Adsorption and Transport in Nanoporous Materials

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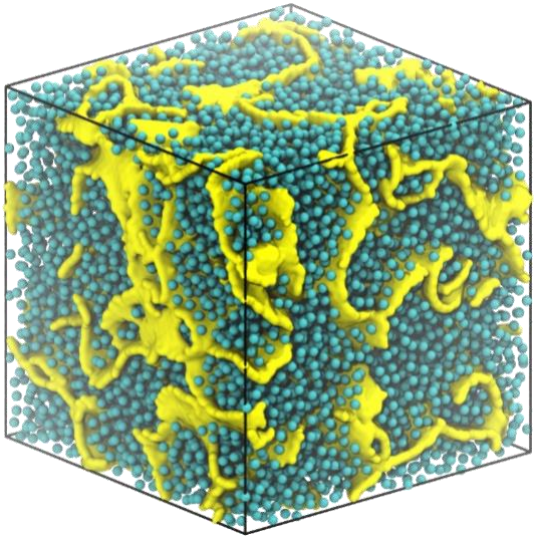
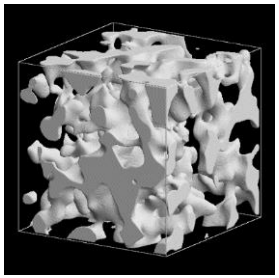
https://benoitcoasne.github.io/



Coll.: C. Bousige, K. Falk, A. Obliger, A. Schlaich, C. Picard, L. Bocquet, P. Levitz

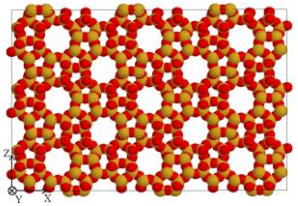
Feb. 22, 2023

Nanoporous Materials

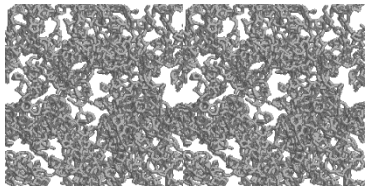


Courtesy
P. Levitz

A material that consists of solid domains coexisting with pore voids having one of their dimensions in the nm scale

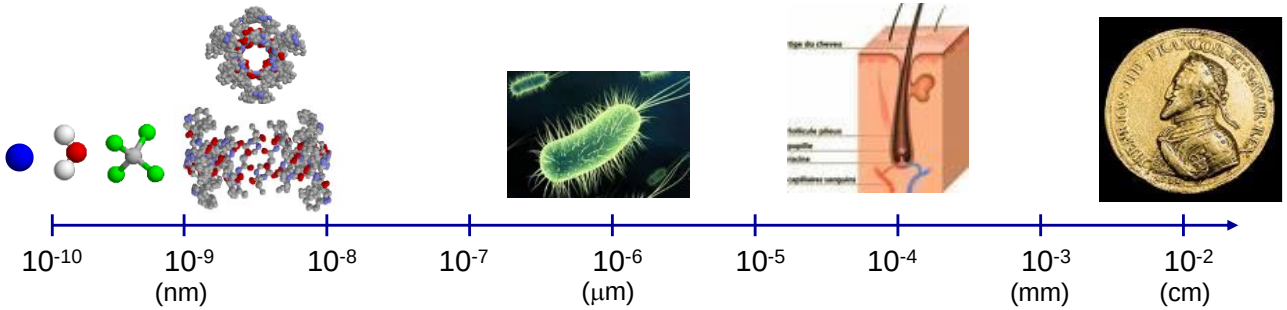


Aluminosilicate zeolite

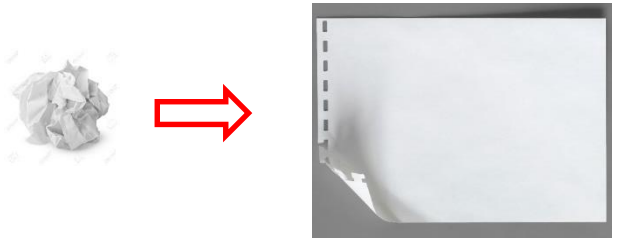


Activated carbon

- Nanoporous solids (with one dimension ~ *nm*)

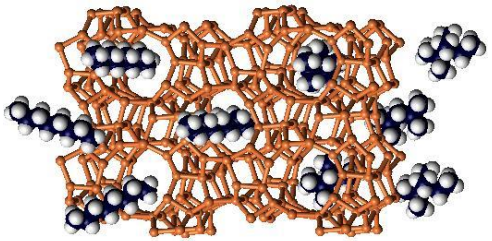


- Large surface areas ~1000 m^2/g



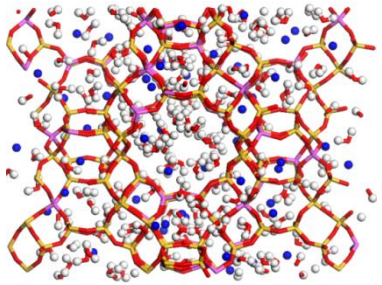
Catalysis, Separation, Exchange, etc.

- Catalysis



Cracking, isomerisation and hydrocarbon synthesis for oil industry

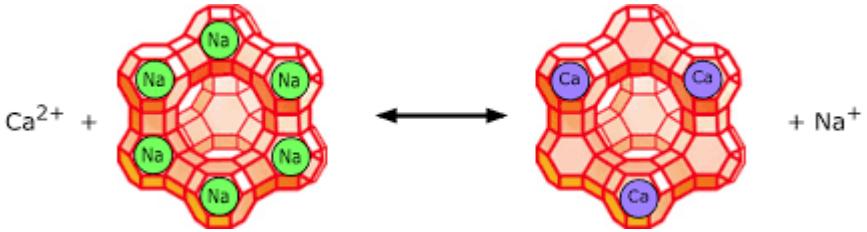
- Phase separation



Separation of xylenes from hydrocarbons,

O_2 bottles from ambient air

- Ion exchange



- Fertilizers, Substrate, Cat litter, etc.

