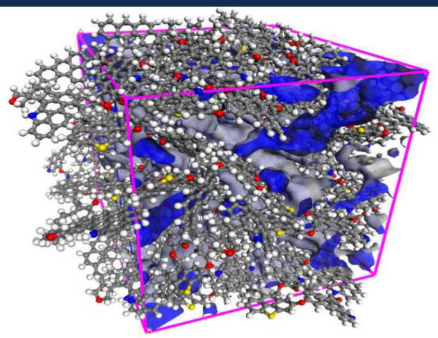
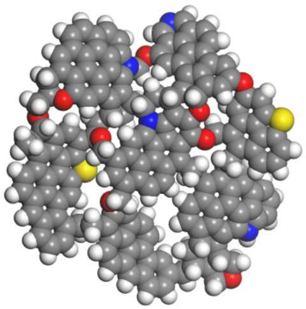
SAND2019-3395C





Molecular Simulation of the Multicomponent Interaction in Shale Nanopores

Tuan Ho, Yifeng Wang, Louise Criscenti, Anastasia Ilgen

Sandia National Laboratories

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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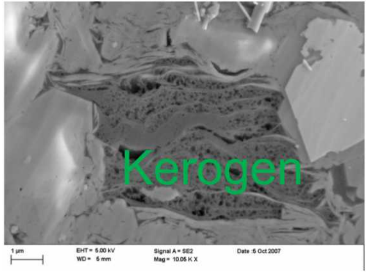
Introduction

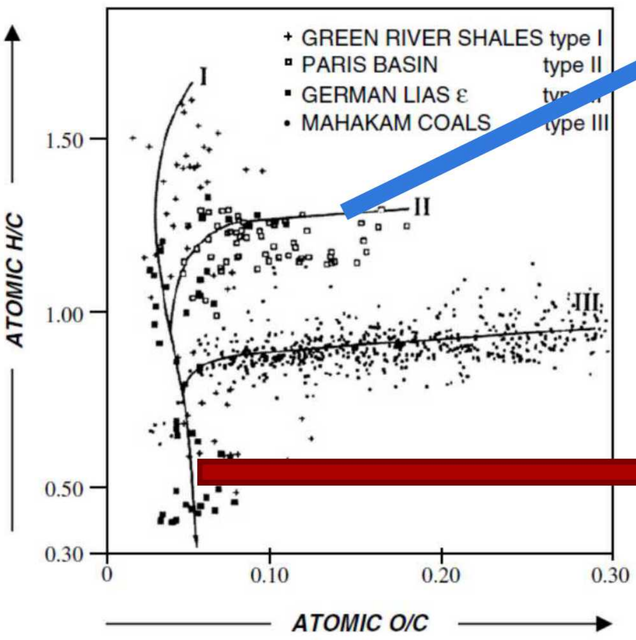
Kerogen

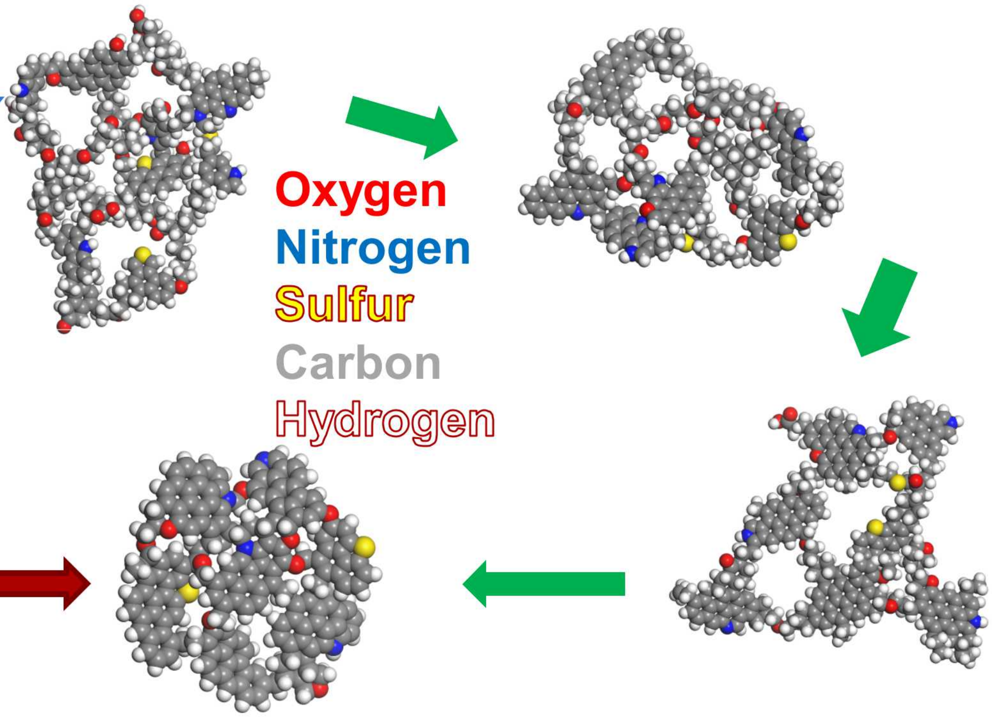


- Insoluble organic matter found in sedimentary rocks (geochemistry)
- Cracks into petroleum products (kerogen maturation, petroleum generation)

  Van Krevelen diagram

Organic Geochemistry 38, 719-833 (2007)





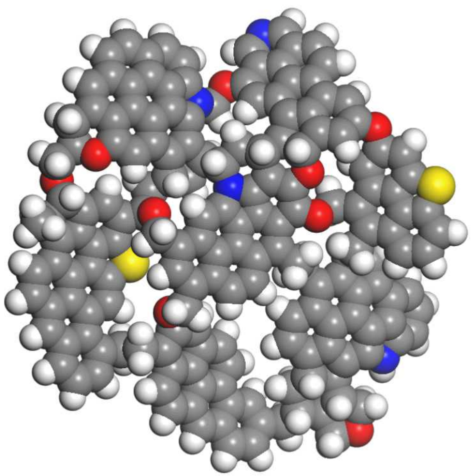
Ungerer et al., Energ Fuel 29, 91-105

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

Overmature Kerogen

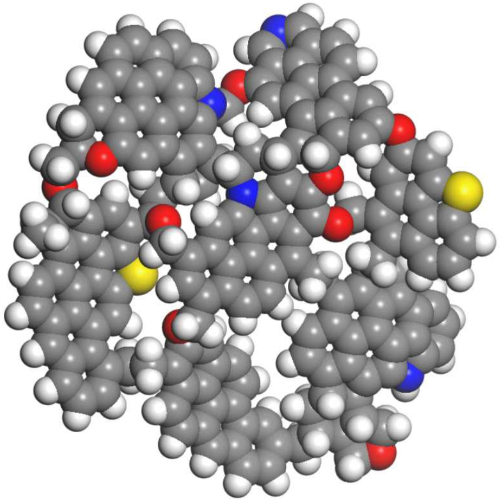
- Use the available elemental analysis and functional data from XPS and ^{13}C NMR
  - *(Energy & Fuels, 2007, 21, 1548-1561)*

Oxygen
Nitrogen
Sulfur
Carbon
Hydrogen



	II-D analytical data	II-D model unit
H/C	0.56	0.58
O/C	0.047	0.051
N/C	0.021	0.023
S/C	0.01	0.011
% of aromatic carbon from XPS(a) or NMR(b)	72(a), 80(b)	79
avg. number of C atoms per aromatic cluster	20	19.9
fraction of aromatic carbons with attachments (sp^3 C, N, S, O)	0.24	0.28

