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Sandia National Laboratories

Subsurface Processes at the Nanoscale

Molecular Simulation

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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INTRODUCTION TO MOLECULAR MODELING & APPLICATIONS

- Like regional-scale models, molecular models can be used to simulate different scenarios depending on chemistry (fluid compositions and solid compositions), T, P.
- Processes important in the subsurface often occur/start at interfaces: fluid mixing, solute adsorption, mineral precipitation and dissolution, crack formation and propagation.
- Validation with simple system experiments is important. Then models can be used to predict/hypothesize how other systems might behave.
- Provide input for new constitutive equations for field-scale models.

EXAMPLES:

- Water-scCO_2 Interface
- Brine-scCO_2-Mineral Interface
- CO_2 and CH_4 in Kerogen
- Nanoparticle Aggregation & Porosity
- Subcritical Fracture in Geomaterials

MOLECULAR SIMULATIONS OF CARBON DIOXIDE AND WATER
CATION SOLVATION AND WETTABILITY

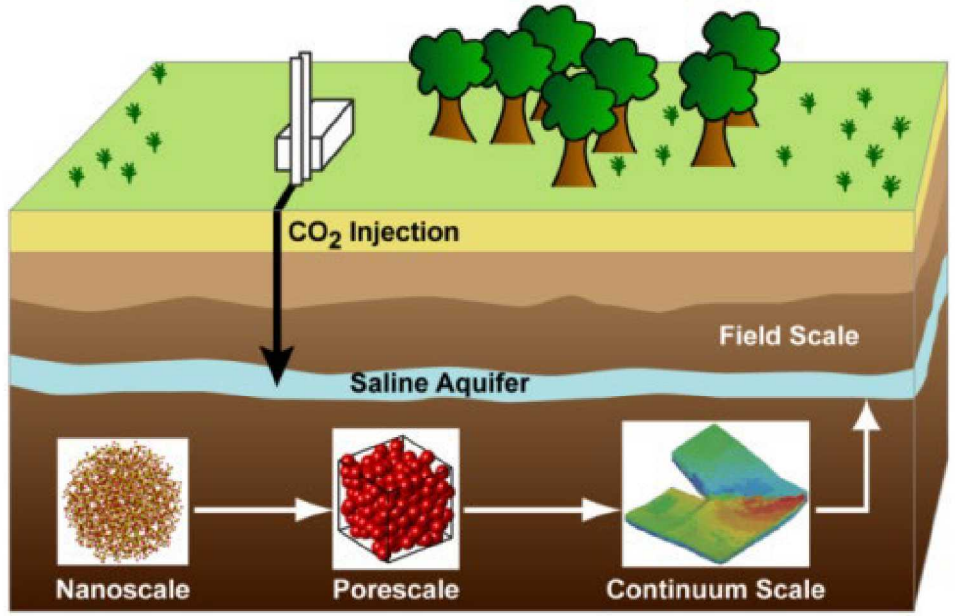
Goal: To model the behavior of $scCO_2$ as it is pumped into subsurface reservoirs and the interaction of $scCO_2$ with resident fluids and minerals over time.

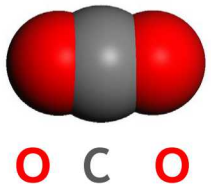
Overview:

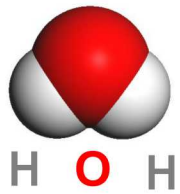
To develop accurate regional-scale models of $scCO_2$ sequestration scenarios, we need to assess the exchange of solutes across the $scCO_2$-water interface.

As a first approximation, these models neglect the solubility of water, salts, metals in $scCO_2$, largely due to lack of data.

What is the impact of ignoring salt solubility? Use computational chemistry methods to explore this subject.



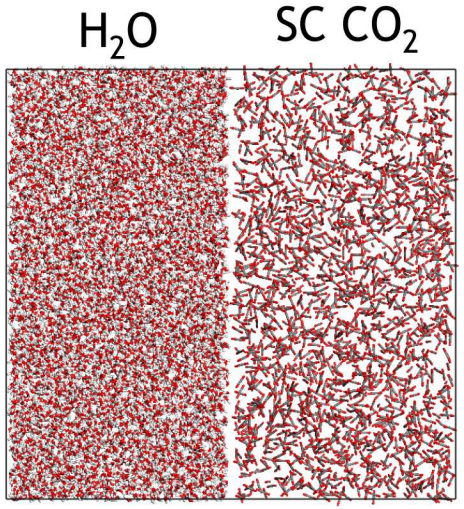




Criscenti, L.J. and Cygan, R.T. (2013) Molecular Simulations of Carbon Dioxide and Water: Cation Solvation. Environmental Science & Technology 47, 87-94.

WATER-SUPERCRITICAL CO_2 INTERFACE: LARGE-SCALE MOLECULAR DYNAMICS

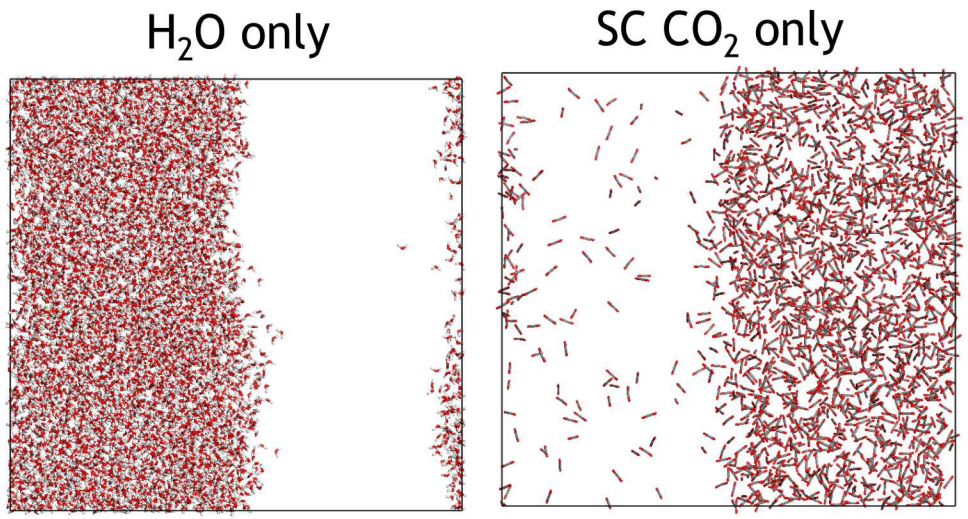
Initial Simulation Cell

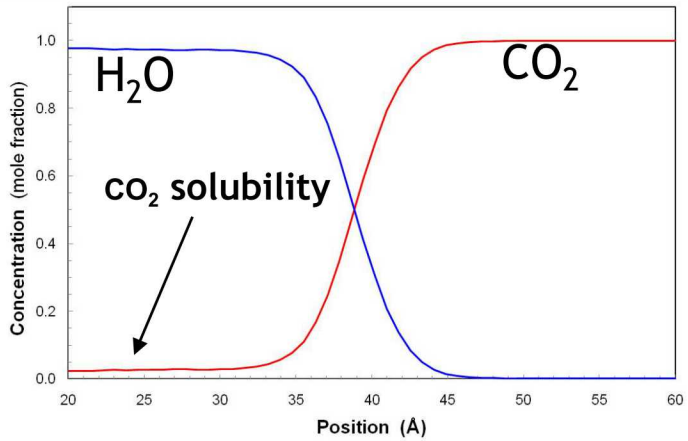


78 Å x 78 Å x 78 Å

NVT ensemble
6,912 H_2O molecules
2,048 CO_2 molecules
Densities at 20 Mpa
(800 m depth)

