Adsorption and Transport in Nanoporous Materials

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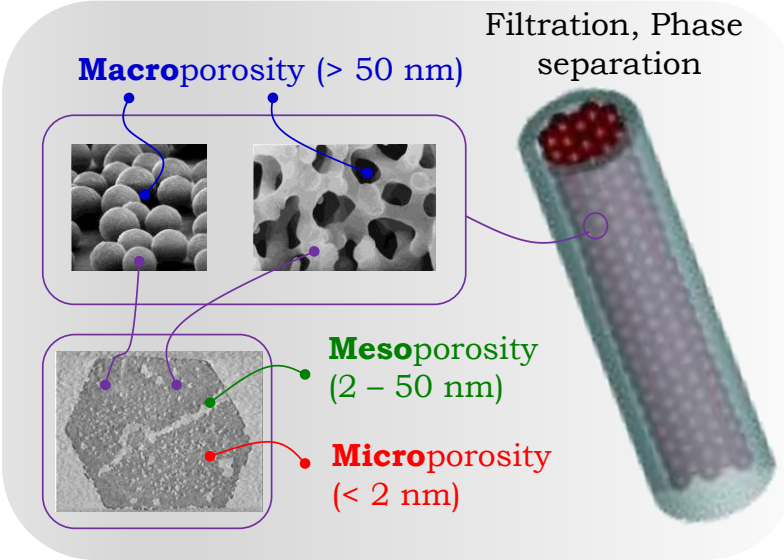
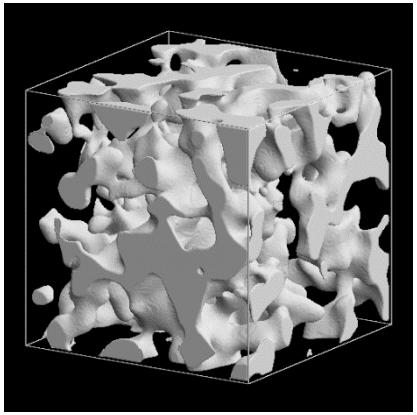


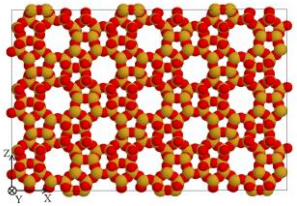
Porous Materials

A material that consists of solid domains and pore voids

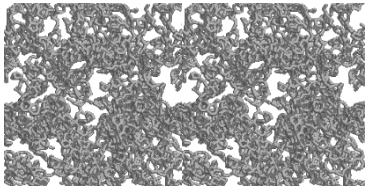


Courtesy of P. Levitz, reconstruction of Vycor

- **Large surface areas** (ex. ashes ~m^2/g) but much larger surfaces can be reached with zeolithes, activated carbon ~1000 m^2/g



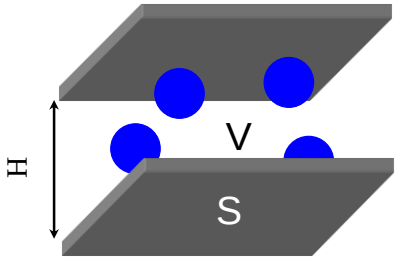
zeolite: aluminosilicate nanoporous crystal

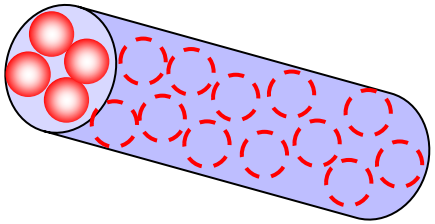


Activated carbon: a disordered porous carbon

Length Scales and Confinement

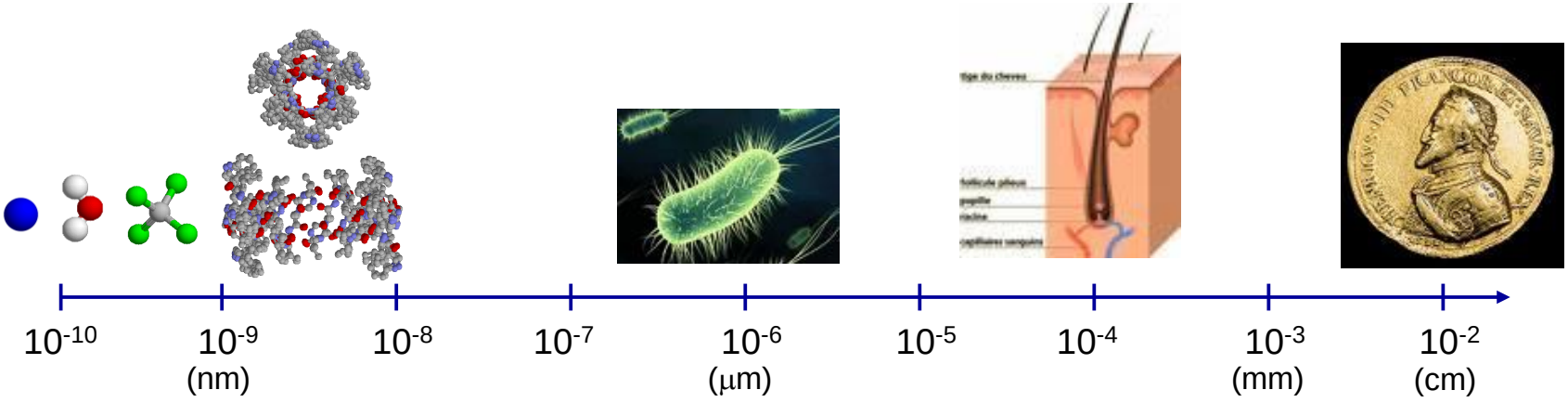
- **Confinement**





Independently of the pore morphology, decreasing the pore size H increases the surface to volume ratio S/V ~ 1/H

