D Pore Network Model

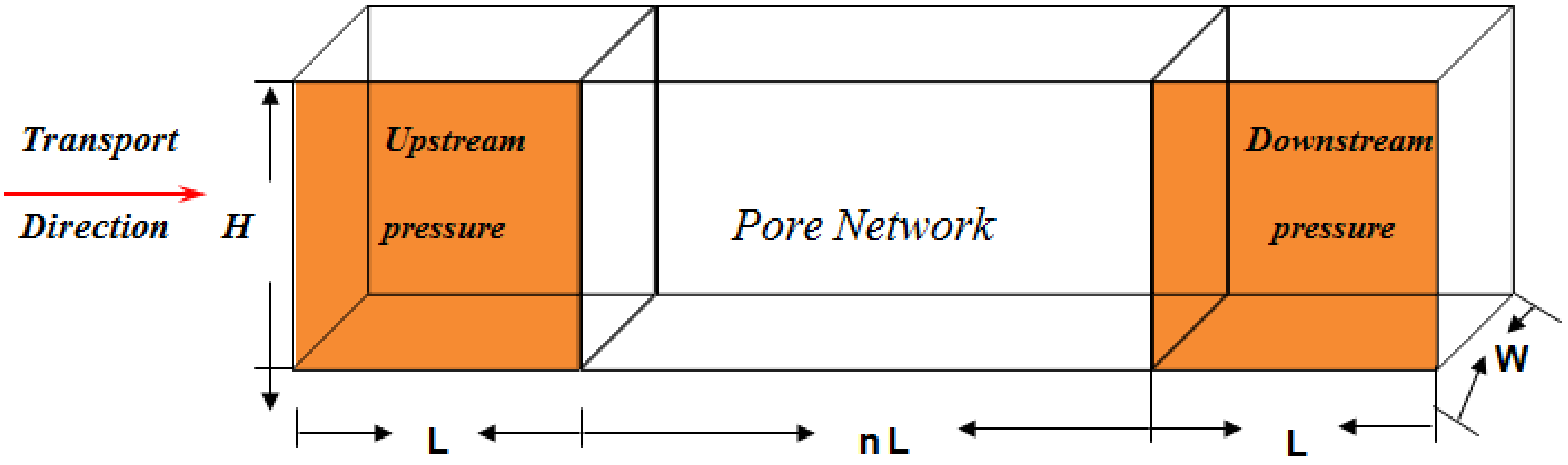


- The dimensions of the system modeled are ~ 10 x 10 x 10 nm
- 3-D molecular pore network model based on the *Voronoi* tessellation method
- To generate the molecular pore network model:
  - Create a 3-D simulation box of structural atoms corresponding to porous structure
  - Tessellate the atomic structural box
- The pore space is created by specifying the desired porosity and # polyhedra → total volume fraction = specified porosity
  - pore space consists of interconnected pores of various shapes and sizes