After 0.5 ns at 350K



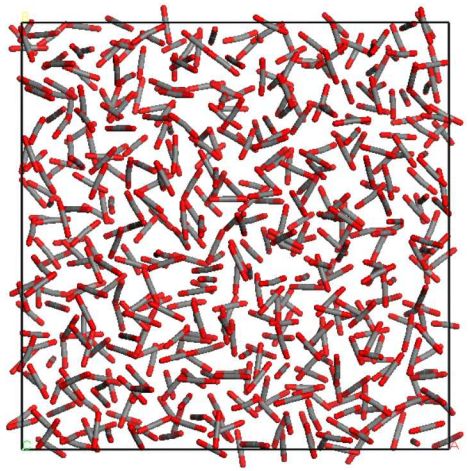


- CO_2 molecules diffuse into water.
- Dissolved CO_2 concentration similar to experimental value.
- Only a trace of H_2O in $scCO_2$ phase.

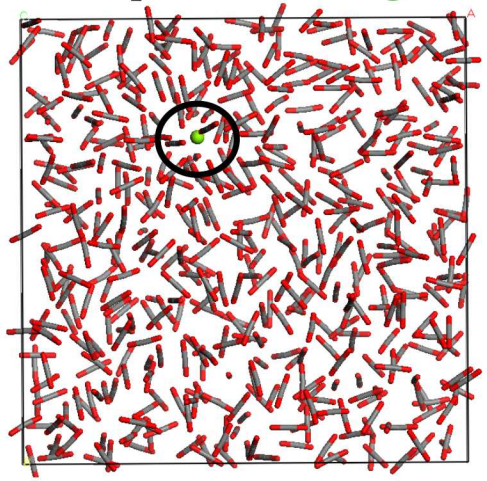
Criscenti, L.J. and Cygan, R.T. (2013) Molecular Simulations of Carbon Dioxide and Water: Cation Solvation. Environmental Science & Technology 47, 87-94.

CATION SOLVATION BY LIQUID CARBON DIOXIDE

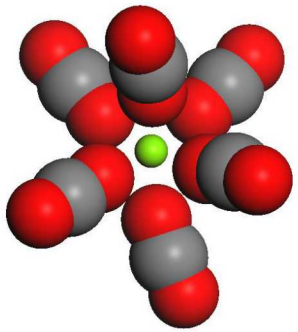
Liquid CO_2

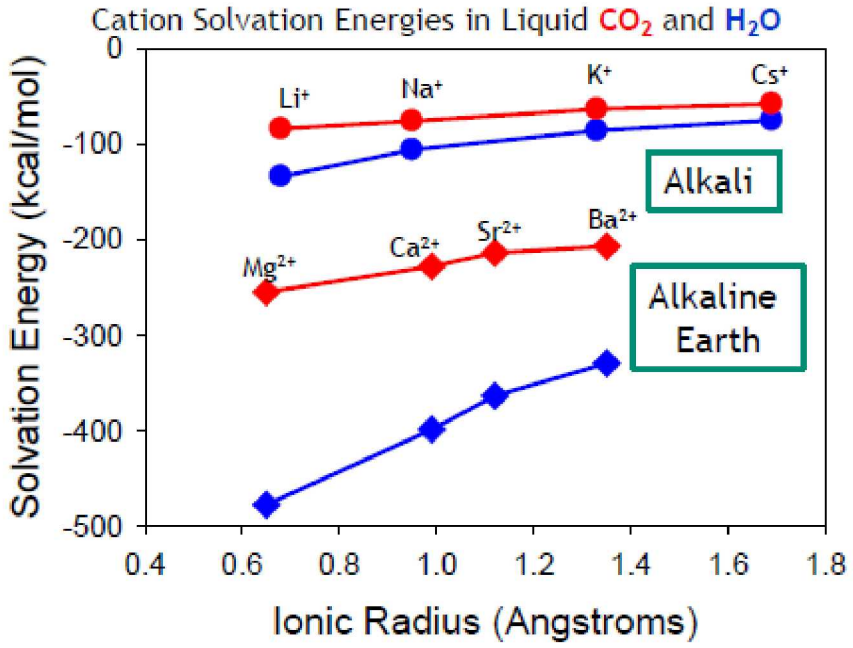


Liquid CO_2+ Mg^{2+}



$CN_{Mg^{2+}} = 6$





- Compared cation solvation in liquid CO_2 (8MPa, 300K) to liquid H_2O (0.1MPa, 300K)
- The most likely cations to partition into CO_2 are K^+ and Cs^+
- Assuming cations do not partition into $scCO_2$ may not be appropriate in regional-scale models.

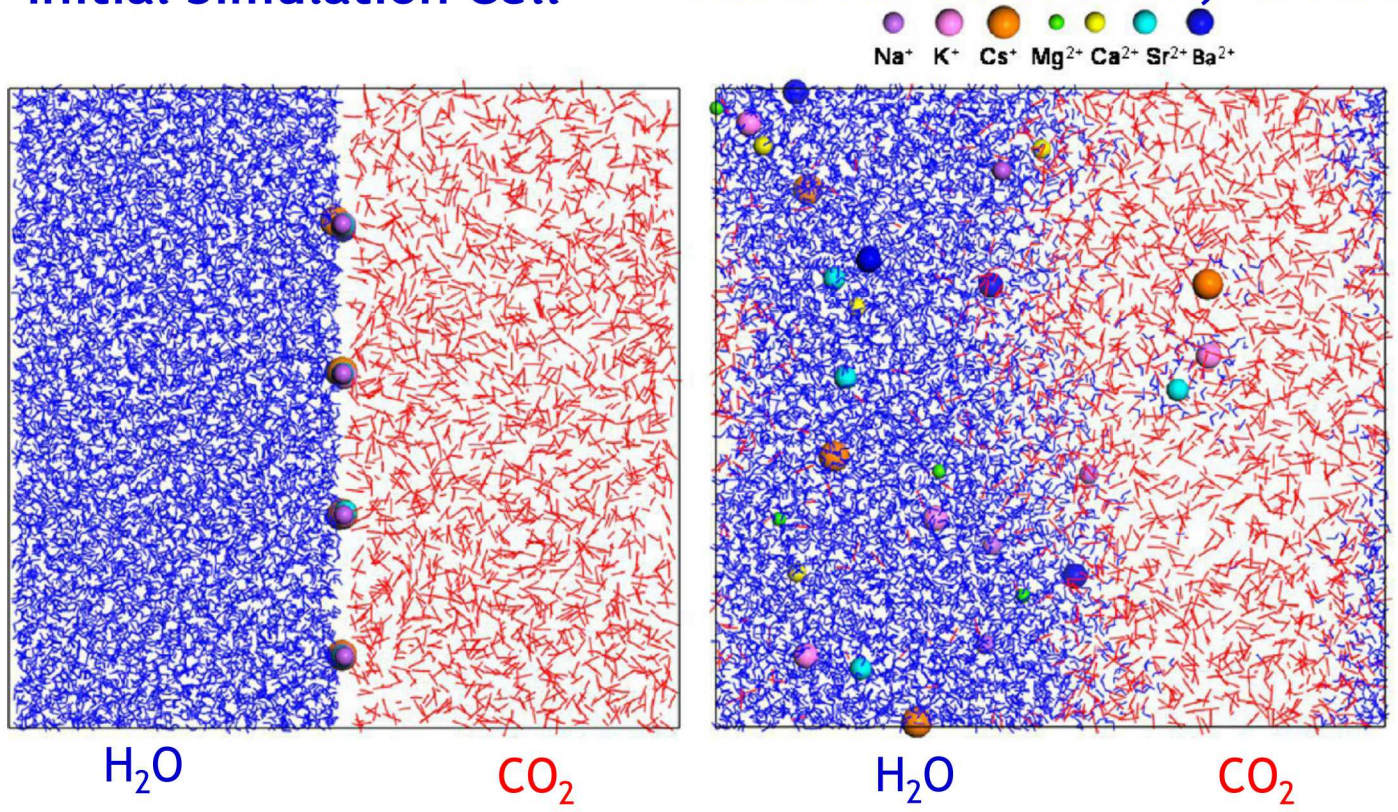
- The solubility of salts (e.g., KCl) in $scCO_2$ may be larger than anticipated.
- New constitutive equations for salt partitioning between water and $scCO_2$ may be required.