Nanoporous solids D ~ ξ



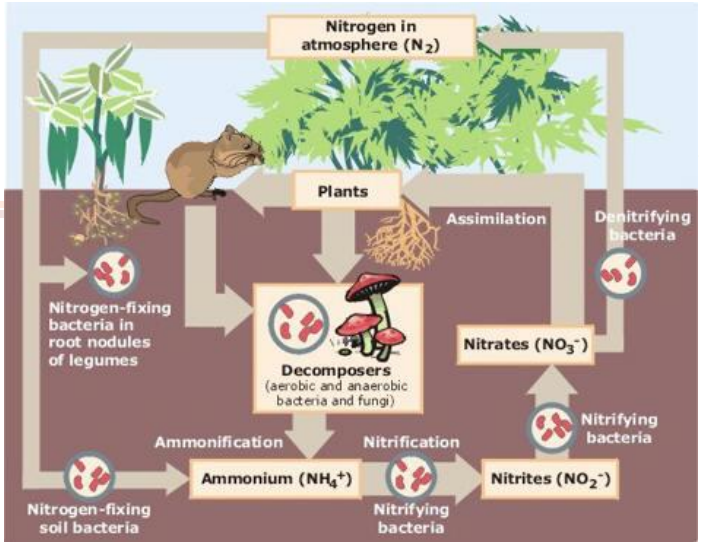
Porous Materials

Both thermodynamics and dynamics
of nanoconfined fluids are modified
with respect to their bulk counterpart

New phenomena such as phase transitions driven
by surface or confinement (ex: Equation de Kelvin)

Interplay between adsorption and transport
The rich and complex behavior of confined fluids

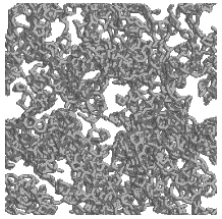
In our everyday life



- Soil (multi-scale) porosity is crucial for the nitrogen and carbon cycles as it ensures exchange between the soil and the atmosphere

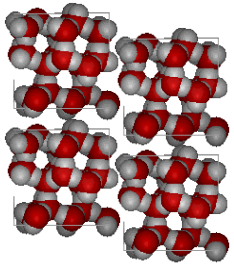
Water vapor produced by fuel combustion

+



Carbon soot produced by the aircraft engine

=



Ice clusters

Fomation + impact on the environment of these ice clusters still poorly understood (difficult to get samples upon the same conditions ~above 8000 m and -40°C)

In our everyday life

Concrete is responsible for 7-8% of CO_2 emission on Earth

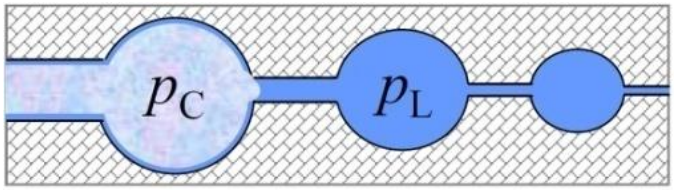
Understanding their properties including their ageing and sensitivity to external conditions is therefore of key importance

[Beaudoin and Mc Innis, 1974]

Cement pore saturated with benzene
Same effect as with water

(photo : Cours de H. Van Damme, Ecole thématique 2003)

Cryosuccion

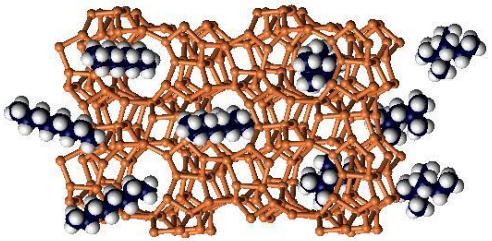


$$P_C - P_L = \Delta S(T - T_m)$$

Olivier Coussy
(1953-2010)

Applications: Catalysis, Separation

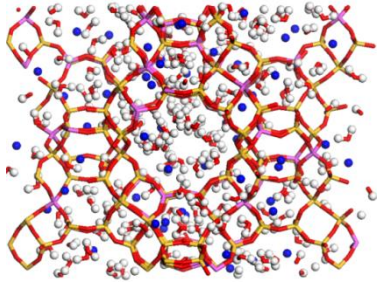
- Catalysis



From Beck's group at UMich

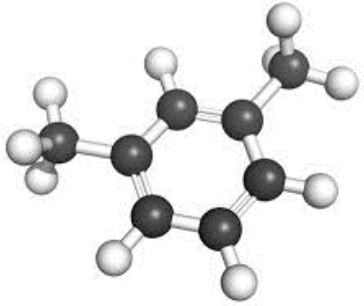
Cracking, isomerisation and hydrocarbon synthesis for oil industry

- Phase separation



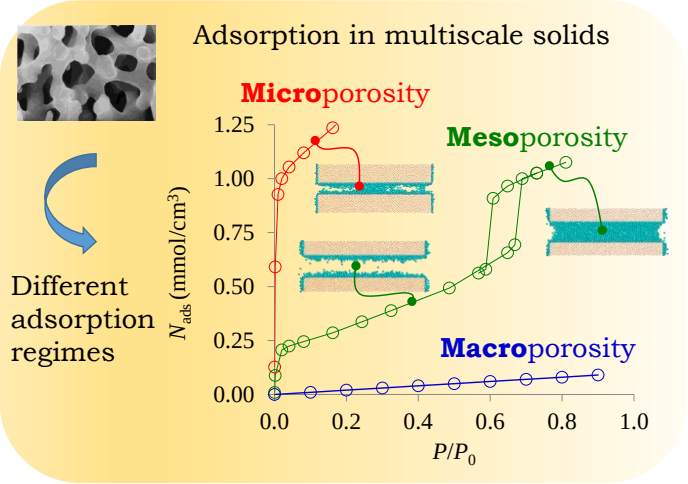
Separation of xylenes from hydrocarbons,

