MODÉLISER LES PHÉNOMÈNES DE TRANSPORT À TRAVERS LES ÉCHELLES

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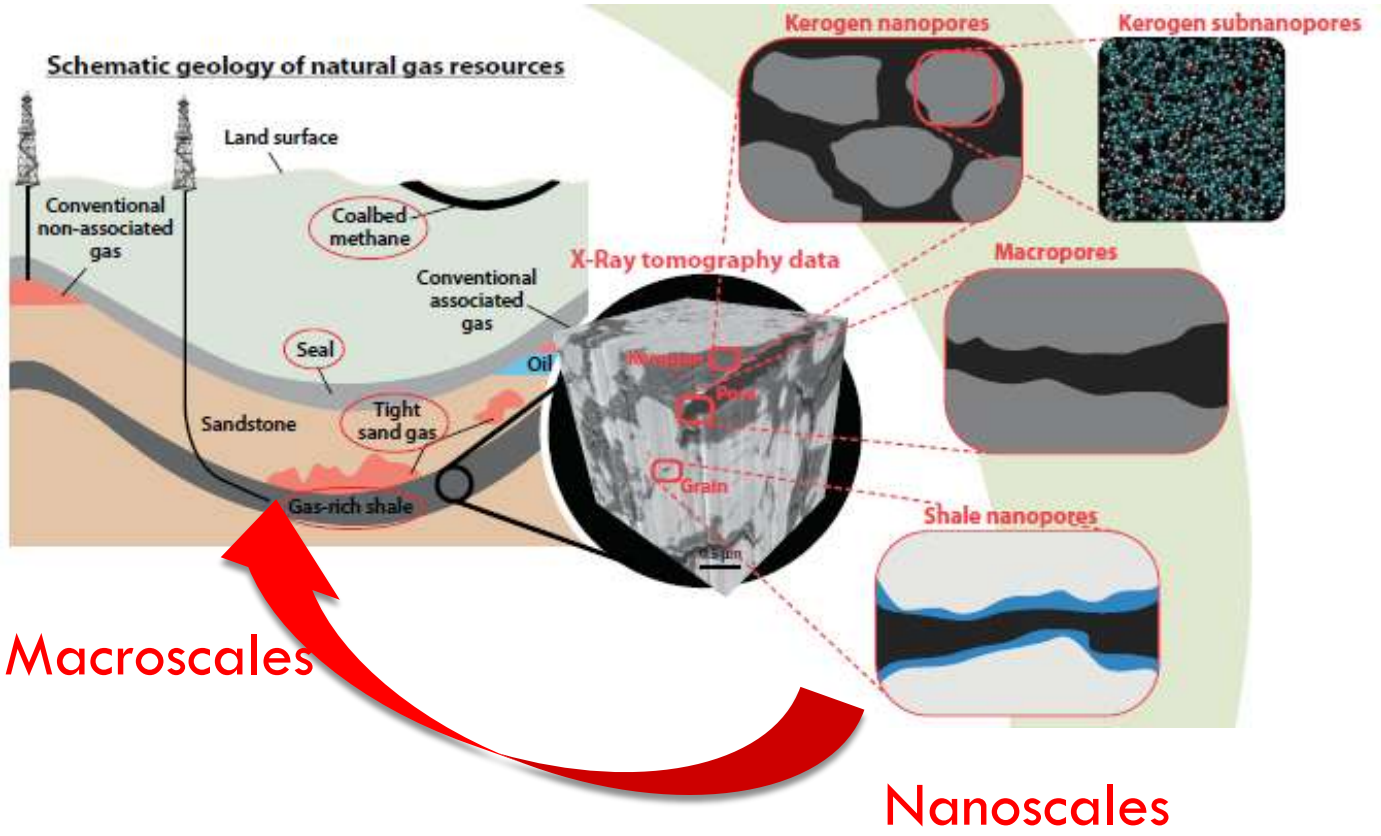
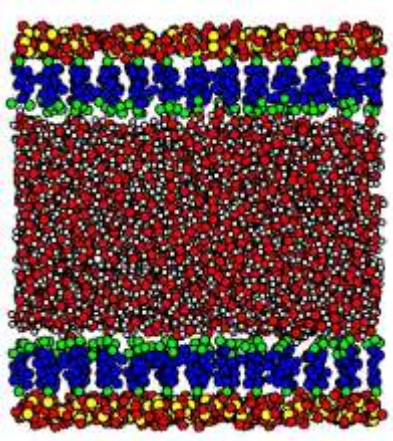
- Overview of recent works performed at UMI-MIT by B. Coasne, R. Pellenq, F. Ulm, collab. L. Bocquet
- Students K. Falk and A. Botan