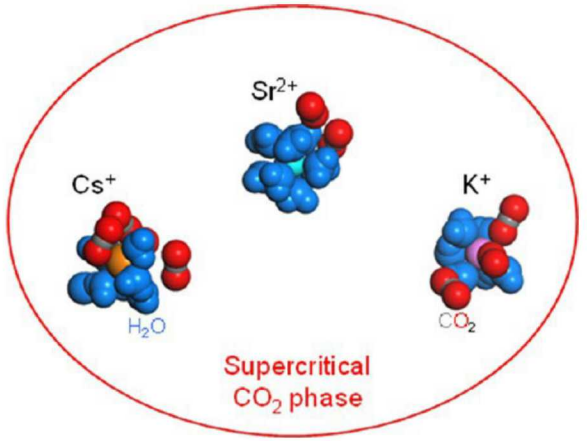
Criscenti, L.J. and Cygan, R.T. (2013) Molecular Simulations of Carbon Dioxide and Water: Cation Solvation. Environmental Science & Technology 47, 87-94.

INTERFACE BETWEEN WATER AND SUPERCRITICAL CO_2

Initial Simulation Cell

After 0.5 ns at 350K, 20 MPa





- Several cations coexist in the CO_2 phase, partially or fully coordinated by water molecules.
- **IMPACT:**
  - May increase water solubility in $scCO_2$.
  - May increase rate of $scCO_2$-water mixing & acidification of repository

Criscenti, L.J. and Cygan, R.T. (2013) Molecular Simulations of Carbon Dioxide and Water: Cation Solvation. Environmental Science & Technology 47, 87-94.

CAPILLARITY AND WETTABLITY

- Wettability of reservoir rocks and minerals controls CO_2 invasion and lateral spread, caprock breakthrough pressures, and leakage.
- Wettability (i.e., contact angle) varies with mineral type, pressure, temperature, and salinity
- Use molecular modeling to investigate wettability as a function of conditions.

Young-Laplace Equation

$$P_c = \frac{\psi \sigma_{fl} cos\theta}{d}$$

P_c = capillary entry pressure

ψ = pore shape parameter

σ_{fl} = CO_2-water interfacial tension

θ = contact angle

d = minimum pore size

Young-Dupré Equation

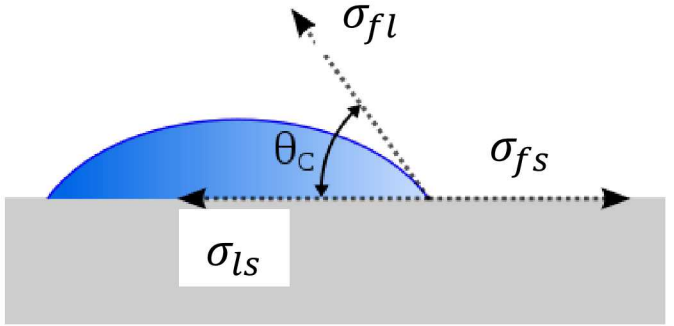
$$cos\theta = \frac{(\sigma_{fs} - \sigma_{ls})}{\sigma_{fl}}$$