O_2 bottles from ambient air

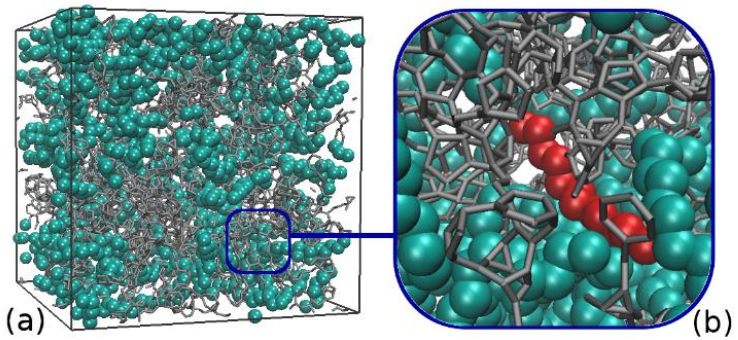


Outline

- 1. Adsorption in Nanoporous Materials



Coasne et al., Chem. Soc. Rev. 2013



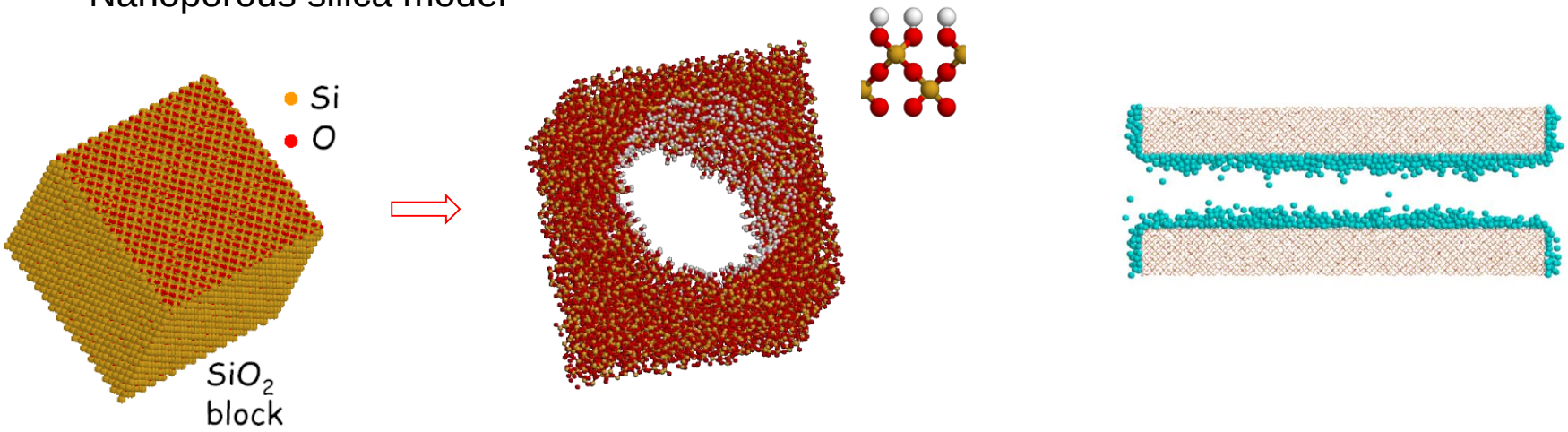
Falk et al. Nature Comm. 2015

Obliger et al. J. Phys. Chem. Lett. 2016

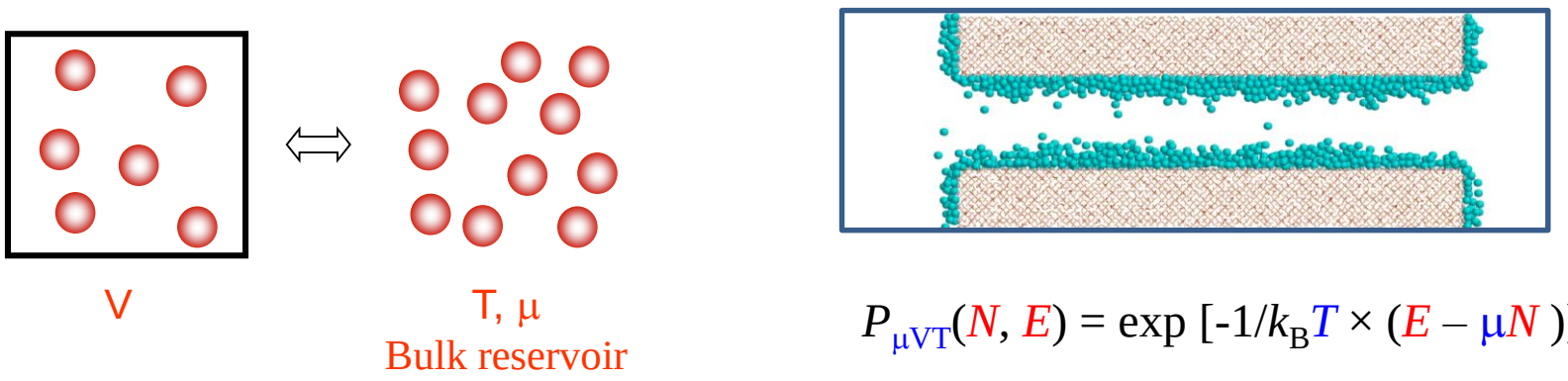
- 2. Transport at the Nanoscale

Molecular Simulation

- Nanoporous silica model



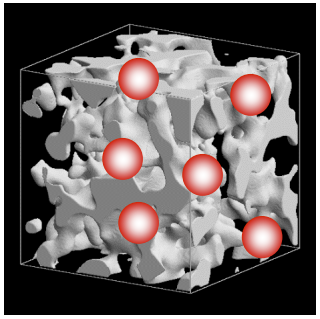
- Grand Canonical Monte Carlo simulations