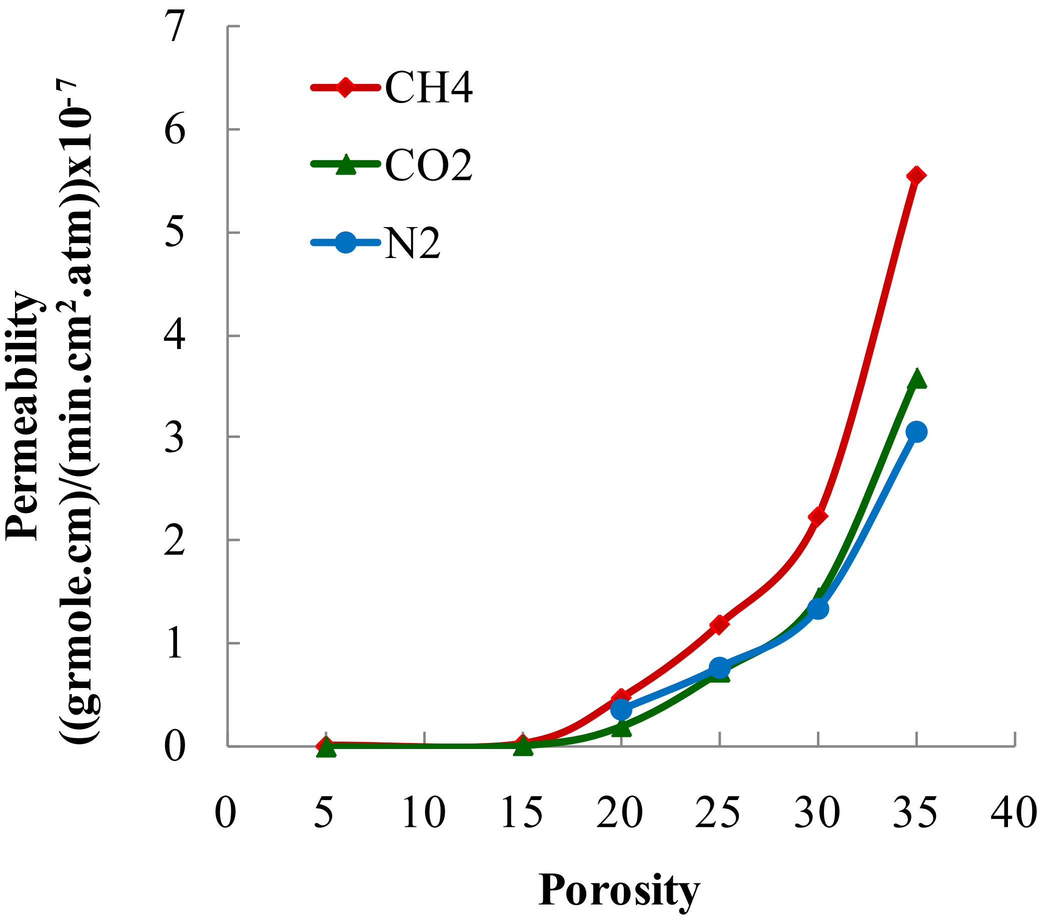
Modeling Transport with MD

- The pore network model previously described will be used
- Non-equilibrium molecular dynamics (NEMD) simulations are carried out
- The system (pore network) is exposed to an external driving force (chemical potential or pressure gradient) in a specified direction
- Flux and permeability predictions are carried out



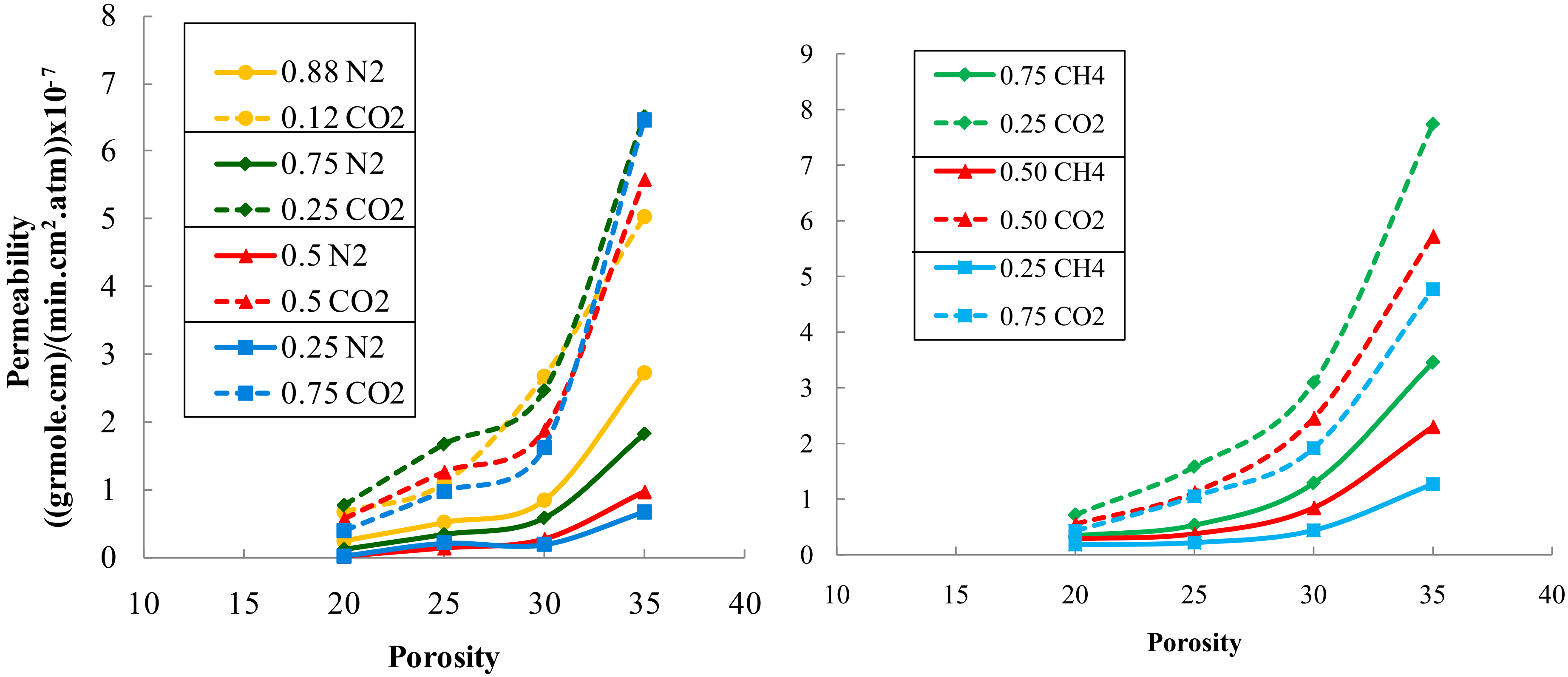
Permeability of Pure Components vs Porosity

- The permeability of CH_4, CO_2 and N_2 will increase with increasing porosity
- When the porosity is higher the pores are more connected assisting molecular transport through the pore network
- CH_4 is the more permeable species in the absence of CO_2
- CO_2 crosses over N_2 at ~ 30% porosity
- In small pores CO_2-surface interactions dominate



Permeability of CH_4, CO_2 and N_2 with ***average pore diameter of 1.2 nm [12 Å]*** *and 5%, 15%, 20%, 25%, 30% and 35% porosities*

Permeability of N_2/CO_2 and CH_4/CO_2 Mixtures



Permeability of N_2 / CO_2 (left) and CH_4 / CO_2 (right) mixtures with ***average pore diameter of 1.2 nm [12 Å]*** *and 20%, 25%, 30% and 35% porosities*