θ = contact angle

σ_{ls} = water-solid interfacial tension

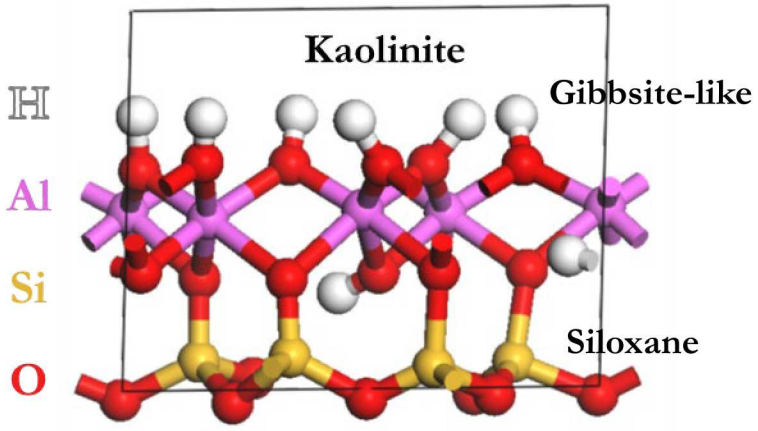
σ_{fs} = CO_2-solid interfacial tension

σ_{fl} = CO_2-water interfacial tension



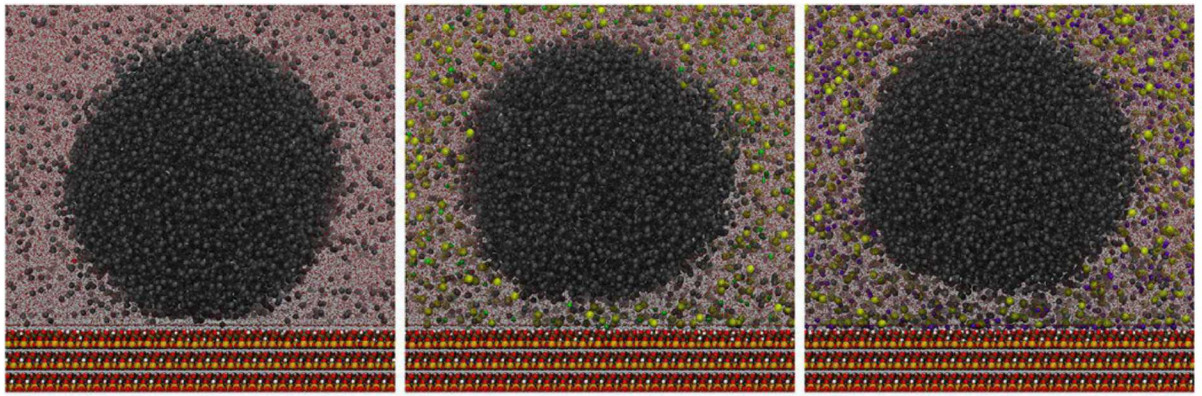
Espinoza and Santamarina, 2010

CONTACT ANGLE CALCULATIONS FOR $SCCO_2$ DROPLETS IN WATER AND BRINE



Supercritical CO_2 droplet separated from surface by distinct layers of water

Hydrophilic Gibbsite-like Surface

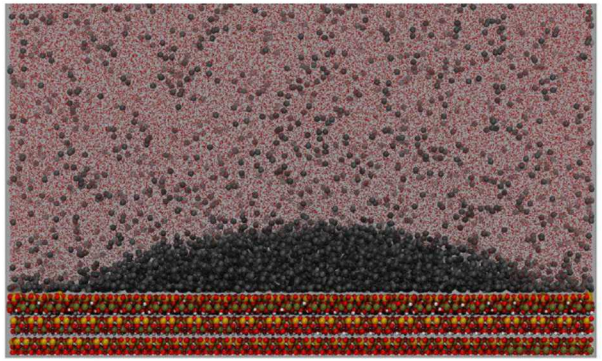


(a) water (b) $CaCl_2$ brine (c) NaCl brine

- In brines ($CaCl_2$ and NaCl), the CO_2 droplets on the gibbsite surface of kaolinite detach completely from the mineral surface.
- CO_2 wets siloxane surface and forms a nonwetting droplet on the gibbsite-like surface (the opposite of water).
- The addition of salt to solution does not impact CO_2 wetting of the siloxane surface
- These types of calculations can be used to investigate other three-phase systems and scenarios.

Hydrophobic Siloxane Surface

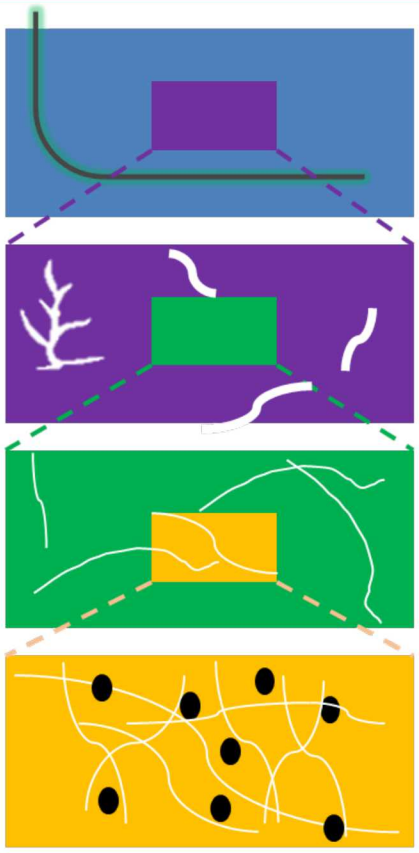
Strong wetting of surface by $scCO_2$ (330K, 20 MPa)



(a) CO_2 droplet in water

Tenney, C.M. and Cygan, R.T. (2014) Molecular Simulation of Carbon Dioxide, Brine, and Clay Mineral Interactions and Determination of Contact Angles. Environmental Science & Technology 48, 2035-2042.

THE RETENTION OF CO_2 AND CH_4 IN KEROGEN AND ITS IMPORTANCE IN ENHANCED GAS RECOVERY



Macroscale: gas flow to the wellbore

Mesoscale: micro-fractures network

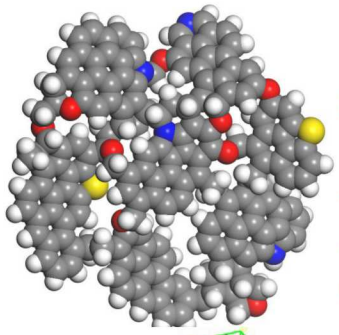
Microscale: nanopores network

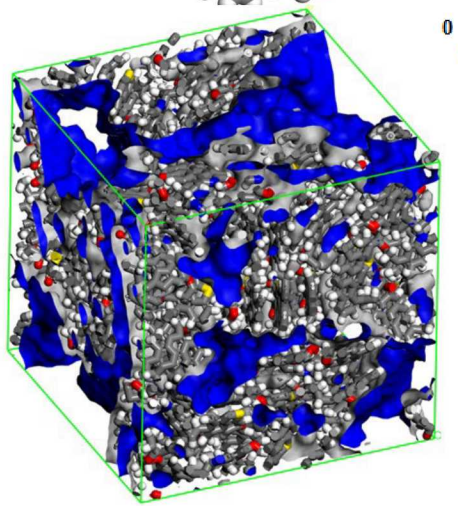
Nanoscale/Sub-nanoscale: Gas diffusion from kerogen/clay porous structure to nanopores.

JCPT 46, 55 -61 (2007)

Kerogen IID

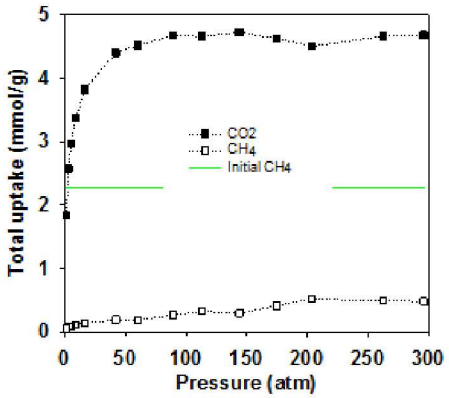
Ungerer et al., Energ Fuel 29, 91-105



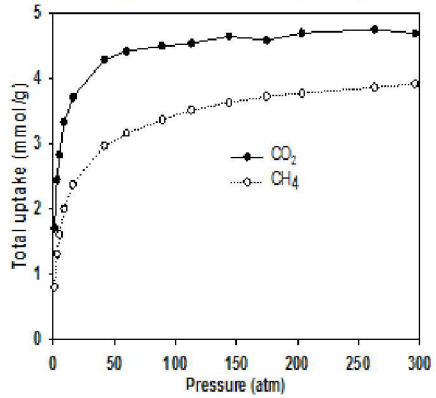


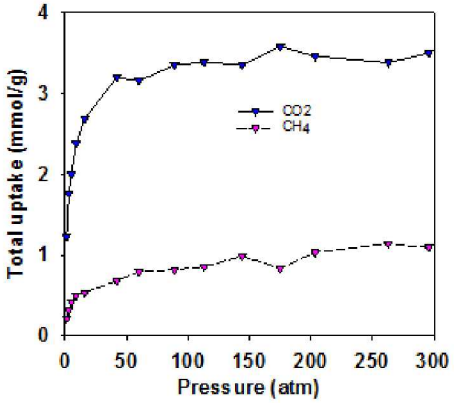
Competitive adsorption of CH_4 and CO_2 in Kerogen