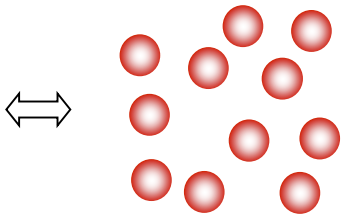
$$P_{\mu VT}(N, E) = \exp\left[-1/k_B T \times (E - \mu N)\right]$$

Adsorption in Porous Materials

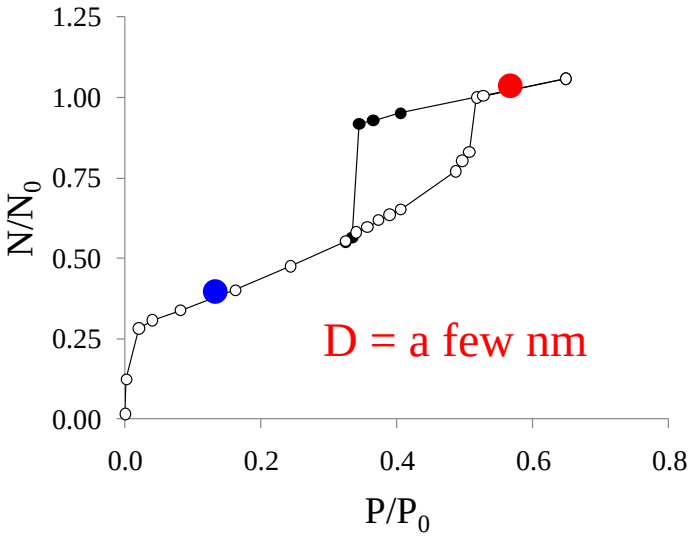
Open System (Grand Canonical Ensemble)

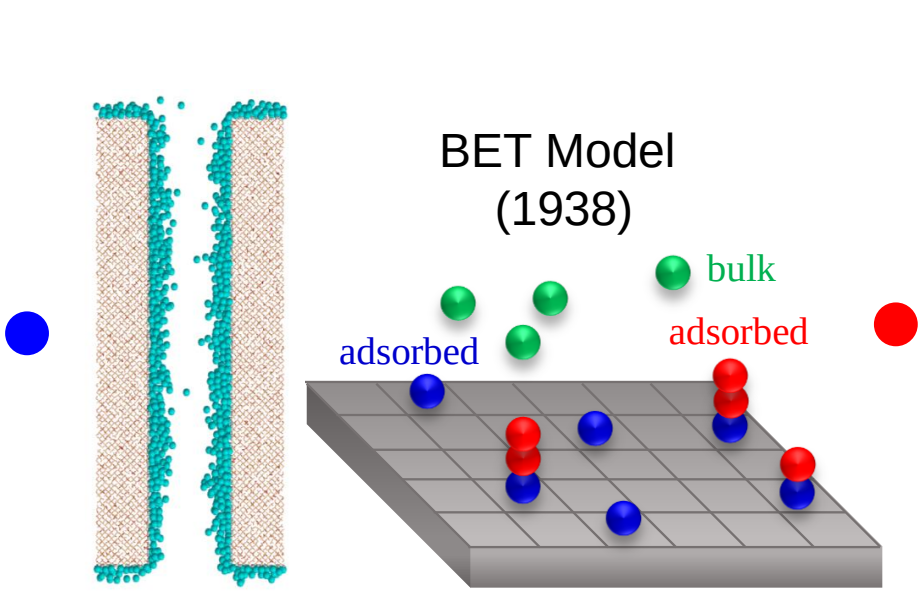


V



T, μ
Bulk reservoir





Laplace Pressure

$P_G - P_L = 4\gamma/D$

+

Chem. potential Equality

$\mu_G = \mu_L$

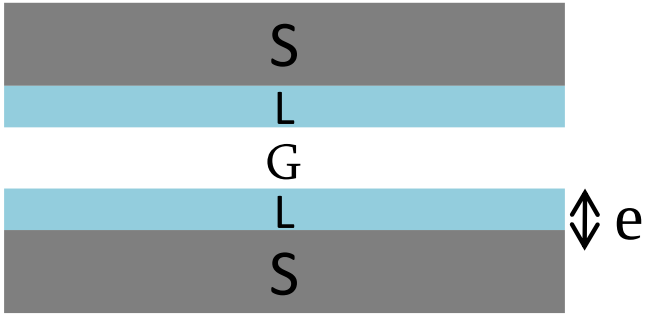
$\Rightarrow$ $kT \ln P/P_0 = 4\gamma/\rho D$