Formation of condensed kerogen



$C_{175}H_{102}O_9N_4S_2$

Energy Fuels 2015, 29, 91-105

24 Kerogens in $10 \times 10 \times 10 nm^3$ box, 1000K

NVT

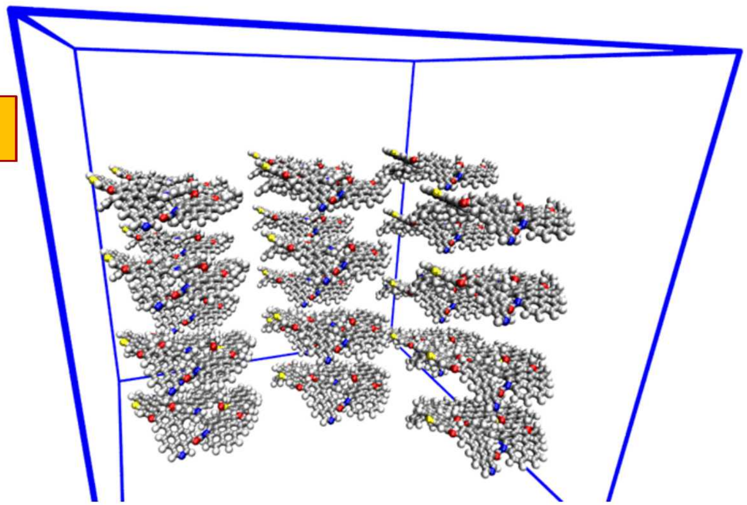
9 snapshots

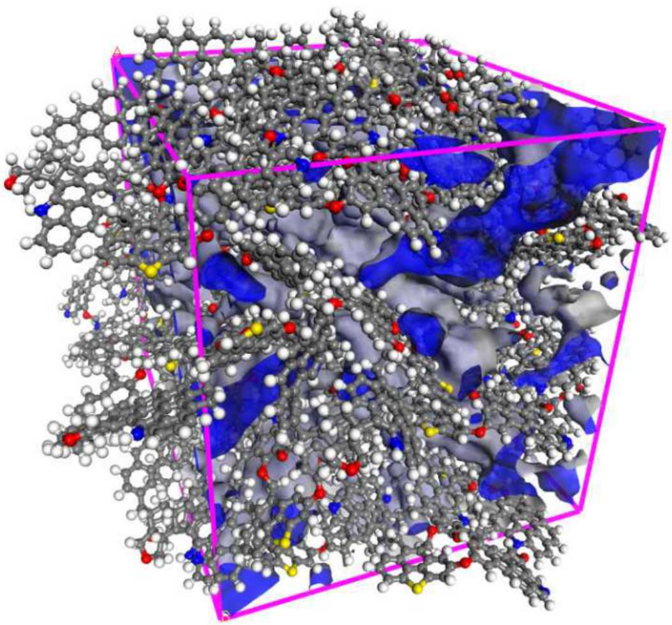
NPT, 100at, 900K to 300K

300K and 100atm

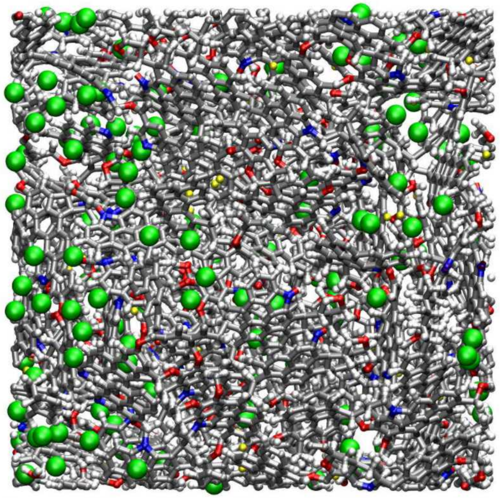
NPT, 1atm, 300K

9 samples at 300K and 1atm





Characterization

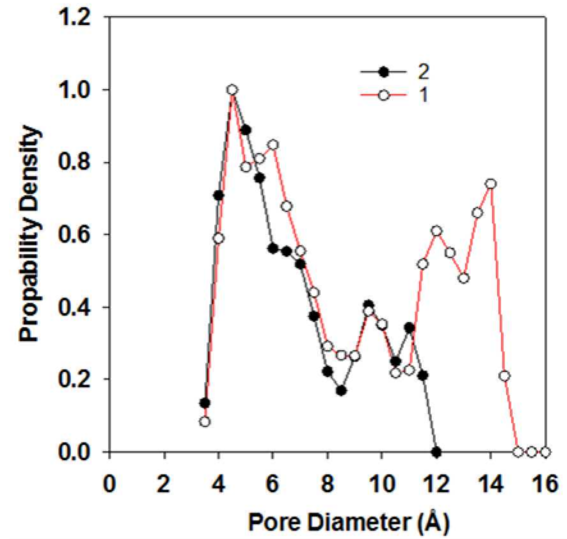


Density

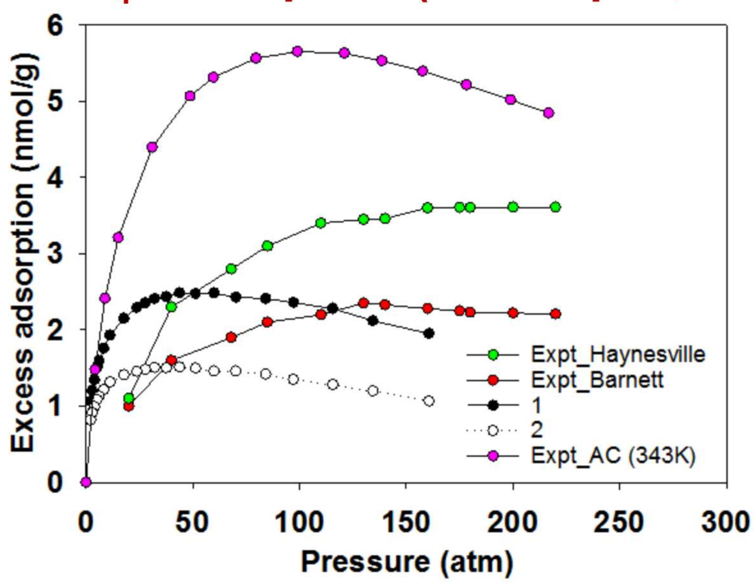
Average :1.22±0.04 g/cm^3
Experiment: 1.28±0.3g/cm^3

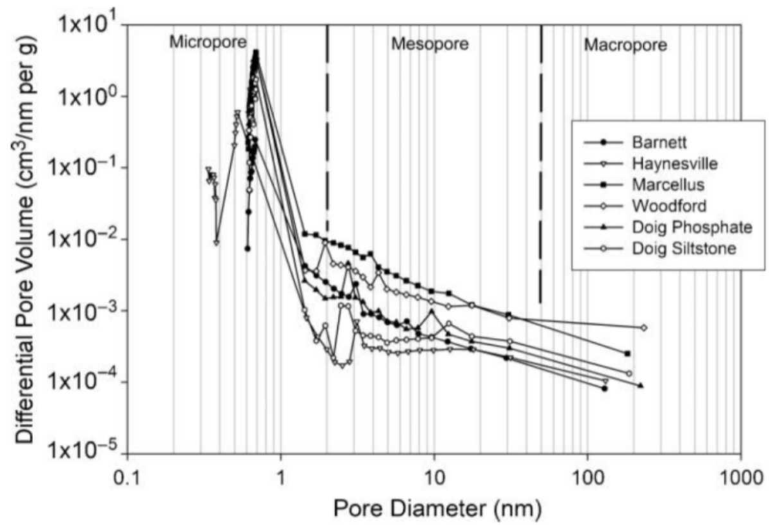
Stankiewicz A, *et al.* (2015) Kerogen density revisited – lessons from the Duvernay Shale. *In: Paper URTeC 2157904 at the Unconventional Resources Technology Conference, San Antonio, Texas, July 2015*

Pore size distribution



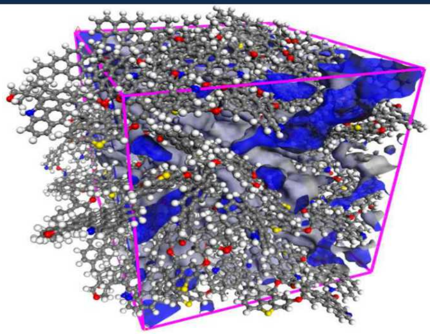
CH_4 Adsorption (Sci. Rep. 6, 28053)

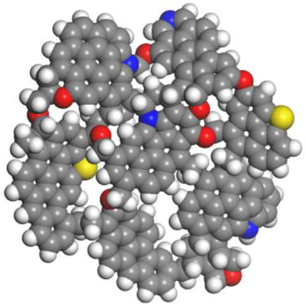




AAPG 96 (2012), 1099-1119

Molecular Simulation of the Multicomponent Interaction in Kerogen Nanopores





Outline:

1. CH_4/CO_2 adsorption onto kerogen

2. Kerogen swelling

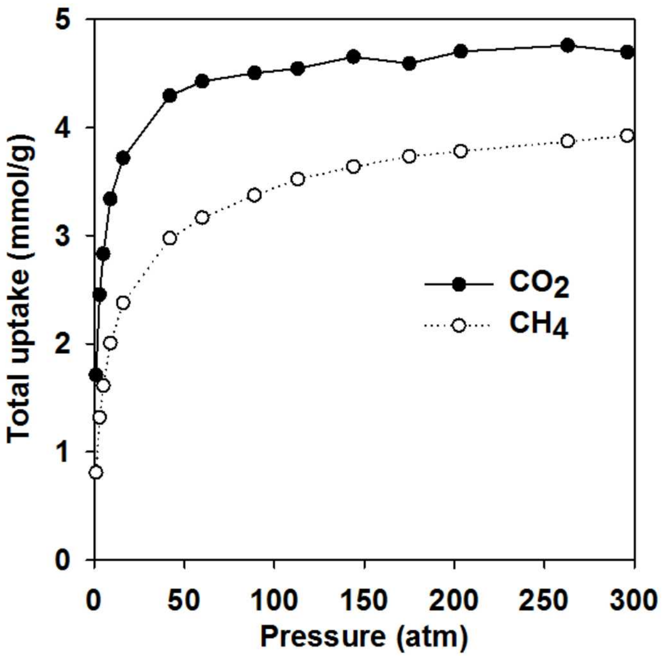
3. Wettability

4. Oil transport in shale nanopores

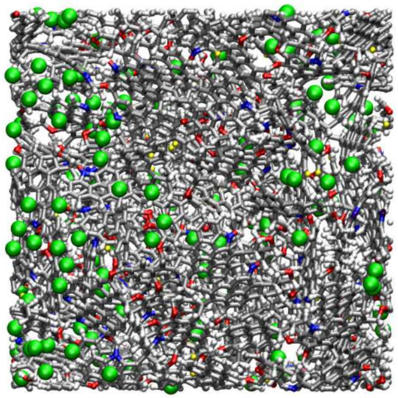
Differential retention and release of CO_2 and CH_4 in kerogen nanopores (Fuel 220, 1-7, 2018)

