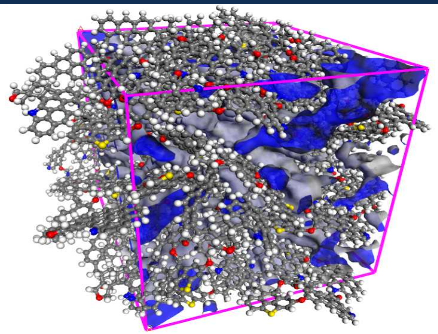
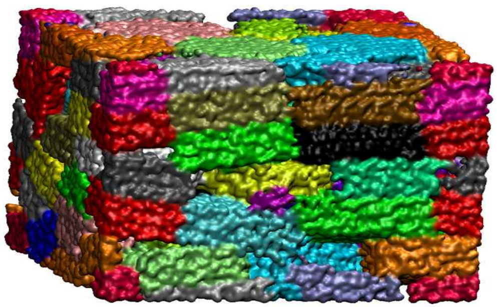
Sandia Postdoctoral Development

SAND2017-10449PE





Molecular modeling of gas adsorption and release from subsurface porous media

Tuan Anh Ho (8865)

U.S. DEPARTMENT OF ENERGY NNSA National Nuclear Security Administration

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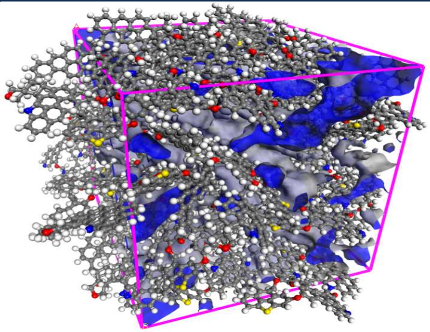

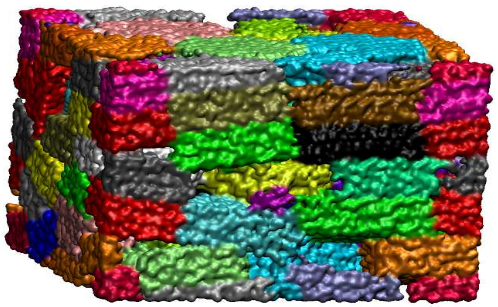

Molecular modeling of gas adsorption and release from subsurface porous media

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LDRD/NETL: **Fundamental understanding of the methane-carbon dioxide-water interactions in shale nanapores under reservoir conditions.**

BES: **Interfacial geochemistry of nanopores: Molecular behavior in subsurface environments.**

CFSES: **CO_2 sequestration.**

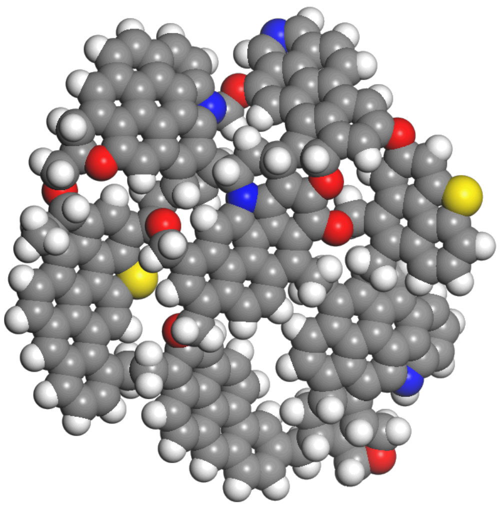
Introduction

Sandia National Laboratories

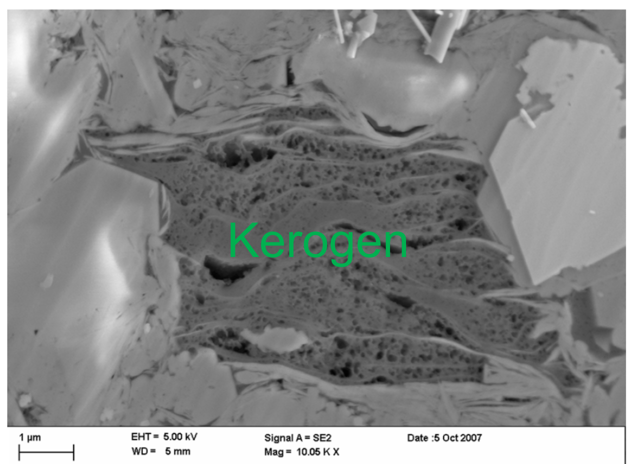
Subsurface porous media

Organic matter
Kerogen

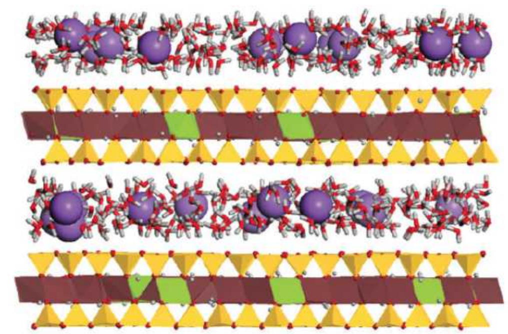
Inorganic matter
Clay



Energy Fuels 2015, 29, 91-105



SPE 124253 (2009)

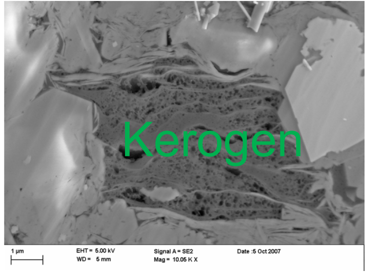


Na-Montmorillonite

JCCP 2005, 7, 3580

Introduction

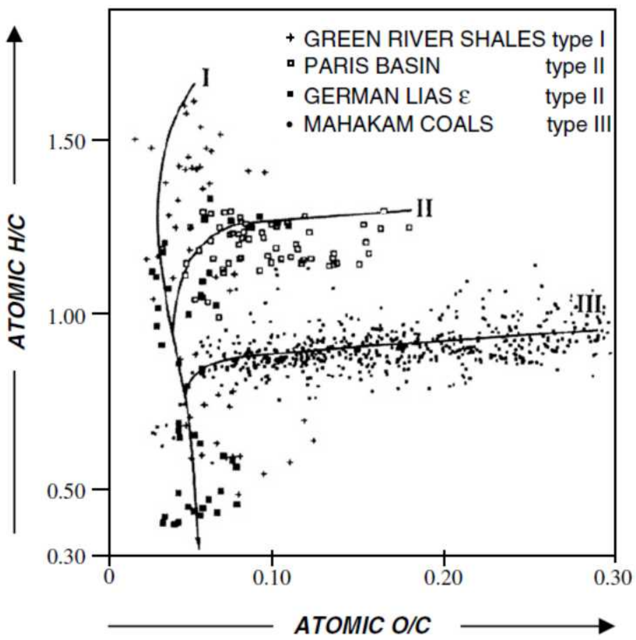
Kerogen

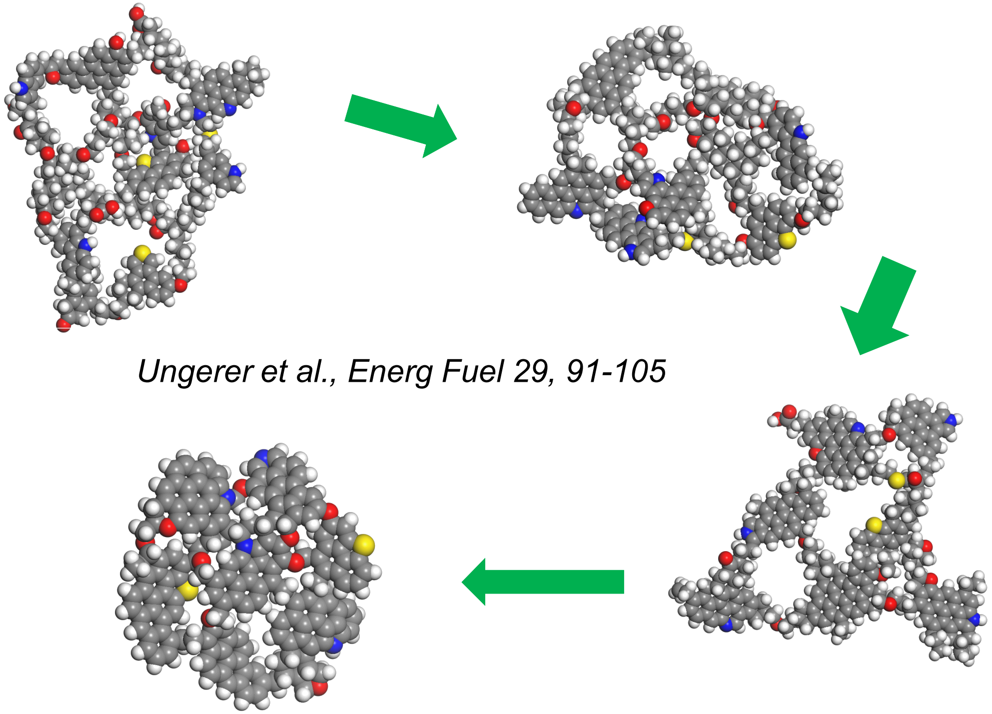


- Insoluble organic matter found in sedimentary rocks (geochemistry)
- Cracks into petroleum products (kerogen maturation, petroleum generation)

Van Krevelen diagram

Organic Geochemistry 38, 719-833 (2007)





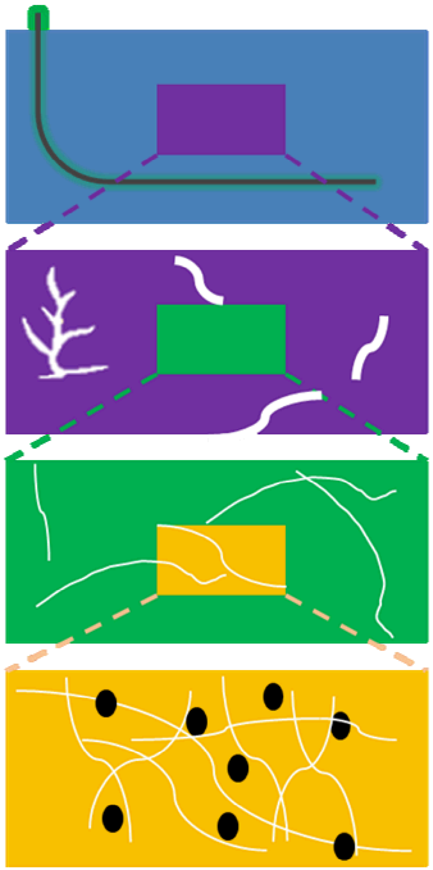
Ungerer et al., Energ Fuel 29, 91-105

- **Hosts pore space responsible for petroleum storage and transport**

Kerogen Research Motivations

Sandia National Laboratories

Hosts pore space responsible for petroleum storage and transport
Shale gas revolution



Macroscale: gas flow to the wellbore

Mesoscale: micro-fractures network

Microscale: nanopores network

Nanoscale/Sub-nanoscale: Gas diffusion from kerogen/clay porous structure to nanopores.

JCPT 46, 55 -61 (2007)

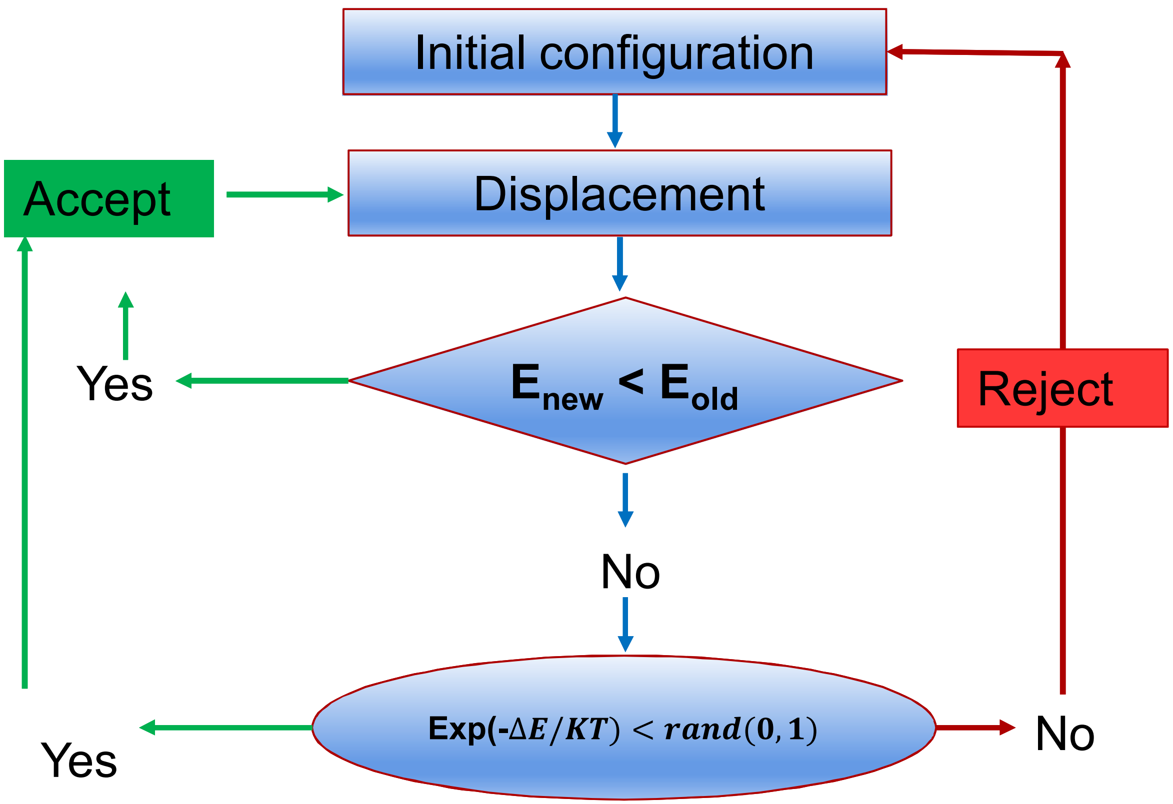
Understand gas adsorption and release from kerogen nanopores