Fundamental science for dirty problems

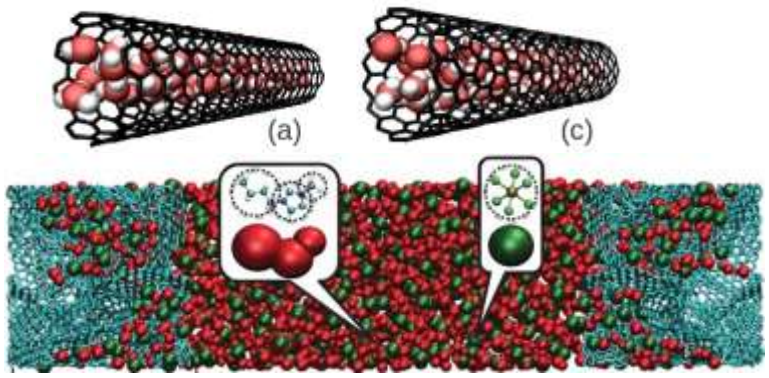


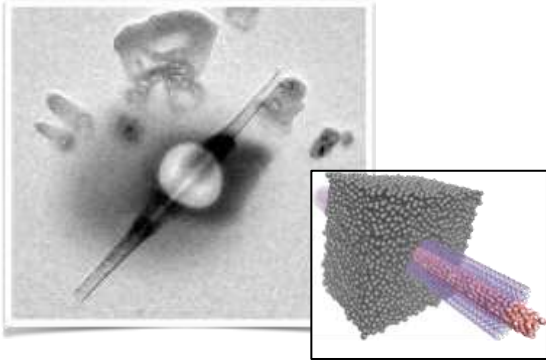
Fundamental science for dirty problems

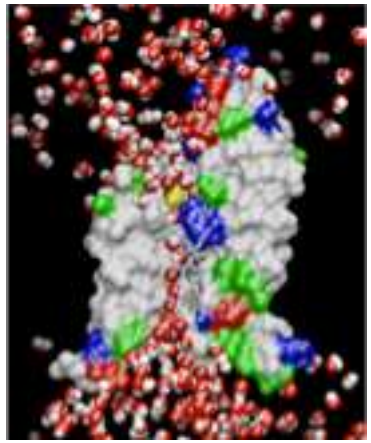
- This echoes directly state-of-the-art questions in fundamentals of liquid transport



Water, alcanes, ionic liquids in carbon nanomaterials







AQP-1

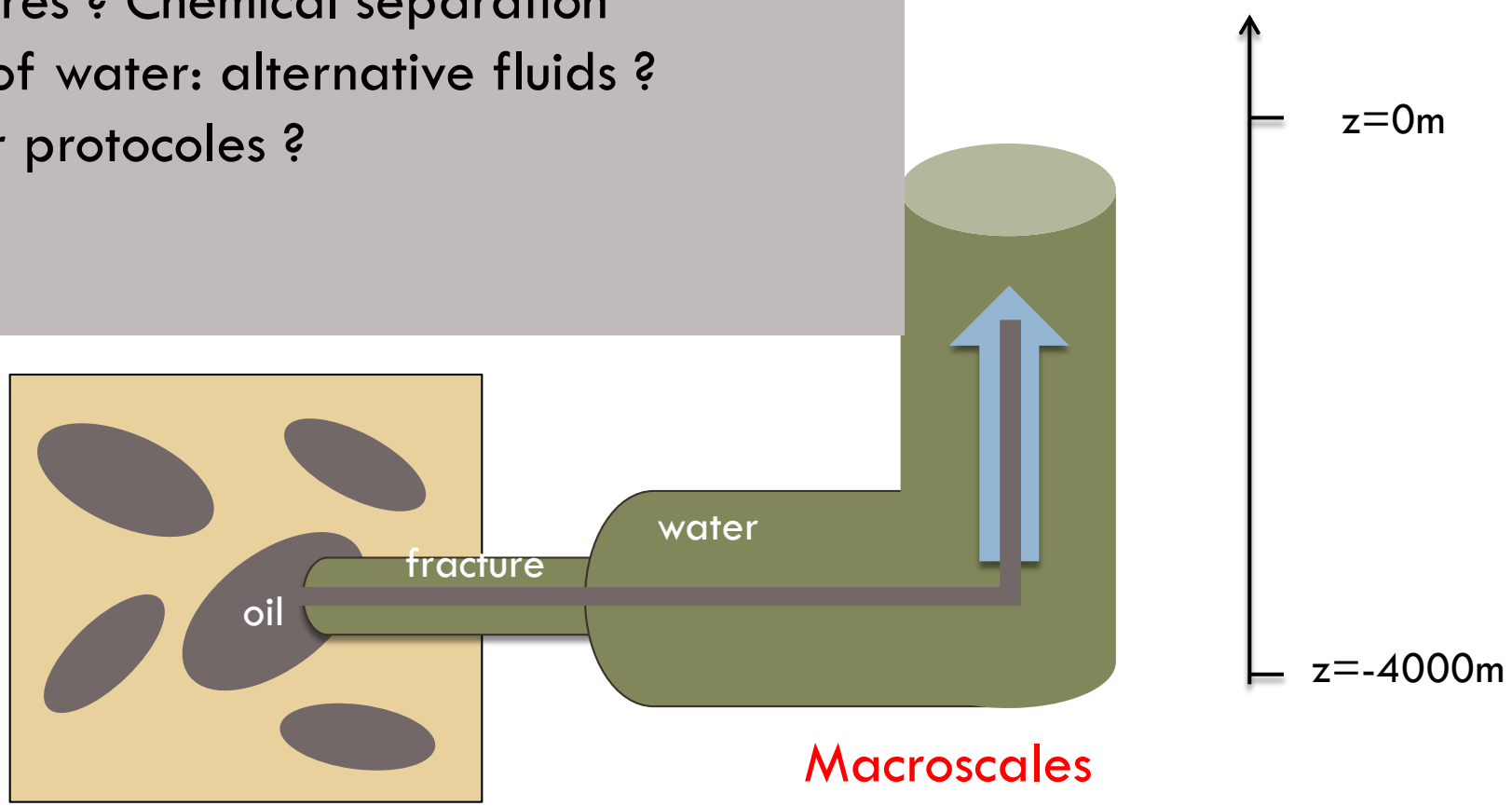
Liquid transp
confinement
Applications

NEW PROPERTIES/ NEW PHYSICS

on
tc.