Problem Statement

⇨ New adsorption and transport phenomena

- Adsorption/transport interplay
- Complex hydrodynamics

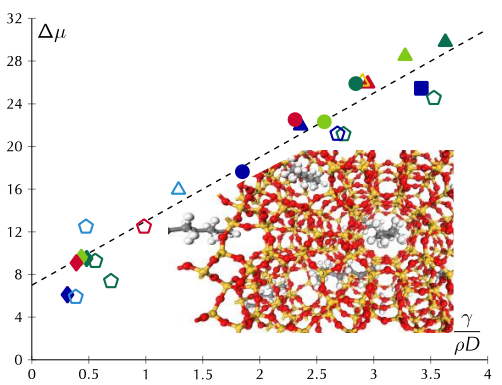
e.g. slippage, interfacial transport, and non-viscous effects

↪ Theory/molecular modeling of adsorption and transport in nanoporous media

Thermo. in nanopores

Coasne et al. Chem. Soc. Rev. 2013

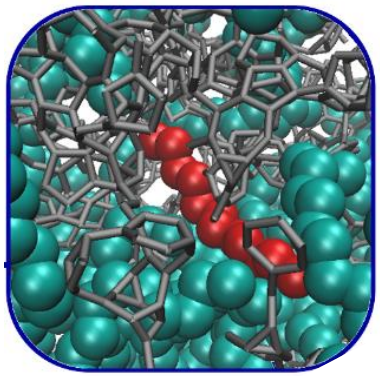
Deroche et al. Nature Comm 2019



Transport in subnanopores

Falk et al. Nature Comm. 2015

Bousige et al. Nature Comm 2021

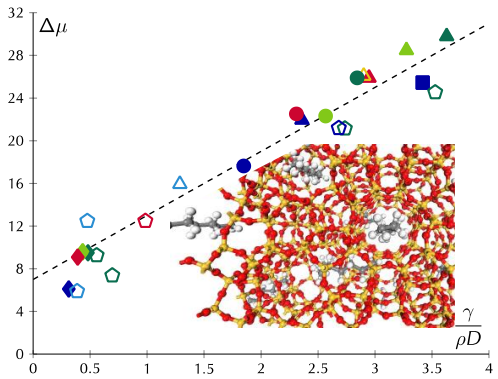


Outline

⇨ Part 1

Fluid adsorption and criticality in porous media

Coasne et al. Chem. Soc. Rev. 2013
Deroche et al. Nature Comm 2019

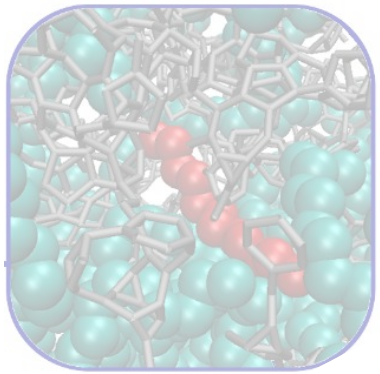


Part 2

Transport in subnanopores

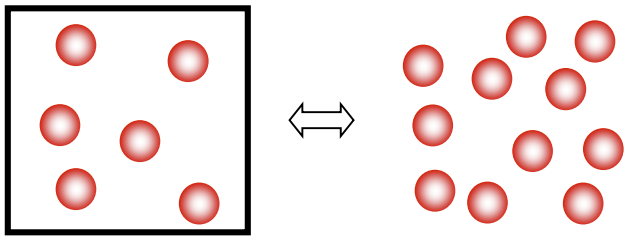
Falk et al. Nature Comm. 2015

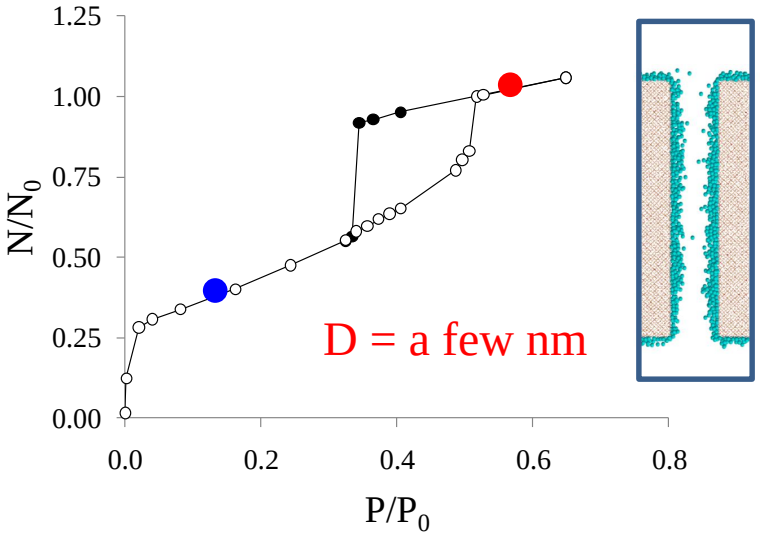
Bousige et al. Nature Comm 2021

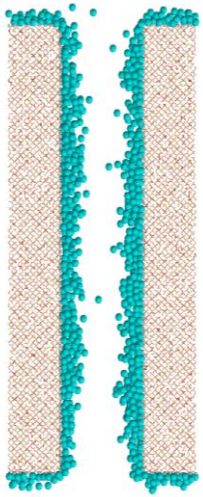


Adsorption in Porous Materials

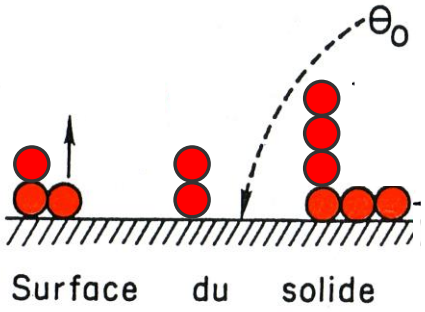
Open System (Grand Canonical Ensemble)