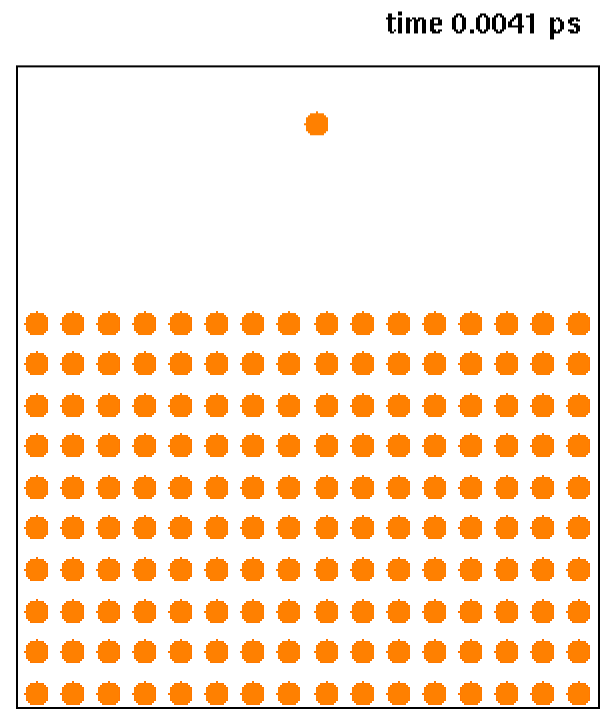
My research on kerogen

Molecular modeling of gas adsorption and release from kerogen

Techniques:

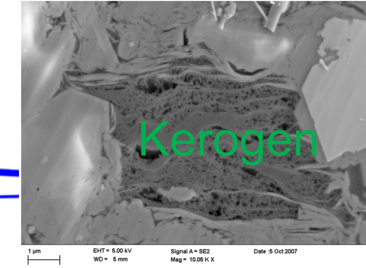
- **Molecular dynamics simulation**: Numerically solving Newton's equations of motion F=ma
- **Monte Carlo molecular simulation:**

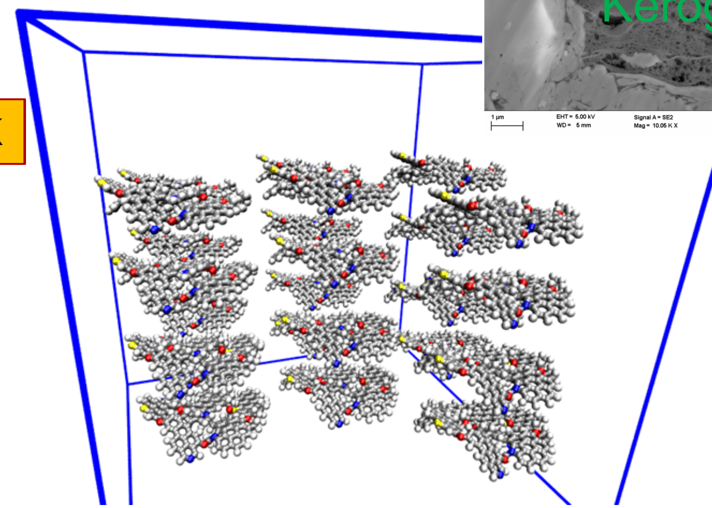


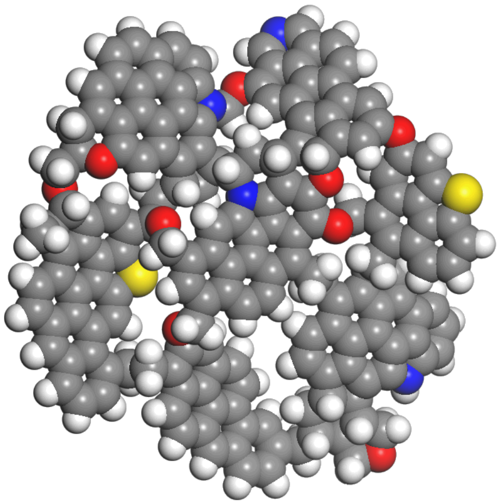


(Wikipedia)

Formation of condensed kerogen







$C_{175}H_{102}O_9N_4S_2$

Energy Fuels 2015, 29, 91-105

24 Kerogens in 10x10x10nm^3 box, 1000K

NVT

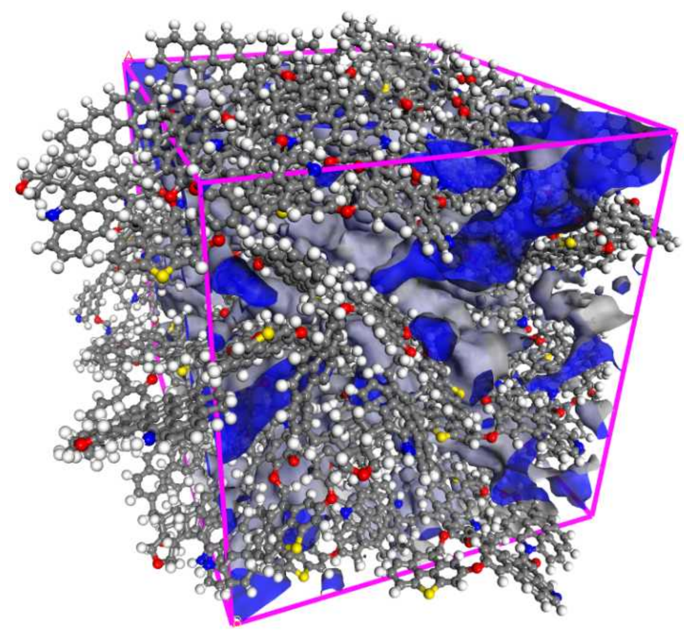
9 snapshots

NPT, 100at, 900K to 300K

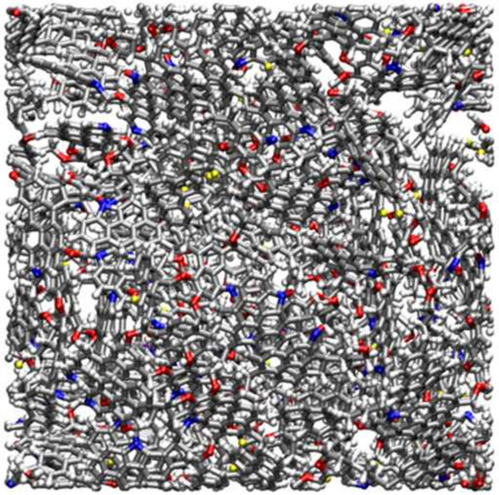
300K and 100atm

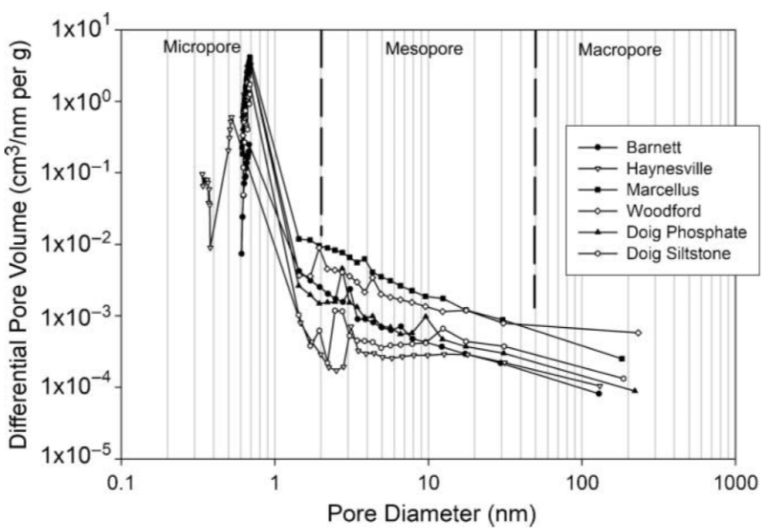
NPT, 1atm, 300K

9 samples at 300K and 1atm



Characterization





AAPG 96 (2012), 1099-1119

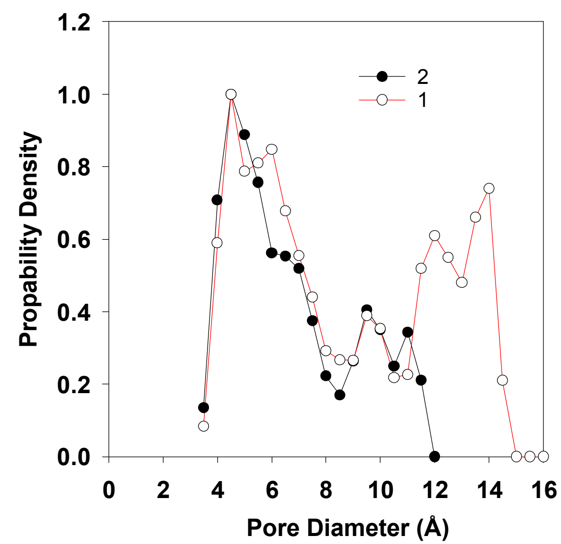
Density

Sample 1: 1.172g/cm^3
Sample 2: 1.287g/cm^3

Average :1.22±0.04 g/cm^3
Experiment: 1.28±0.3g/cm^3

Stankiewicz A, *et al.* (2015) Kerogen density revisited – lessons from the Duvernay Shale. *In: Paper URTeC 2157904 at the Unconventional Resources Technology Conference, San Antonio, Texas, July 2015*

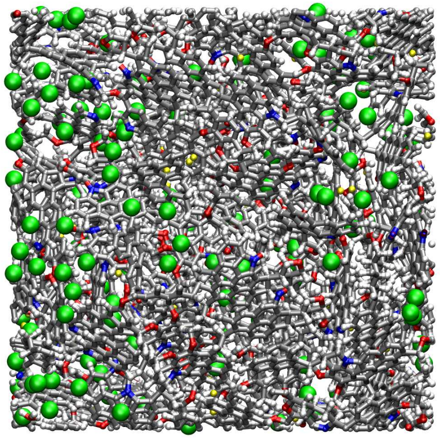
Pore size distribution



Method: Bhattacharya S & Gubbins KE (2006) *Langmuir* 22:7726-7731

Nature materials

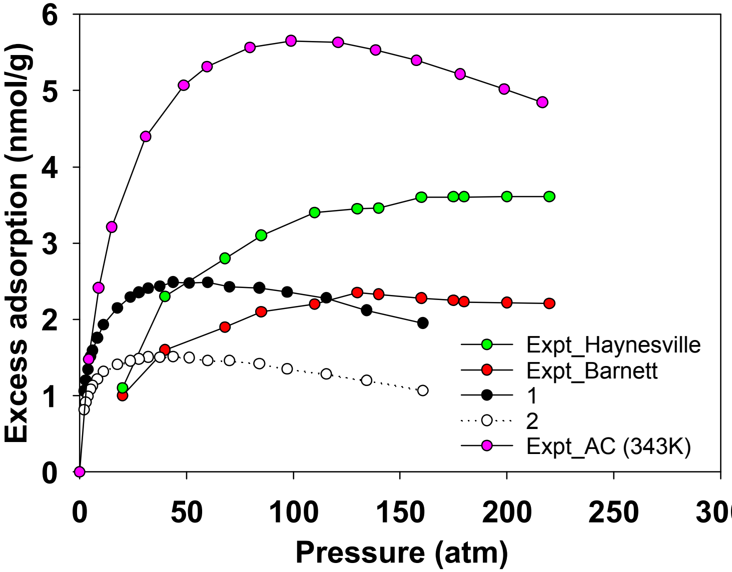
Methane adsorption



Total adsorption
Excess adsorption

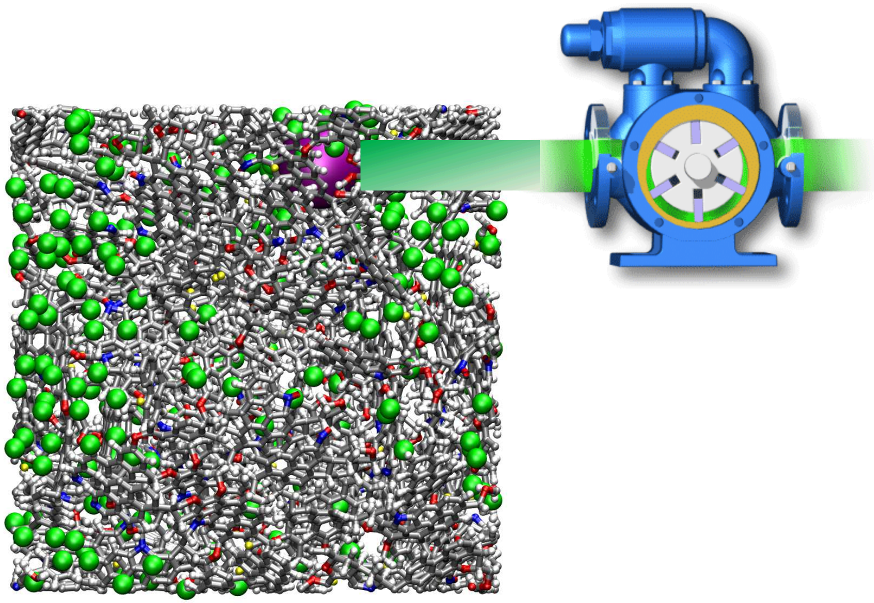
$$n_{excess} = n_{total} - \rho_{P,T} V_{free},$$