Implications for gas enhanced recovery and carbon sequestration

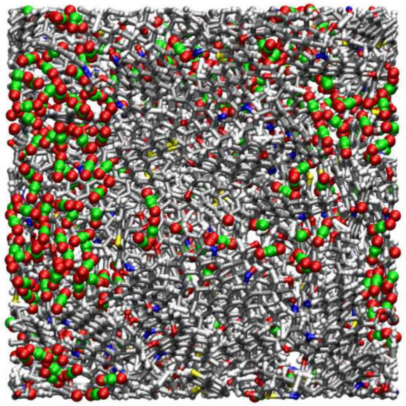
Pure gas adsorption



CH_4



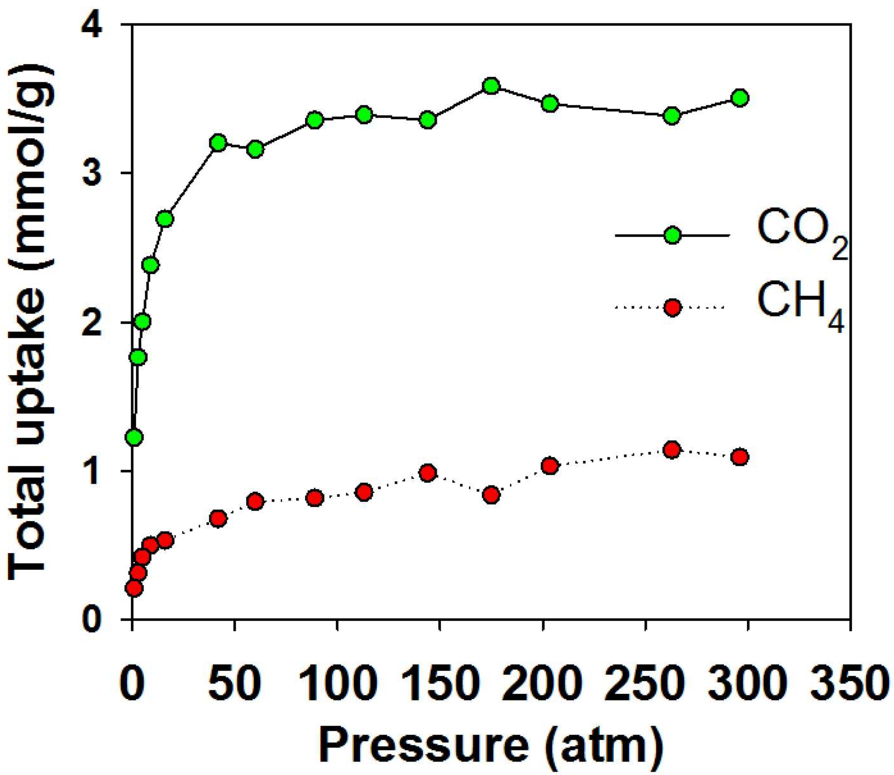
CO_2



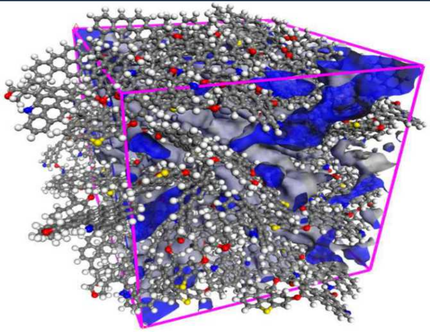
Differential retention and release of CO_2 and CH_4 in kerogen nanopores (Fuel 220, 1-7, 2018)

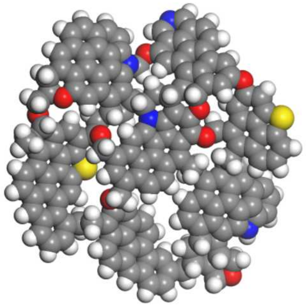
Implications for gas enhanced recovery and carbon sequestration

1:1 binary gas adsorption



Kerogen preferentially retains CO_2 over CH_4





Molecular Simulation of the Multicomponent Interaction in Kerogen Nanopores

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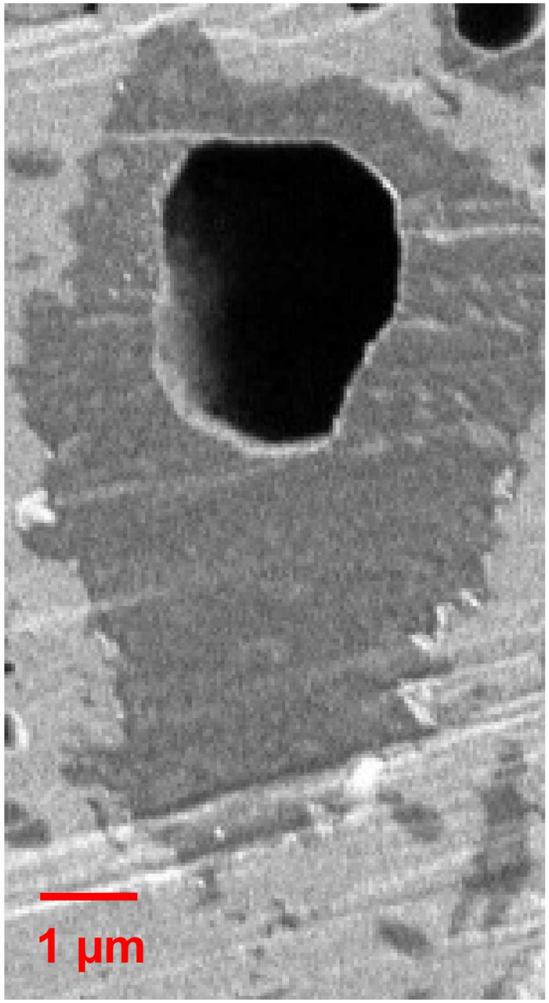
Kerogen swelling

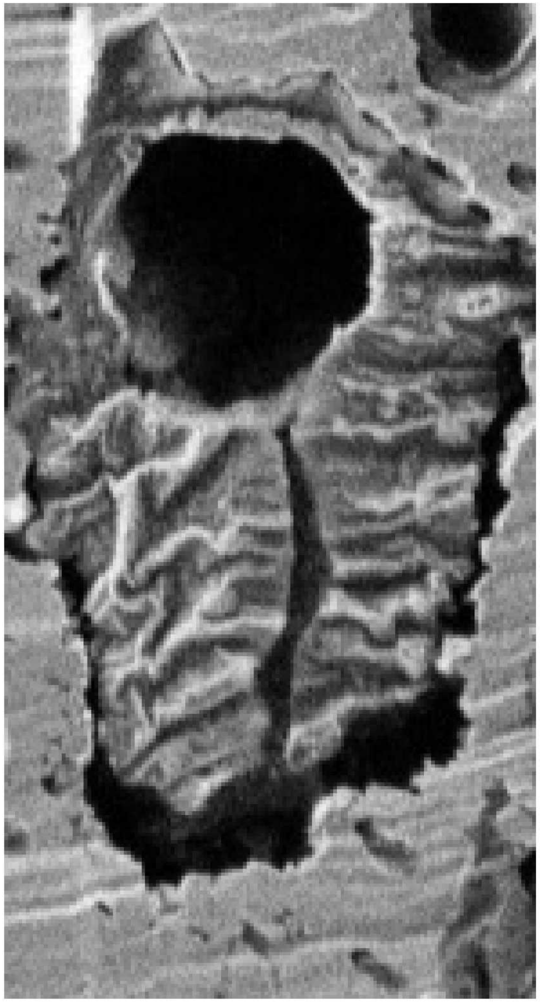
Rubber swelling in oil

From: **Drew Pomerantz**, Schlumberger

Will kerogen swell upon gas adsorption?