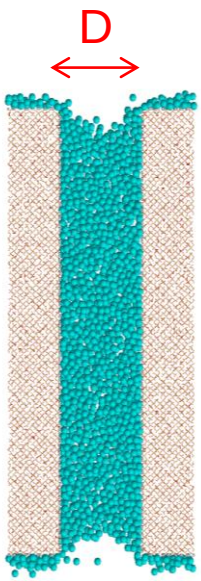






BET (Ising-like) Model (1938)





Laplace Pressure

$P_G - P_L = 4\gamma/D$

+

Chem. potential Equality

$\mu_G = \mu_L$

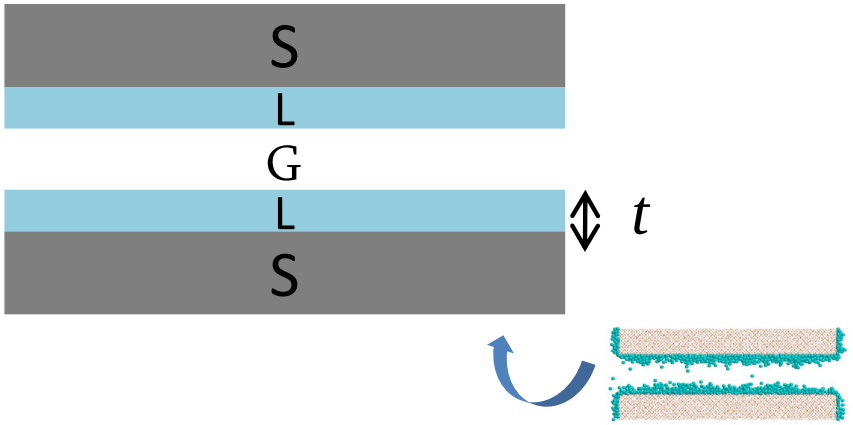
$\Rightarrow$ $kT \ln P/P_0 = 4\gamma/\rho D$

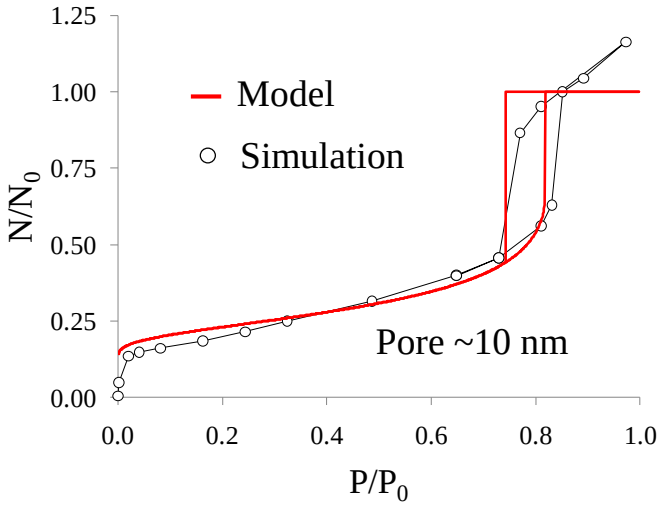
Derjaguin's model

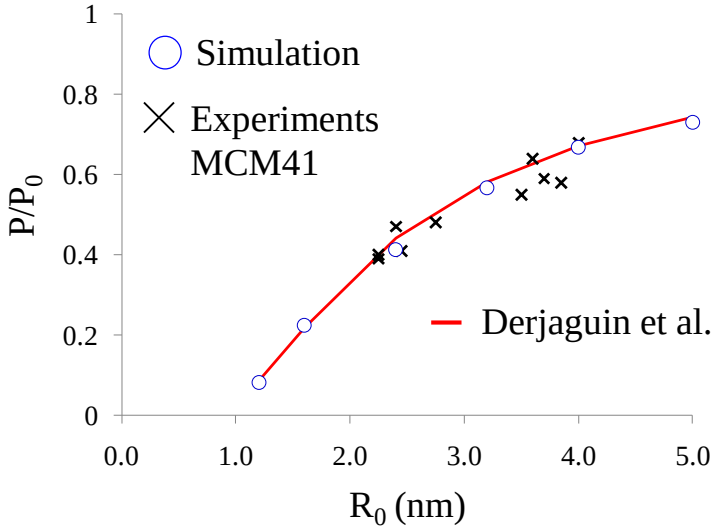
$$\Omega = -P_G V_G - P_L V_L + A_{SL}\gamma_{SL} + A_{LG}\gamma_{LG} + A_{SL}W(t)$$

$$\Pi(t) = -\,dW(t)/dt = P_G - P_L$$

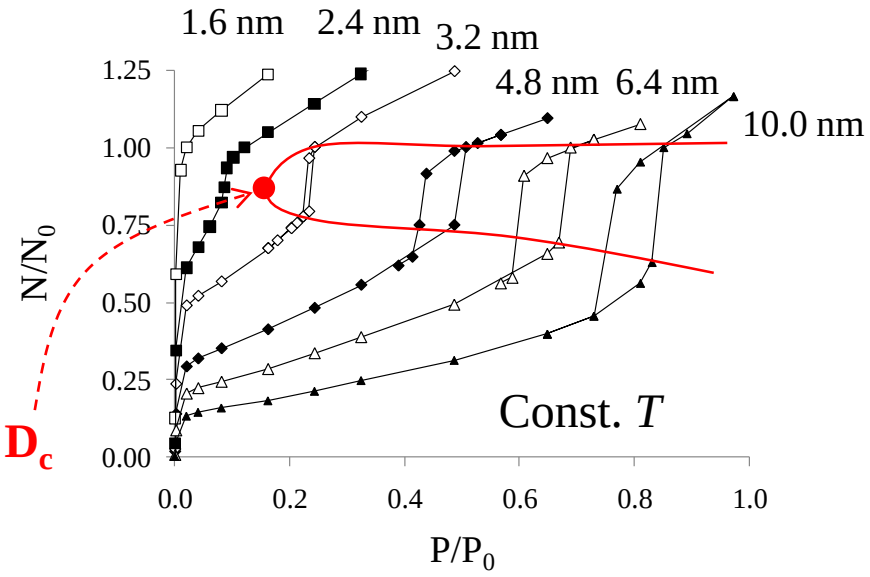
$W(t) \sim S \exp[-t/\xi]$
with $S = \gamma_{sg} - \gamma_{sl} - \gamma_{lg}$