Pure CH_4 and Pure CO_2



binary mixture CH_4:CO_2

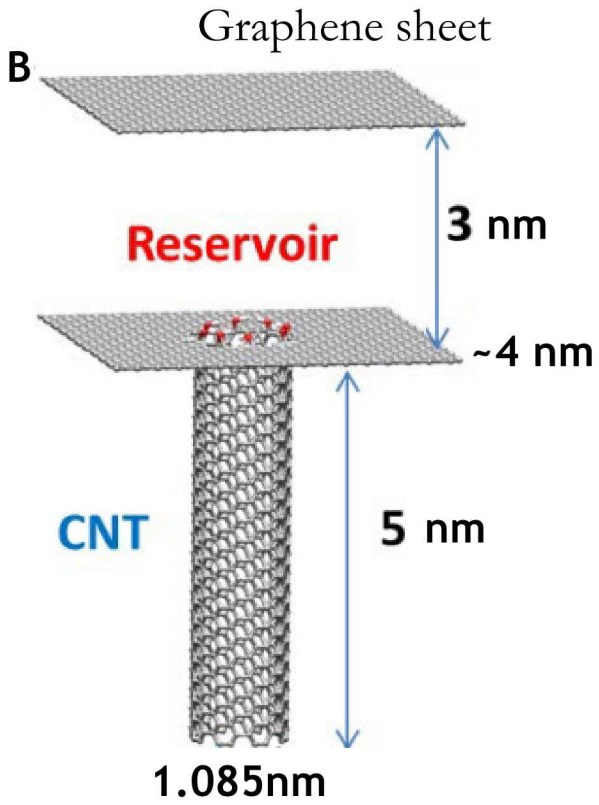


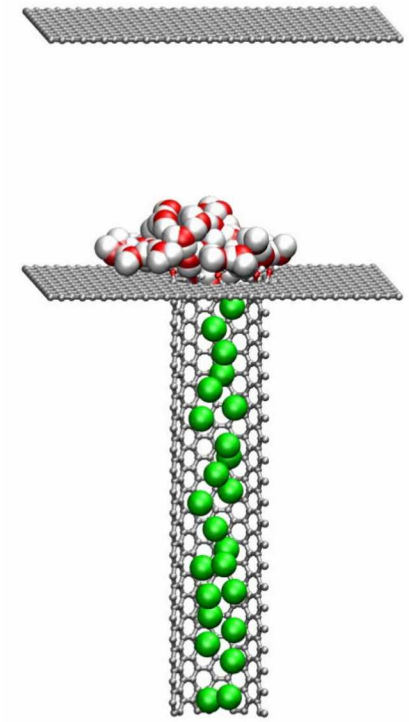


Enhanced methane gas recovery

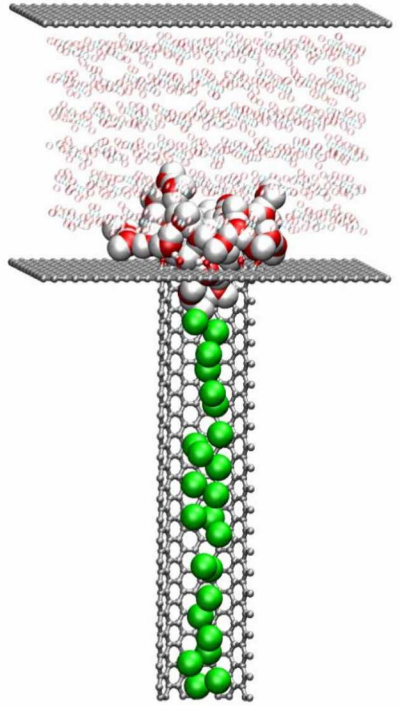
Ho, T.A., Wang, Y., Xiong, Y. and **Criscenti, L.J.** (2018) Differential retention and release of CO_2 and CH_4 in kerogen nanopores. Fuel 220, 1-7.

IMPACT OF H_2O AND CO_2 ON METHANE RECOVERY





Assume that water drop blocks the pore entrance.



CO_2 invades through water and replaces CH_4 in the nanopore.

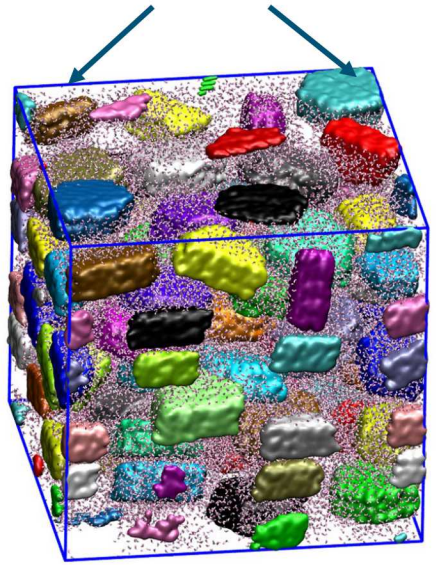
- Water can block CH_4 release.
- CO_2 may enhance CH_4 release because dissolved CO_2 can migrate through water and exchange for adsorbed methane in kerogen nanopores.

Ho, T.A., Wang, Y., Xiong, Y. and **Criscenti, L.J.** (2018) Differential retention and release of CO_2 and CH_4 in kerogen nanopores. Fuel 220, 1-7.

PARTICLE AGGREGATION AND POROSITY

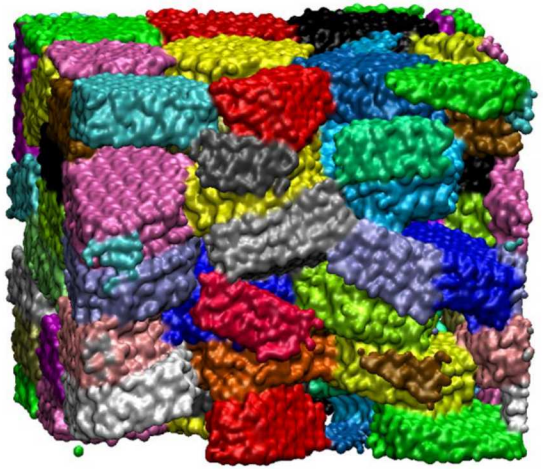
Effect of dewatering rate on aggregate structure