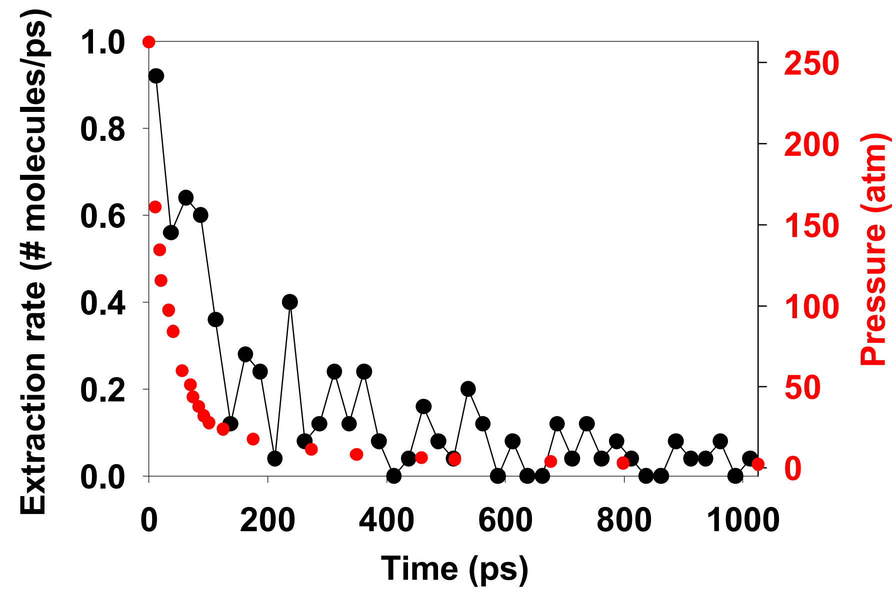
Method: GCMC simulations

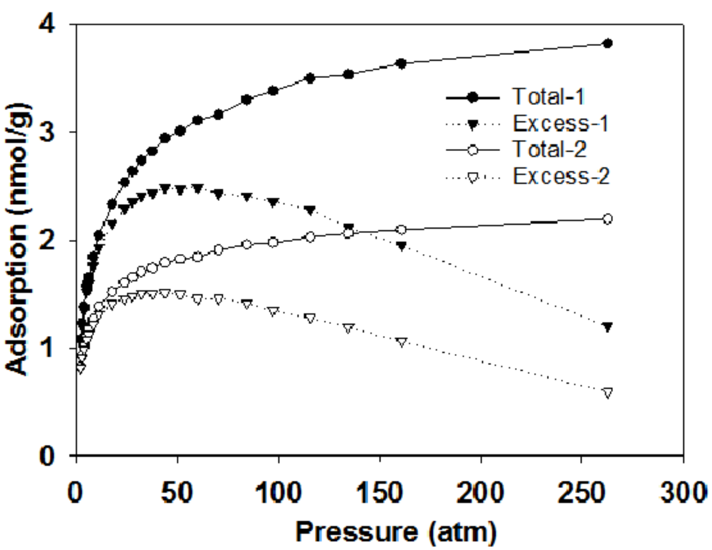


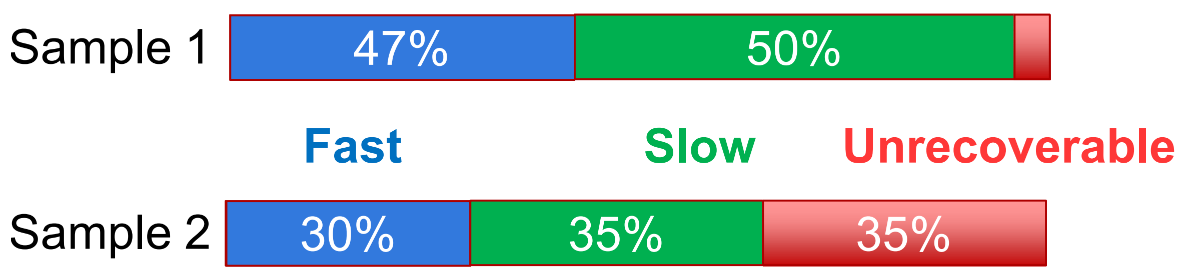
Int J Coal Geol **123**, 34-51 (2014)

Methane extraction from kerogen

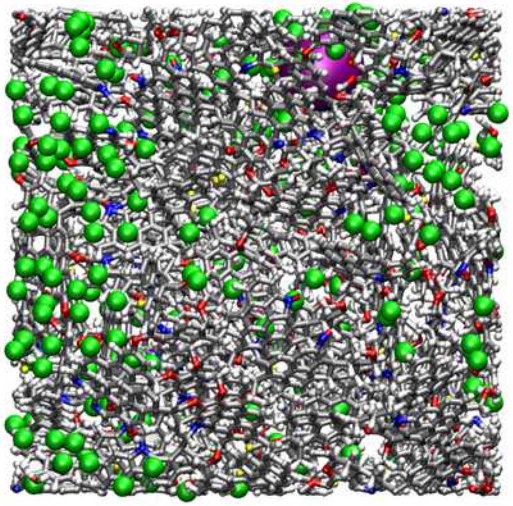


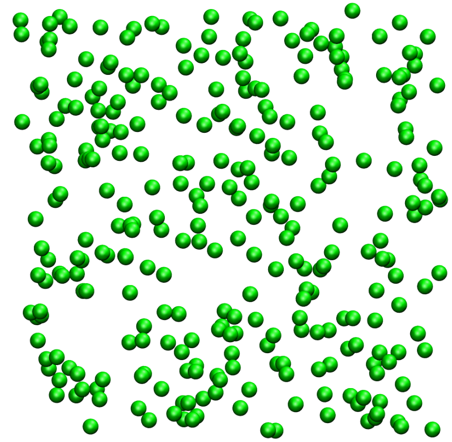


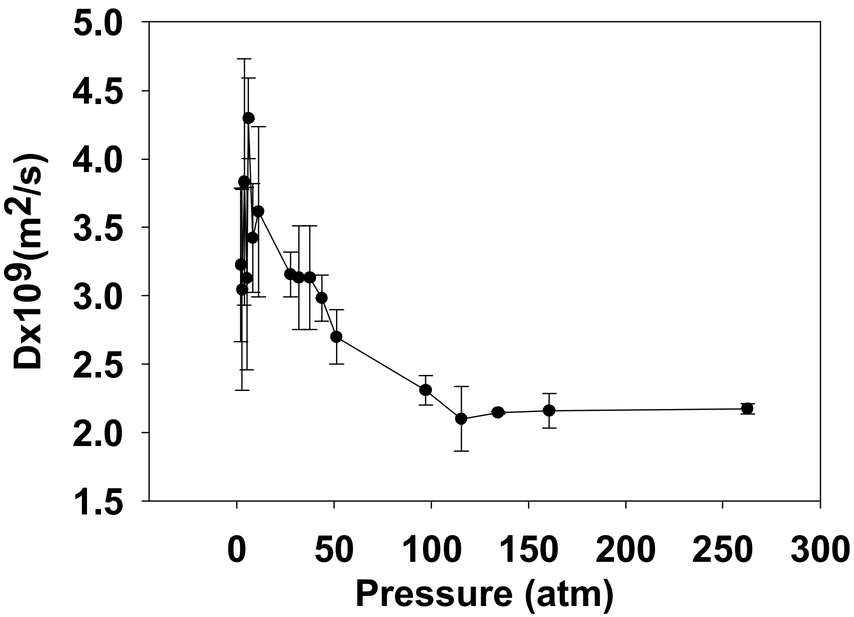


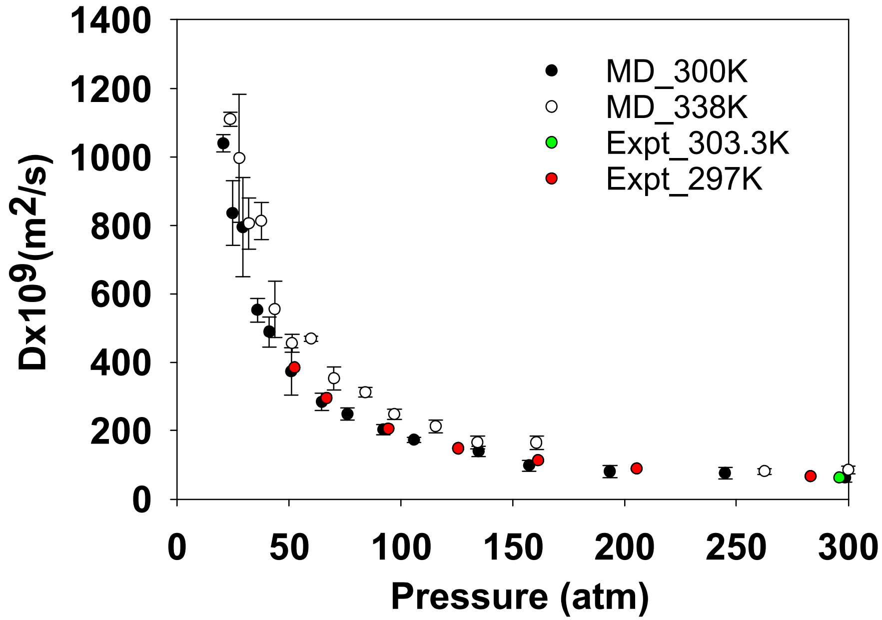


Properties of methane in kerogen







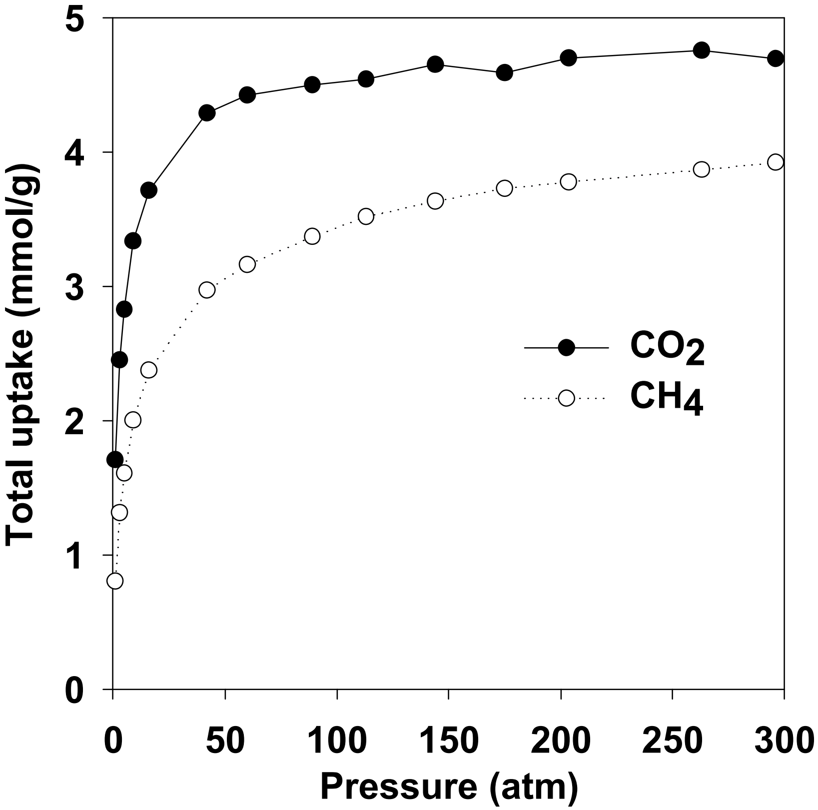


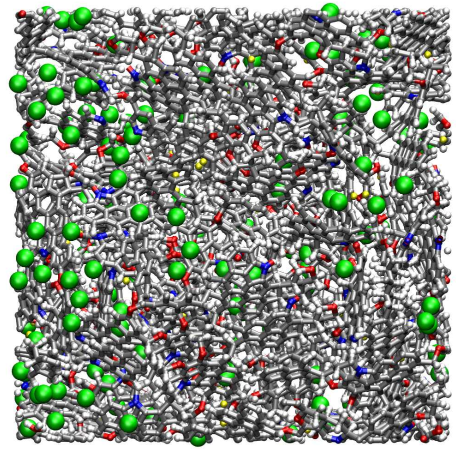
J Chem Eng Data **41**, 598-603 (1996)
Aiche J **16**, 725 (1970)