Many Qs:

- ✓ Can one predict the flux of oil ?
- ✓ Nanoscale confinement effects ?
- ✓ Mixtures ? Chemical separation
- ✓ Role of water: alternative fluids ?
- ✓ Other protocoles ?
- ✓ …

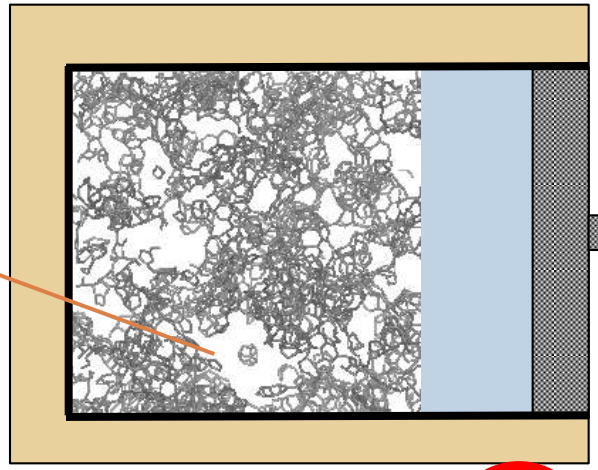


P_{down}=250bar
T_{down}=420K

Permeability

- Limiting factor: fluid transport at the *nanoscales*

methane, propane, hexane, nonane, dodecane, ...



ΔP

$k \propto a^4$

Darcy's law

$$\Phi_{fluid} = -\frac{k}{\eta_f} \times \nabla P$$

Fluid viscosity

(mass) Permeability= THE key quantity for extraction

- Central Q: is Darcy law valid in nanopores?

$$\Phi_{fluid} = -\frac{k}{\eta_f} \times \nabla P$$

  - The pores are in the few Angströms range
  - Question the validity of continuum fluid equations (Navier-Stokes)
  - The notion of viscosity has no real validity at such scales

Example of water in nanopores

- For water (CNTP)
  - Navier-Stokes equation valid down to 1nm ! (3 water molecules)
  - Confirmed by molecular dynamics simulation

Underlying idea: time scale separation needed to be able to describe a collection of particule as a continuum

$$\tau_{hydro} \gg \tau_{micro}$$

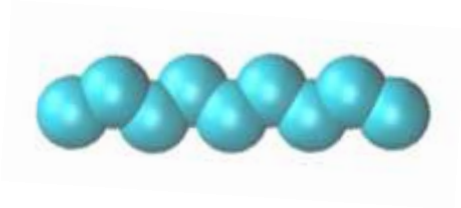
$$L \gg L_c = \sqrt{\frac{\eta_f}{\rho} \times \tau_{micro}} \approx \sqrt{\frac{\eta_f^2}{\rho \cdot G}}$$

$$L_c \sim 1nm$$

Water (CNTP)

Bocquet-Charlaix, Chem Soc Rec (2010)

- For alcanes (C_n)



  - Typically: viscosity $\eta_f \propto n$ Length of chain

Size threshold L_c increases with chain length: $L_c \approx \sqrt{\frac{\eta_f^2}{\rho \cdot G}} \propto n$

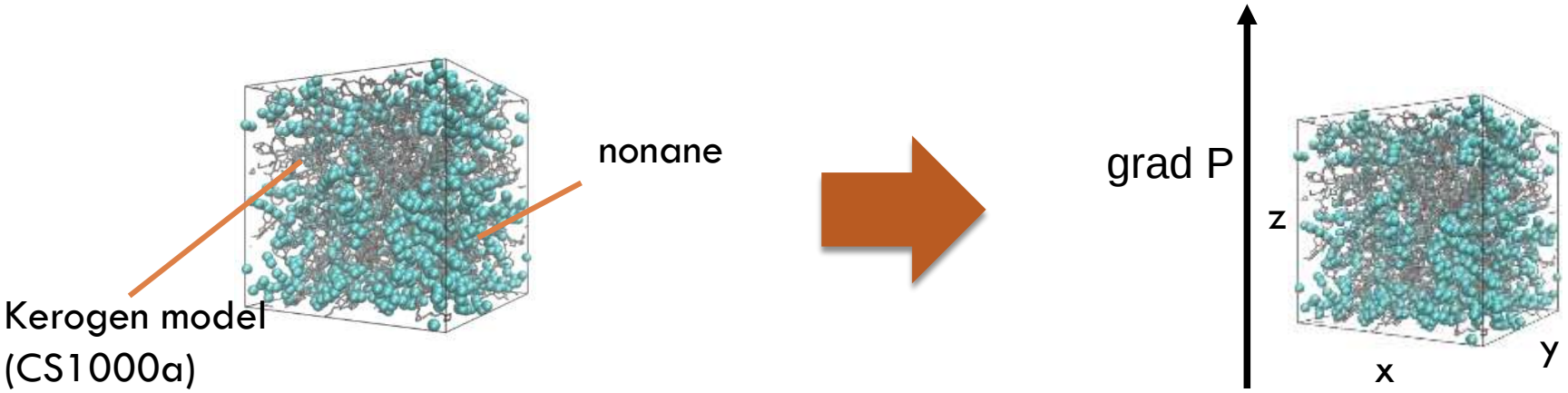
Nano Pore size smaller than threshold for long chains

  - Hydrodynamics and Darcy expected to break down

  - Needs for new transport models ?