Clay (gibbsite) nanoparticles

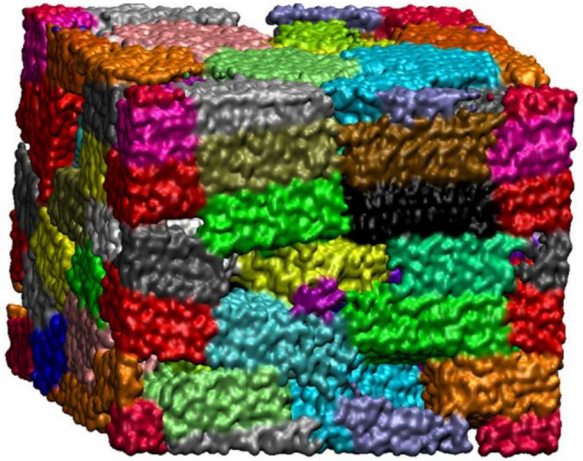


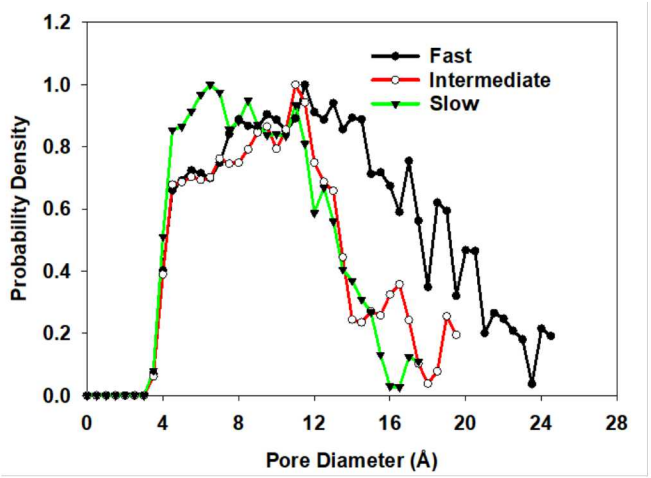
Particle Diameter: ~2-3 nm

Fast



Slow



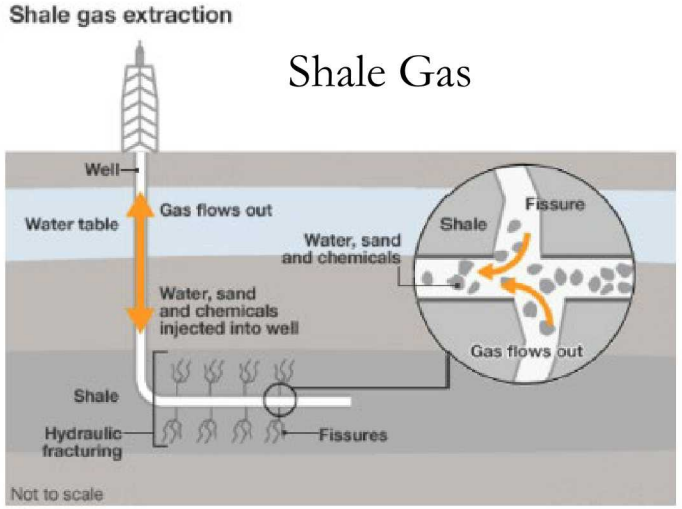


Possible Next Steps:

- Fluid flow through nanoporous mineral aggregates
- Average affects of clay interlayer and inter-particle porosity
- Create models that mimic porosity of actual shales.

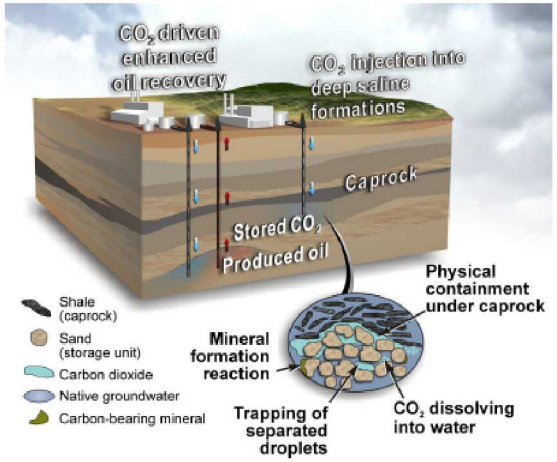
Ho, T.A., Greathouse, J.A., Wang, Y. and **Criscenti, L.J.** (2017) Atomistic structure of mineral nano-aggregates from simulated compaction and dewatering. Scientific Reports 7.

CHEMO-MECHANICAL FRACTURE OF ROCK



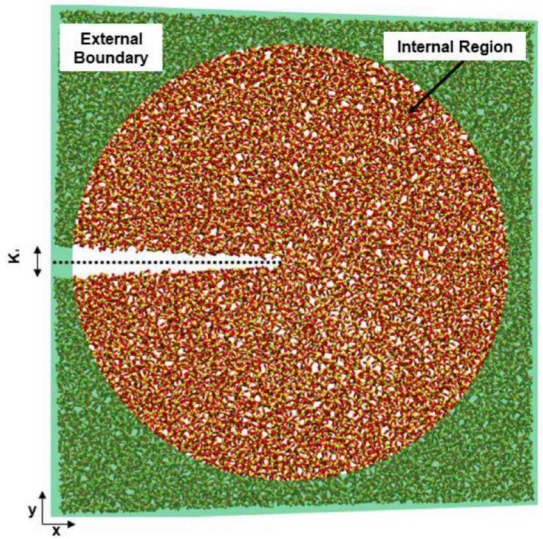
Shale Gas

CO_2 Sequestration



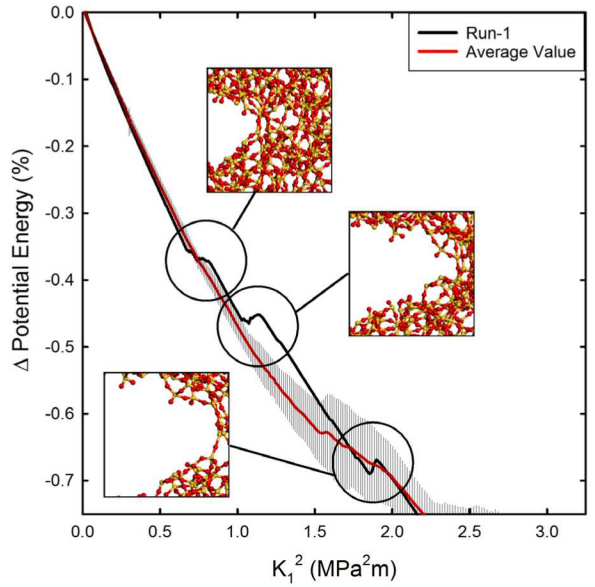
Motivation:
How does fluid composition affect fracture toughness and propagation?

Simple System: Method Development/Validation



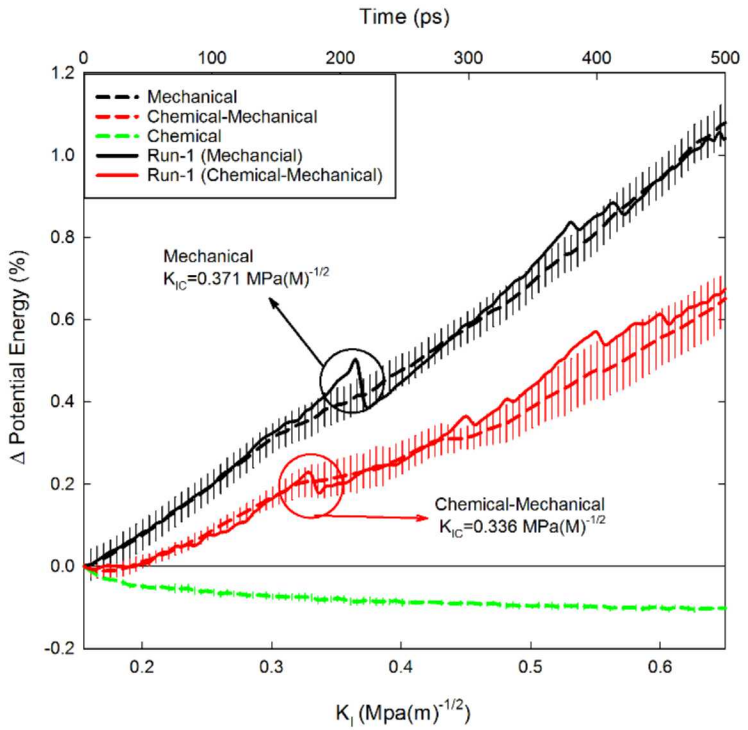
Start with amorphous SiO_2
Fracture in Vacuum

Fracture toughness (K_{IC}) is defined by the first deviation of the potential energy from the expected trend.

