Nano/Molecular Scale Petrophysics and Fluids

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Research interests:
• Nano-scale and molecular phenomena
• Shale petrophysics
• Fluid flow, transport and reactions in heterogeneous porous media

Related Publications:
Wasaki, A., and Akkutlu, I.Y., 2015. Permeability of Organic-rich Shale. SPE-170830, paper presented during the SPE ATCE in Amsterdam, the Netherlands, October 27-29. Accepted for publication in SPEJ


Multi-scale Pore Network

shale core plug

SEM Evidence of Porosity in Kerogen

1 μm

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Mercury Injection Porosimeter

Steady-state permeability measurements shown on the Double-slip Chart

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MC Simulation of Fluid Adsorption

4nm, 3,000 psi (20.7MPa) pore pressure and 176°F (80°C) temperature

VMD visualization of methane-ethane mixture in slit-pore

Adsorbed fluid 41

Free fluid

pore half length, Å

$\text{r}^*\text{CH}_4, (1000*\text{Å}^{-3})$

4nm, 3,000 psi (20.7MPa) pore pressure and 176°F (80°C) temperature

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Adsorption in SWCNT

Structured density profile across the tube under thermodynamic equilibrium conditions:

- 2 nm
- 3 nm
- 5 nm
Density Profile in Organic Pores and Channels

Under equilibrium conditions, discrete density profile has three regions:

- **adsorbed layer**
- **transition layers**
- **free fluid**

**methylene in 4,000 psi and 175 F**

**phase distribution in nanopore**

**Distance from the wall (Å)**

**Density (g/ml)**

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Shale Gas-in-place Calculations

Old Methodology

Void space measured by porosity measurement

+ Sorbed mass measured by adsorption experiment

= Total GIP

New Methodology

Void space measured by porosity measurement

+ Sorbed mass measured by adsorption experiment

- Free gas volume taken up by sorbed gas

= Total GIP

\[ G_f = \frac{32.0368}{B_g} \left[ \frac{\phi(1 - S_w)}{\rho_b} - \frac{1.318 \times 10^{-6} \dot{M}}{\rho_{ads}} \left( \frac{G_{sL}}{p + p_L} \right) \right] \]

\[ correction \ for \ adsorption \ layer \ effect \]
Phase diagrams of bulk methane, n-butane and n-octane obtained from Peng-Robinson equation of state and GCMC simulations in this work. The dots indicate critical points.
Phase Diagrams of Methane, Butane and Octane under Confinement

**Methane**

**Butane**
Implications – Uncertainty in Analysis

ternary (C_1, C_4, C_8) mixture

Reservoir Pressure, psia

Reservoir Temperature, F

Oil
Gas
Condensate
Wet Gas

ternary (C_1, C_4, C_8) mixture

T=210°F

Bulk

3nm

2nm
Fluid Transport in SWCNT

- Driving force generated using piston-like arrangement, controlling source and sink volumes to emulate pressure gradient

- Transport properties measured through the tube, e.g. velocity profile, to infer the effects of free and adsorbed phases on the overall transport
Fluid Density and Velocity Profiles: High Pressures

Average pressure: 1,687 psi
\[ \Delta p = 50 \text{ psi} \]

Distance from capillary center (nm)
Mass Flux Profile across Nanocapillary

Adsorption phase transport contribute a large portion to the total mass flux
Field Application I: (Bundle of Capillaries Approach)

Marcellus shale permeability correction for the organic capillaries

\[ k_\bullet = k \left[ f(r_{\text{tube}}) \right] R_{me} \]

where \( f(r_{\text{tube}}) \) = organic pore size distribution (fraction)

A flow cutoff of 2 nm applied

\[ (f \cdot R_{me}) = 1.573 \]

\( k_a = 1.573 \, k \)

57.3% enhancement in permeability
Field Application I: (Organic-rich Shale Permeability)

$$k_{gas} = k_m + \mu D_c g + \mu D_s \frac{G_s L \rho_{grain} B_g}{\varepsilon_{ks}} \frac{p_L}{(p + p_L)^2}$$

$$k_m = k_o \left(1 - \left(\frac{p_{conf} - \alpha p}{p_1}\right)^m\right)^3$$

Molecular transport effects of organic nanopores

Geomechanical effect of inorganic pores only
Because of relatively high pressure near the fracture, molecular transport effects become less influential.
Nano-group Researchers

Ten researchers with in alphabetical order:

• Sara Abedi, *Petroleum Eng Dept.*
  Experimental and theoretical microporomechanics, nano-
  chemomechanical characterization of geomaterials

• Yucel Akkutlu, *Petroleum Eng Dept.*
  Multi-component, multi-phase molecular effects in organic nano-
  capillaries and scaling up

• Perla Balbuena, *Chemical Eng Dept.*
  Nanopore confinement effects on hydrocarbon phase behavior

• Khoa Bui, *Petroleum Engineering Dept.*
  Multi-phase flow and capillarity in nanoporous materials

• Tahir Cagin, *Chemical & Materials Eng Dept.*
  Nano-scale mechanical investigations of water-shale interactions and
  rock failure mechanism
Nano-group Researchers, cont.