Need for molecular models

- Molecular dynamics approaches



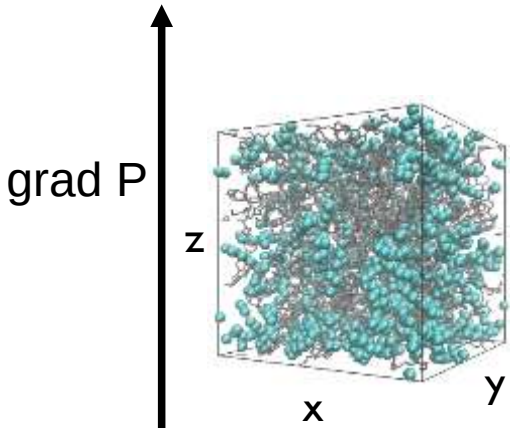
Falk, et al.

All atoms dynamics simulated on a computer

Model for kerogen structure, alcanes, interactions, …
Adsorption of the alcanes under thermodynamic conditions

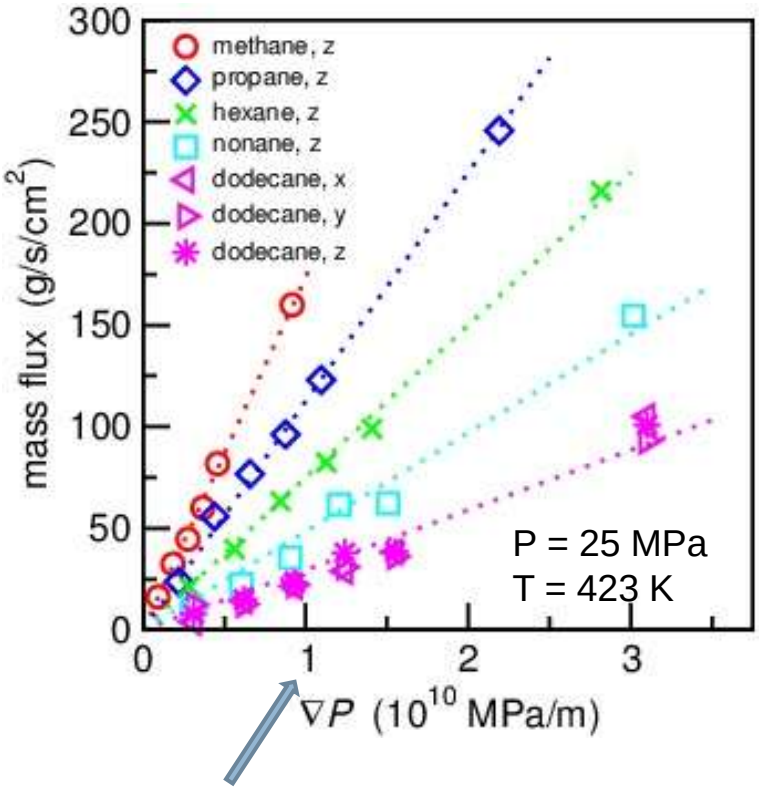
Pressure driven flow (@ 25 MPa)

pressure gradient applied to fluid in CS1000a
(periodic boundary conditions)



$$\Phi_{fluid} = -\frac{k}{\eta_f} \times \nabla P$$?

linear response

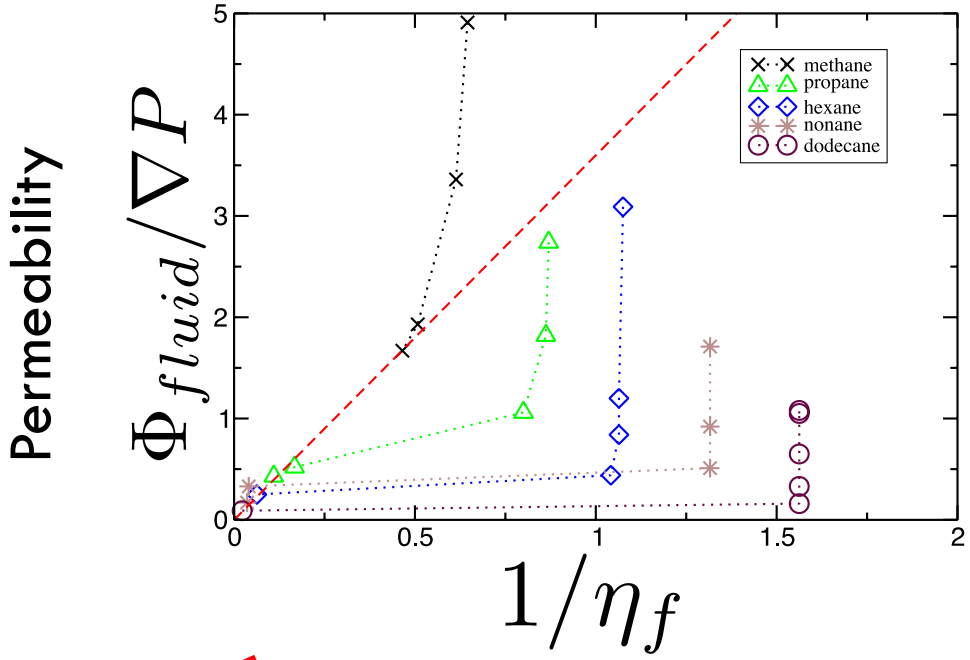


$4.79.10^{11}$ Psi/ft

Falk et al.