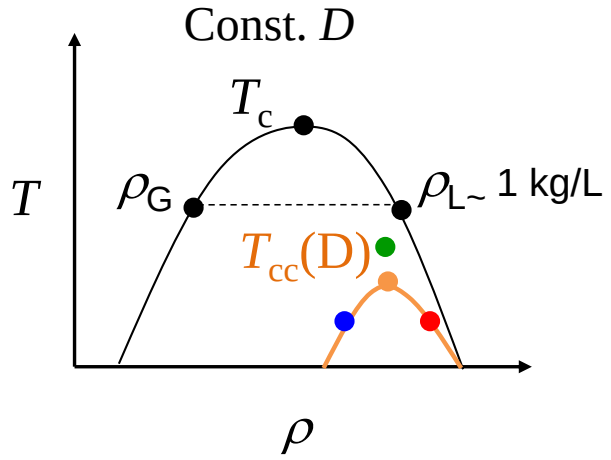


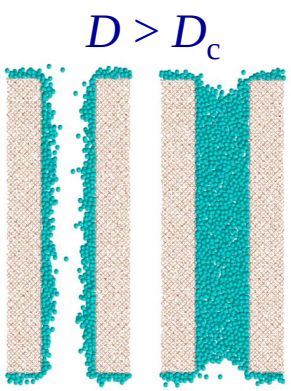




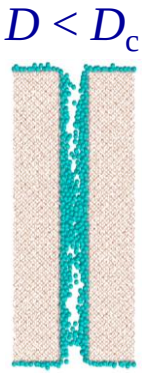
Criticality



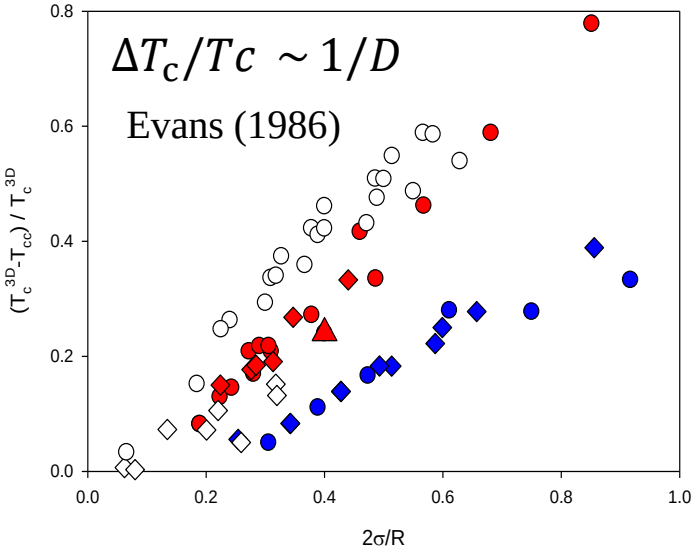




Irreversible,
Discontinuous



Reversible,
Continuous



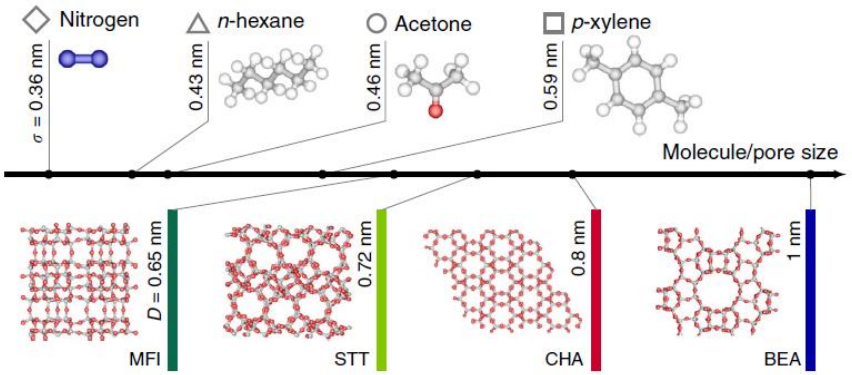
Coasne et al. Chem. Soc. Rev. 2013
Deroche et al. Nature Comm 2019

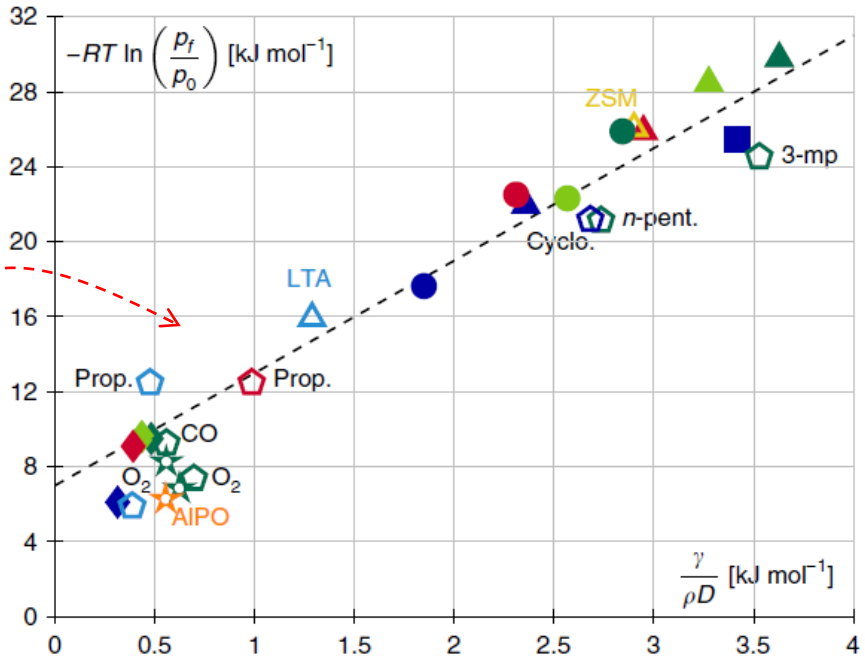
Reminiscent Capillarity

Reminiscent Capillarity in Angstropore!