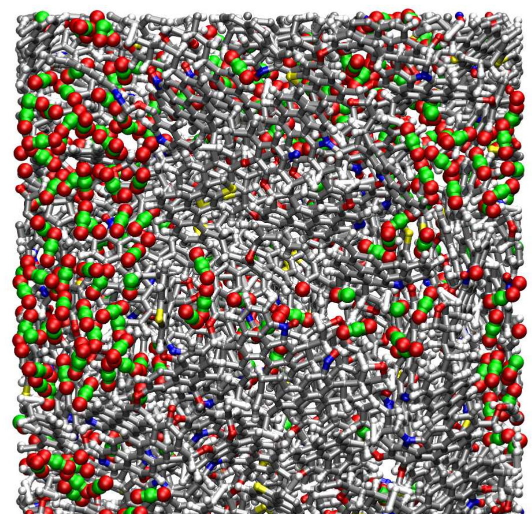
Differential retention and release of CO_2 and CH_4 in kerogen nanopores

Implications for gas enhanced recovery and carbon sequestration

Pure gas adsorption

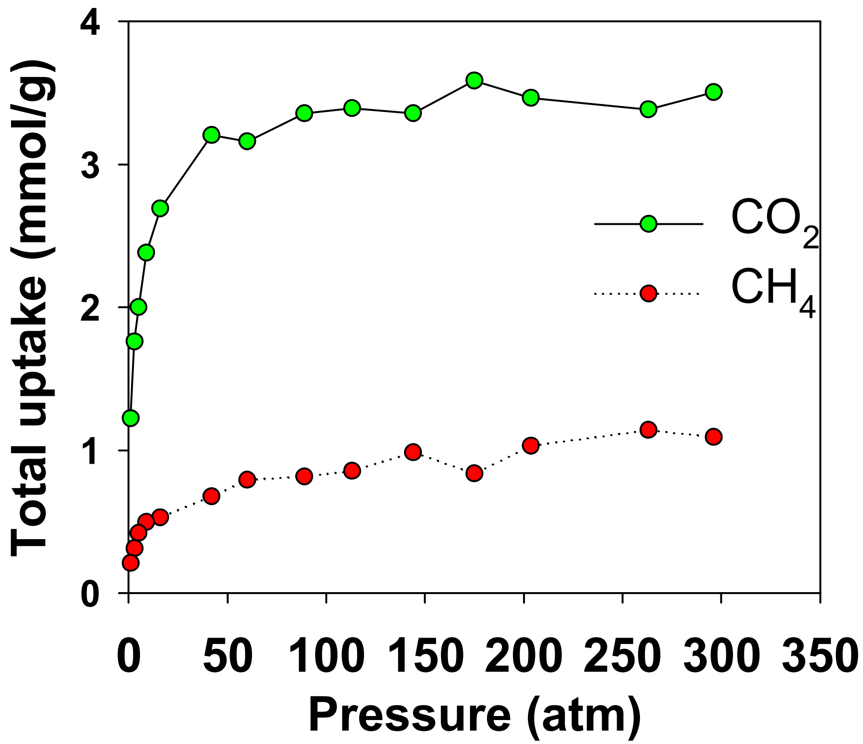






Differential retention and release of CO_2 and CH_4 in kerogen nanopores

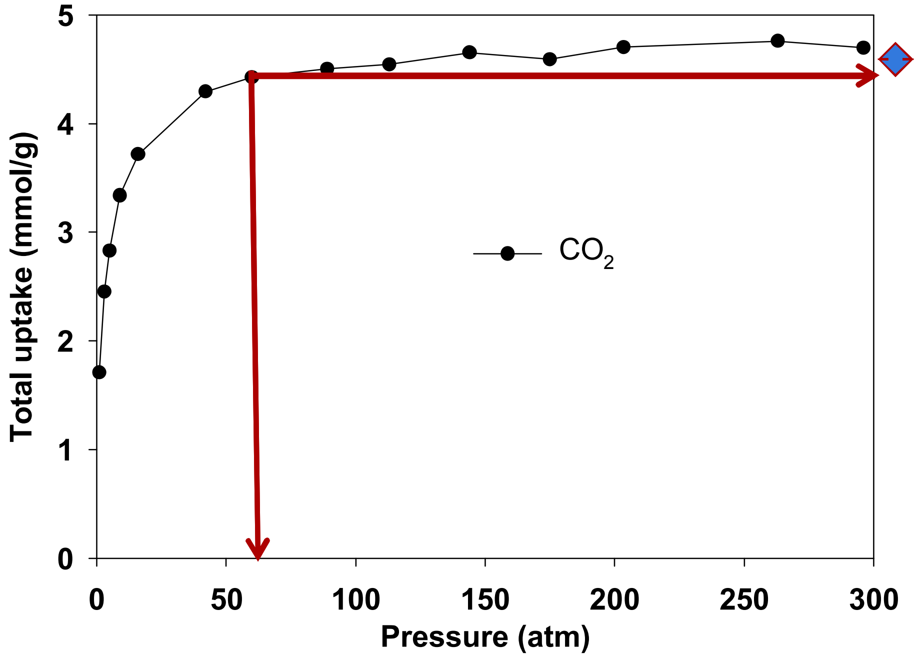
1:1 binary gas adsorption



Kerogen preferentially retains CO_2 over CH_4

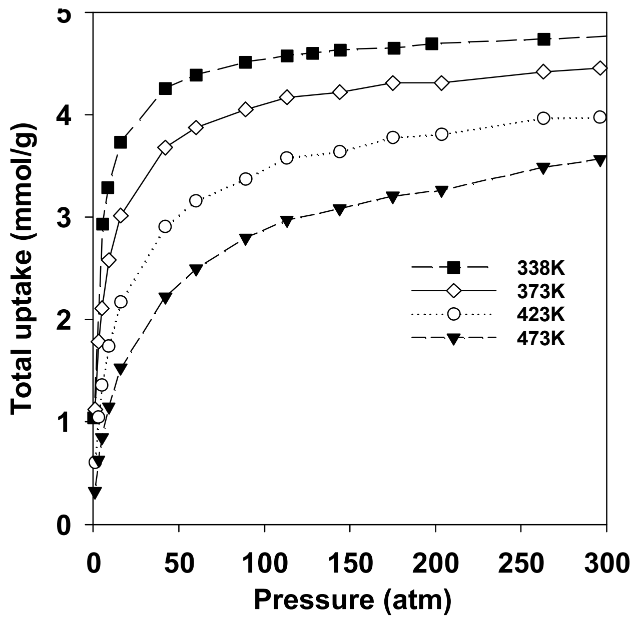
CO_2 release

Adsorption of pure CO_2 in kerogen



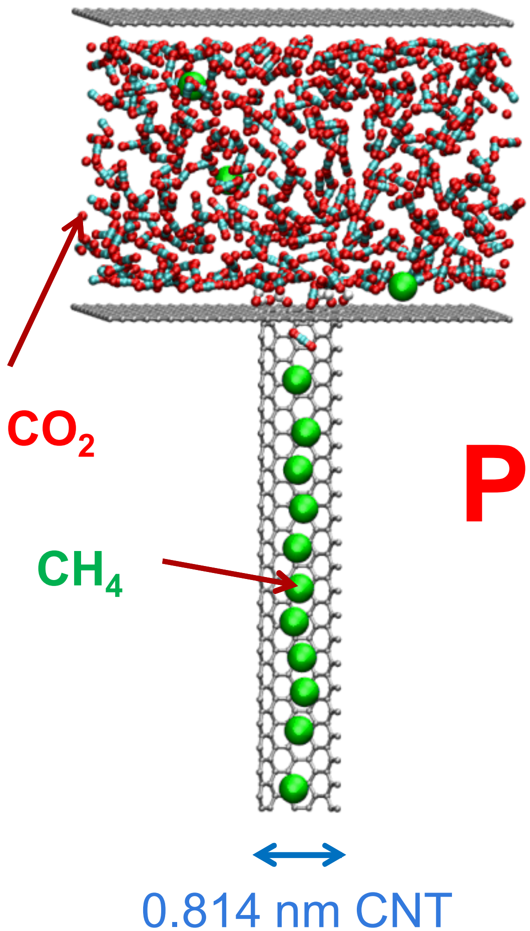
Decrease P from 300 atm to CO_2 supercritical pressure will release small amount of CO_2

Most of CO_2 generated during kerogen maturation might be trapped in kerogen unless P < supercritical CO_2



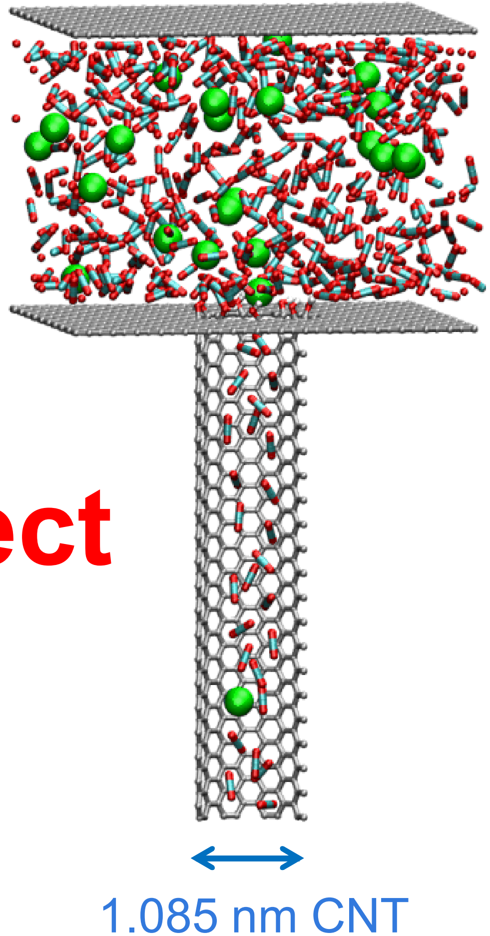
Increasing temperature due to increasing burial depth during kerogen maturation also causes CO_2 to desorb. However, a large amount of CO_2 still trapped in kerogen at P > supercritical P

Pore specific effects on enhanced gas recovery



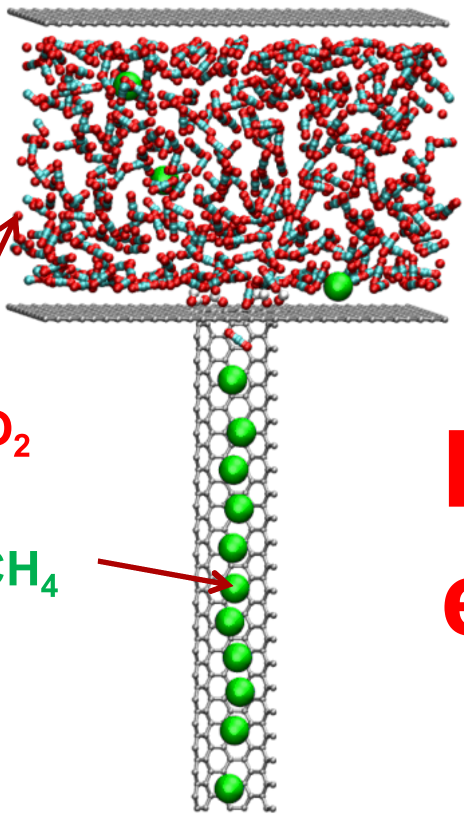
Pore is too small for the invasion of CO_2