Even worst than expected

- Complete breakdown of Darcy !



@ various imposed chemical potential

Inverse viscosity of the alcane (Tabulated/calculated)

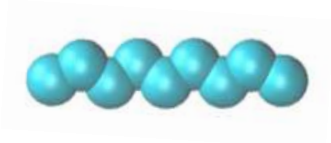
$$\Phi_{fluid} = \frac{k}{\eta_f} \times \nabla P$$

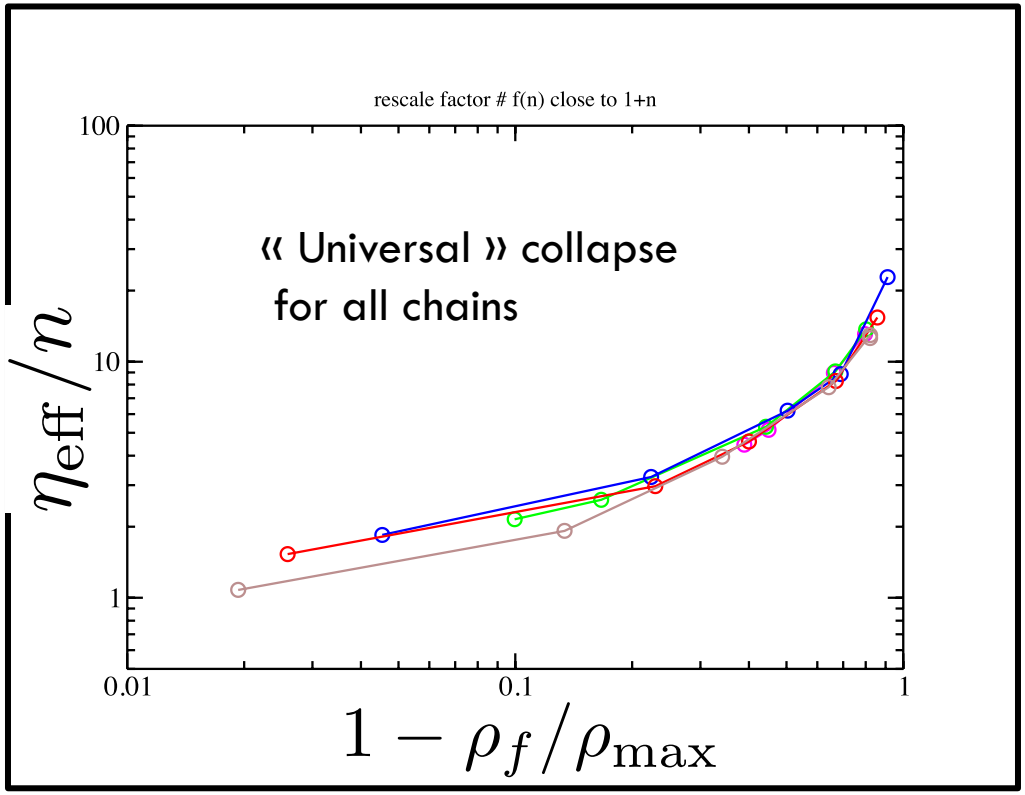
Data rescaling and effective viscosity

- But, still …

$$\frac{\Phi_{fluid}}{\nabla P} \equiv \frac{k_0}{\eta_{\text{eff}}}$$

$$\eta_{\text{eff}} \approx n \times \eta_0$$



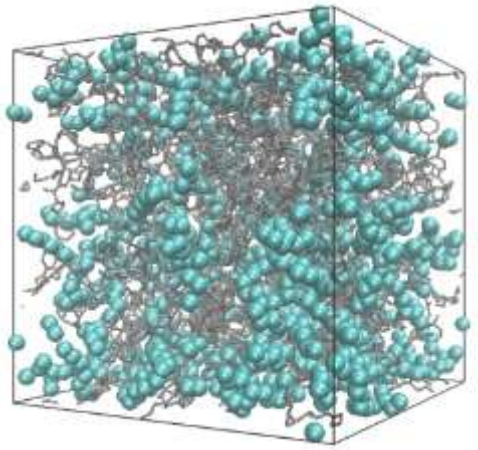


What one learns:

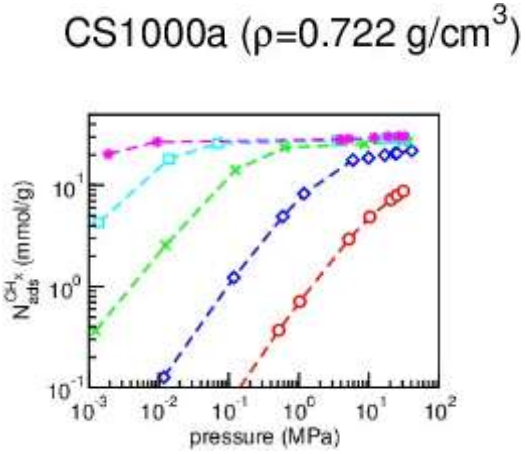
- the fluid inside exhibits an *effective* viscosity…
- This viscosity differs strongly from the bulk one

Physical origin: adsorption

- The alcanes 'condense' in the porous materials
  - Strong alcane/kerogen interactions
  - Properties are fully different from bulk
  - Much higher density in the pores than in the bulk



Key measurement: *fluid adsorption in the porous material*



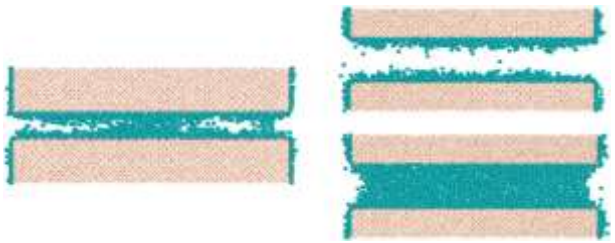
Key quantity: adsorbed density
strong dependence on applied Pressure (and T)

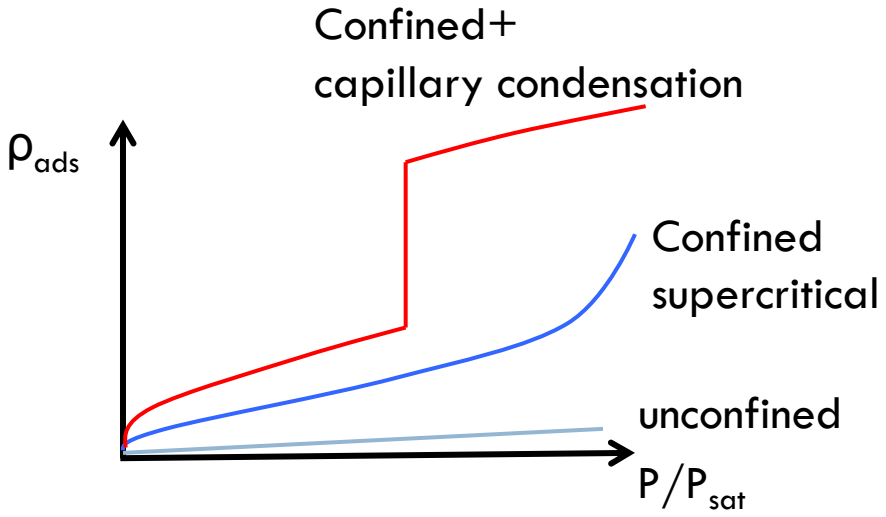
Thus: transport in subnanoscale materials is strongly coupled to adsorption
Effective viscosity = f(adsorption)

Suggests hints how to develop framework

Thermodynamic routes ?