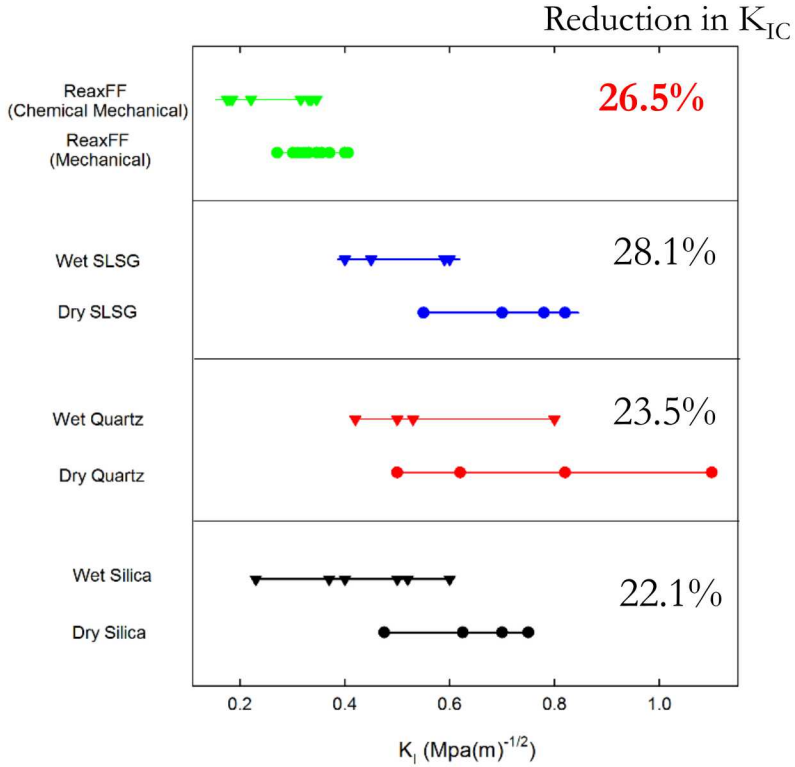


Rimsza, J.M., Jones, R.E. and **Criscenti, L.J.** (2018a, 2018b, 2019)

Subcritical Fracture of $amSiO_2$ in Water



Change in potential energy for silica systems in mechanical, chemical, and chemical-mechanical conditions.



Experimental K_{IC} data for amorphous silica, quartz , and soda-lime silicate glasses in dry and aqueous environments compared with simulations.

eK_{IC} for $amSiO_2$ in Different Environments

Environment	K_{IC} (MPa√m)
Vacuum	0.34±0.04
Water	0.20±0.06
1M NaCl	0.28±0.09
1M NaOH	0.19±0.05

Possible Next Steps:

- Subcritical fracture in minerals
- Subcritical fracture in aggregates
- Different solution compositions
- Temperature effects
- Etc.

Rimsza, J.M., Jones, R.E. and **Criscenti, L.J.** (2018a, 2018b, 2019)

SUMMARY

- Brine-scCO$_2$ Interface:
  - Molecular simulation can be used to test the validity of constitutive expressions used in regional-scale models and guide their improvement.
- Brine-scCO$_2$-Mineral Interface:
  - Molecular simulation can be used to investigate the relative wettability of different minerals) to various fluids under different P, T conditions.
- CO$_2$ and CH$_4$ in Kerogen
  - Molecular simulation can be used to explore the interaction of oil and natural gas components with organic (e.g., kerogen) and inorganic (e.g., clay minerals).
- Nanoparticle Aggregation & Porosity
  - Molecular simulation can be used to investigate the properties of more complex porous materials such as clay aggregates.
- Subcritical Fracture in Geomaterials
  - Molecular simulation can be used to examine subcritical fracture of materials in different solution compositions.
- **Molecular modeling is a useful tool to test various hypotheses and scenarios; it is a useful complement to experiments and larger-scale models.**

Posters tomorrow!!

Tuan Ho,
CO$_2$ Sequestration
In Organic-Rich Shales

Jeff Greathouse,
Molecular Modeling for
Fossil Energy

CFSES CENTER FOR FRONTIERS OF SUBSURFACE ENERGY SECURITY

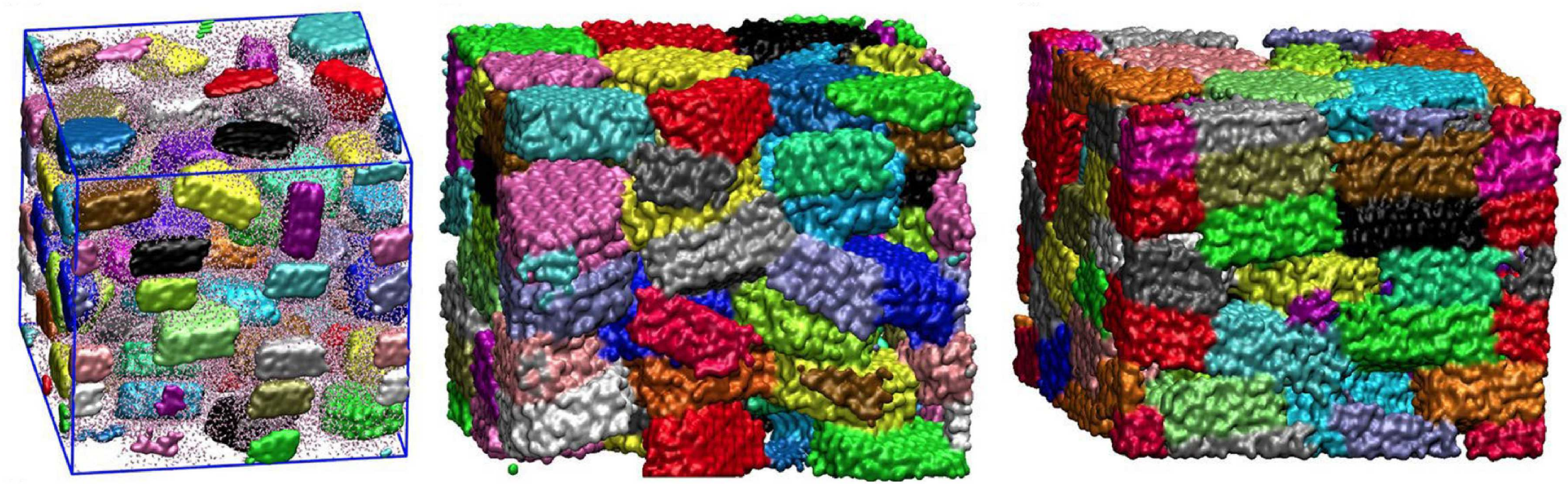
U.S. DEPARTMENT OF ENERGY | Office of Science