Intact shale with swollen kerogen

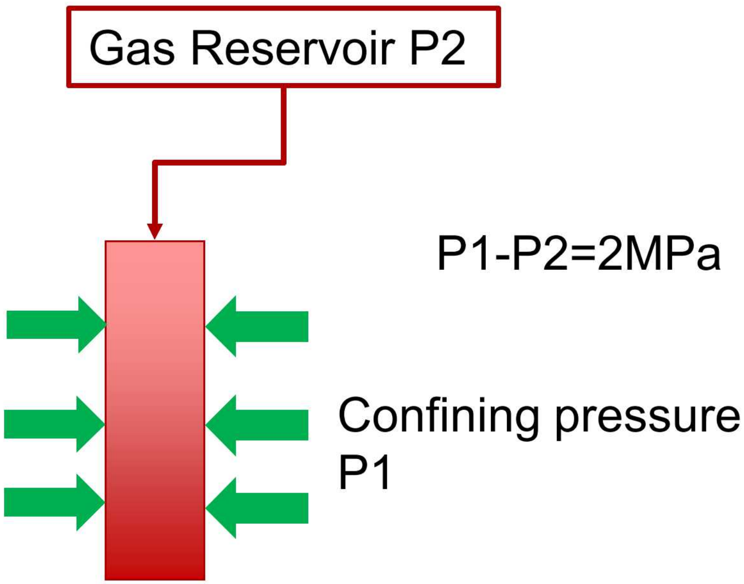


Bitumen-extracted shale with collapsed kerogen

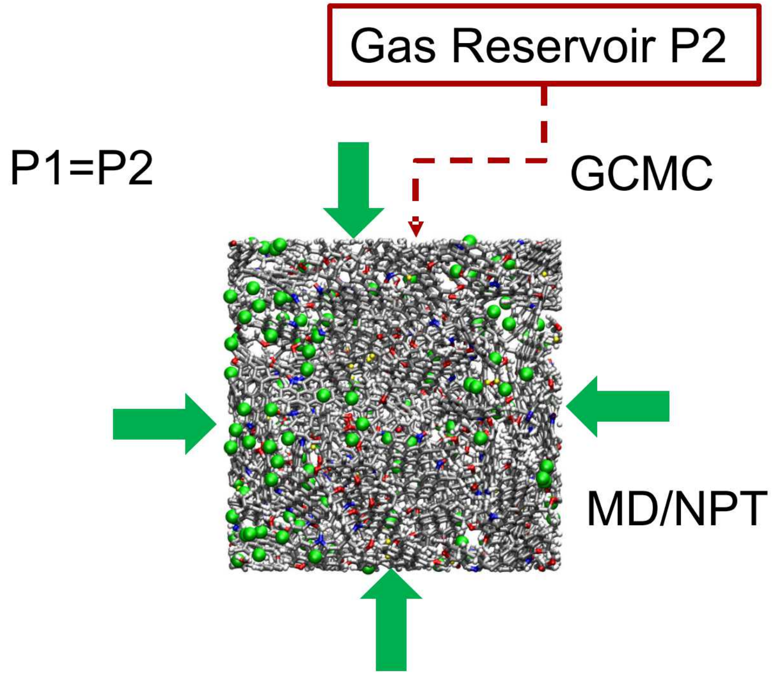
Chemo-mechanical coupling in kerogen gas adsorption (PCCP 20, 11390, 2018)

Experimental setup

(J. Unconv. Oil Gas Resour., 2014)



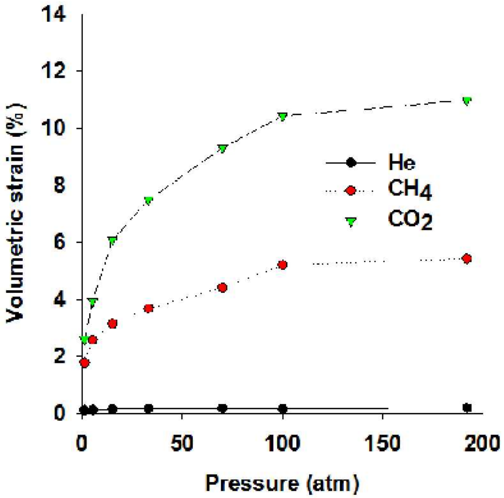
Simulation: Hybrid MD/MC

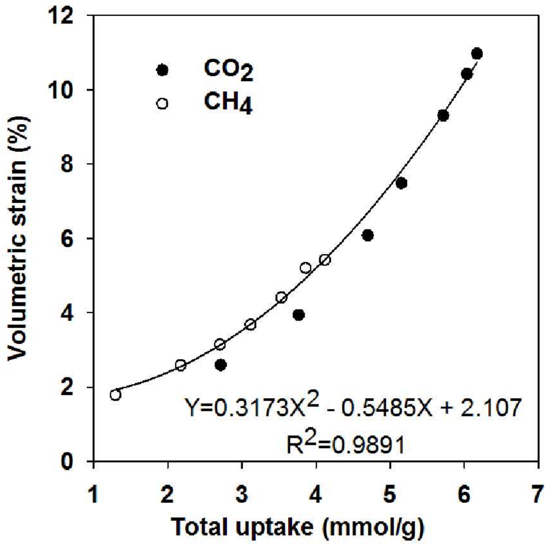


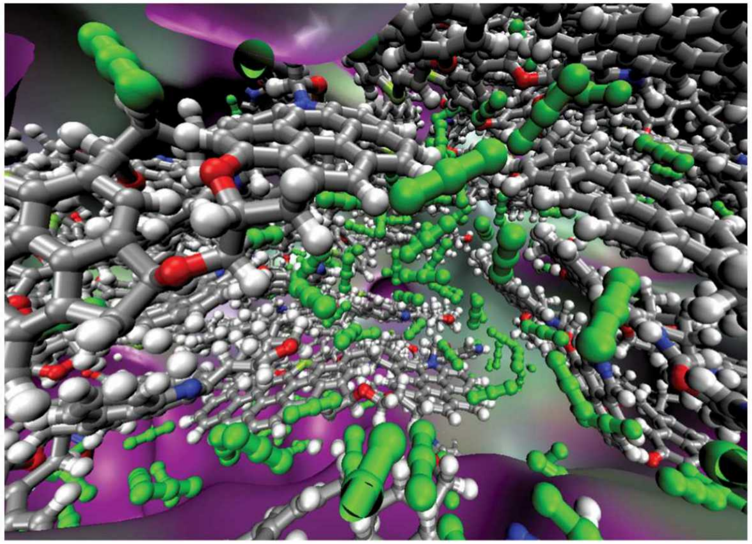
$$Volumetric\ strain = \frac{V - V_o}{V_o}$$

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

Chemo-mechanical coupling in kerogen gas adsorption (PCCP 20, 11390, 2018)







Highlighting shale gas research from the Geoscience Group, Sandia National Laboratories, NM, USA. This work was conducted by Dr Tuan Ho, thanks to funding granted to Dr Yifeng Wang by the DOE National Energy Technology Laboratory.

Chemo-mechanical coupling in kerogen gas adsorption/desorption

We use an integrated experimental and modeling approach to fundamentally understand the interaction of gas and fluid with kerogen and clay under reservoir conditions. Specifically, nanostructural properties of subsurface porous media, gas adsorption and release from the kerogen network, deformation of shale associated with adsorption and lithostatic stress, and wettability of inorganic and organic matter.

As featured in:

See Tuan Anh Ho *et al.*, *Phys. Chem. Chem. Phys.*, 2018, 20, 12390.

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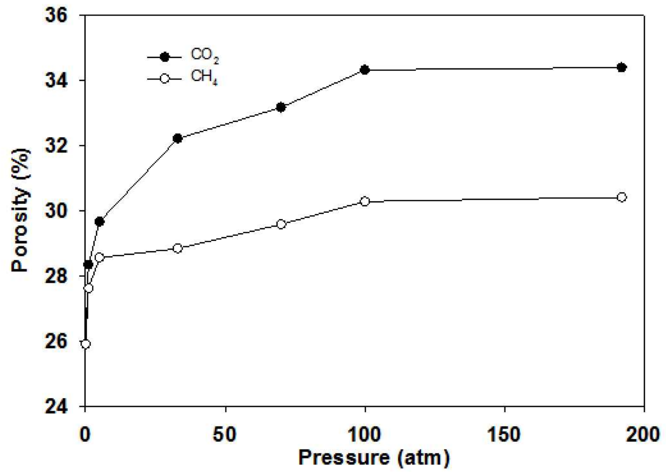
Upon shale gas extraction kerogen shrinks

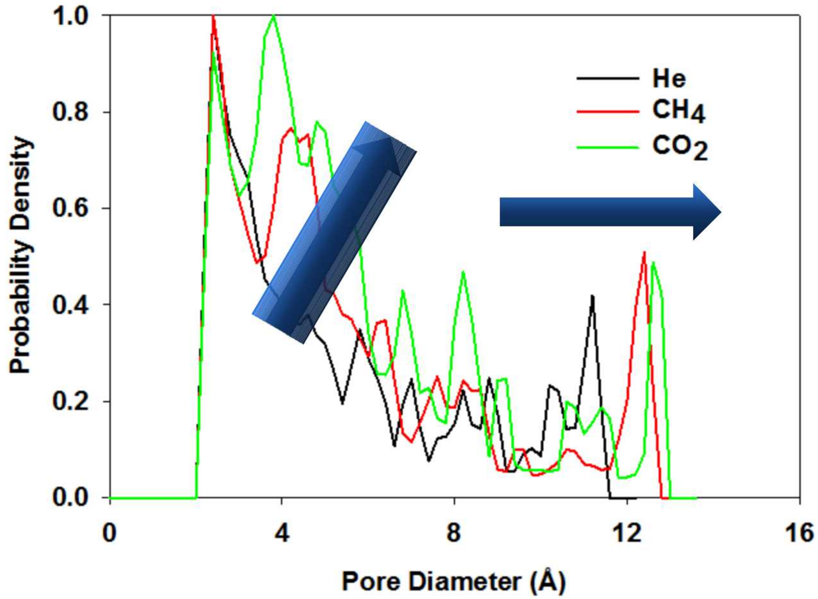
Kerogen swelling with gas (PCCP 20, 11390, 2018)

