New experimental techniques and modeling methods for the study of flow in porous media from the nanometer to the centimeter

Some Up-scaling issues

Benoît Noetinger, IFPEN

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summary

- Stakes
- Goals of up-scaling between these scales
- Issues for cap rocks, shales, clay swelling
- Bias in molecular simulations

Conclusions and perspectives.

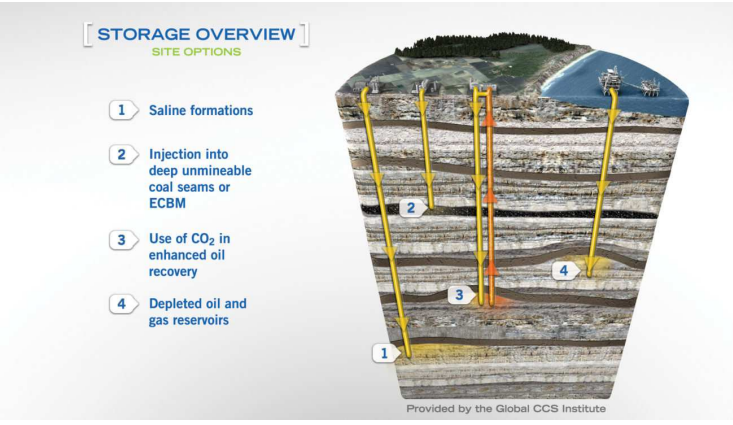
Stakes

- Understanding flow and transport processes in nanopores are of increasing importance for many applications:
  - Shale gas flow understanding and modelling
  - Thermodynamics in nanopores
  - Cap rock modelling in CCS applications
  - Battery modeling, fuel-cells
  - Hydrogen storage
  - Membrane modelling such as water desalinization, blue energy (osmotic energy harvesting)
  - Refining, chemical engineering etc….
- Nanoscale data are more and more available, as well as detailed simulation methods such as molecular dynamics, lattice Boltzmann

Goals of up-scaling from nano to cm

- In analogy to the change of scale from pore-scale to Darcy description, to be able to build a physically sound macroscopic model describing transport in nanopores.
- Surface effects may become dominant, as well as coupling with other physical effects (eg clay swelling)
- Adsorption effects
- So two tasks:
  - finding an effective description (like Darcy's law)
  - determining the associated parameters (like poro/perm etc…) from microscopic data

Understanding diffusion in cap rocks for CCUS, for nuclear waste disposal…



Some open questions regarding cap rocks: oversolubility of HC in nanopores

- Molecular dynamics simulation show an increase in solubility due to interactions between the gases, the wall molecules and water

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Diffusive transport of gases in saturated nanopores: Caprock leakage from a molecular simulation perspective

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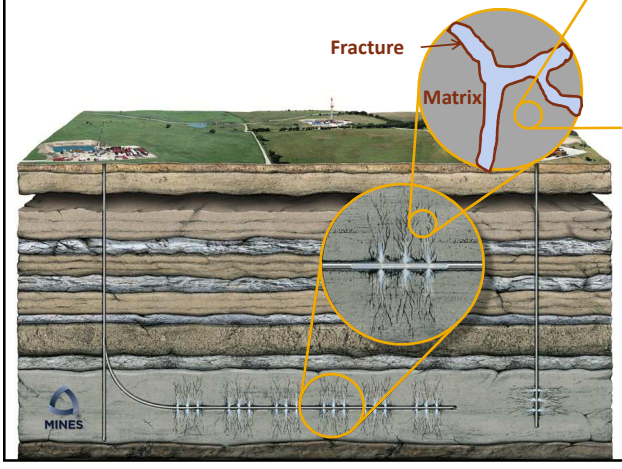
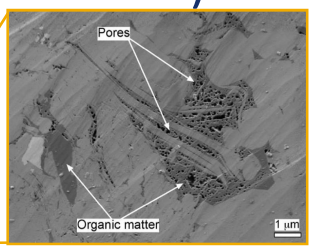
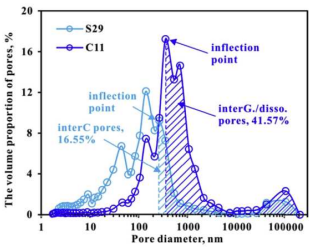
Shale gas modelling, from nano to km scales! (From Sobecki et al)





Scanning electron microimage of Barnett Shale (Wang et al. 2009)



Pore size distribution of 2 tight rock samples (Zhang et al. 2016).