- With mixtures of N_2, at high CO_2 concentrations, permeability is lower below a 30% porosity
- With mixtures of N_2, 25% CO_2 has the greatest permeability
- In gas mixtures of N_2 and CH_4, CO_2 is always the more permeable species in 1.2 nm pores

Gas Slippage - The Klinkenberg Effect

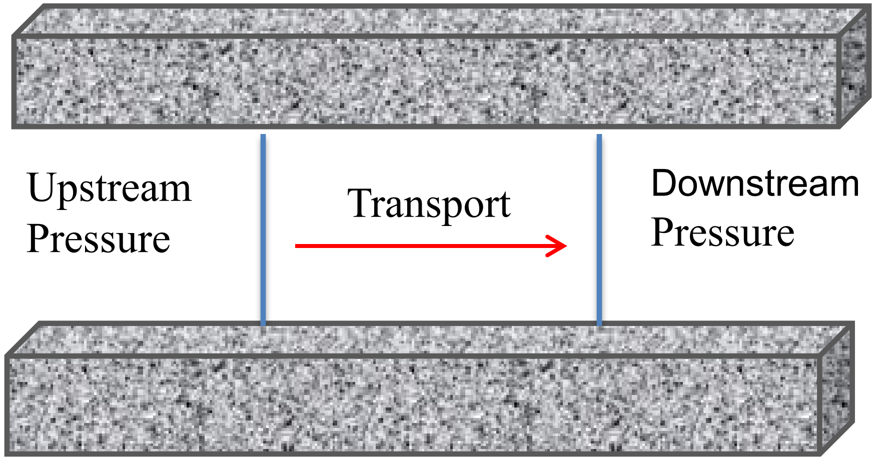
- Research on gas transport through tight sand, coal-bed methane, and unconventional gas reservoirs are examples of cases where more reliable and well supported modeling results could provide useful
- Knudsen # = mean free path ÷ pore diameter: $K_n = \frac{\lambda}{d}$
- As $d\uparrow$, $K_n\downarrow \rightarrow$ wall effects are minimized (commonly call this D_m)
- As $d\downarrow$, $K_n\uparrow \rightarrow$ wall effects begin to play a role
- Knudsen diffusion is independent of of pressure

Continuum	$K_n < 10^{-3}$
Gas Slippage	$10^{-3} < K_n < 10^{-1}$
Transition	$10^{-1} < K_n < 10$
Surface diffusion	$K_n > 1$

[†] M.C. Bravo, Journal of Applied Physics **102**, 074905, 2007

Demystifying the Klinkenberg Effect

- Transport of equimolar binary mixture of CH_4 and CO_2 has been modeled using NEMD simulations in a slit pore model
- The pore wall is assumed smooth and the interaction between molecules and pore wall was modeled by the Steele and fluid-fluid by the LJ potentials
- Verlet algorithm was used to solve the equations of motion

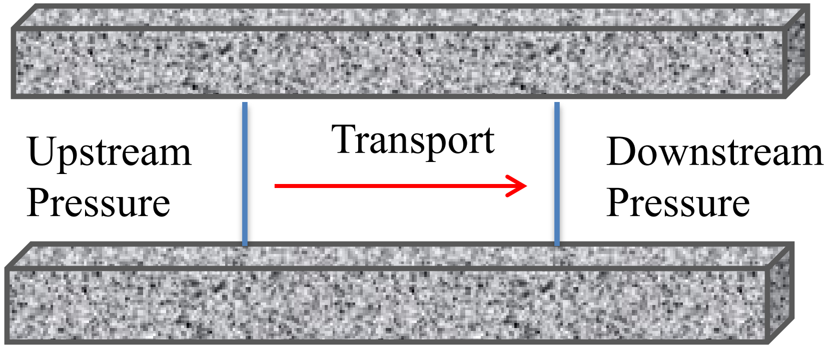


Length = 15.2 nm [152 Å]
Width = micro to mesopore range

Upstream pressure = 3 atm, Downstream pressure = 1 atm, Temperature = 298 K

CH_4/CO_2 Velocity Profiles in Micro and Mesopores

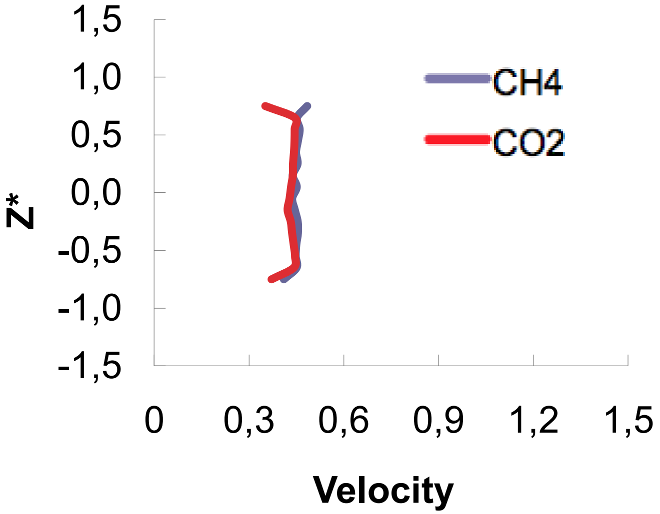
- In small pores the velocity profile is plug flow and becoming parabolic at approximately 4 nm pores for CH_4 and greater than 10 nm pores for CO_2