$$RT \ln P/P_0 \sim \gamma/\rho D$$

Experiment/Simulation of many fluids/zeolites





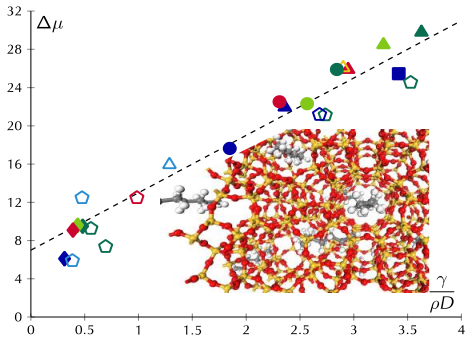
Deroche et al. Nature Comm 2019

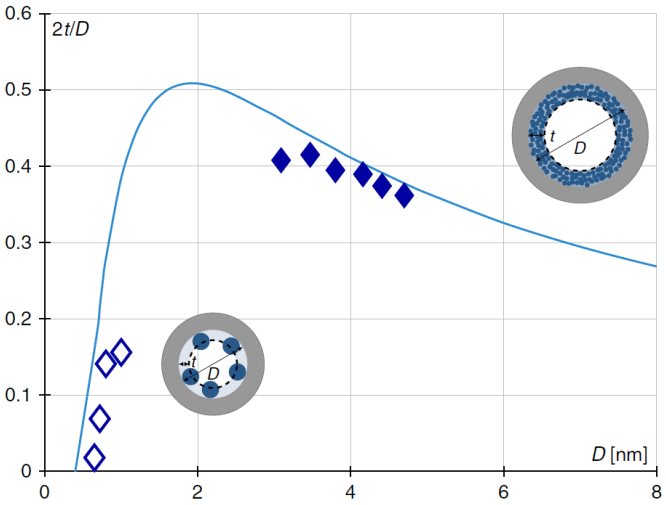
Reminiscent Capillarity

$$\Omega = -P_G V_G - P_L V_L + A_{SL}\gamma_{SL} + A_{LG}\gamma_{LG} + A_{SL}W(t)$$

$$RT \ln \frac{p_V^e(D)}{p_0} = -\frac{6\gamma_{LV}}{\rho_L D}\left[1 + \frac{2t + 2\xi}{D - 2t - 2\xi}\right]$$