Sandia National Laboratories

Effects of kerogen swelling on porosity



Effects of kerogen swelling on pore size distribution



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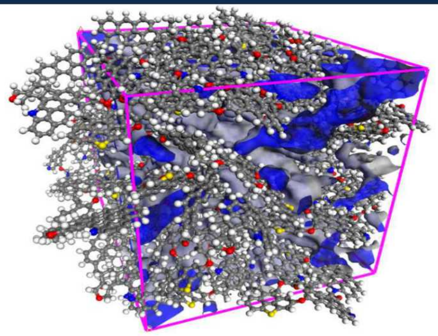

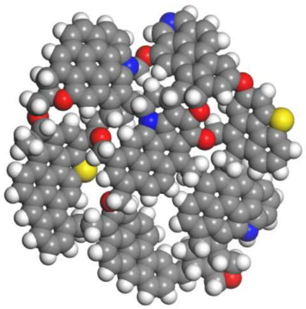

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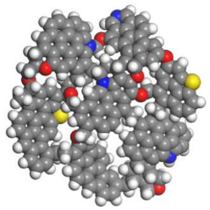
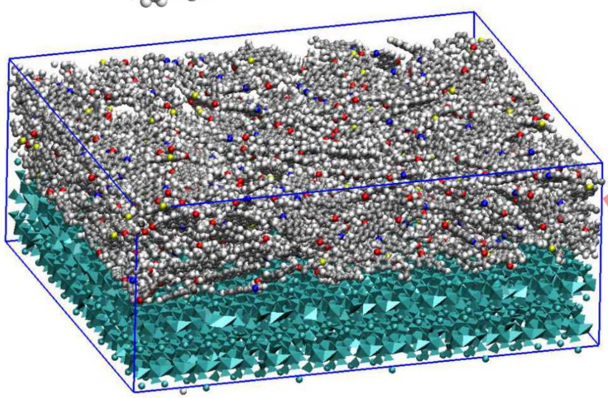
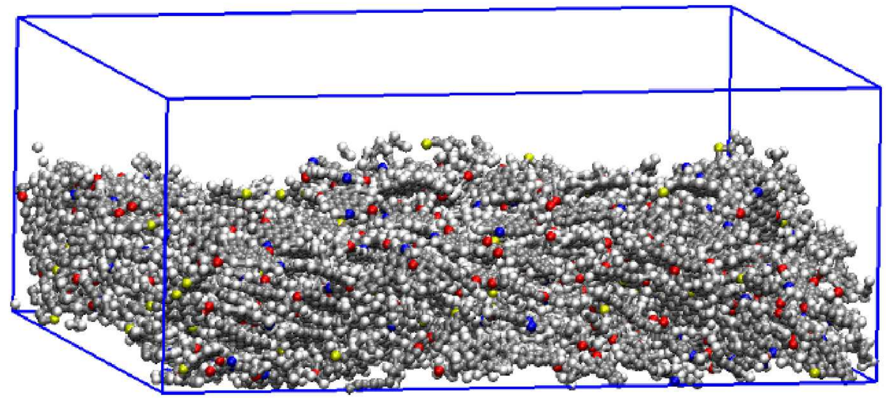
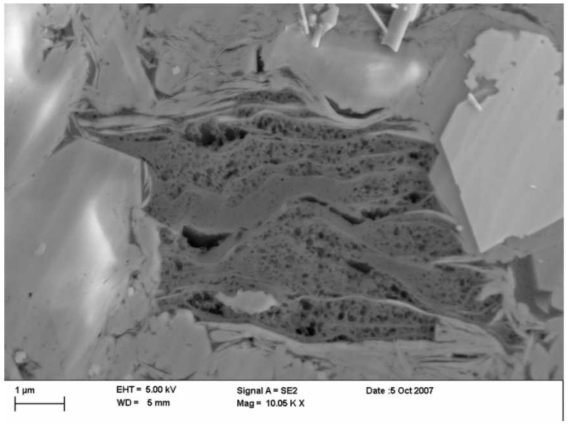
Kerogen wettability and fluid flow (Nanoscale 10, 19957)