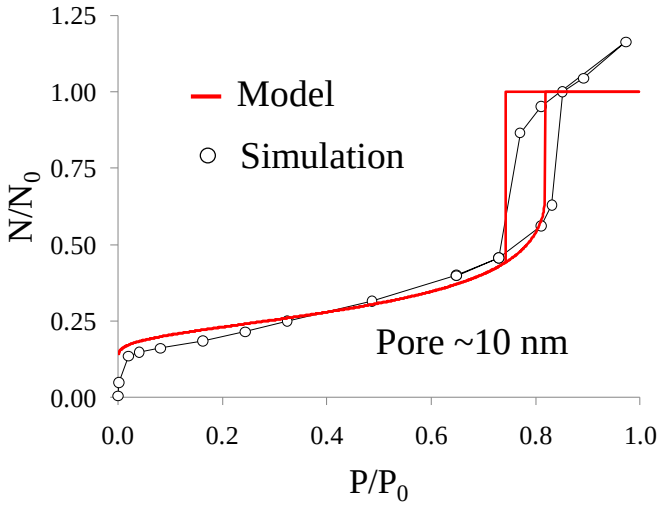
Derjaguin's model

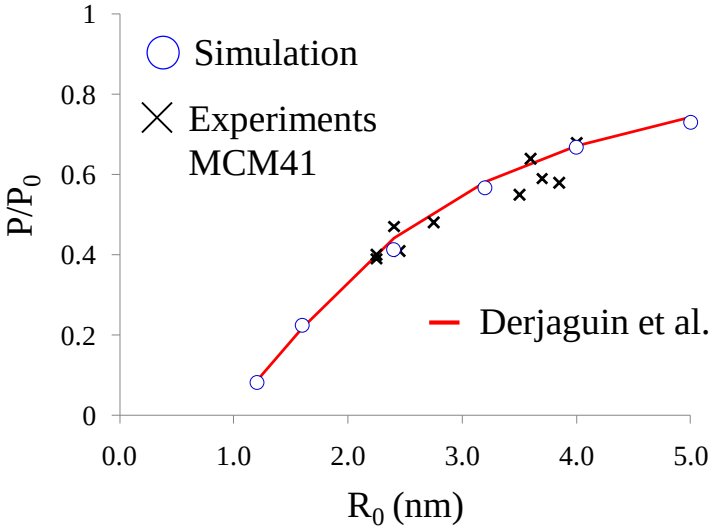
$$\Omega = - P_G V_G - P_S V_S - P_L V_L + 2A\gamma_{SL} + 2A\gamma_{LV} + 2AW(e)$$

$$\Pi(e) = - dW(e)/de = P_G - P_L$$

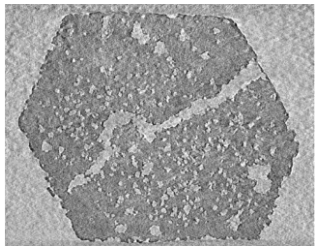
$$W(e) = - A_{SLV}/12\pi e^2 \text{ (van der Waals forces)}$$







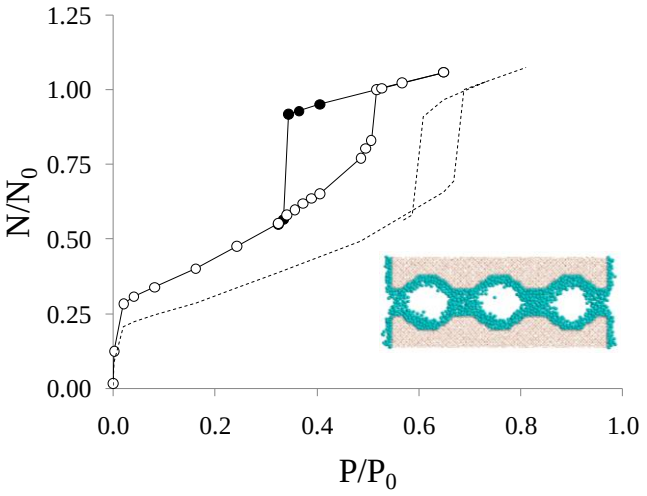
Nucleation vs Surface Pinning

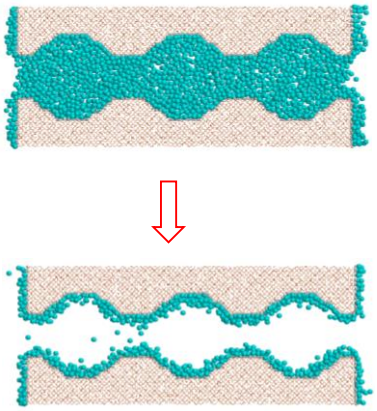


De Jong,
Fajula et al.

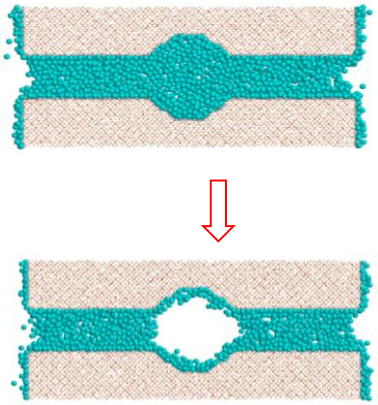
Condensation pressure is always lower than for a regular pore of the same diameter

Desorption occurs either through « pore blocking » or cavitation





If $D > D_0$ desorption through pore blocking

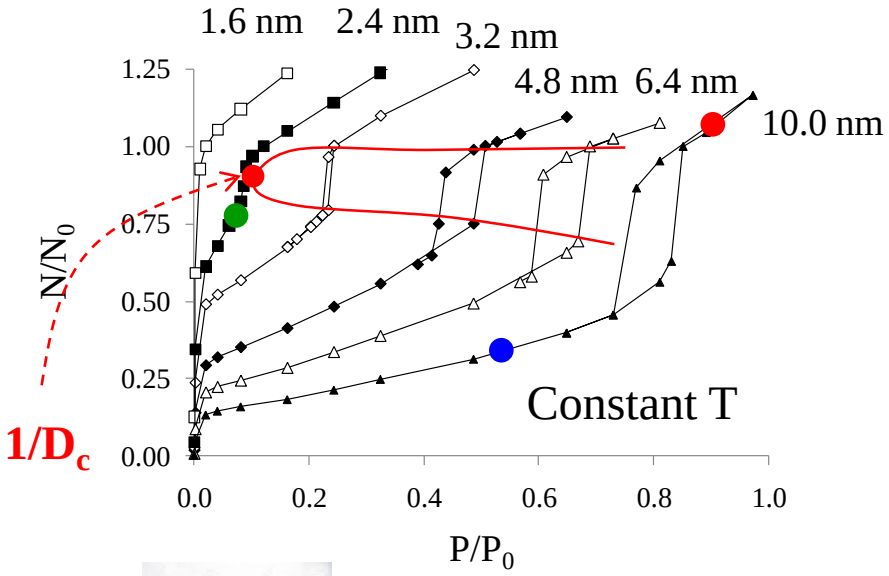


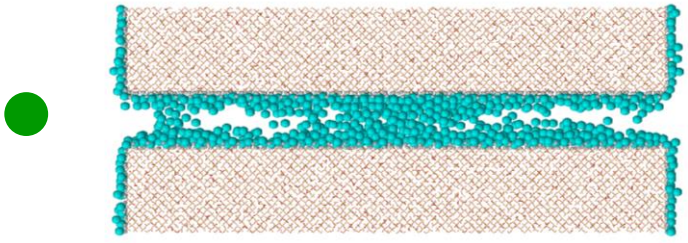
If $D < D_0$ desorption through cavitation