$$RT \ln P/P_0 \sim \gamma/\rho D$$





- Large pores $t, \xi << D$

  $RT \ln P/P_0 \sim \gamma/\rho D$

- Small pores $t << D$

  $RT \ln P/P_0 \sim \gamma/\rho D + K(D,\xi)$

  with K/RT ~ constant

Deroche et al. Nature Comm 2019

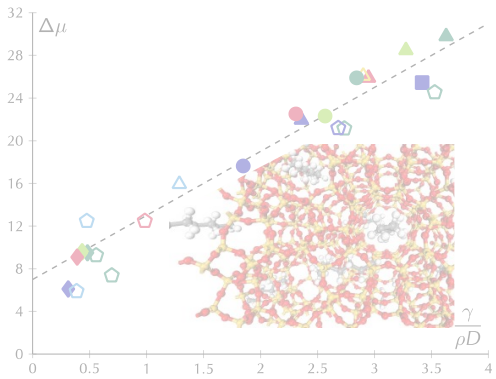
Outline

Part 1

Fluid criticality in porous media

Coasne et al. Chem. Soc. Rev. 2013

Deroche et al. Nature Comm 2019

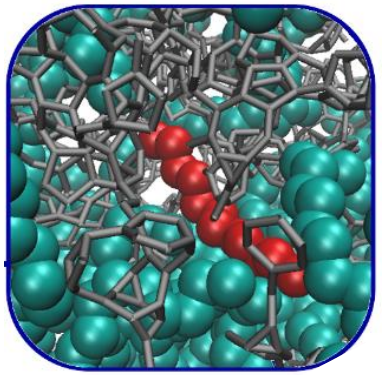


⇨ Part 2

Transport in subnanopores

Falk et al. Nature Comm. 2015

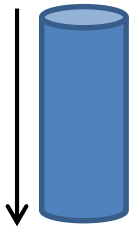
Bousige et al. Nature Comm 2021



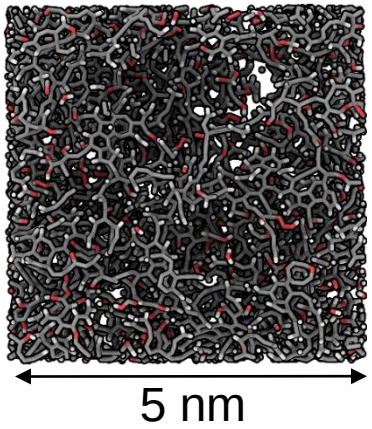
Permeability

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

Darcy law

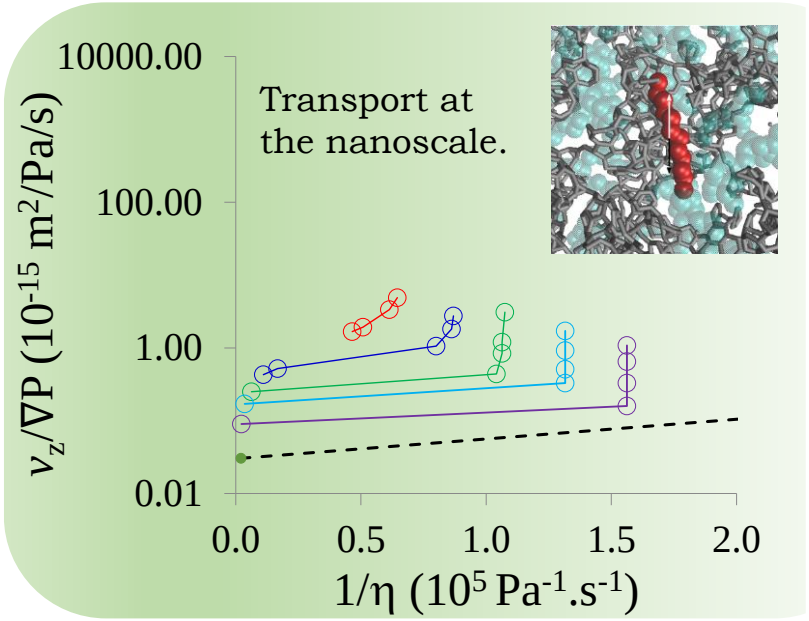


A realistic molecular model of kerogen



Falk, Coasne, Bocquet, et al. Nature Comm. 2015

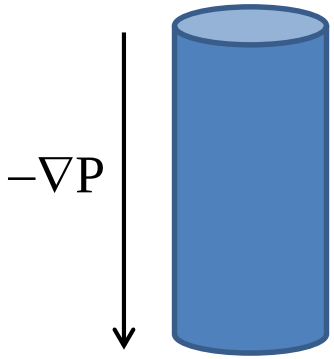
Bousige, et al. Nature Materials 2016



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

Transport at the *nm* scale

Barrat and Hansen, Basic Concepts for Simple and Complex Liquids (Cambridge Univ., 2003).



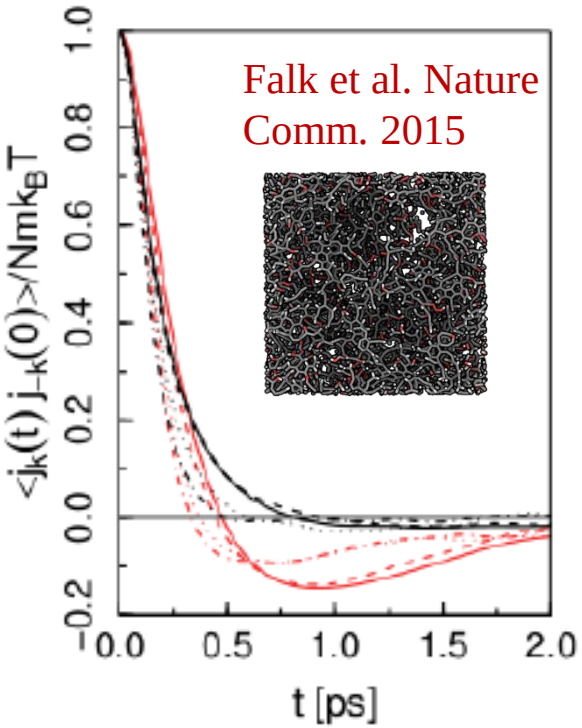
$$\rho \frac{\partial \boldsymbol{v}}{\partial t} = -\nabla \mathrm{P} + \eta \nabla^2 \boldsymbol{v} - \zeta \boldsymbol{v}$$

$$\Rightarrow \quad \rho \frac{\partial \boldsymbol{v}}{\partial t} = \eta \nabla^2 \boldsymbol{v} - \zeta \boldsymbol{v} \qquad \text{[perpendicular to } \nabla \mathrm{P}\text{]}$$

$$\Rightarrow \quad \frac{\partial \boldsymbol{j_k}}{\partial t} = \left(-\nu k^2 - \zeta\right) \boldsymbol{j_k}$$

$$v(t) = \sum_k j_k(t) \exp\left(ik.r\right)$$

[Solving in the Fourier space]



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

Transport of hydrocarbon in the disordered nanoporous carbon is not viscous (nor visco-elastic)

Viscous 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)

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

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

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

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

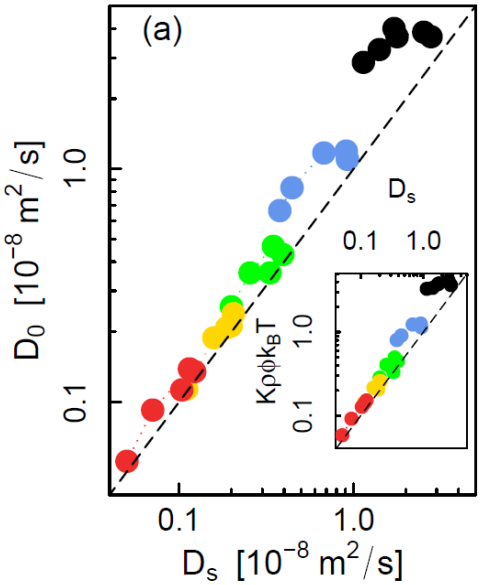
Statistical Mechanics Model

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

[Exact result from the Fluctuation Dissipation Theorem]

$$D_0 = D_s + \int_0^\infty < \sum_{\substack{i,j \\ i \neq j}}^{N} v_i(0) v_j(t) > dt$$

$$D_0 \sim D_s$$

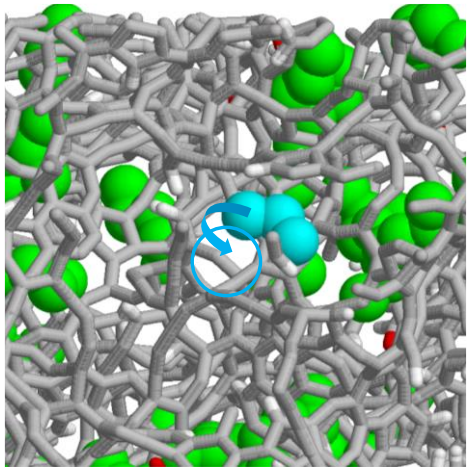


Build a simple microscopic model of hydrocarbon transport based on Statistical Mechanics and express K ~ D_s/ρ