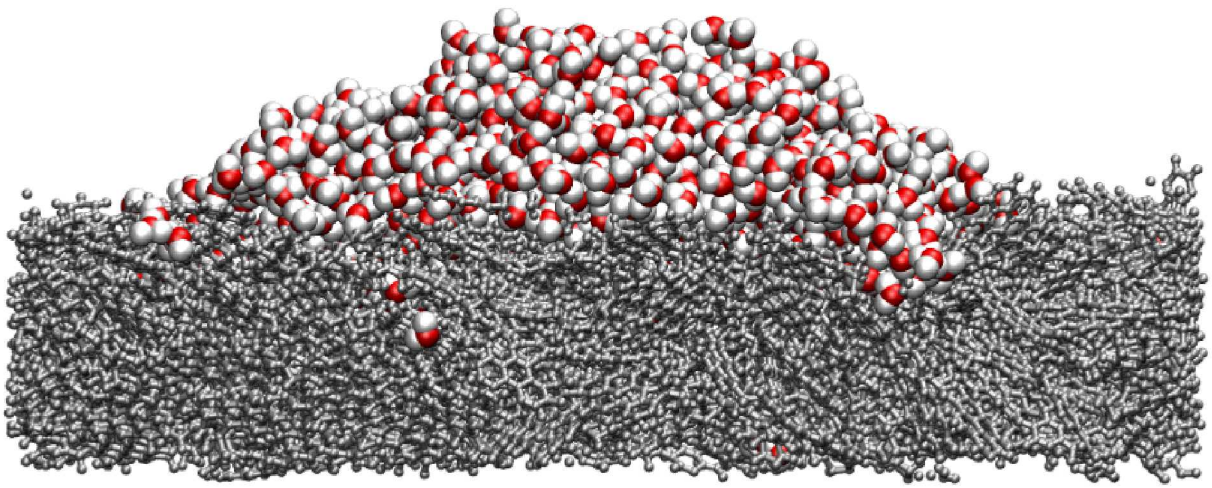






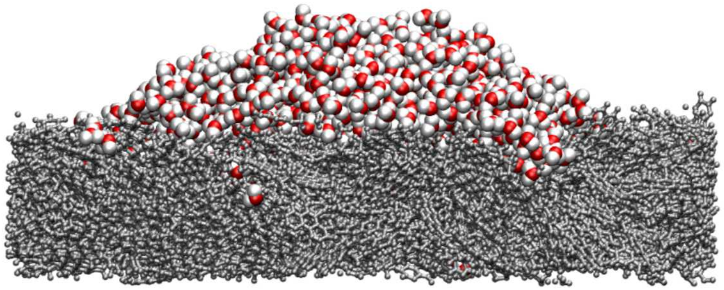


42.8°±6.5°

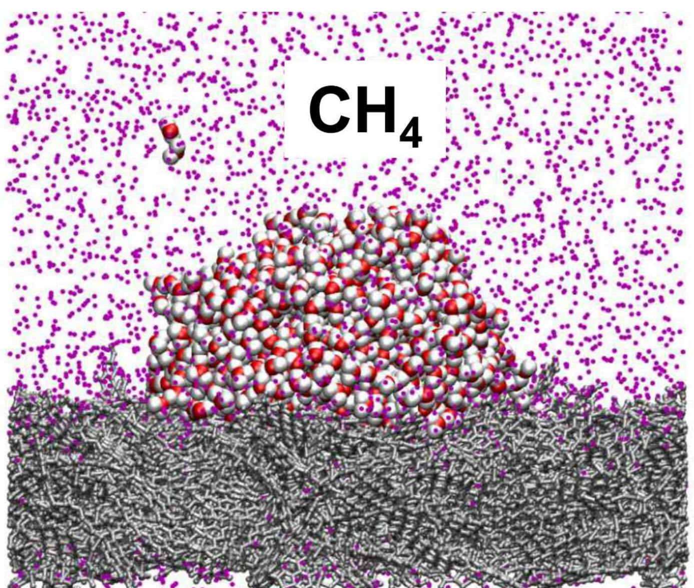


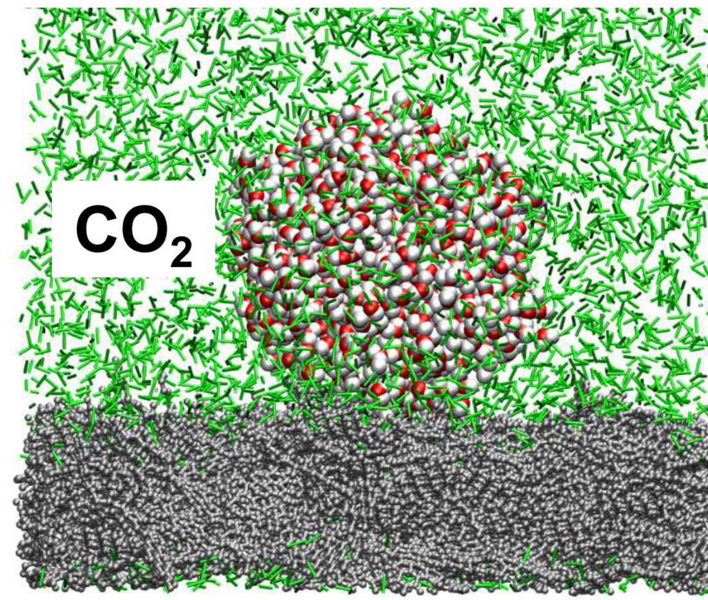
Kerogen wettability and fluid flow

42.8°±6.5°



79.18°±1.97°

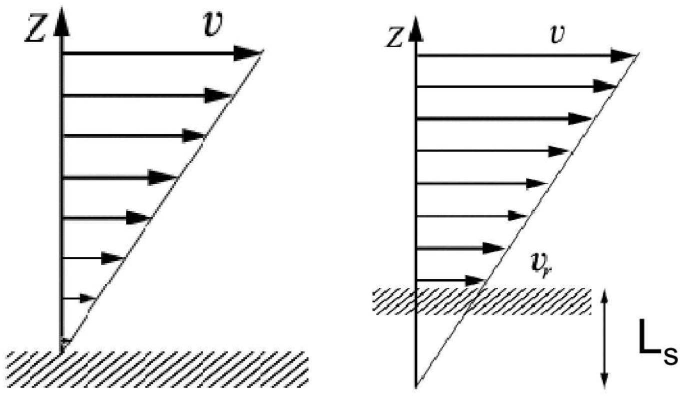




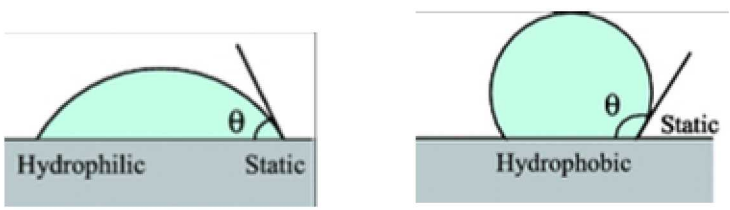
Hydrophilic to hydrophobic transition

Kerogen wettability and fluid flow

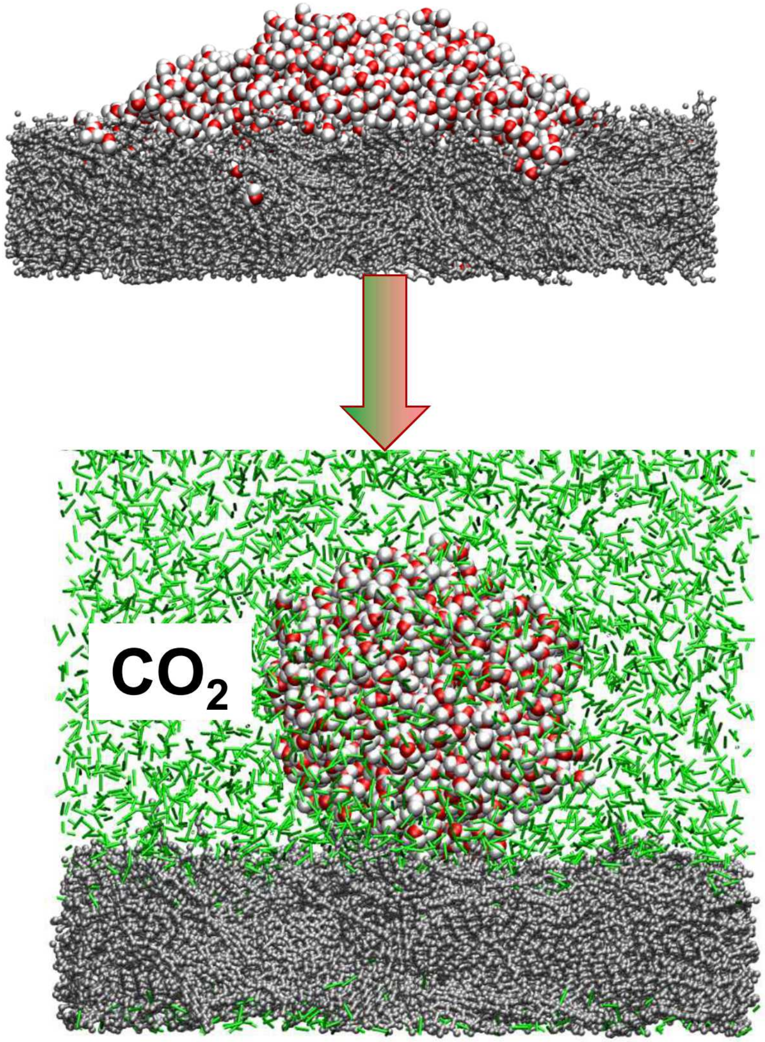
Hydrophilic to hydrophobic transition → Stick to slip flow transition



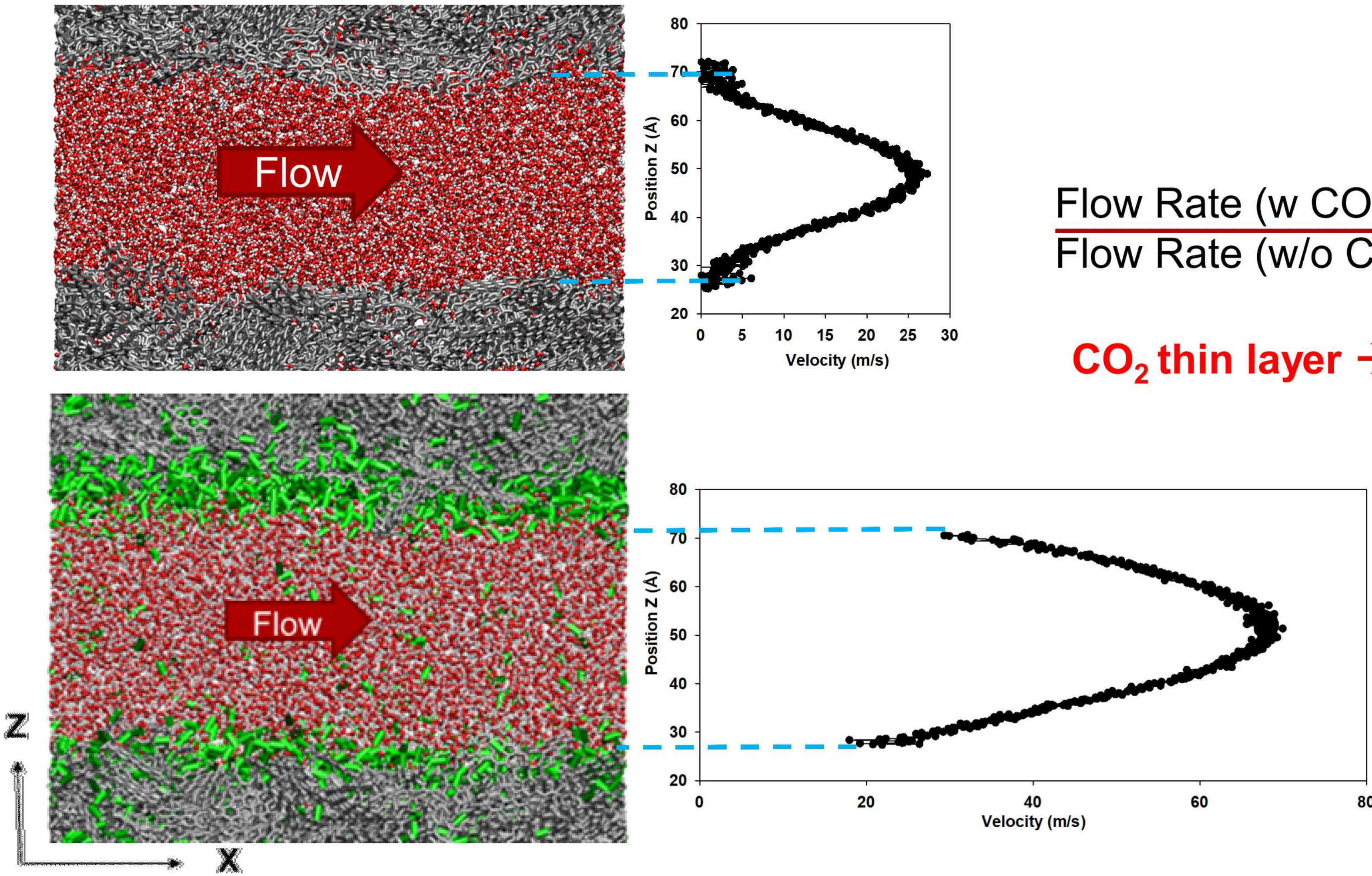
No slip **Slip**



42.8°±6.5°

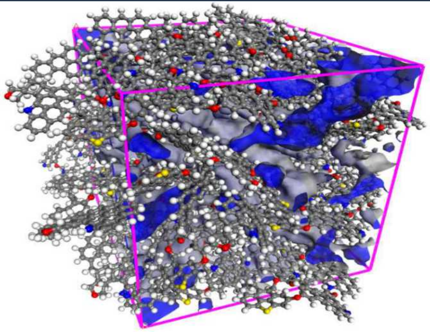


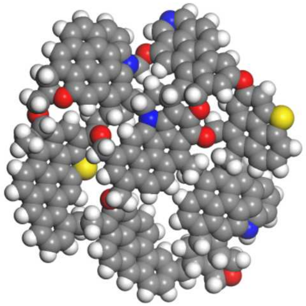
Kerogen wettability and fluid flow



$$\frac{\text{Flow Rate (w } CO_2\text{)}}{\text{Flow Rate (w/o } CO_2\text{)}} \sim 4$$