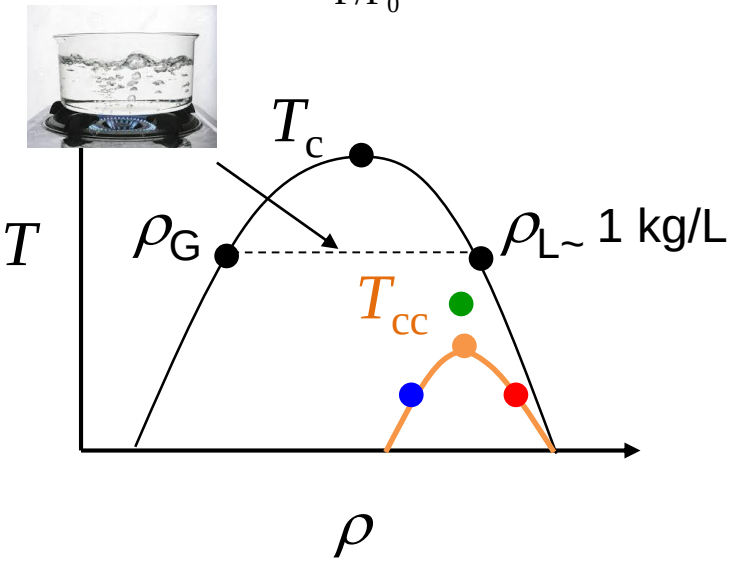
Coasne et al., J. Phys. Chem. 2007

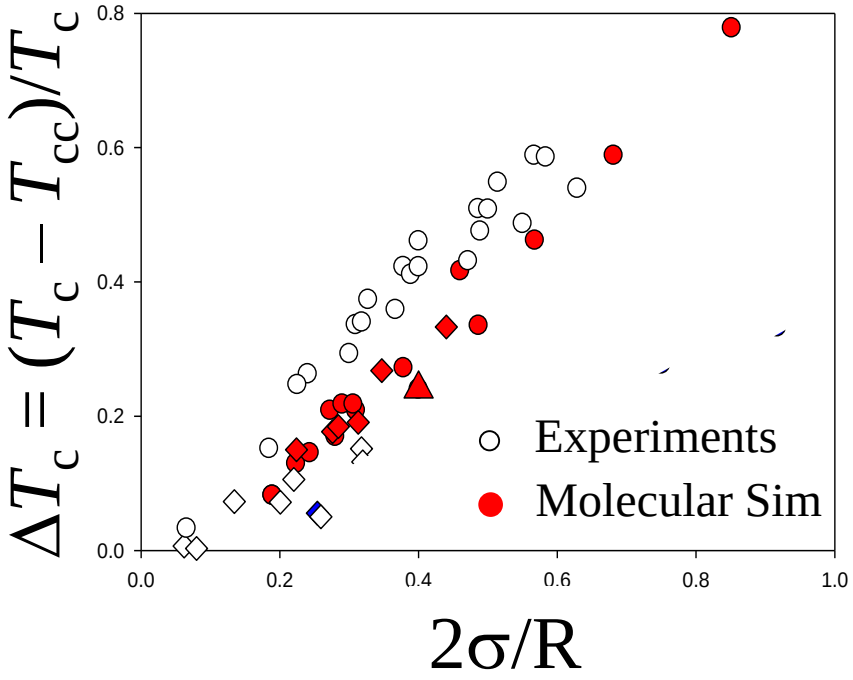
D_0 = 6 nm for N_2 at 77 K

Criticality of Confined Fluids



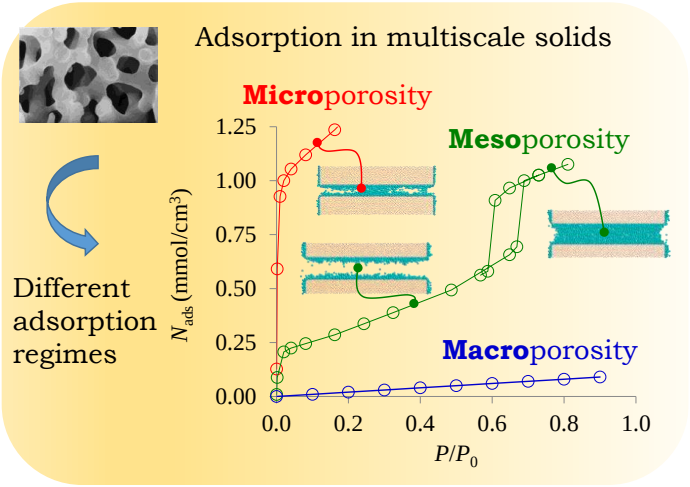




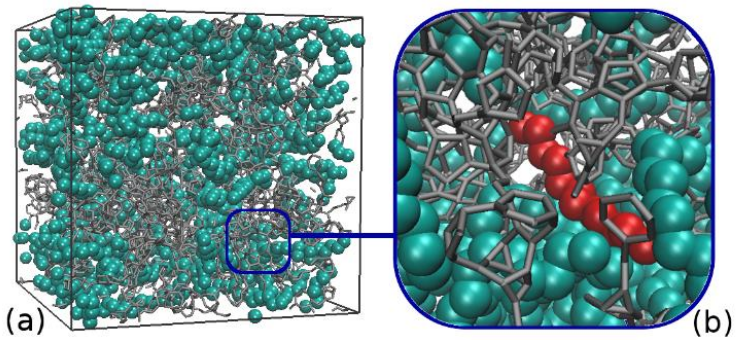


Outline

1. Adsorption in Multiscale Media



Coasne et al., Chem. Soc. Rev. 2013



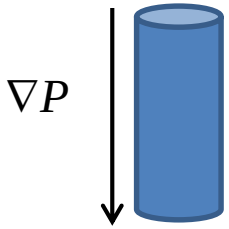
Falk et al. Nature Comm. 2015

Obliger et al. J. Phys. Chem. Lett. 2016

2. Transport at the Nanoscale

Darcy law and Poiseuille flow

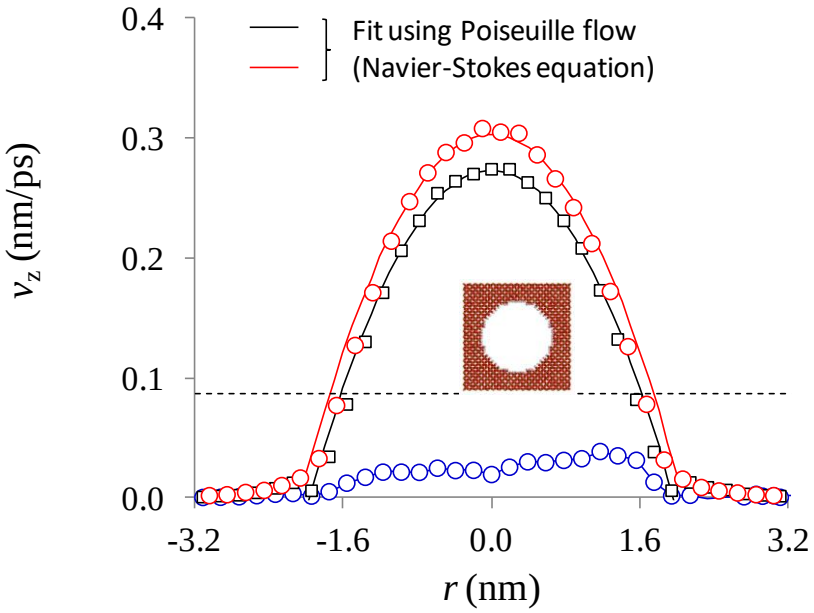
Darcy law



$$J = -\rho\bar{v}$$

$$\bar{v} = -\frac{k}{\eta}\nabla P$$

Poiseuille Flow