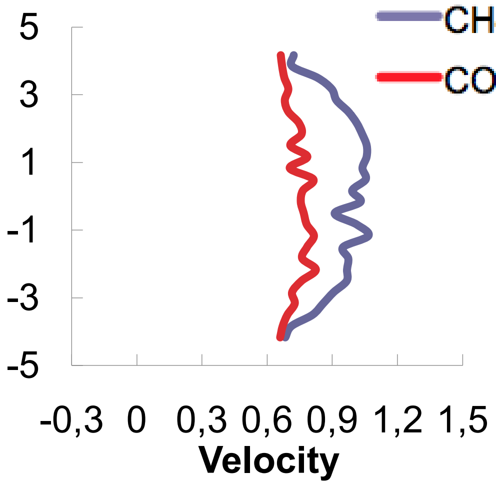
Upstream Pressure

Transport

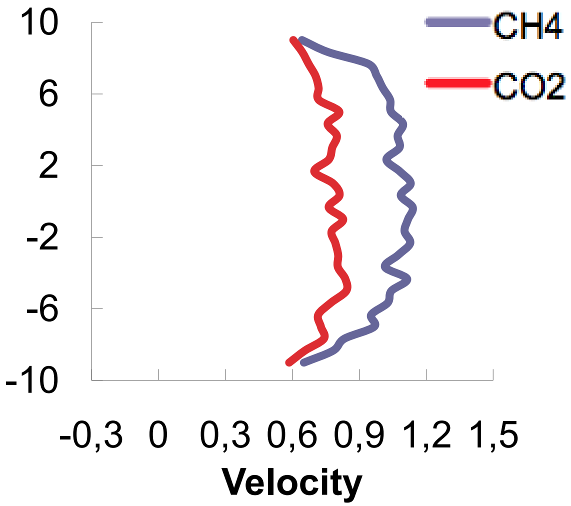
Downstream Pressure



Height = 1.1 nm [11 Å]



Height = 3.8 nm [38 Å]



Height = 7.6 nm [76 Å]

Summary

- **Adsorption (GCMC)**
  - Micro and mesopores dominate surface area and gas containment in coal and organic-rich gas shales
  - Wall densities of pores are fairly independent of pressure, while the core fluid density changes appreciably
  - Experimental PSD has been used to compare predicted vs experimental isotherms → models can aid in understanding adsorption mechanisms (surface functional groups?)
  - Cylindrical pores have enhanced adsorption capacities, with pores less than 1.2 nm

- **Transport**
  - Pure gas-phase permeabilities are different than their gas mixtures
  - CO_2 has greatest permeability at 25 mol% in 1.2 nm pores in CO_2/N_2 gas mixtures
  - Klinkenberg effect is evident for CH_4 in carbon pores less than ~ 3 nm
  - Klinkenberg effect is evident for CO_2 in carbon pores less than ~ 10 nm