• Louise Criscenti, *Sandia National Laboratories, New Mexico*
  Molecular interaction of hydrocarbons with various kerogen types

• Yalchin Efendiev, *Mathematics Dept.*
  Upscaling microscopic phenomena, multi-scale simulations

• Andreas Holzenburg, *Center for Imaging and Microscopy*
  Nano-scale imaging for petrophysics

• John Killough, *Petroleum Engineering Dept.*
  Meso-scale simulations of fluid flow and transport in multi-scale porous media

• Yifang Wang, *Sandia National Laboratories, New Mexico*
  Geochemistry laboratory
Organic rich shales: from nano to macroscale

- Stochastic upscaling
- Tests at elevated temperature

Macro:
- Uniaxial creep
- Acoustic measurement
- Strength
- Fracture toughness

Nano/Micro-
- Micromechanical testing
- Uniaxial creep
- Acoustic measurement
- Strength
- Fracture toughness

Creep
- Elasticity
- Strength
- Fracture toughness

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IFT of Methane in Nanopore

From the local stress tensor, pressures are calculated considering both kinetic and internal (inter- and intra-molecular) contributions:

\[
\gamma = \frac{1}{N_0} \int_0^{L_z} \left[ p_N(z) - p_T(z) \right] dz = \frac{1}{N_0} \int_0^{L_z} \left[ p_{zz}(z) - \frac{p_{xx}(z) + p_{yy}(z)}{2} \right] dz
\]

Value of IFT is 6.65 mN/m across the V-L interface. This value is 45% smaller than that of the bulk IFT.

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EOR for Shale Oil using Nano-emulsion

**Surfactant:** dodecylhepta(oxy-ethylene)ether (C$_{12}$E$_{7}$) contains one hydrophobic tail of 12 alkyl groups, and one hydrophilic head of 7 ethylene oxide groups and 1 terminal OH group.

**Oil:** d-limonene (terpene solvent)
TAMU Center for Imaging and Microscopy: Imaging Modalities across the Scales (continuum)

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Length scales resolved →
Interfacial structure between SiC and nanoscale MgAl$_2$O$_4$ particles. The layer spacing of 0.25 nm is well resolved for the SiC phase.
TAMU Center for Imaging and Microscopy:
...and from Alzheimer’s peptides to zeolite

Small, spherical aggregates

Sheets rolling up

Fibrils

Tin-containing zeolite crystals
Nanogeochemistry: Nanostructures, emergent properties and their control on geochemical reactions and mass transfer

Yifeng Wang
DOE Center for Integrated Nanotechnology

Pioneering work in nanogeochemistry. Access to DOE Center of Integrated Nanotechnology

TRAMANTO: Classical Density Functional Theory

http://www.pflotran.org/applications.html

PFLOTRAN: Reactive transport modeling

High pressure flow-through experiments

Constitutive relationships

Continuum models

Reactive transport modeling

Binding energies of methane sorption

Diffusion rates

Molecular dynamic (MD) modeling

Nano science

• Effects of nanopore confinement on fluid thermodynamic properties

• Effects of nanopore confinement on methane transport (microfluidics in shale)

Upscaling

• Perculation theory

• Fractal representation

• Lattice Boltzmann modeling

Predictive models

Field observations

• Core/outsitop/sample collection

• Quantification of heterogeneities

Material characterization

• Pore structures: SANS, BET, TEM, SEM, etc

• Chemistry & mineralogy: XRD, XRF, etc

Sorption/desorption measurements

• Methane sorption/desorption on model materials

• Methane sorption/desorption under high P & high T

• Chemical/physical stimulations

Gas disposition & release

• Gas in place (GIP)

• Gas migration from matrix into fractures

• Stimulated volume

• Gas for secondary recovery

Column experiments

• Diffusive fluxes

• Advective fluxes

High pressure/high temperature sorption/desorption measurements

Pore structure characterization using small angle neutron scattering

High pressure flow-through experiments

70.00 nm

Synthesis of nanoporous materials

Isolation of kerogen from Mancos shale

Density functional theory (DFT) modeling

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Water-clay interactions using large-scale simulations

50 x 50 x 80 nm³ Kaolinite

- Clay under external stress
- Soak with brine
- Vary salinity, stress, temperature