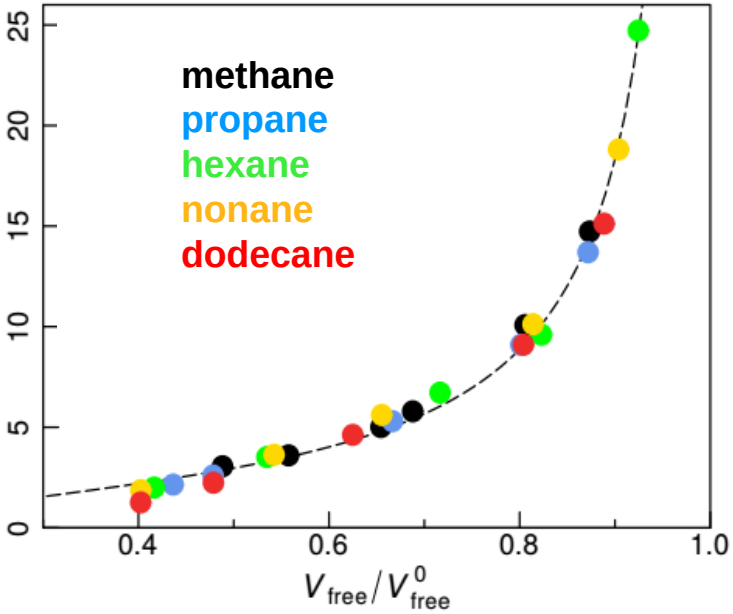
Free Volume Theory

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

with $V(N) = V_{free}(0) - V_{free}(N) \sim N$



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



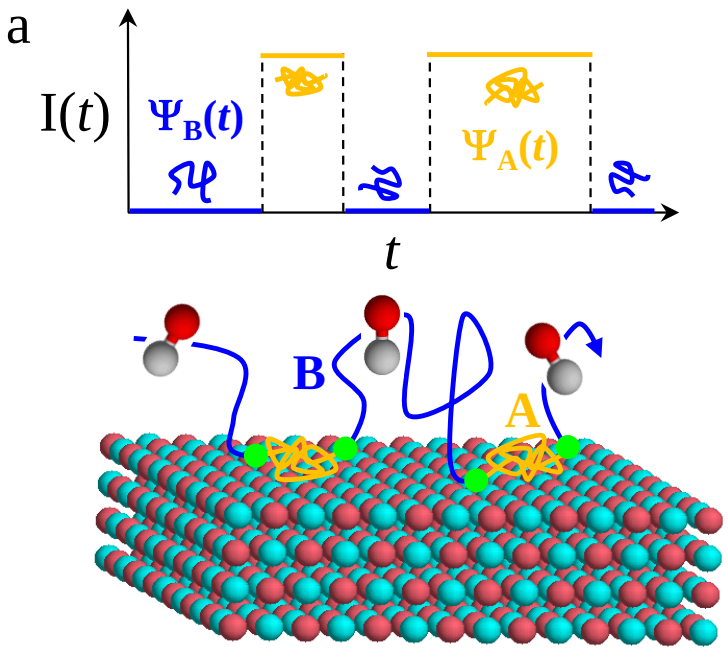
- A simple "Stat Mech" model is built
- This model does not use macro concepts (e.g. viscosity)

Falk et al. Nature Comm. 2015

Long Time (Macroscopic) Dynamics

Intermittent Brownian Dynamics:

« Trajectory as successive surface residence and relocation steps with underlying first passage distributions »



$$\Psi_A(t) \sim 1/t_A \times \exp[-t/t_A]$$

$$\Psi_B(t) \sim x/[D_s^p\, t^3]^{1/2}$$

$$C(t) = < I(t)\, I(0) > \qquad J(f) = \mathrm{TF}[C(t)]$$

$$J(f) \sim \mathrm{Re}\, \frac{[1 - \tilde{\Psi}_B(f)] - [1 - \tilde{\Psi}_A(f)]}{f^2 \times [1 - \tilde{\Psi}_A(f)\tilde{\Psi}_B(f)]}$$

Levitz et al. Soft Matter 2013
Bousige et al. Nature Comm. 2021

Intermittent Brownian Motion

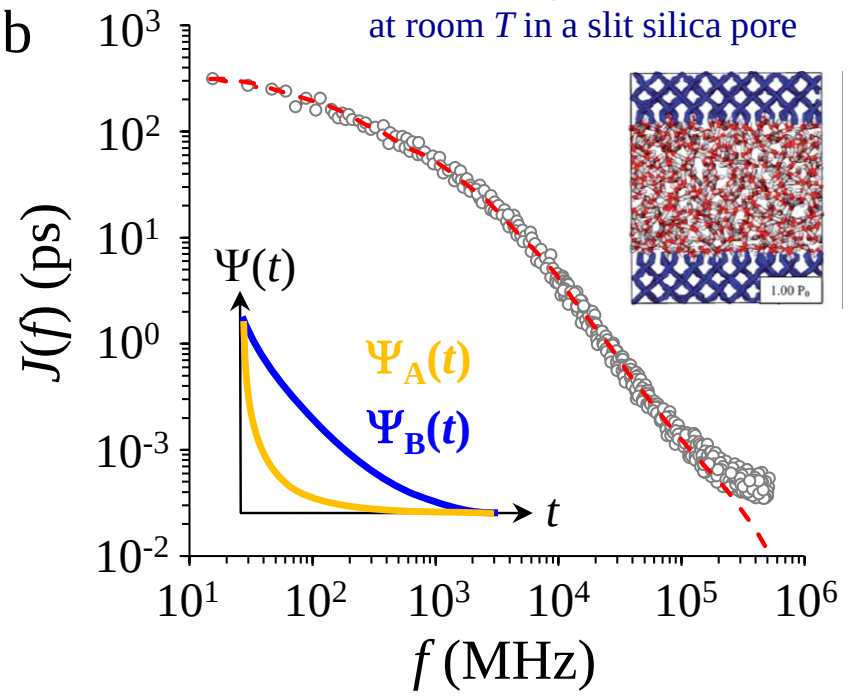
- *Short timescale* $t \leq 10\,ps$ ($f > 10^5$ MHz)
  Dynamics driven by molecular dynamics (collisions, interactions)