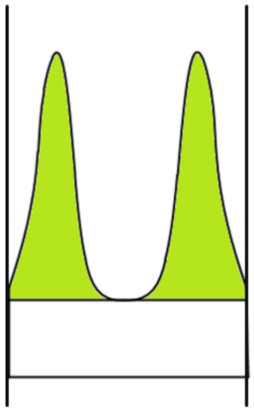
Acknowledgements

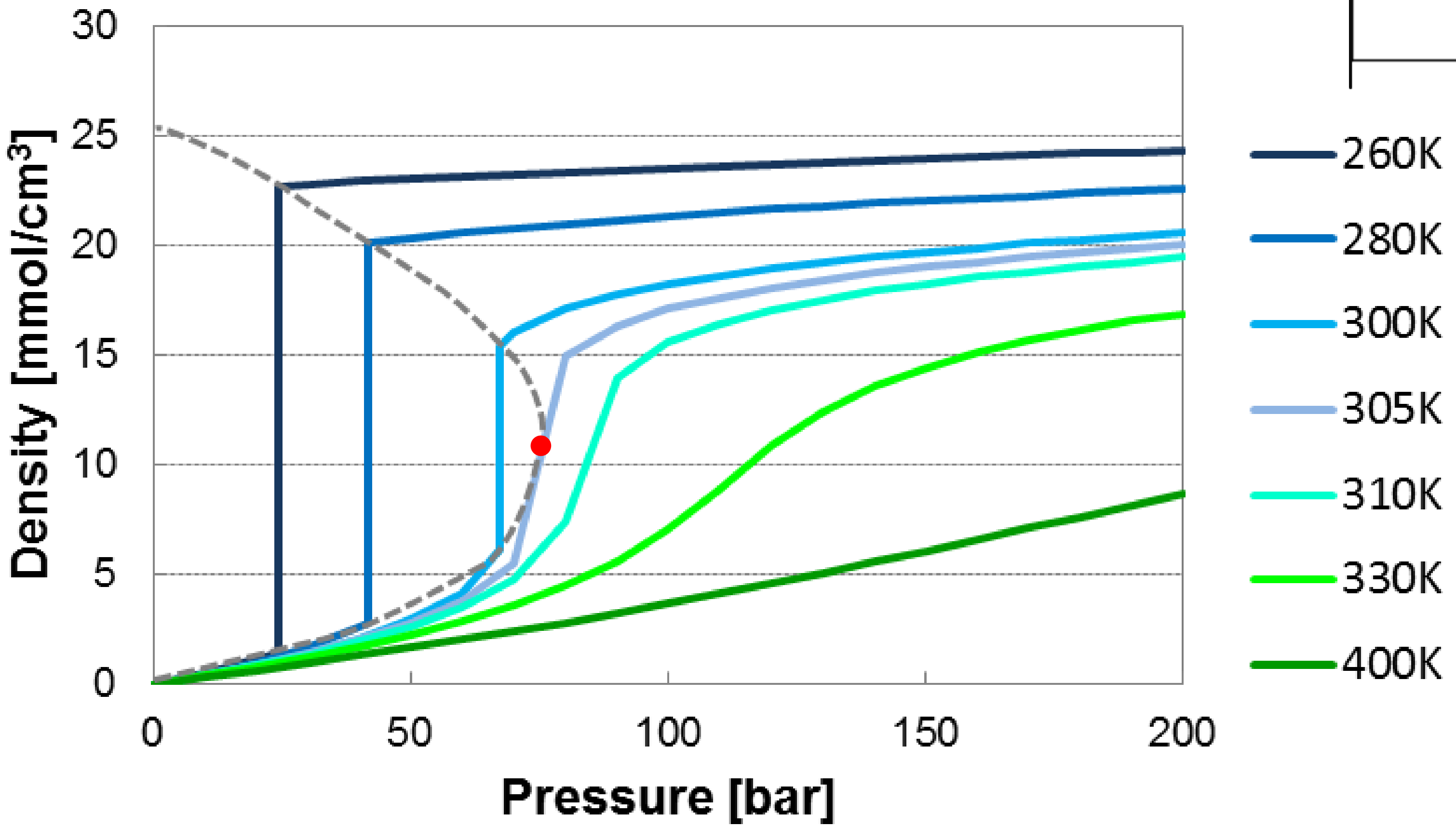
- Experimental Collaborators at ETH, Zurich
  - Marco Mazzotti and Ronny Pini
- Experimental Collaborators at Stanford
  - Mark Zoback, geophysics and Tony Kovscek, ERE
- Computational Resources
  - Stanford Center for Computational Earth & Environmental Science
- Funding
  - DOE-NETL and BP PhD Fellowship

Questions ?

Results and Discussion - Bulk CO_2 Density

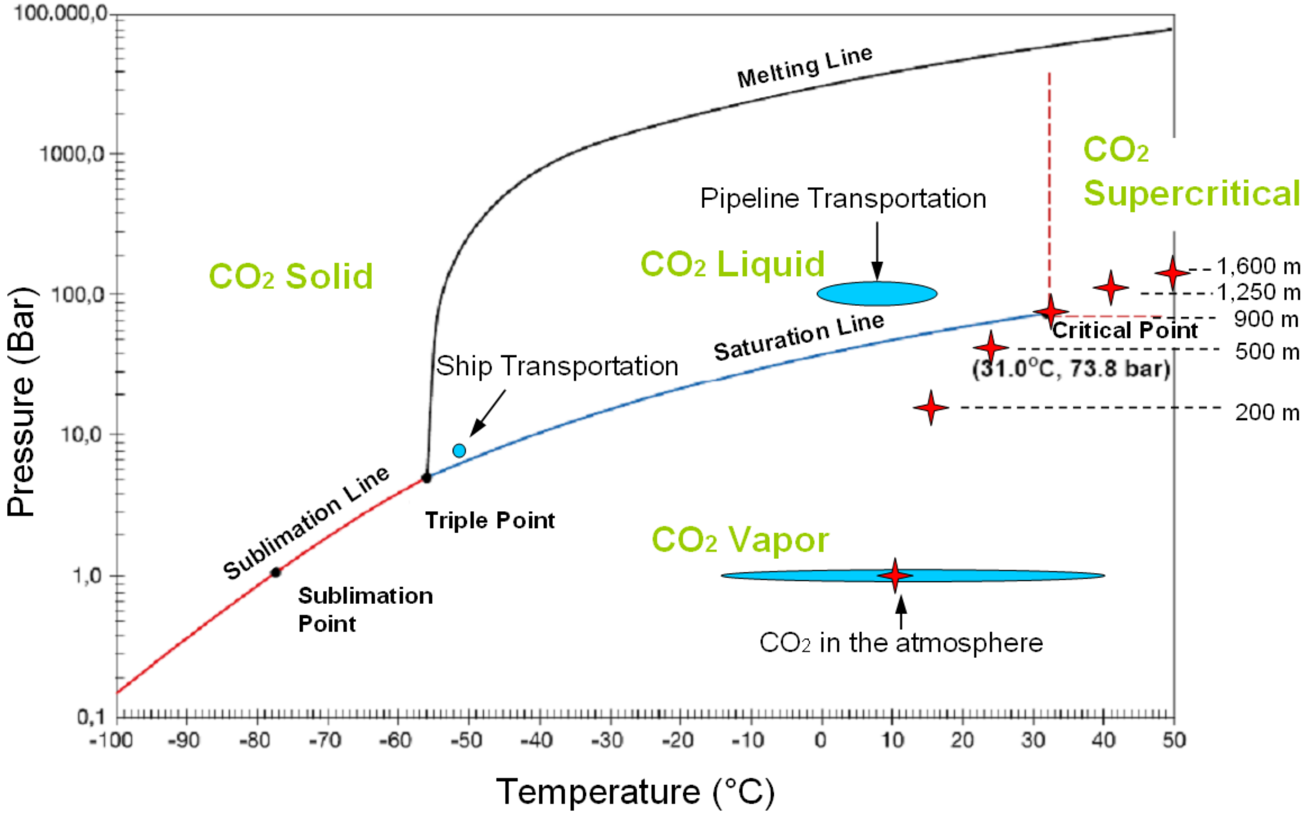
T_c	K	304.1
P_C	Pa	7.376×10^6
V_C	m^3/kmol	0.094
T_b	K	194.7
Quadrupole moment	C m^2	-14.9×10^{-40}
Dipole	D	0