- **Fluid located in kerogen and clay with ultra low permeability (~100nD) and porosity (~0.05)**
- **Strong rock-fluid interaction within nano-pores**
- **Very heterogeous pore size distribution**

Shale gas/tight oil reservoir

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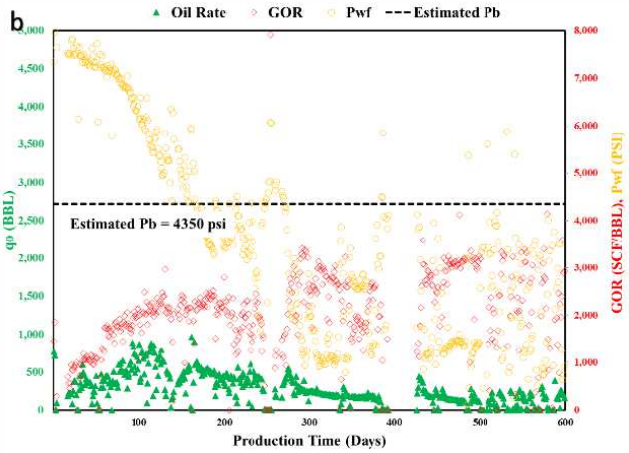
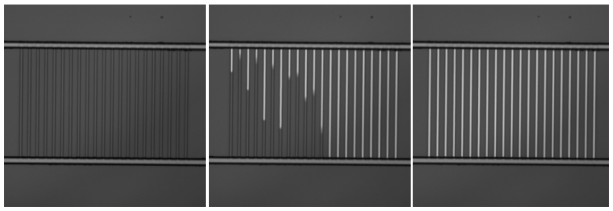
Approaches

- Monte Carlo simulation using molecular modeling
  - PVT, adsorption in nanopores etc…
- Molecular dynamics (transport properties)
  - Diffusion coefficient
  - Soret effect
  - Clay swelling
- Battery modelling etc….

Anomalous GOR



Production of a liquid rich shale oil Eagle Ford well (M. Khoshghadam et al. 2017)



Three consecutive images (0.05s) during the vaporization (L. Wang et al. 2014).

- **Production GOR anomaly**
- **Pore size dependent PVT**

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Thermodynamics in nanopores: may be treated by shifting Tc, Pc using Grand canonical Monte Carlo

RESERVOIR CHARACTERISTICS:
- Strong rock-fluid interaction within nano-pores
- Very heterogeous pore size distribution

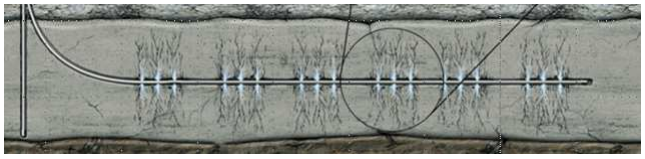
→

CONSEQUENCES ON FLUID AND PRODUCTION:
- Pore size dependent PVT
- Production GOR anomalies

→

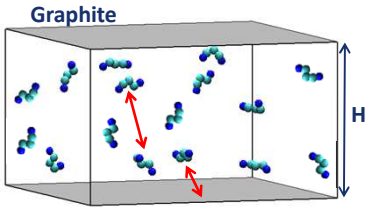
MODELING ISSUES
- Standard thermodynamic flash not adapted
- Conventional simulator not predictive

PROBLEM:
HOW TO MODEL ACCURATELY HYDROCARBON THERMODYNAMIC AND FLOW IN LOW PERMEABILITY RESERVOIR AT LARGE SCALE?



Molecular simulation

Monte Carlo: statistical method based on the Boltzmann distribution of energy at thermodynamic equilibrium



- **Fluid/fluid interaction**:

  Lennard-Jones 12-6 AUA potential

- **Fluid/solid interaction**:

  Steele 9-3/AUA potential

$$u_{sf}(z) = \frac{2}{3}\pi\rho_s\varepsilon_{sf}\sigma_{sf}^3\left[\frac{2}{15}\left(\frac{\sigma_{sf}}{z}\right)^9 - \left(\frac{\sigma_{sf}}{z}\right)^3\right]$$

Grand Canonical Monte Carlo ensemble (µVT)

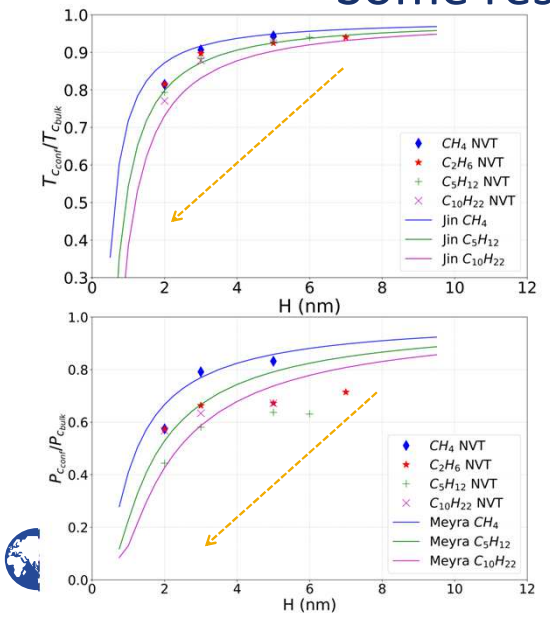
- Lack of precision on the LVE chemical potential
- Inability to give information on pressures