- Various types of adsorption

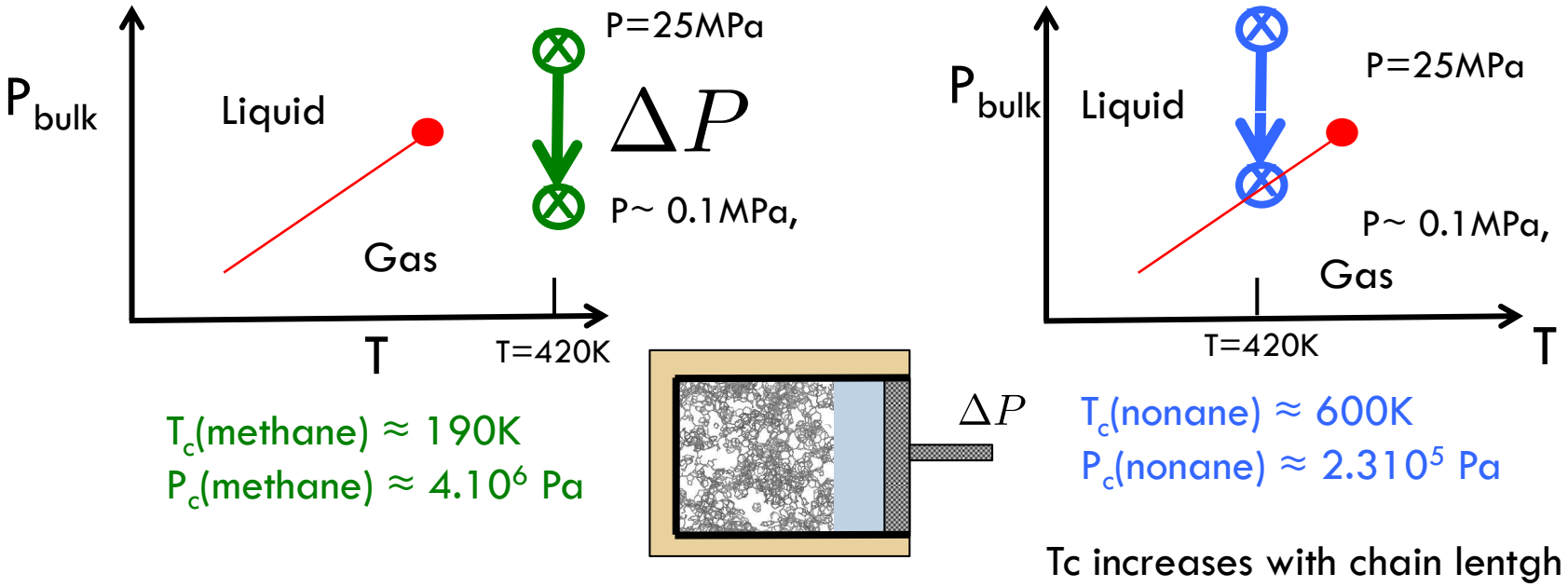




- Will depend on chain length and confinement

Thermodynamic routes ?

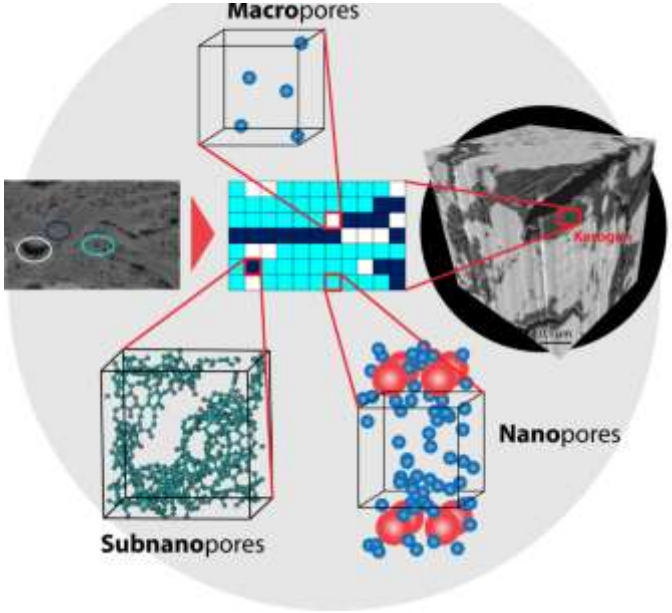
- Direct coupling of *transport and thermodynamics*



Under pressure drop, the various chains behave very differently: their phase behavior directly affects transport

Towards multiscale transport

- Couple transport to adsorption *for all scales*
- Q: *formalize multiscale transport*



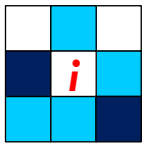
Chemical potential: μ(P,T)

$\rho(\mu)$ Adsorption properties, scale dependent
From MonteCarlo simulations/model

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot \vec{\Phi}$$

$$\vec{\Phi} = -M(\mu)\vec{\nabla}\mu$$

Transport properties,
Scale dependent
From Molecular Dynamics
Simulations or model

Lattice model 

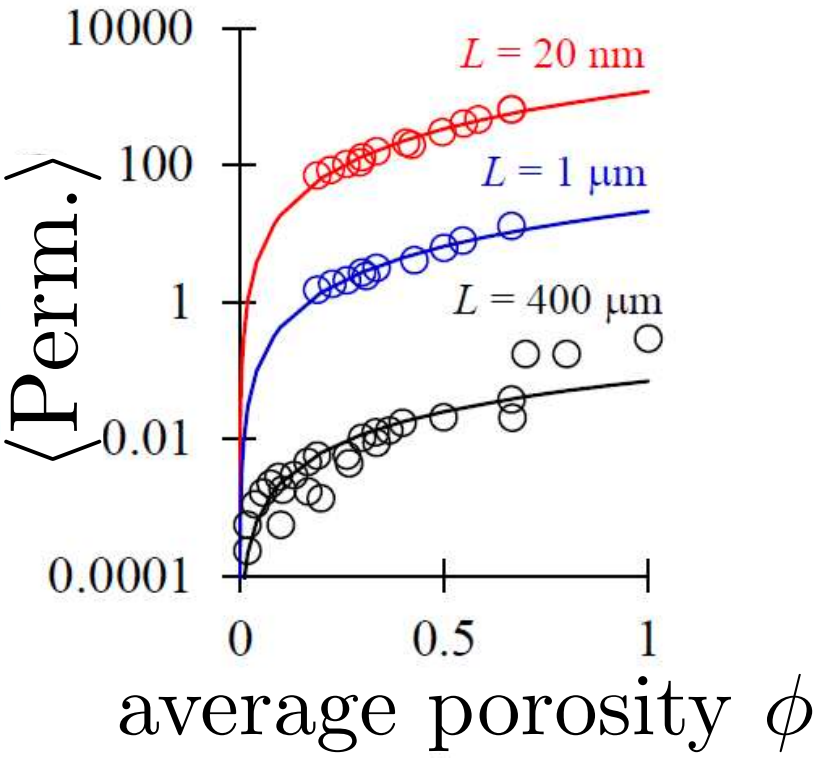
Each scale represented
+ couplings btw scales