Supplement

- Thermodynamic Properties of CO_2

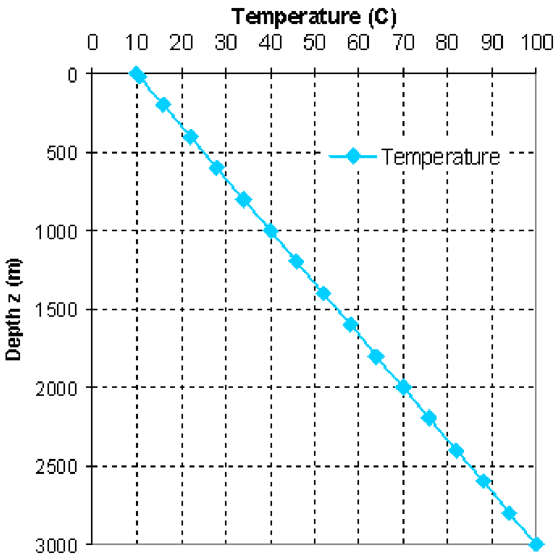


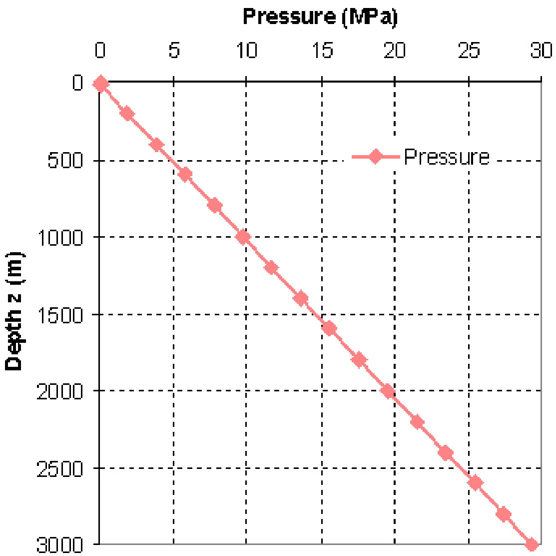
Phase Diagram of CO_2 and the State of CO_2 at Various Conditions

Supplement – Temperature & Pressure

- Subsurface Temperature Conditions: Geothermal Gradient †
  - Temperature increases with depth below the ground surface
  - ΔT/Δz ~ 30˚C/km
  - T_s = mean annual ground surface temperature (assumed to be around 10˚C)
  - Depth of coalbeds ~ 300m → T~300K (Powder River Basin, WY)

$$\boxed{T = T_s + \int_0^d \frac{dT}{dz}\, dz}$$





What is Molecular Dynamics?

- Over the past decades, Molecular Dynamics (MD) simulations have become an important tool for investigating and predicting various static as well as dynamical properties of materials.

- We call *molecular dynamics* a computer simulation technique where the time evolution of a set of interacting atoms is followed by integrating their equations of motion. For a system with *N* molecules, this involves solving a set of 3*N* second order differential equations (Newton's equations of motion):

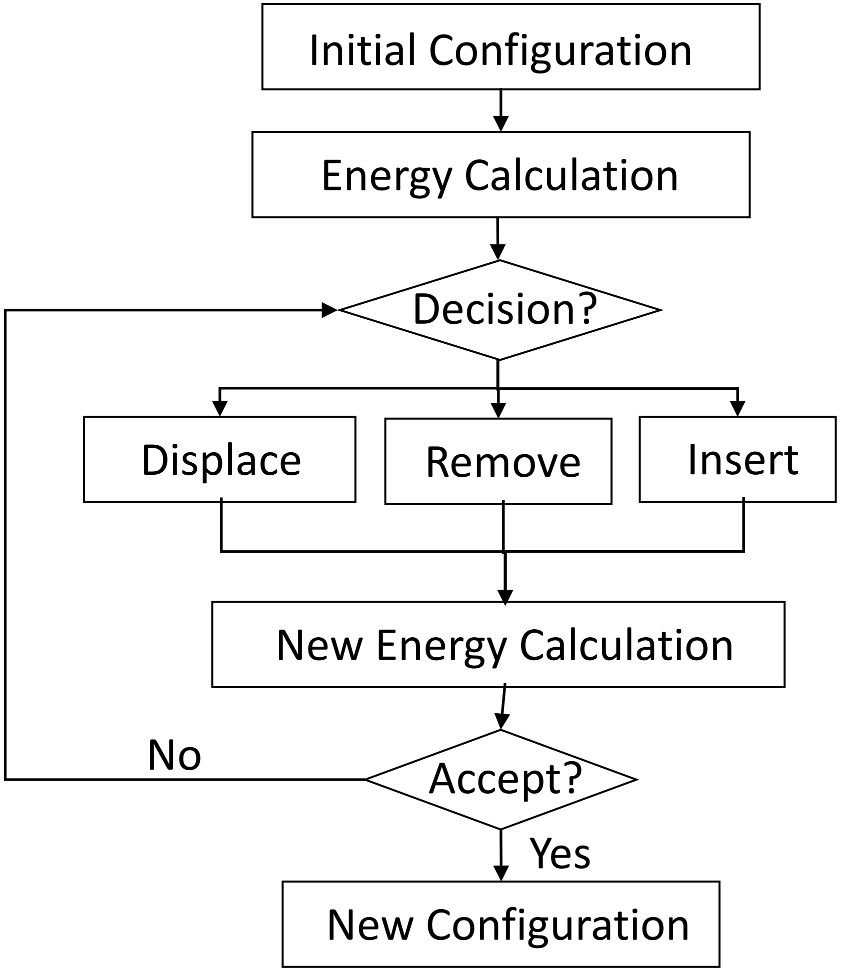
$$F_{x_i} = m_i \frac{\partial^2 x_i}{\partial t^2}, \quad F_{y_i} = m_i \frac{\partial^2 y_i}{\partial t^2}, \quad F_{z_i} = m_i \frac{\partial^2 z_i}{\partial t^2} \qquad \mathrm{i} = 1,2,\ldots\mathrm{N}$$