$$\rho\left(\frac{\partial \boldsymbol{v}}{\partial t} + \boldsymbol{v}\cdot\nabla\boldsymbol{v}\right) = -\nabla \mathrm{P} + \eta\nabla^2\boldsymbol{v}$$

$$\nabla \mathrm{P} = \eta\nabla^2\boldsymbol{v}$$

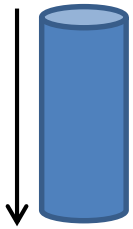
$$v_z(r) = \frac{\nabla_z P}{4\eta} r^2 + C$$

$$\bar{v} = -\frac{R^2}{8\eta}\nabla P \quad \Rightarrow \quad k = -\frac{R^2}{8}$$

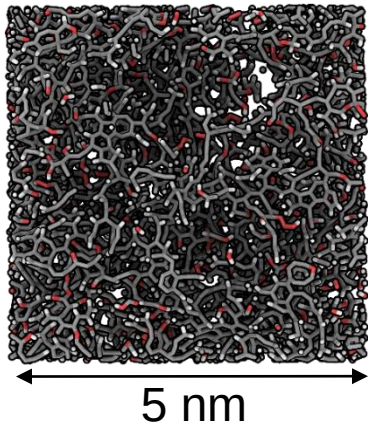
Darcy law

$$J = - \rho \frac{k}{\eta} \nabla P$$

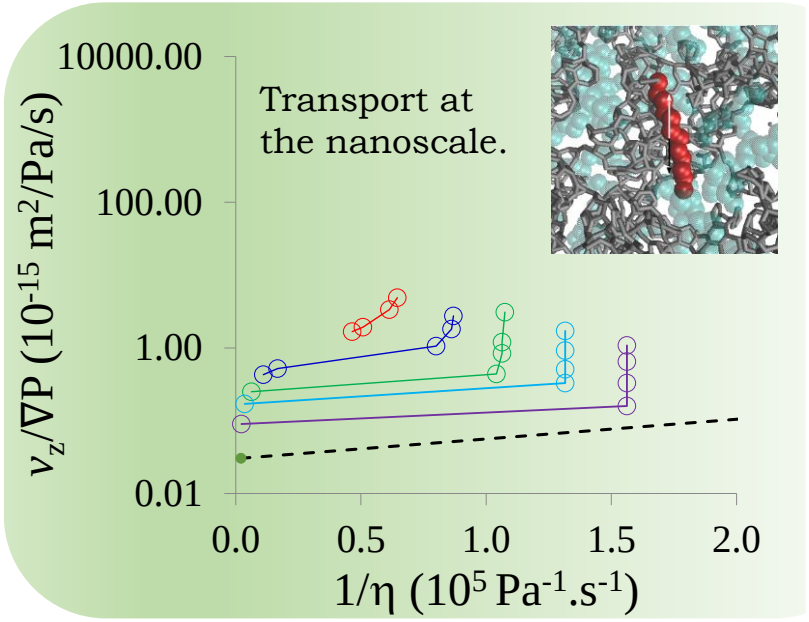
Darcy law



A realistic molecular model of kerogen



Bousige et al. Nature Materials 2016



k permeability is not an intrinsic constant of a material as it depends on fluid, temperature, transport regime, etc.