Pore size effect



Pore is big enough for the invasion of CO_2

Pore specific effects on enhanced gas recovery



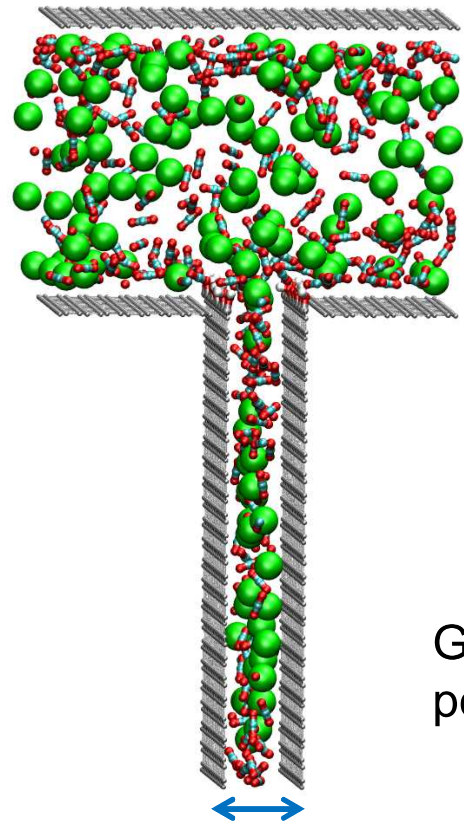
CO_2

CH_4

0.814 nm CNT

Pore is too small for the invasion of CO_2

Pore shape effect

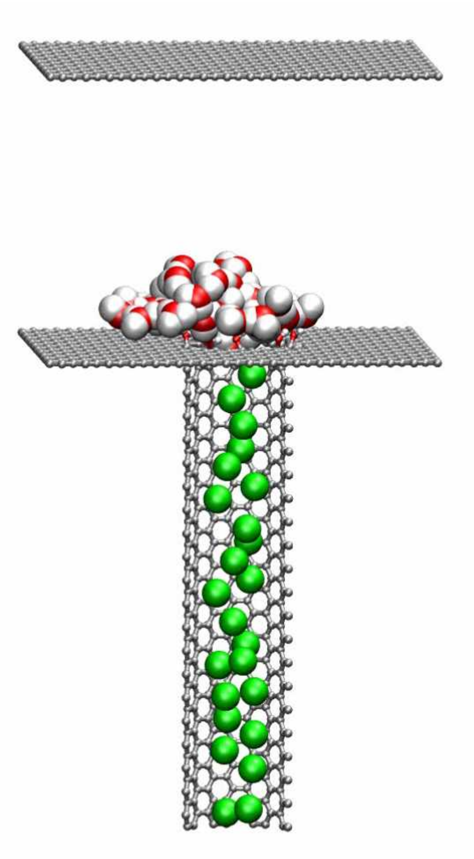


Graphene slit-pore

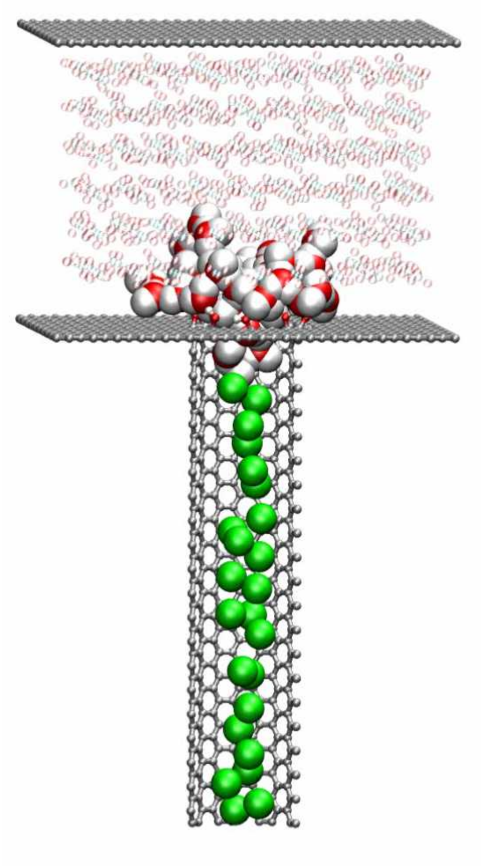
0.814 nm CNT

Methane and CO2 can diffuse in the direction parallel to the slit-pore surfaces

Pore specific effects on enhanced gas recovery



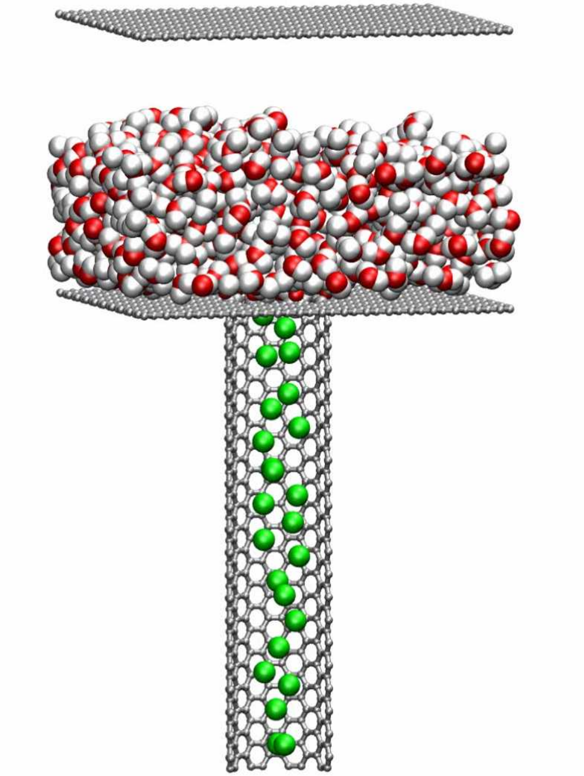
Water effect



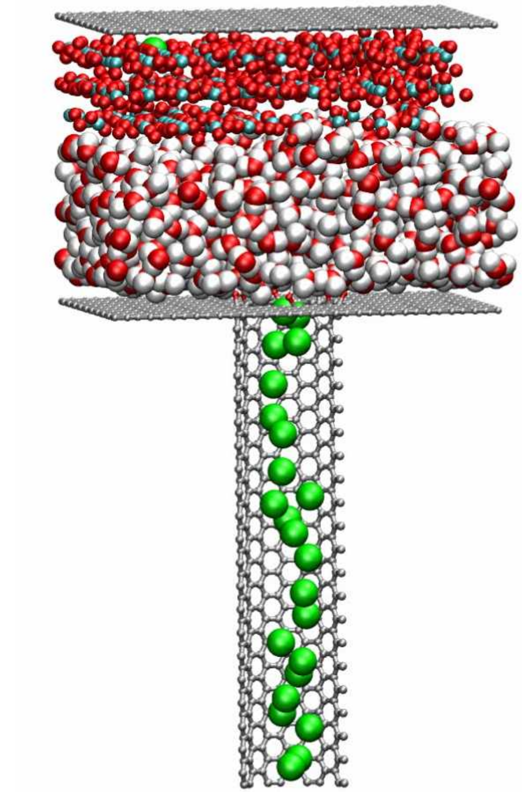
Assume that water drop blocks the pore entrance.

CO_2 invades through water and replaces CH_4 in the nanopore.

Pore specific effects on enhanced gas recovery



Water effect



Assume that water thin films block the pore entrance.

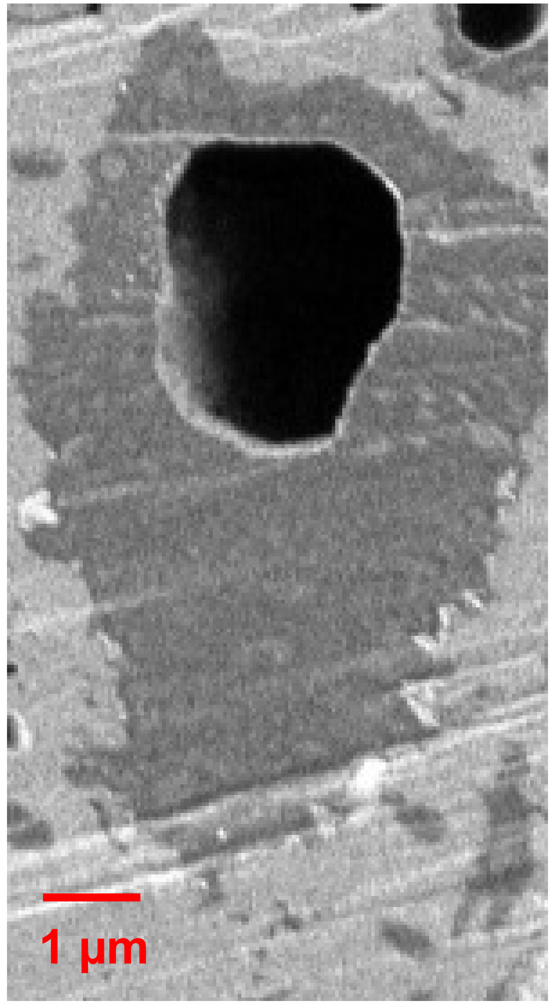
CO_2 invades through water and replaces CH_4 in the nanopore.

Kerogen swelling

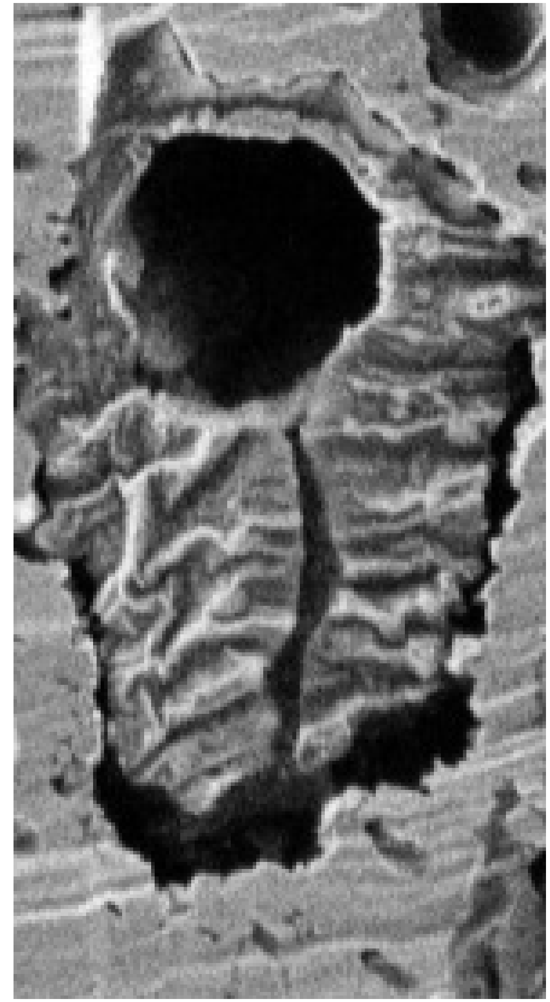
Rubber swelling in oil

From: **Drew Pomerantz**, Schlumberger

Will kerogen swell upon gas adsorption?



Intact shale with swollen kerogen



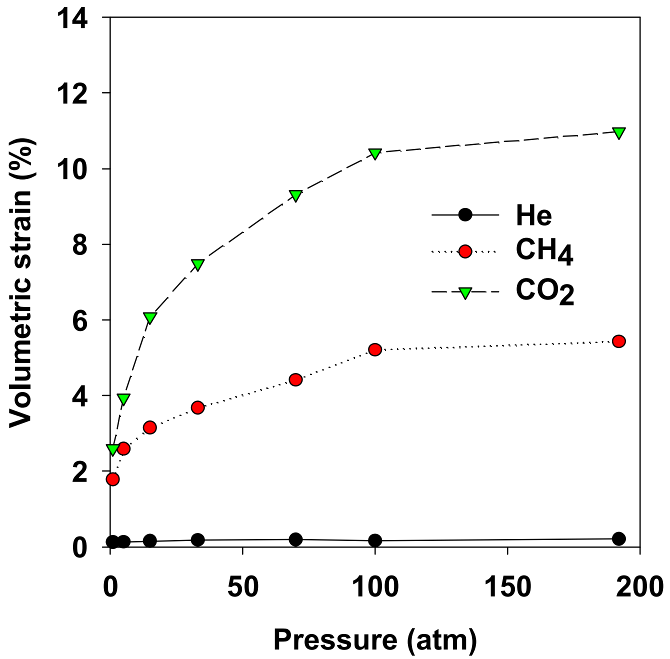
Bitumen-extracted shale with collapsed kerogen

Kerogen swelling with gas

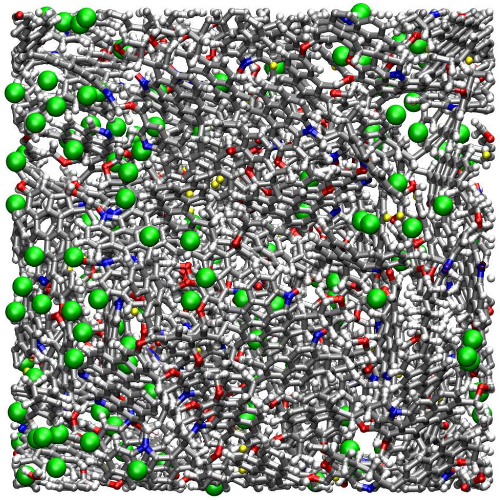
Will kerogen swell upon gas adsorption?