- The force on the *i*th particle is related to the potential energy and the fluid interactions are pairwise additive since the potential calculations are computationally costly.

$$F_{x_i} = -\sum_{j \neq i} \frac{x_{ij}}{r_{ij}} \frac{\partial u(r_{ij})}{\partial r_{ij}} \quad U^{Particle} = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} u(r_{ij})$$

Methodology - GCMC

- Statistical mechanics: the bridge to connect micro- and macroscopic properties
- Grand canonical Monte Carlo (GCMC)
  - Fixed:
    - Chemical potential
    - Pore volume
    - Temperature
  - Adsorbates (e.g., CO_2, N_2, methane):
    - Displace
    - Remove
    - Insert
    - Rotate
    - Swap (different types of particles)
    - …



Initial Configuration

Energy Calculation

Decision?

Displace

Remove

Insert

New Energy Calculation

Accept?

No

Yes

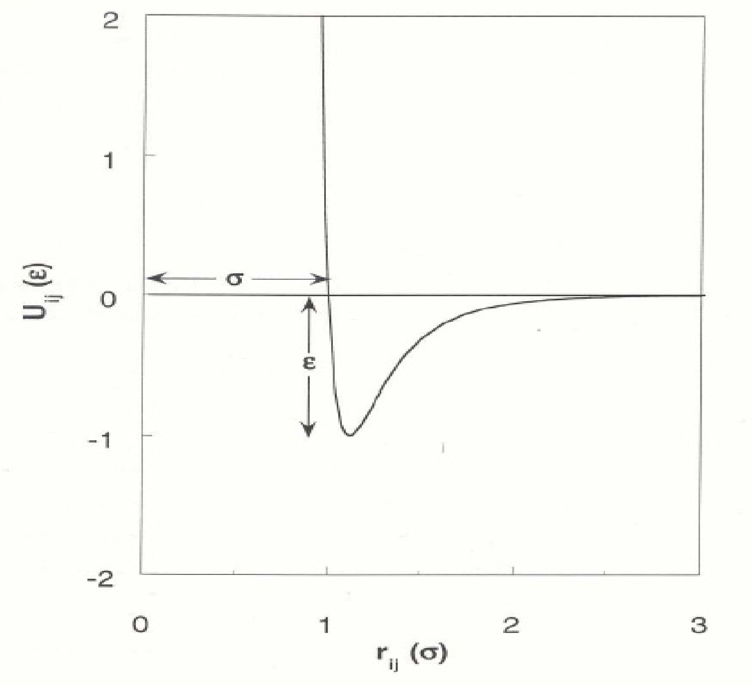
New Configuration

Lennard-Jones Potentials

- In many MD simulations the interaction potential between a pair of particles is represented by the classical Lennard-Jones (LJ) 12-6 potential:

$$u(r_{ij}) = 4\varepsilon\left\{\left(\frac{\delta}{r_{ij}}\right)^{12} - \left(\frac{\delta}{r_{ij}}\right)^{6}\right\}$$

- Where ε is the energy parameter of the potential (the maximum energy of attraction between a pair of molecules), or the LJ well depth, and δ is the size parameter (or the distance at which the LJ potential passes through zero and the potential sharply rises to repulsive values), also called the collision diameter.



The 12-6 Lennard-Jones potential for particles *i and j. The potential energy is in units of ε and the distance between i and j is in units of δ.* When Uij is positive, the interactions for the pair of particles are repulsive. When Uij is negative, their interactions are attractive.