The concept of viscosity at the nanoscale has no clear definition (as it assumes that hydrodynamics remains valid).

Hydrodynamics Breakdown

$$\rho \frac{\partial \boldsymbol{v}}{\partial t} = -\nabla \mathrm{P} + \eta \nabla^2 \boldsymbol{v} - \zeta \boldsymbol{v}$$

Assumes time scale separation between stress relaxation t_R inside the fluid particle and momentum transfer τ

(Bocquet and Charlaix, Chem. Soc. Rev. 2010)

$$\eta = \frac{1}{V k_B T} \int \sigma_{xy}(t)\sigma_{xy}(0)\mathrm{d}t \sim \exp[-t/t_R] \Rightarrow t_R \sim 1 \text{ ps}$$

$$\langle j_k(0) j_{-k}(t) \rangle \sim \exp\left[\left(-\frac{\eta k^2}{\rho} - \zeta\right) t\right] \Rightarrow \tau \sim \frac{\rho}{\eta k^2}$$

Hydrodynamic regime $\rho/\eta k^2 >> t_R$

Breakdown $k \sim 1/L$ (L = 1 nm)

Statistical Mechanics Model

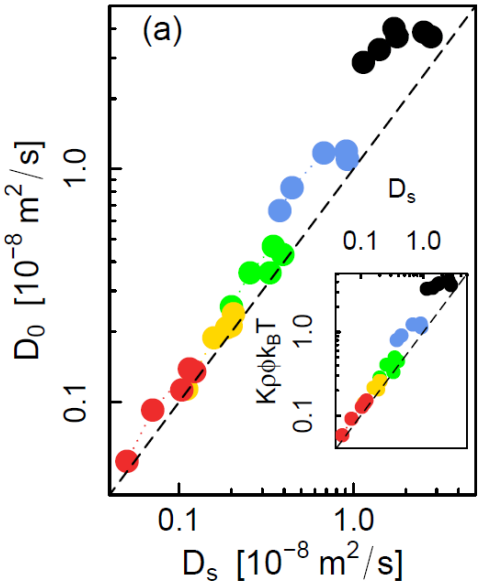
$$J = -\rho \frac{k}{\eta} \nabla P \quad \Rightarrow \quad J = -\rho K \nabla P \qquad \text{with } K \sim \frac{D_0}{\rho k_B T}$$

[Exact result from the Fluctuation Dissipation Theorem]

$$D_0 = \int_0^\infty < v_{COM}(0) v_{COM}(t) > dt$$

$$D_s = \int_0^\infty < v(0) v(t) > dt$$

$$D_s \sim D_0$$



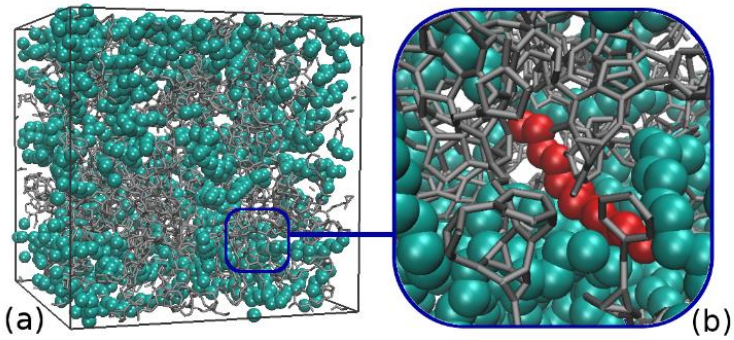
methane
propane
hexane
nonane
dodecane

Build a simple microscopic model of hydrocarbon transport based on Statistical Mechanics and express K ~ D_s/ρ

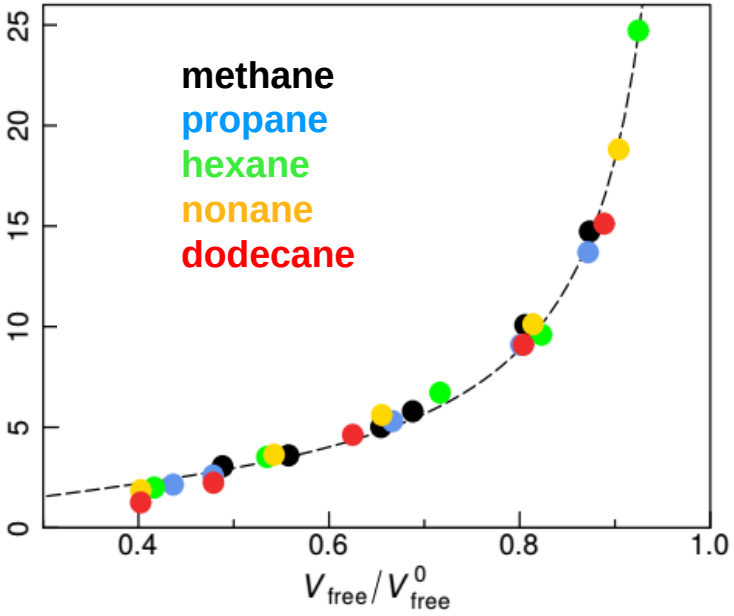
Free Volume Theory

$$D_s(N) \sim D_s(0) \exp\left[-a \frac{V_{mol}(N)}{V_{free}(N)}\right]$$

$$V_{mol}(N) = V_{free}^{0}(N) - V_{free}(N) \sim N$$



$K(n+n_0) \sim D_s/\rho kT$



- A simple "Stat Mech" model is built by using the fluctuation-dissipation theorem
- This model does not use macro concepts (viscosity) and relies on simple concepts such as free volume

Falk et al. Nature Comm. 2015

Conclusion

- Nanoscale transport requires statistical mechanics modelling to avoid the use of macroscopic concepts such as viscosity

- A simple multiscale model is developed to capture adsorption/transport in porous media

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