↓

Adapt Gibbs Ensemble Monte Carlo ensemble (NVT)

- Considers liquid and vapor boxes at equilibrium
  - Gives information on pressures
  - Needs good initial condition to converge

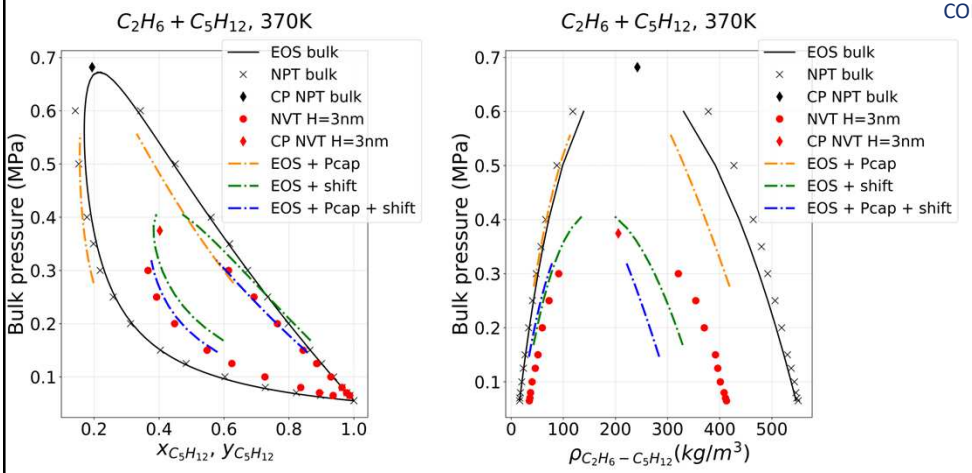
Some results



PURE COMPONENT RESULTS: CRITICAL POINT

- **Different shifts of critical temperature and pressure**
- **Critical temperature shift can be modeled by *Jin et al, 2013* correlation**
- **Critical pressure shift can be modeled by *Meyra et al, 2005* correlation**

Results for mixtures



COMPARISON WITH MOLECULAR SIMULATION RESULTS

- **Good match without any fitting with Flash+Pc with shift Tc Pc**
- **Need of density correction**

Up-scaling Approaches for pore size distribution (PSD), 3 porosity model

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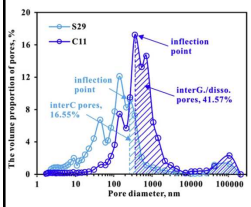
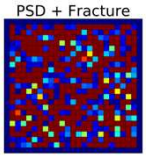
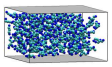
PSD from lab



PSD achieved through N2GA and MIP (Zhang et al. 2016).

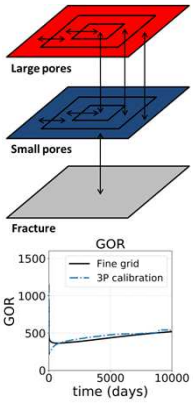
Fine grid matrix/fracture simulation for a PSD



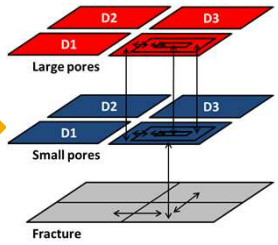


EOS+Pcap+shift calibrated by Molecular simulation

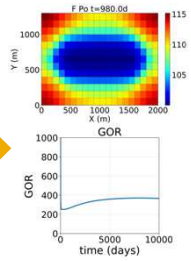
Concept of 3P model and calibration for a PSD



Building of the 3P model with different PSD



SRV simulation



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- **Molecular simulation**
  - Test the methodology developed on other pure components, mixtures and pore sizes
  - Test alternatives to Monte Carlo molecular simulation such as Density functional theory (DFT)
- **PVT modeling**
  - Improve calibration of modified EOS and test new EOS
  - Speed up convergence and improve robustness of the flash algorithm using deep learning for example
- **Matrix/fracture interaction**
  - Investigate the gravity effect using 3D simulation cases
  - Investigate the impact of correlation length for the PSD
- **Triple porosity model**
  - Test the robustness of the methodology developed on discrete fracture network and 3D reservoir model
  - Take into account direct fluid flow between two matrix cells

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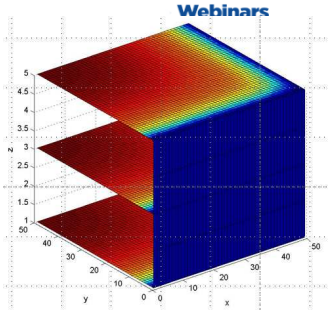