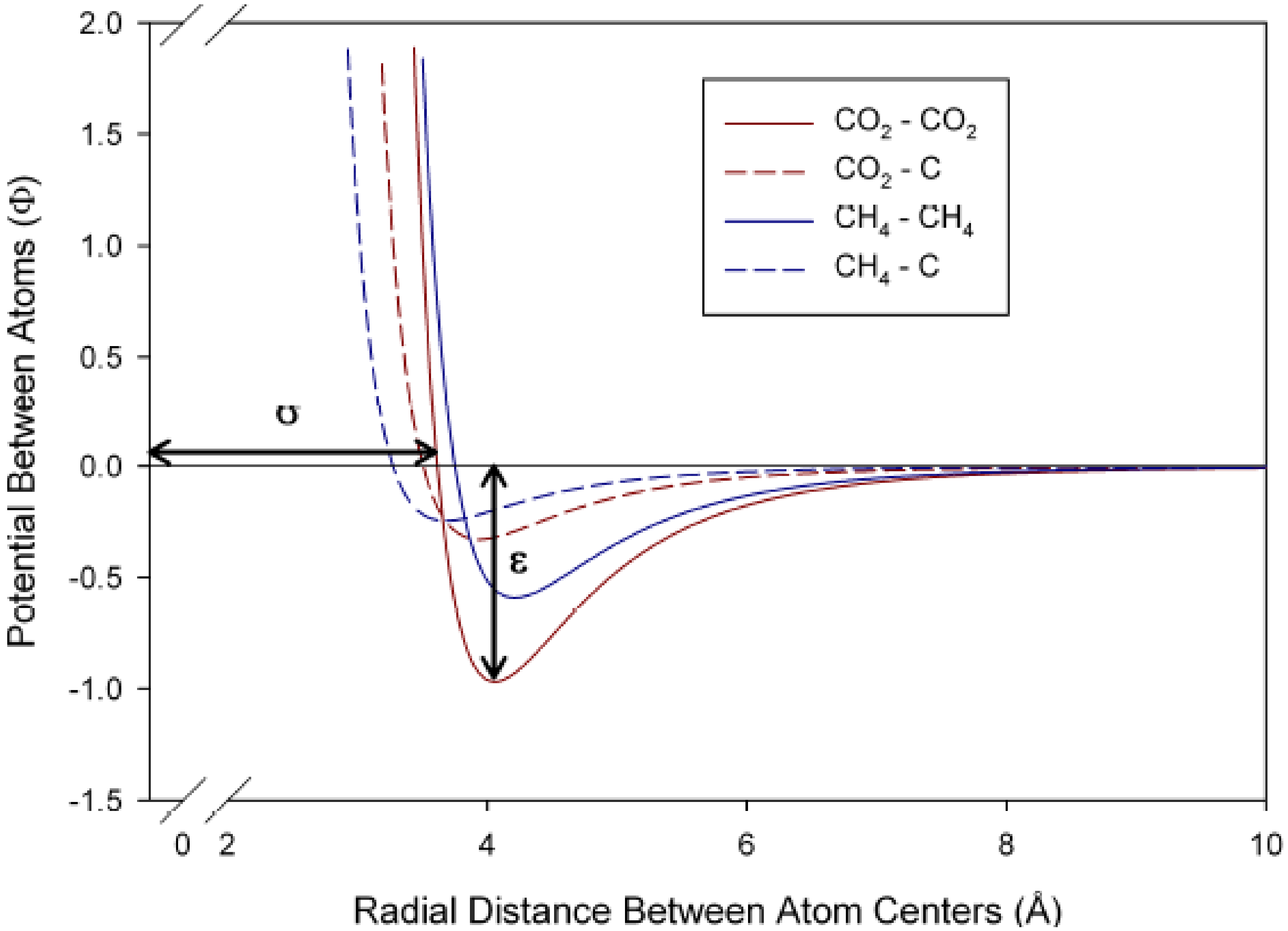


Figure 3.2: Lennard-Jones Plot of Carbon, Methane, and CO_2

Flux and Permeability Calculations

- The flux for each component is calculated by measuring the net number of particles crossing a given *yz* plane of area A_{yz}:

$$J_i = \frac{N_i^{LR} - N_i^{RL}}{N_{\mathrm{MD}} \Delta t A_{yz}}$$

where N_i^{LR} and N_i^{RL} are the number of the molecules of type *i* moving from the left to the right and vice versa, respectively, Δt is the MD time step (we used $\Delta t^* = 5 \times 10^{-3}$ = 0.00685 ps, where t* is the dimensionless time), and N_{MD} is the number of the MD steps over which the average was taken (we used NMD = 50,000); the system is assumed to reach steady state when the fluxes calculated at various *yz* planes are within 5% of the averaged values

- The permeability of species *i* are 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 species *i* along the pore, with x_i is the mole fraction of component *i*, and ΔP the total pressure drop across the pore

M. Firouzi, *et. al.,* Journal of Chemical Physics 119(13) (2003), pp. 6810-6822.

Coal and Gas Shale Properties

- Adsorption and surface diffusion characteristics are affected strongly by micro-pore (i.e., < 2nm) size distributions
- Total porosity of coal is a complex function of the coal rank and may vary from 4% to 20%
  - high-rank coals, the total porosity could be 4–8%
  - low to medium-rank coals (e.g., lignite and bituminous), total porosity could be 15-20%
- The total porosity of Barnett shale is 3-10% considering the organic kerogen in the rock (accounts for less than 10% of the rock mass) and contains most of the free porosity
- Pore size distribution and pore connectivity have been generated using pore network modeling (based on a graphitic structure) and will be benchmarked by experiments

F.Y. Wang, Z.H. Zhu, P. Massarotto, V. Rudolph, Chemical Engineering Science, 2007, 62, 3268-3275; S. J. M. Butala, Energy and Fuels, 2000, 14(2), 235-259.