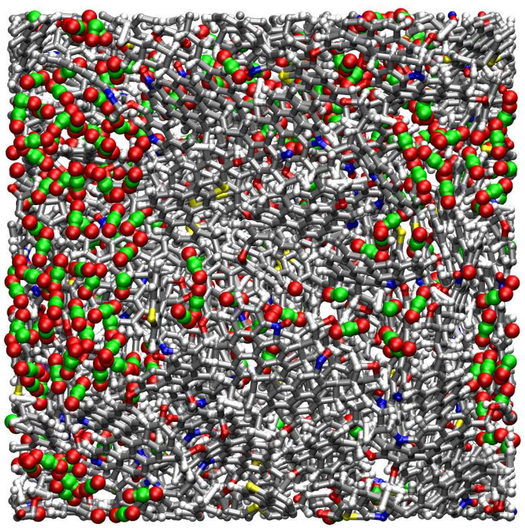
$$Volumetric\ strain = \frac{V - V_o}{V_o}$$

V: kerogen volume after gas adsorption
V_o: kerogen volume before gas adsorption



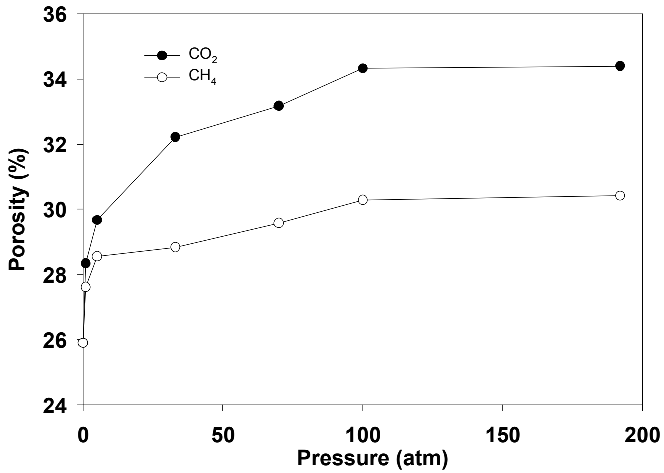
Upon shale gas extraction kerogen shrinks

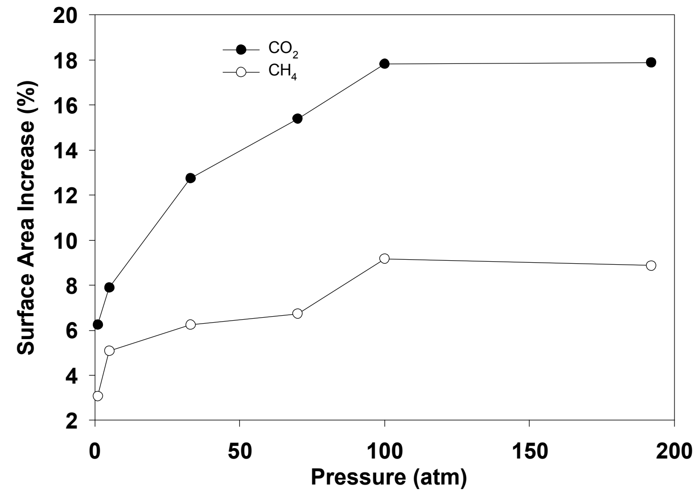




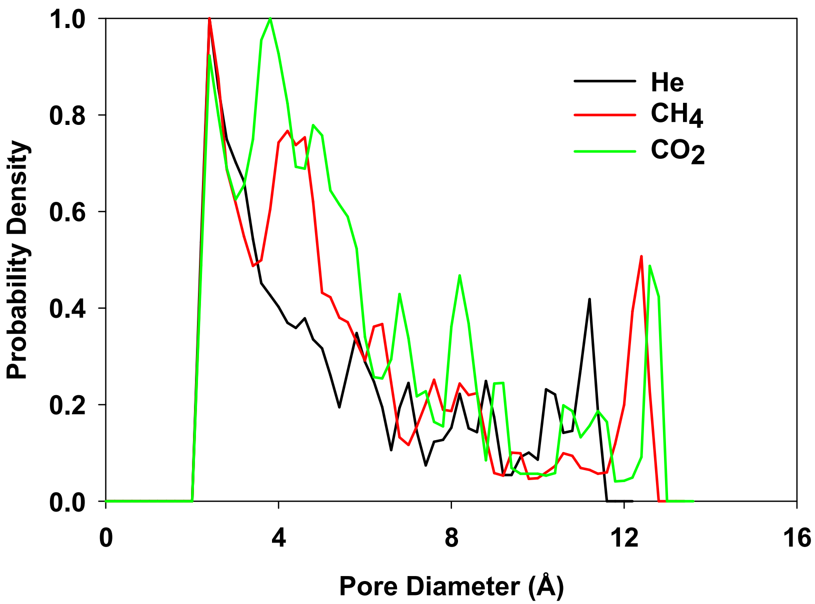
Kerogen swelling with gas

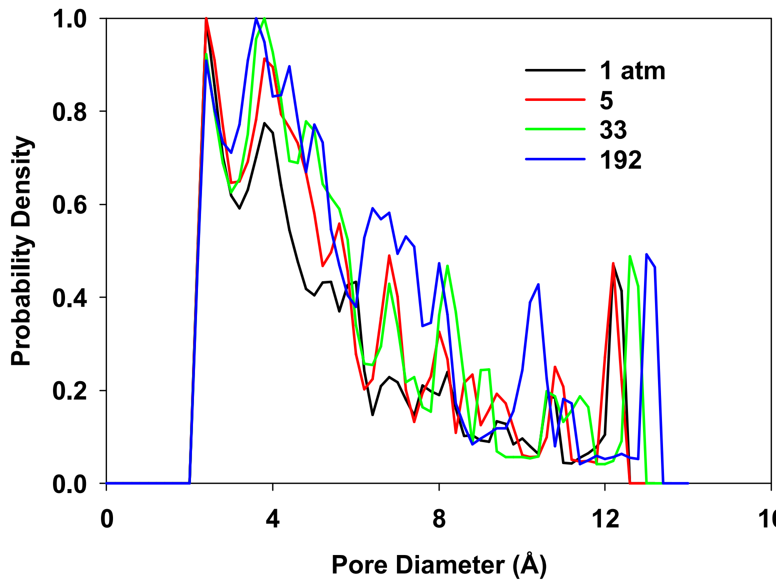
Effects of kerogen swelling on porosity and surface area





Effects of kerogen swelling on pore size distribution





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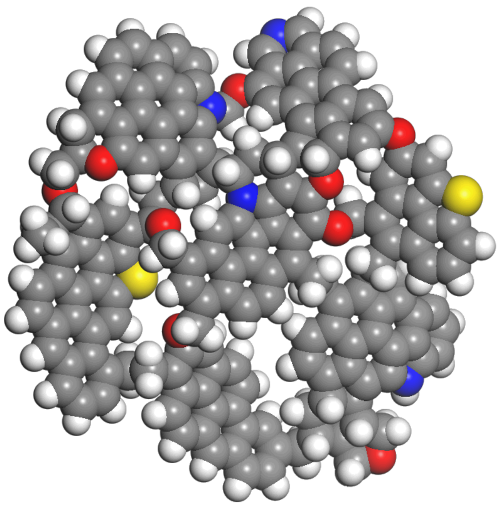
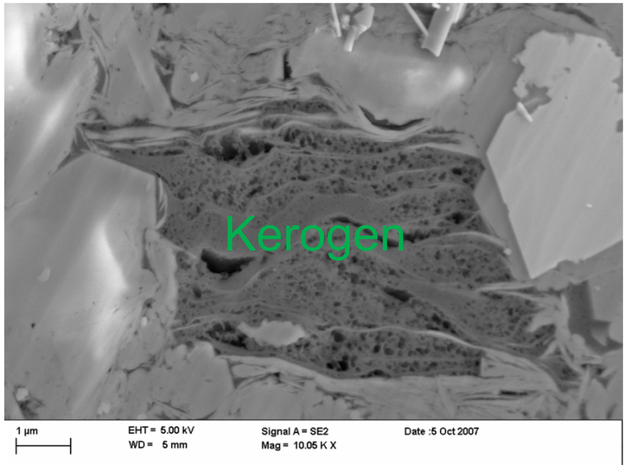
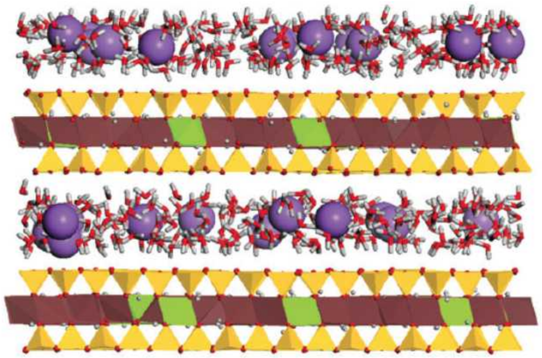


Energy Fuels 2015, 29, 91-105



SPE 124253 (2009)

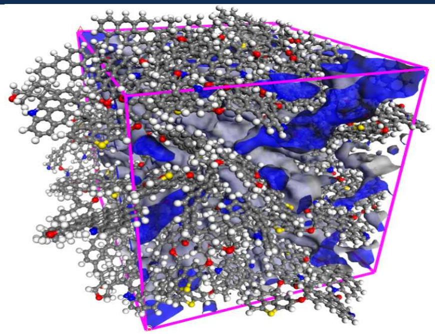


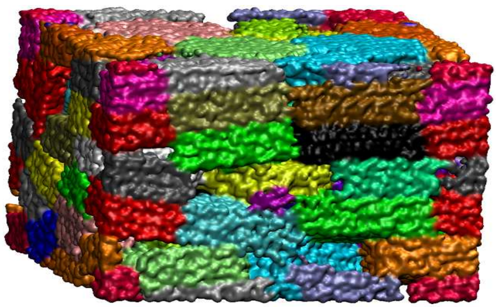
Na-Montmorillonite

JCCP 2005, 7, 3580

Molecular modeling of gas adsorption and release from subsurface porous media

Tuan Anh Ho (8865)





LDRD/NETL: Fundamental understanding of the methane-carbon dioxide-water interactions in shale nanapores under reservoir conditions.

BES: Interfacial geochemistry of nanopores: Molecular behavior in subsurface environments.

CFSES: CO_2 sequestration.

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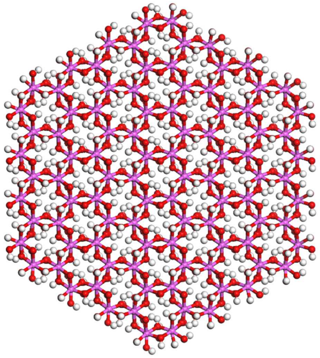
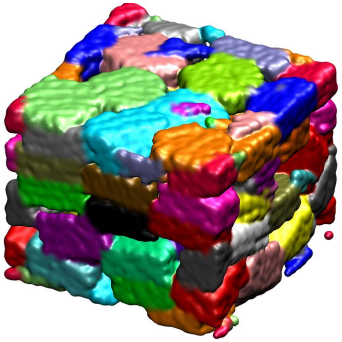
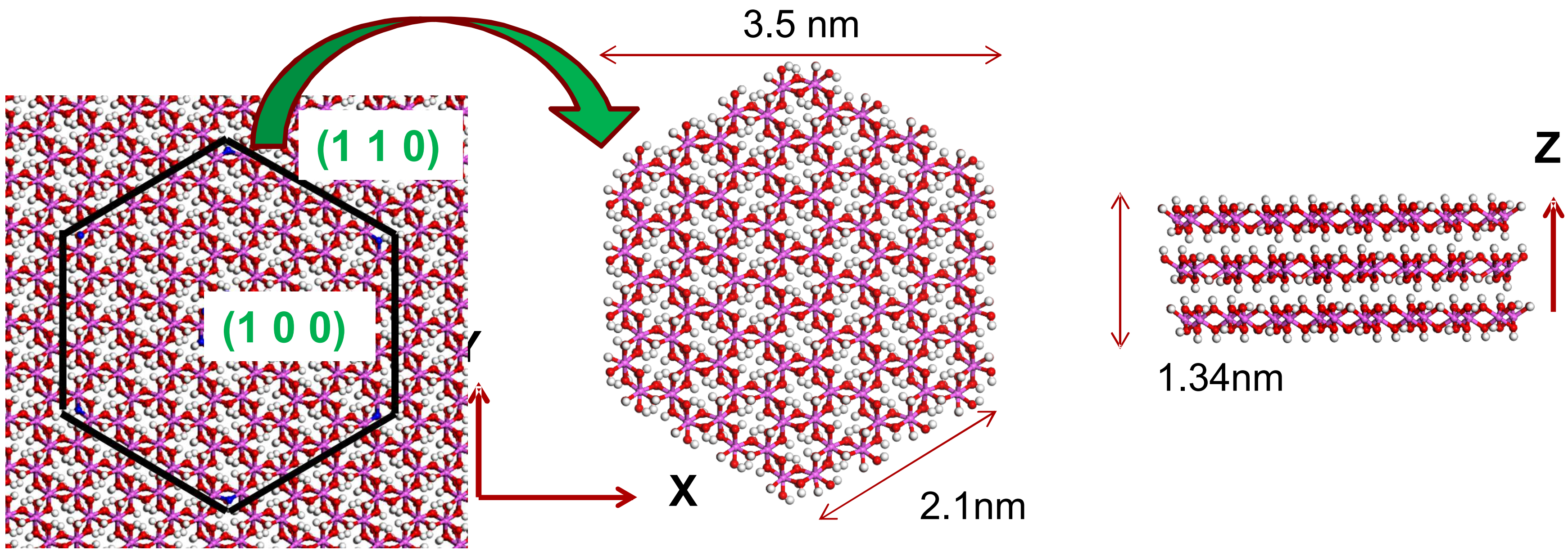




Atomistic Structure of Mineral Nano-aggregates from Simulated Compaction and Dewatering

Gibbsite nanoparticle construction



ClayFF force field:

Lennard-Jones:σ (Å), ϵ (Kcal/mol)

Al: 4.27132, 1.3297e-06

O:3.165, 0.1554

H: 0, 0

Charge

Al :1.575e

O : -0.95e

H : 0.425 e

Bond: OH harmonic

Additional term:

Al-O-H angle harmonic

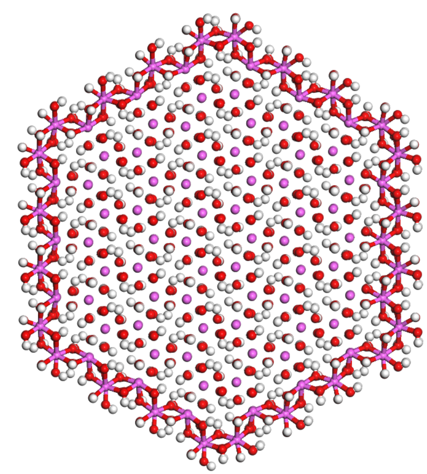
110^o

Al-O-Al angle harmonic

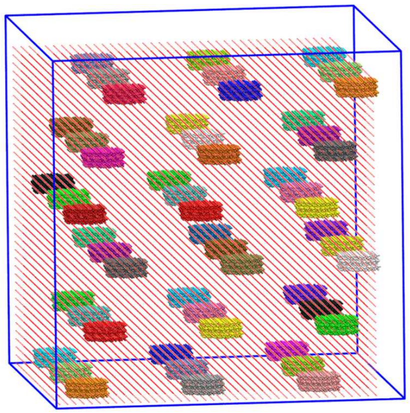
(edge surfaces)

100^o

k = 800Kcal.mol^{-1}.rad^{-2}

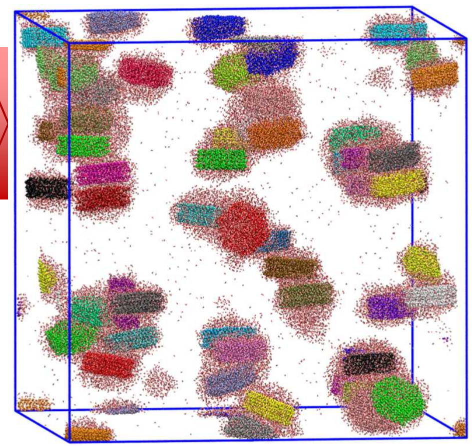


Gibbsite aggregate



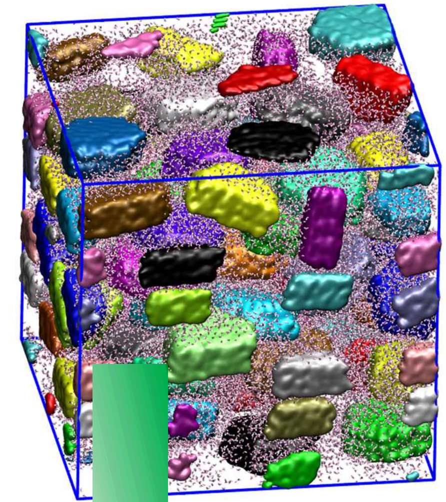
54 NPs, 55008 H_2O
$30x30x30nm^3$

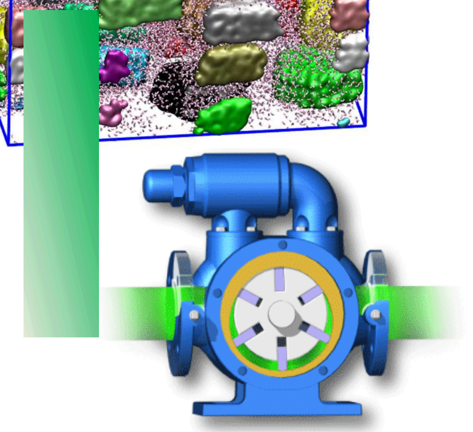
NVT, 0.3ns, 300K PPPM



NPT, 0.3ns, 300K, 100MPa Short-range

$15.4x15.5x14.9nm^3$





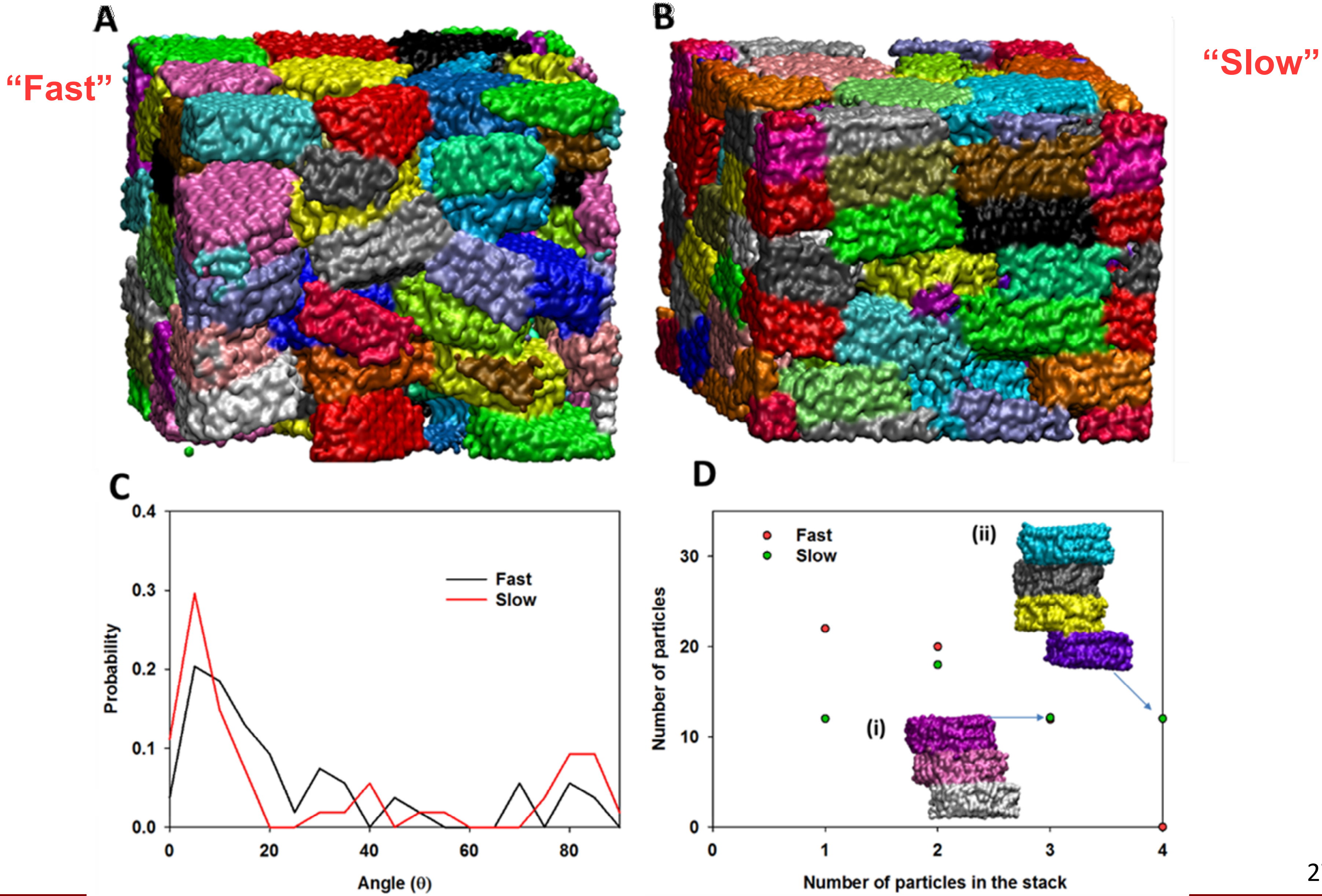
Effect of dewatering rate:

- Delete all water: "Fast"
- Delete 100 H_2O/100 steps: "Intermediate"
- Delete 10 H_2O/100 steps: "Slow"

Effect of water content:

- 1 water layer around each particle: 1W (22.5wt%)
- 2 water layers around each particle: 2W (37.2wt%)
- Additional withdraw water from 2W: 2W_dewatering (6wt%)
- Dry: 2W_dry

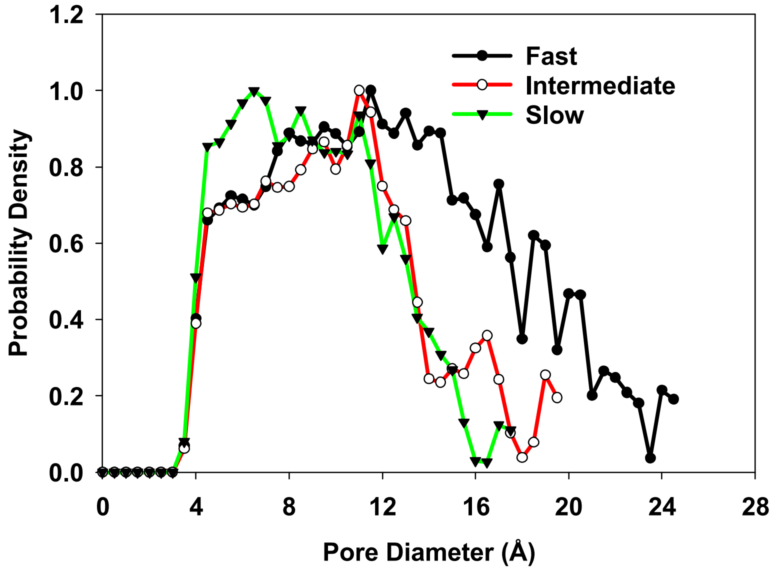
Aggregate structure



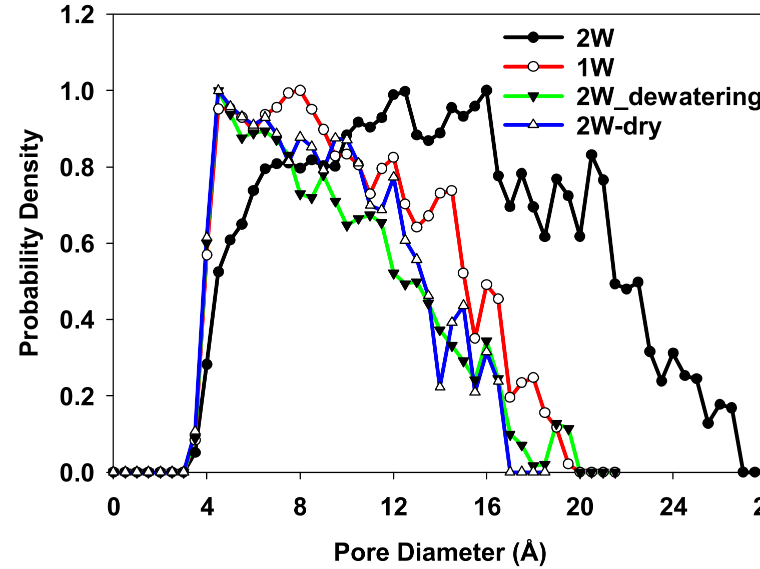
Results

Sandia National Laboratories

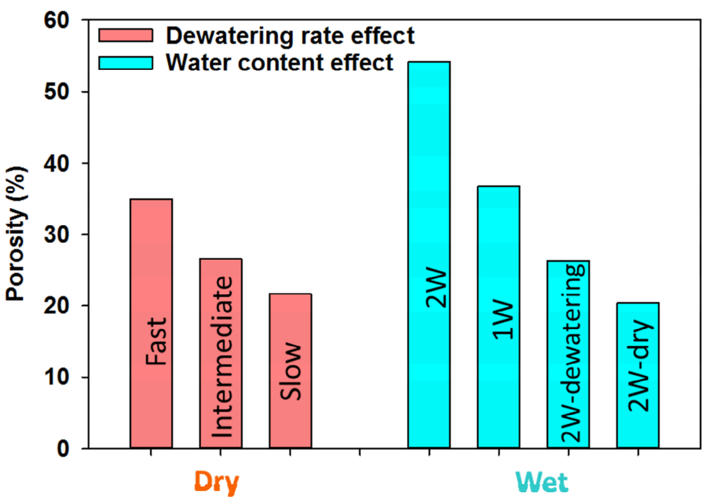
Effect of dewatering on PSD

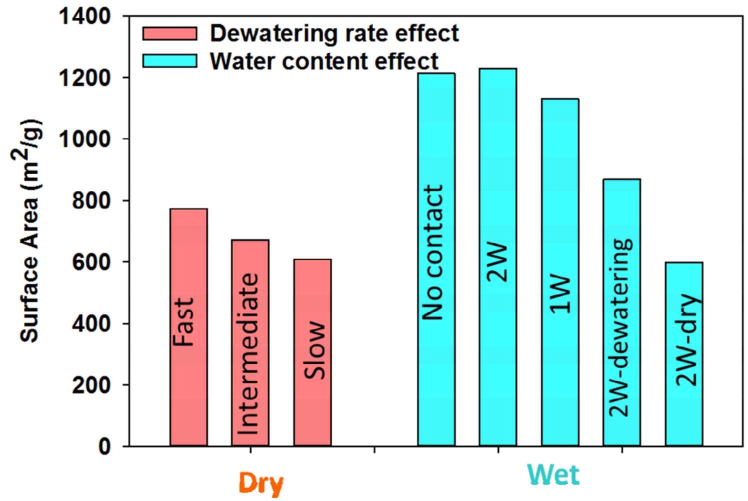


Effect of water content on PSD



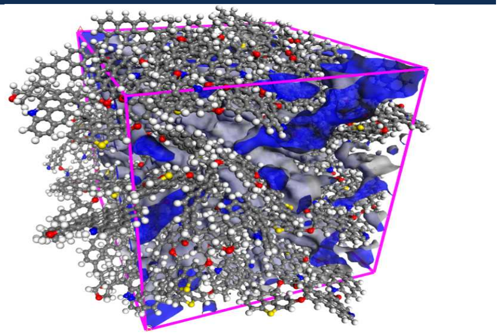
Effect of dewatering rate and water content on porosity and surface area

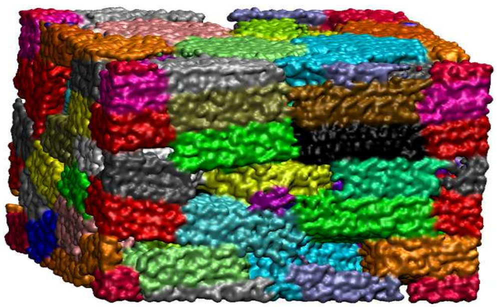




Molecular modeling of gas adsorption and release from subsurface porous media

Tuan Anh Ho (8865)



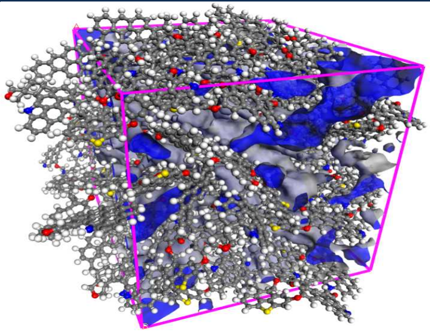


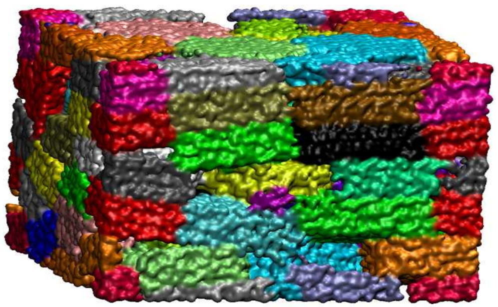
LDRD/NETL: Fundamental understanding of the methane-carbon dioxide-water interactions in shale nanapores under reservoir conditions.