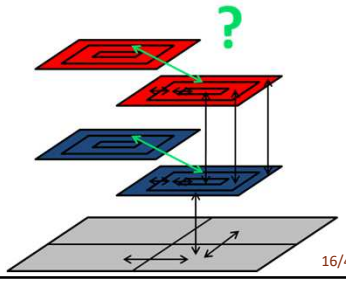

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Other exemple: modelling clay swelling

- Important for nuclear waste disposal in clay structures (like in Callovo-Oxfordian layer in Bures, France)
- Understanding the interaction between clay and various gases e.g. hydrogen coming from nuclear wastes

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Molecular Dynamics Simulation of Hydration and Swelling of Mixed-Layer Clays

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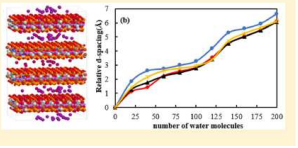
ABSTRACT: Swelling of clay minerals is important to a broad class of problems in science and engineering. While the problem has been extensively studied experimentally, past molecular modeling of the phenomenon was focused on pure clays of one type or another. In practice, however, there is a diverse class of mixed-layer clays (MLCs) in sedimentary rock with intermixed stacking sequence of two or more types of distinct layers within a single crystal. In fact, more than 60% of sedimentary rocks in the U.S. contain various types of MLCs. We present the results, to our knowledge, of the first molecular dynamics simulation of hydration energetics and



Application for CO2 injectivity control

- Major applications for geomechanics issues

International Journal of Greenhouse Gas Control 76 (2018) 193–199

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Geological and geomechanical factors impacting loss of near-well permeability during CO_2 injection

Malin Torsæter*, Pierre Cerasi

SINTEF Petroleum Research, Trondheim, Norway

Once clay swelling is quantified, up-scaling can be achieved by a cascade of multiple porosity models

Journal of Petroleum Science and Engineering 165 (2018) 596–615

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Modeling the swelling of shale matrix in unconventional reservoirs

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Unconventional Natural Gas and Oil Institute, Colorado School of Mines, 1500 Illinois St, Golden, CO, 80401, USA

Molecular simulation: solving Newton equation of motion of N particles in nanopores represented as realistic fixed molecules.

- Very expansive calculations, imply relatively narrow simulation boxes implying important numerical erros that can be corrected analytically

JCTC Journal of Chemical Theory and Computation — Article — pubs.acs.org/JCTC

Diffusion under Confinement: Hydrodynamic Finite-Size Effects in Simulation

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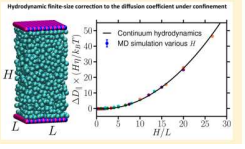
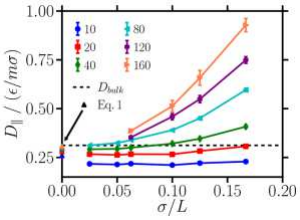
ABSTRACT: We investigate finite-size effects on diffusion in confined fluids using molecular dynamics simulations and hydrodynamic calculations. Specifically, we consider a Lennard-Jones fluid in slit pores without slip at the interface and show that the use of periodic boundary conditions in the directions along the surfaces results in dramatic finite-size effects, in addition to that of the physically relevant confining length. As in the simulation of bulk fluids, these effects arise from spurious hydrodynamic interactions between periodic images and from the constraint of total momentum conservation. We derive analytical expressions for the correction to the diffusion coefficient in the limits of both elongated and flat systems, which are in excellent agreement with



Correcting the bias

- Theory for diffusion coefficient in a very long nanopore

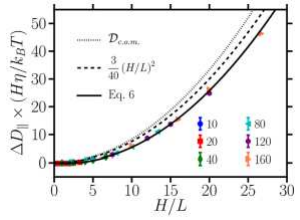
$$D_{\parallel}(H, \infty) \approx D_{\text{bulk}}\left[1 + \frac{9}{16}\frac{\sigma}{H}\ln\left(\frac{\sigma}{2H}\right)\right]$$



- But strong bias due to too small simulation box

- The bias can be corrected analytically thanks to An hydrodynamical calculation

$$\Delta D_{\parallel}(H > L) = \frac{k_B T}{\eta}\left[\frac{3}{40}\frac{H}{L^2} - \frac{3\ln(1+\sqrt{2})}{4\pi L}\right]$$



Conclusions & perspectives

- Experimental and molecular simulation methods allow deeper qualitative and quantitative understanding of transport in nanopores.
- Upscaling approaches using a combination of molecular simulation, hydrodynamics, multiporosity models and geomechanics can be set up to get results useful for the practitionner.
- Big computational facilities are required, as well as big data and AI for huge simulation data postreatment.
- Plenty of other issues (slip boundary conditions of importance for membrane modelling) etc….

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