CO_2 thin layer → Lubricant





Molecular Simulation of the Multicomponent Interaction in Kerogen Nanopores

Outline:

1. CH_4/CO_2 adsorption onto kerogen
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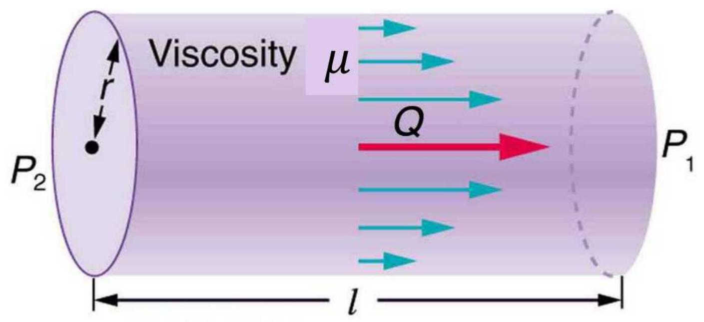
3. Wettability
4. Oil transport in shale nanopores

Enhancement of oil flow in shale nanopores

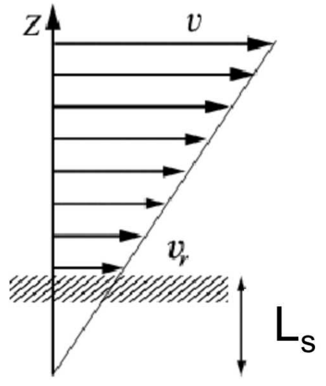
(Submitted)



$$Q_{no-slip} = {}^{\pi r^4 \Delta P}/_{8\mu L}$$

$$Q_{slip} = Q_{no-slip}\left(1 + \frac{8L_s}{2r}\right)$$

$L_s = \mu/\lambda$ (viscosity/friction coefficient)

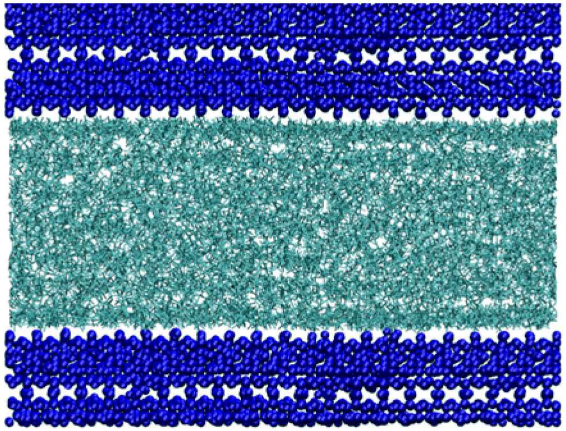


Slip

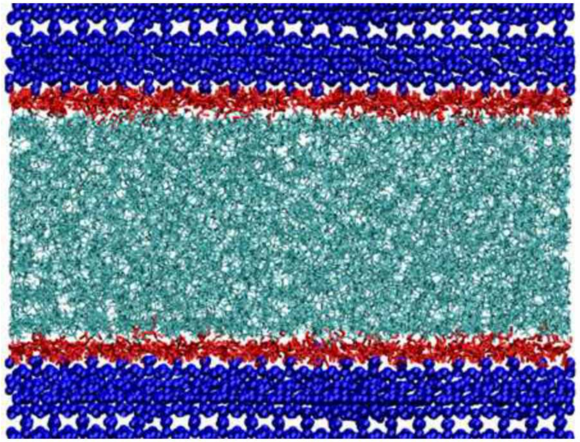
$$Q_{slip} = \left({}^{\pi r^4 \Delta P}/_{8\mu L}\right)\left(1 + \frac{8\mu}{2r\lambda}\right)$$

Viscosity$_{bulk}$ ≠ Viscosity$_{nanoconfinement}$

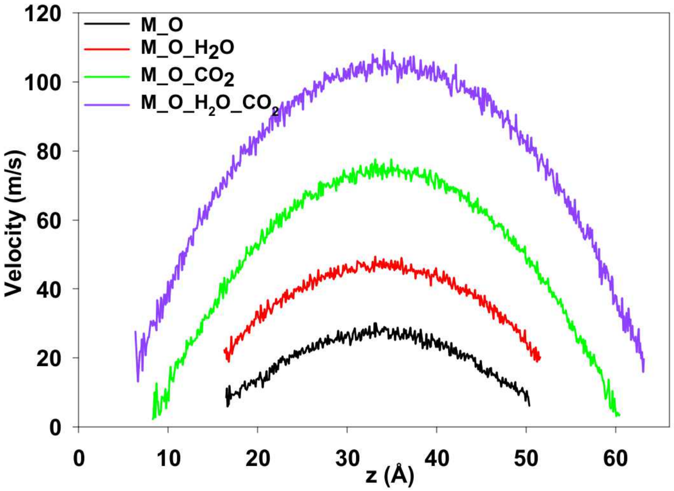
Enhancement of oil flow in shale nanopores

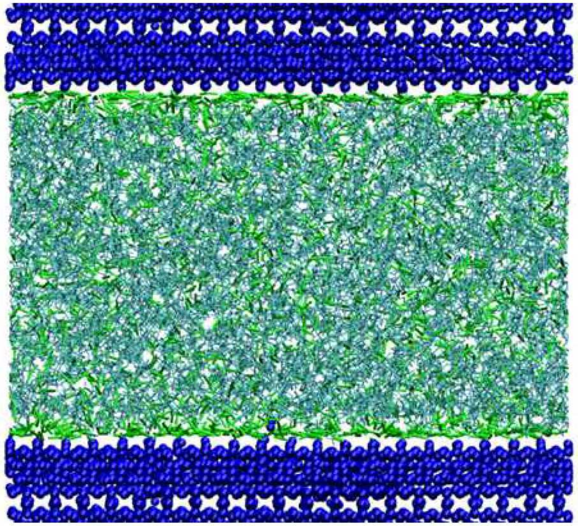


M_O
(Muscovite and Octane)