U.S. DEPARTMENT OF ENERGY | NETL NATIONAL ENERGY TECHNOLOGY LABORATORY

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

Extra Slide

PARTICLE AGGREGATION AND POROSITY/ PERMEABILITY

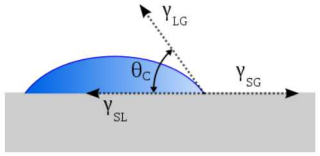


(Ho et al., 2017)

GAS-LIQUID-SOLID INTERFACES: CONTACT ANGLE CALCULATION

Introduction

- CO_2 injected into a porous media will replace present-day pore fluids including water, oil and air.
- Need to understand the relative wettability of the sandstone and shale to these fluids to predict outcome of CO_2 sequestration.
- If water and oil adhere to rocks better than CO_2, then CO_2 will not stay sequestered over time; if CO_2 adheres strongly to mineral surfaces then more likely to remain sequestered over long periods of time.



Hydrophilic

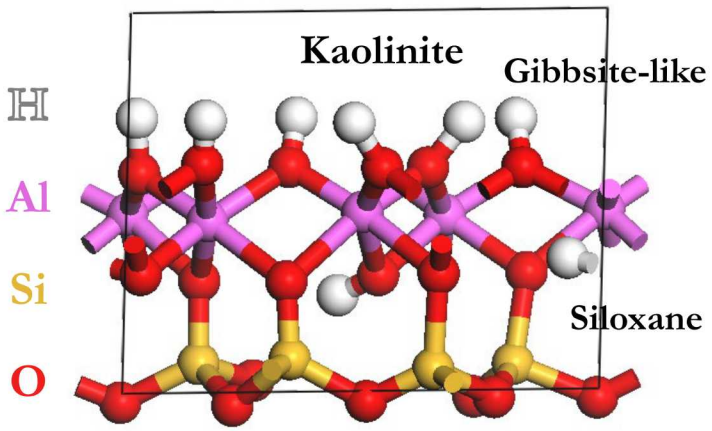
Contact angle of 12.6°

Experimental values ~17-20° *(Shang, et al. 2008)*

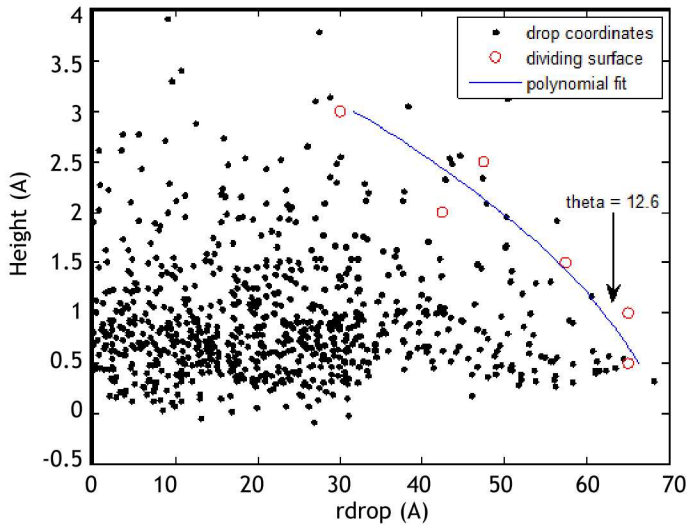
Hydrophobic

Contact angle of 110°

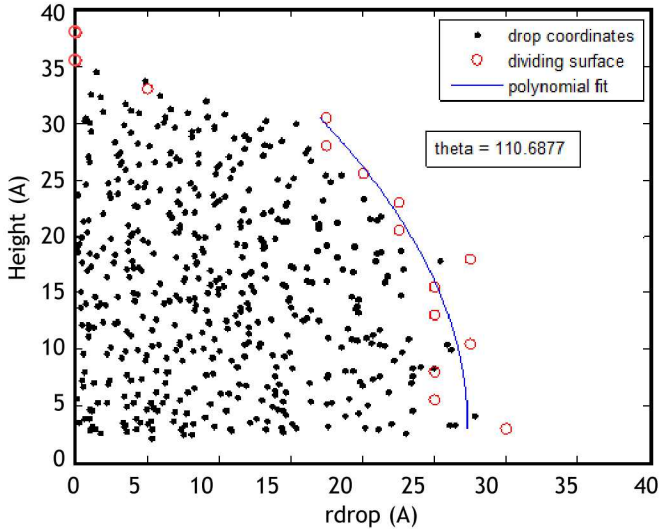
Similar to other calculations *(Chai, et al. 2009)*



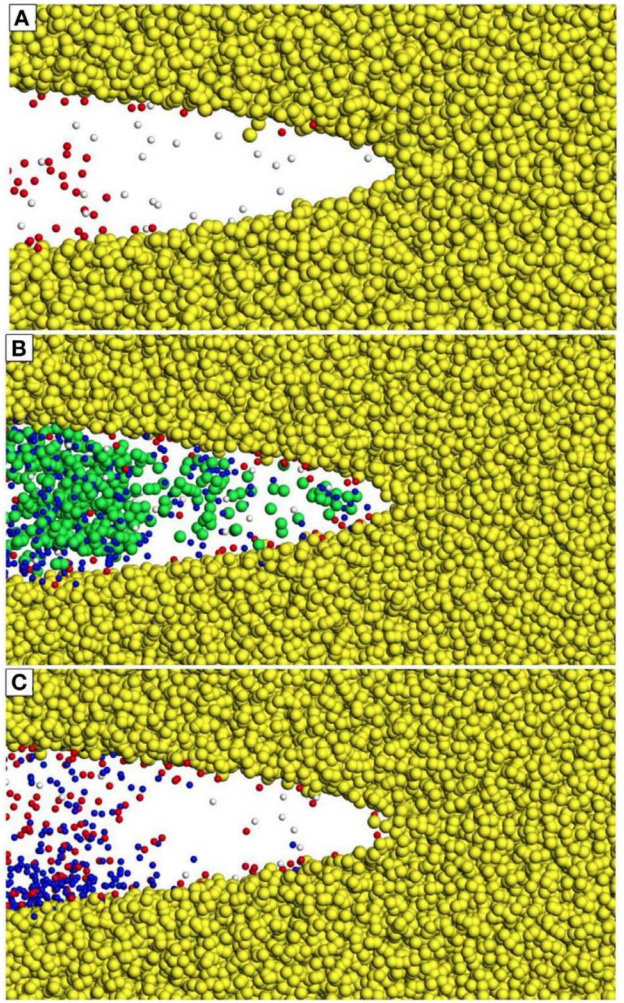
Gibbsite-like Surface



Siloxane Surface



Criscenti, L.J. and Bracco, J. Molecular Modeling in Support of CO_2 Sequestration and Enhanced Oil Recovery, SAND2011-0257.


A
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