First typical results

Ex: methane in model kerogen

$$\text{Gas Flux}/\Delta P \propto \phi \; ?$$

Flux J versus average porosity
for various multiscale porous media



⇨ *Unconventional Flux-porosity relationship*

$$\langle \text{Perm.} \rangle \propto \phi^m$$ with m = 1.5-1.8

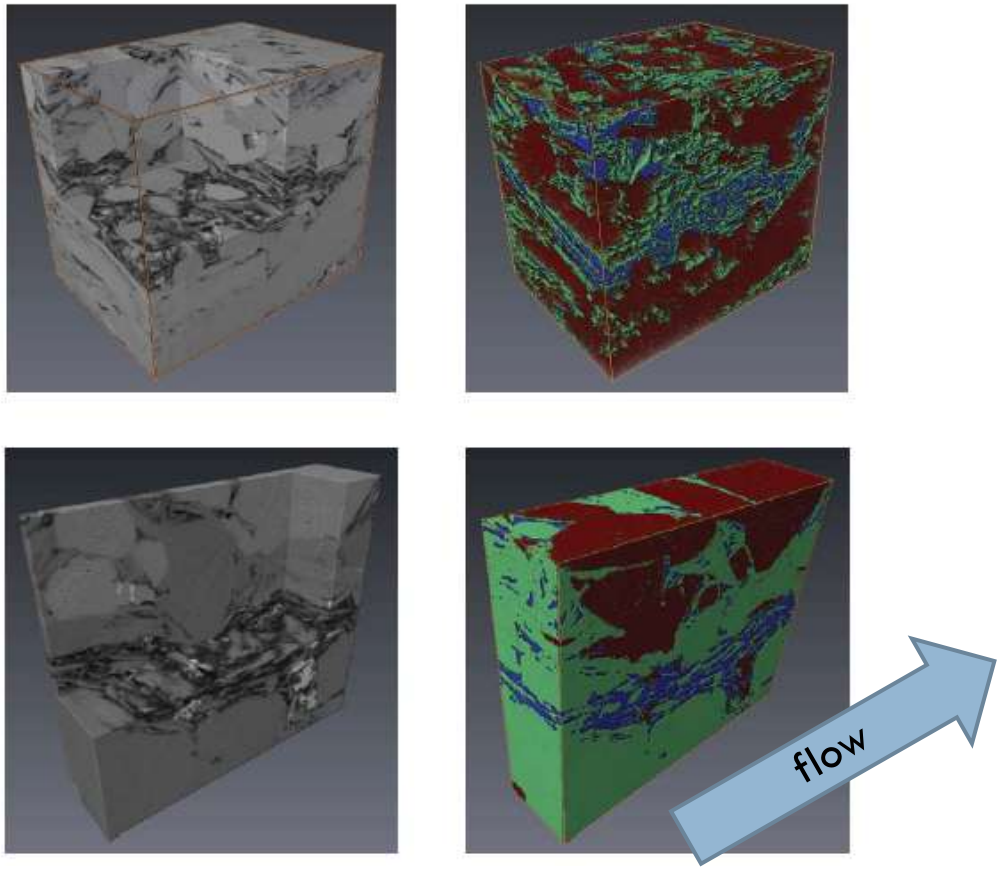
This multiscale approach recovers empirical "Archie's" type of transport law
Collective behavior

Q: Scaling laws for heterogeneous transport ?

Botan et al. (submitted)

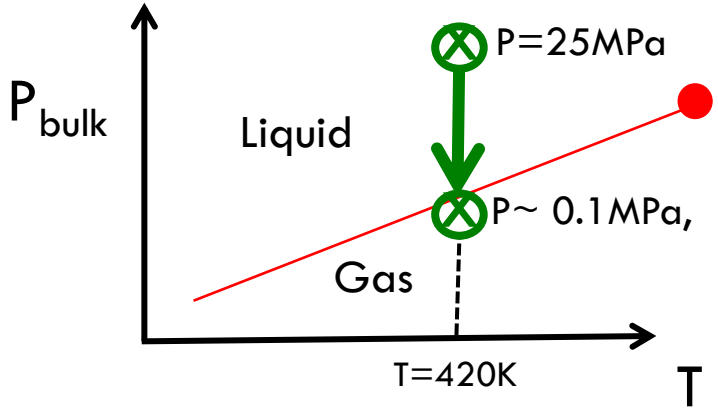
Towards realistic systems

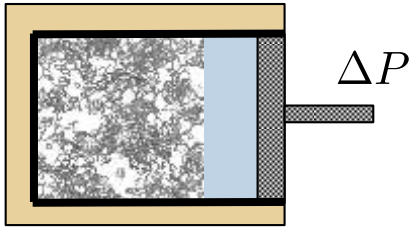
- An efficient tool for transport in real shale sample



What about the fracking fluid ?

- Water used as fracking fluid: also acts as the *pressure transmitting fluid* to extract oil





T_c(water) ≈ 650K
P_c(water) ≈ 2.10^6 Pa

Expect various behavior: water phase transition, nucleation, …

Is water a bad pressure transmitter ?

Suggestions:

- Try new depressurization protocoles
- Use alternative fluid (CO_2 ?) as fracking fluid/pressure transmiter ?

Conclusion/Perspectives/Questions

- Interesting fundamental science:
  - Coupling thermodynamics to transport
- Lack of lab experiments
  - 'in vitro' experiments for nanoporous materials under controlled conditions
  - Benchmarkings on model situations
- Think out of the box
  - Water is maybe not the best choice

    eg, CO_2 or …: revisit protocoles