BES: Interfacial geochemistry of nanopores: Molecular behavior in subsurface environments.

CFSES: CO_2 sequestration.

Sandia Postdoctoral Development





Molecular modeling of gas adsorption and release from subsurface porous media

Water

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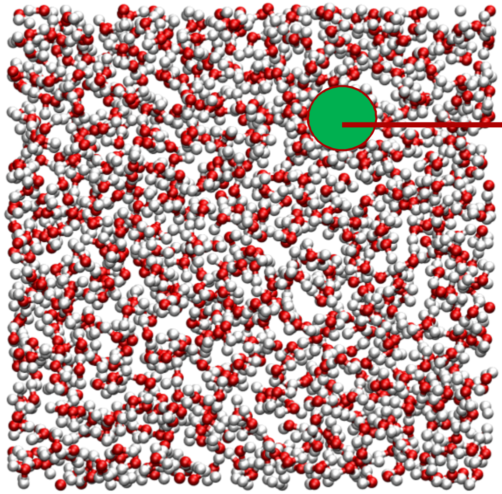
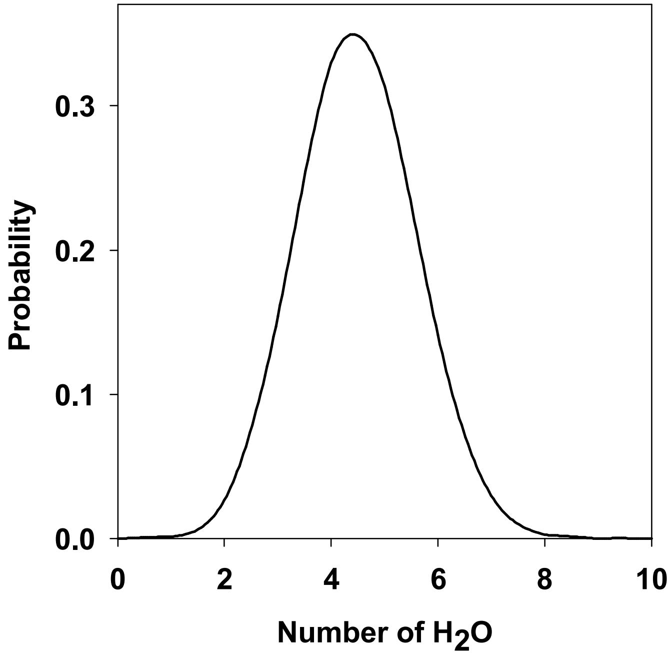
Density fluctuation and cavity formation



Probe volume R=3.3Å

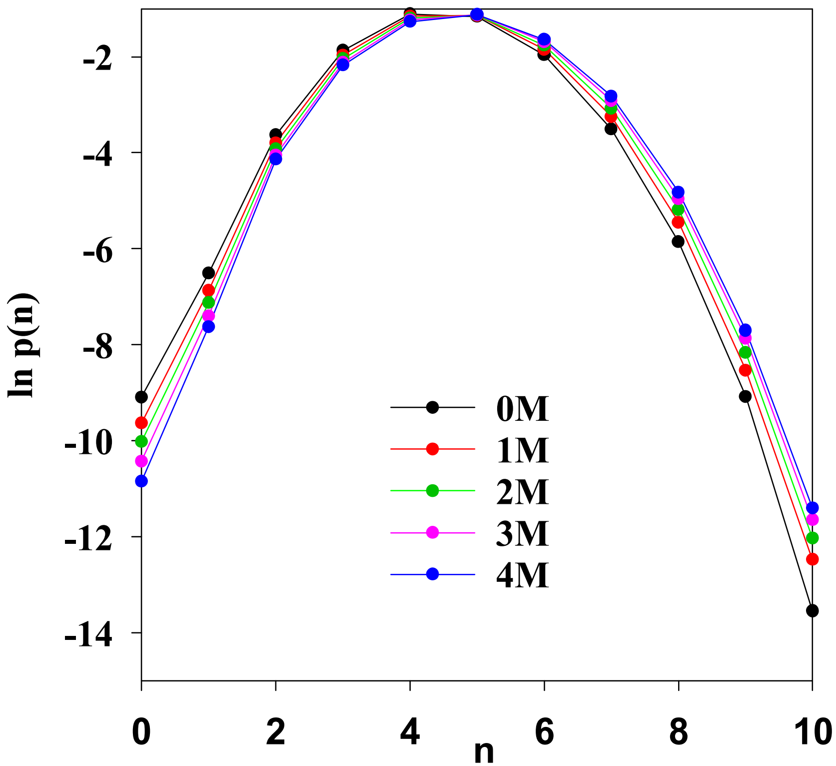
Density of water: 1g/ml → 5 water molecules in the probe volume



Water - Cavity

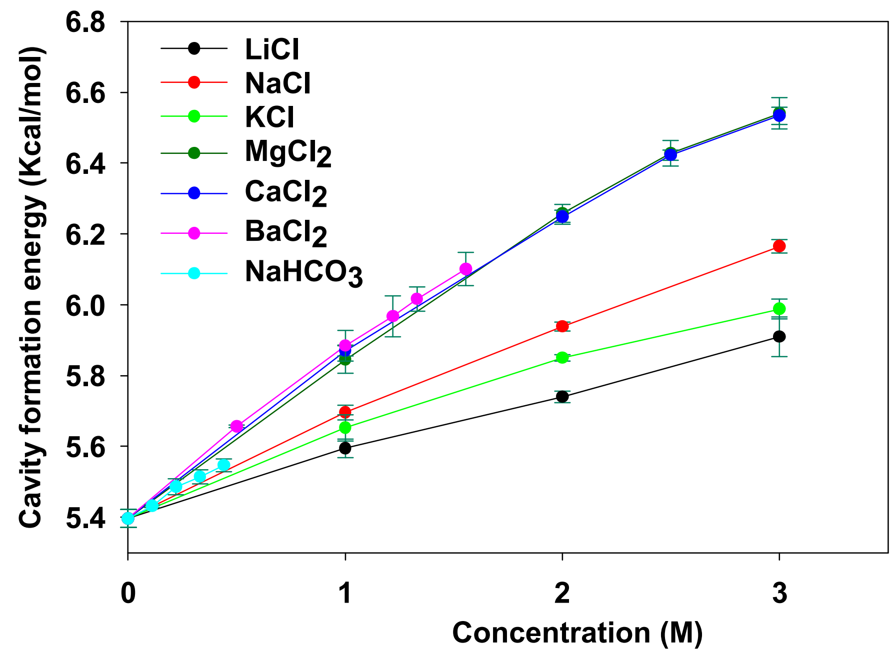
Zero water → cavity

Density fluctuation and cavity formation



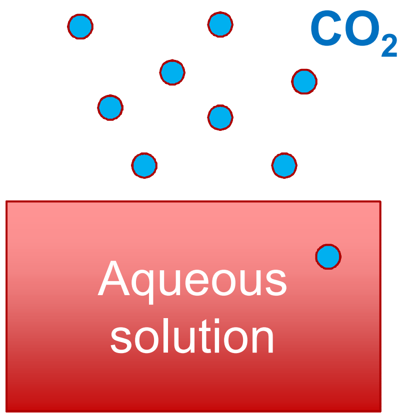
Cavity formation energy

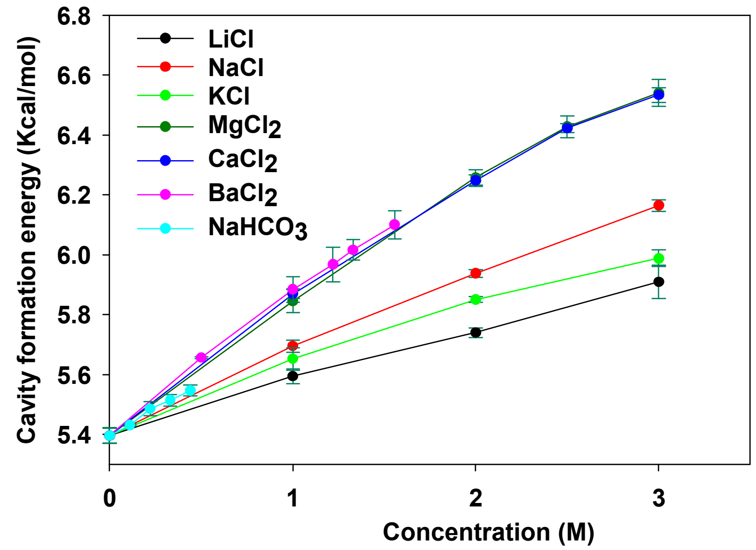
$$\mu = -k_B T ln[P(n = 0)]$$

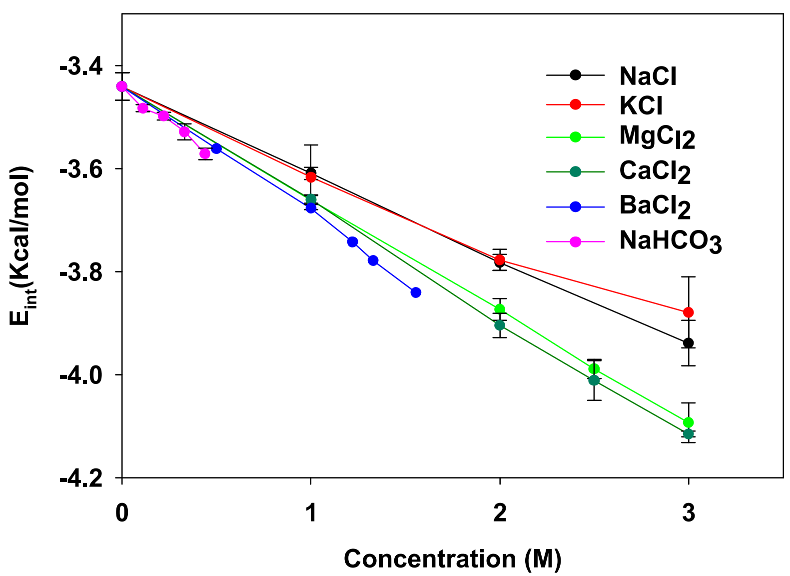


Effects of cavity formation on CO_2 solubility

$$\Delta G = \Delta G_{cavity} + E_{int}$$







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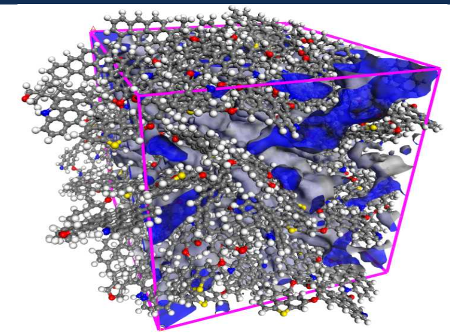

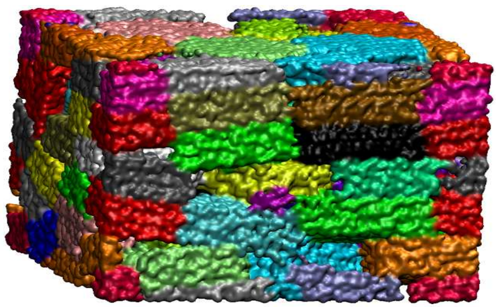

Molecular modeling of gas adsorption and release from subsurface porous media

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- DOE-BES
- CFSES

Thank you for your attention!

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NNSA National Nuclear Security Administration

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