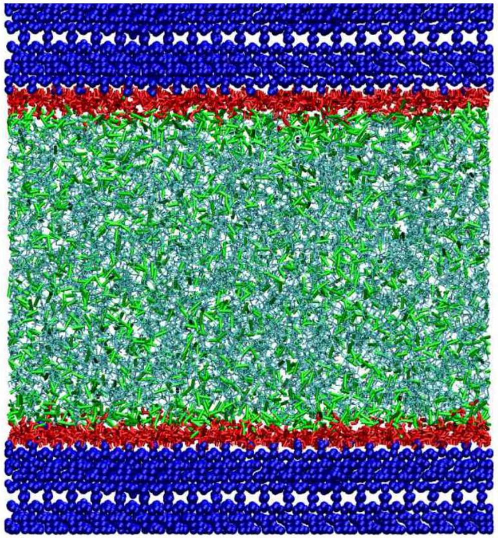


M_O_H_2O



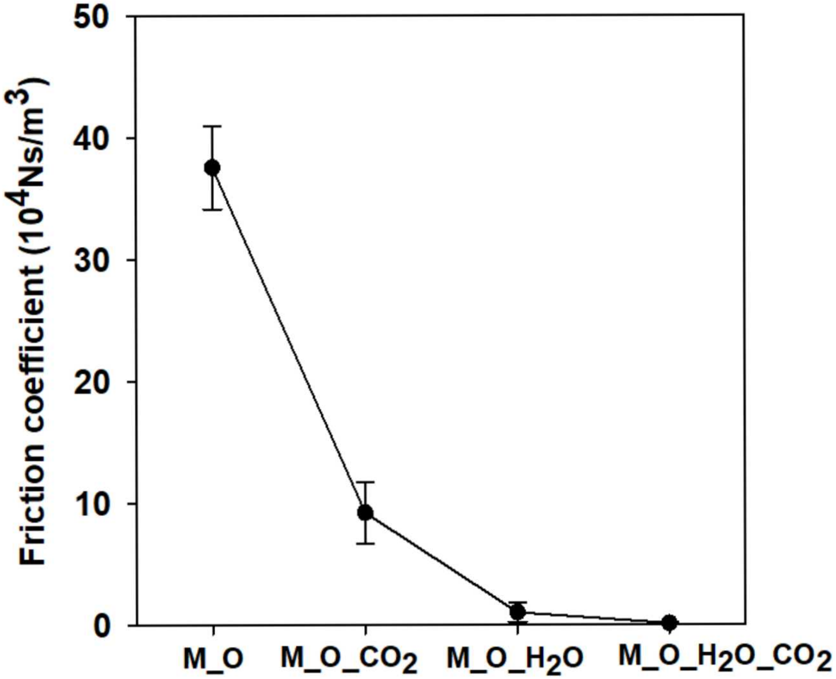


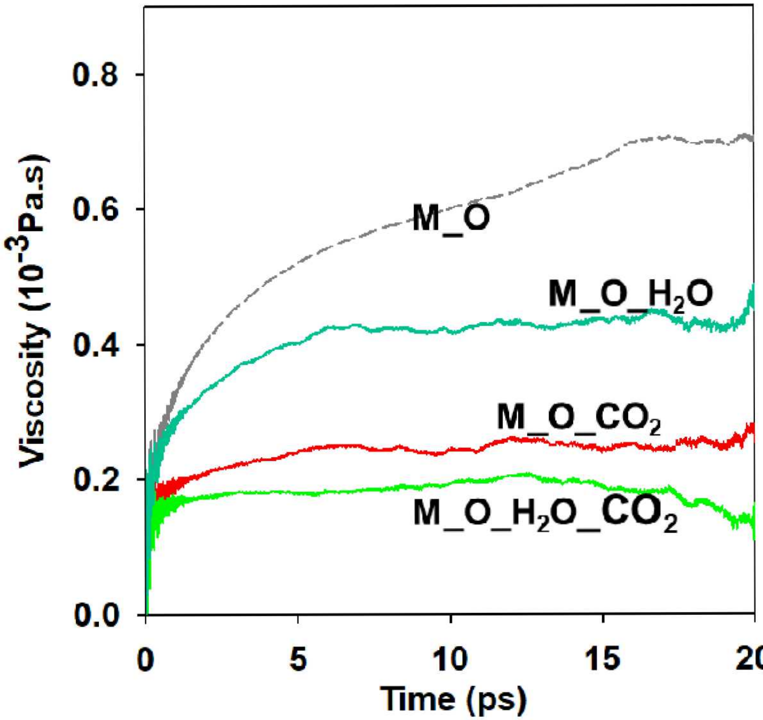
M_O_CO2



M_O_CO2_H2O

Enhancement of oil flow in shale nanopores



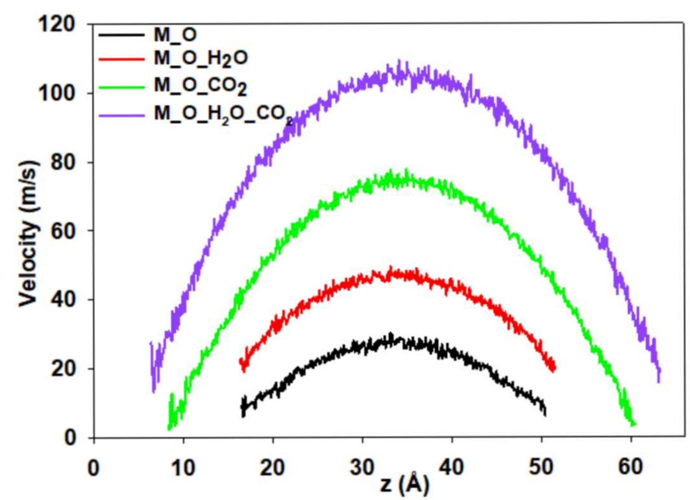


$$Q_{slip} = \left({}^{\pi r^4 \Delta P}/_{8\mu L}\right)\left(1 + \frac{8\mu}{2r\lambda}\right)$$

$$\frac{Q_{M\_O\_H_2O}}{Q_{M\_O}} = 1.95$$

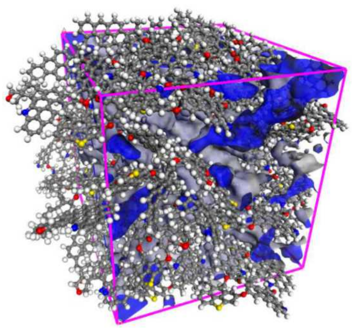
$$\frac{Q_{M\_O\_CO_2}}{Q_{M\_O}} = 3.84$$

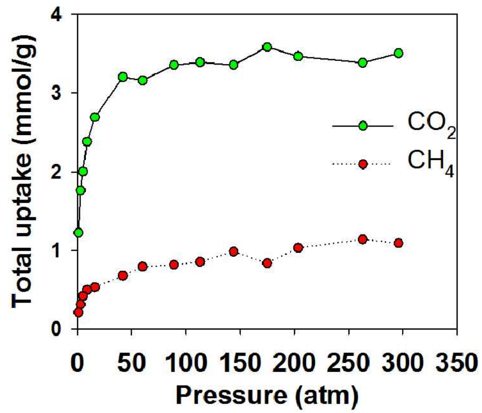
$$\frac{Q_{M\_O\_CO_2\_H_2O}}{Q_{M\_O}} = 6.37$$



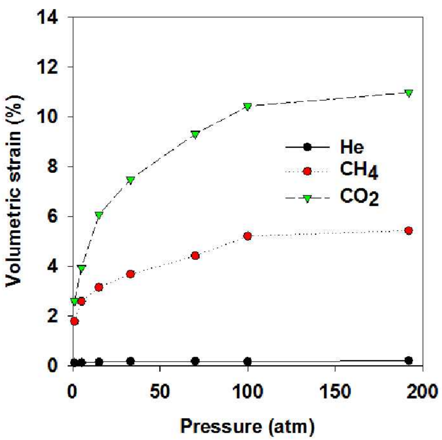
Summary

1. CH_4/CO_2 adsorption onto kerogen
(Fuel 2018 & Sci. Rep. 2016)

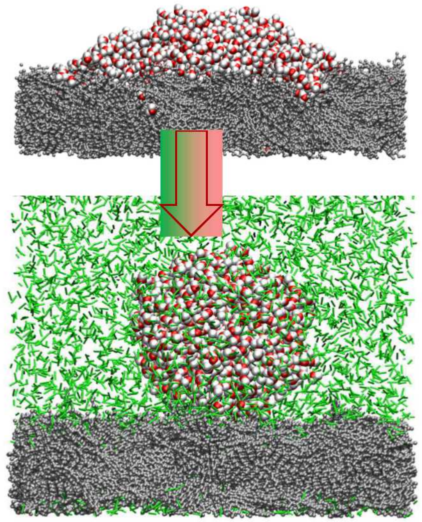


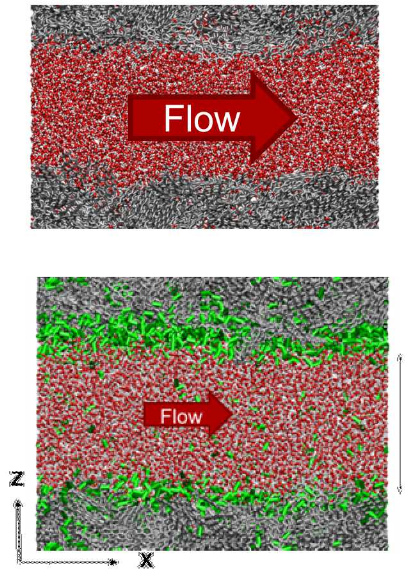


2. Kerogen swelling
(PCCP 2018)

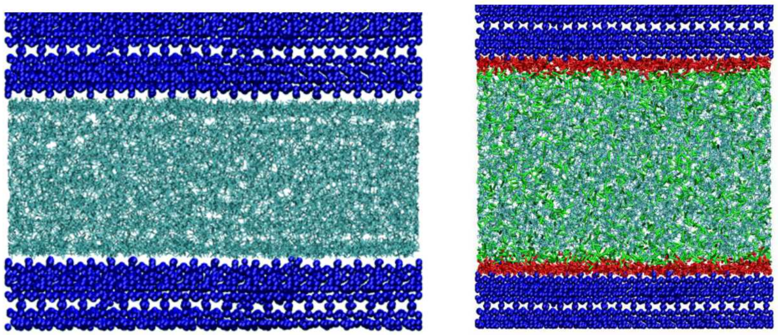


3. Wettability
(Nanoscale 2018**)**

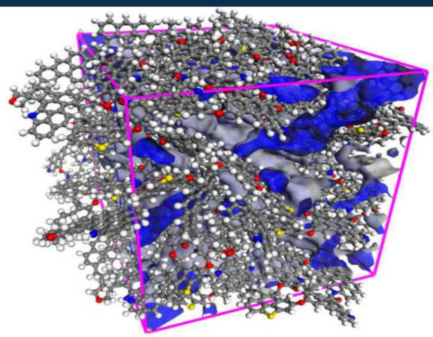


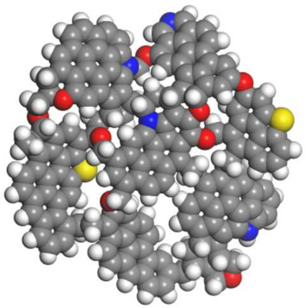


4. Oil flow enhancement (submitted)



$$Q_{slip} = \left(\pi r^4 \Delta P / 8\mu L\right)\left(1 + \frac{8\mu}{2r\lambda}\right)$$





Molecular Simulation of the Multicomponent Interaction in Kerogen Nanopores

Tuan Ho, Yifeng Wang, Louise Criscenti, Anastasia Ilgen

Sandia National Laboratories

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