  ⇨ IBM = coarse grained picture with random walk diffusion and statistical distribution of residence times

- *Long timescale* $t > 10$ ps ($f < 10^2$ MHz)
  Molecular dynamics is correctly captured by IBM

  ⇨ IBM can be used to predict from molecular dynamics ingredients the macroscopic behavior beyond timescales accessible through Molecular Dynamics (typically t > 10-100 ns, f < 10^2-10^3 MHz)

Molecular dynamics of water at room *T* in a slit silica pore

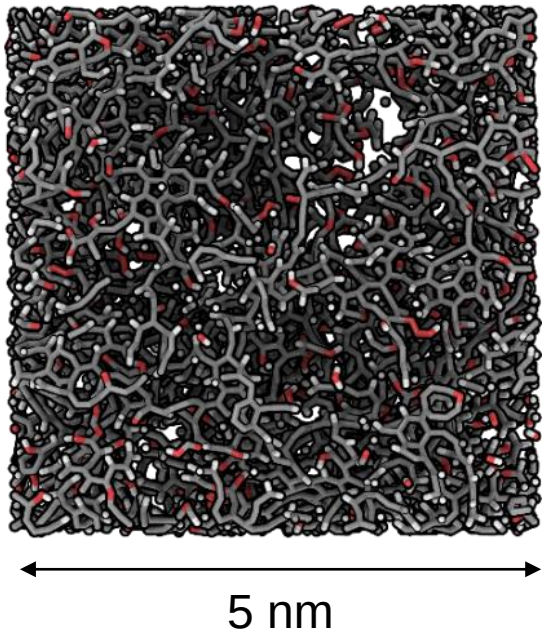


$$J(f) = \mathrm{TF}[C(t)]$$

Levitz, Coasne et al. Soft Matter 2013

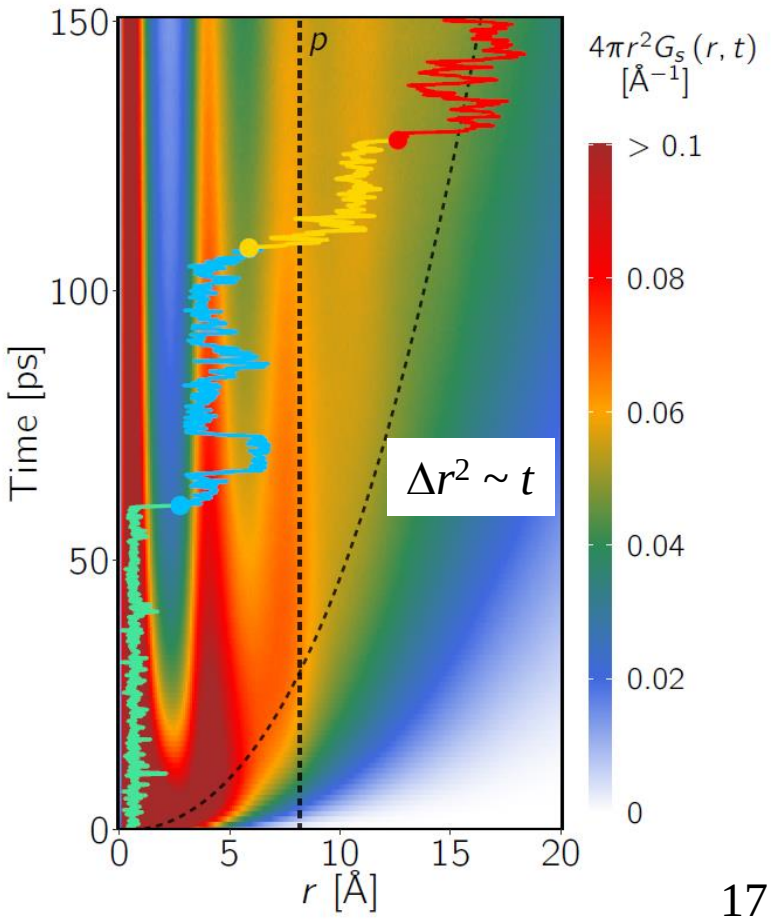
“Stop and Go” Diffusion

Various fluid/wall ε and pore sizes *D*



$$t_A = t_A(d,\varepsilon) \qquad t_B = t_B(d,\varepsilon)$$

Propagator $G_s(r,t)$
[prob. that a molecule is translated by a quantity r over a time t]



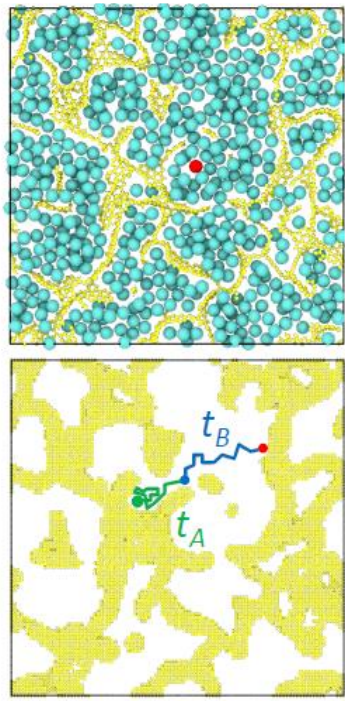
Bousige, Levitz, Coasne, Nature Comm. 2021

Mapping Micro/Mesoscopic Dynamics

Intermittent Brownian Dynamics

- Exact, robust formalism but complex, ill-defined residence and relocation times because of disordered geometry

- Mapping between self-diffusivity seen by molecular dynamics simulations and by random walk approach with residence time



MD

RW

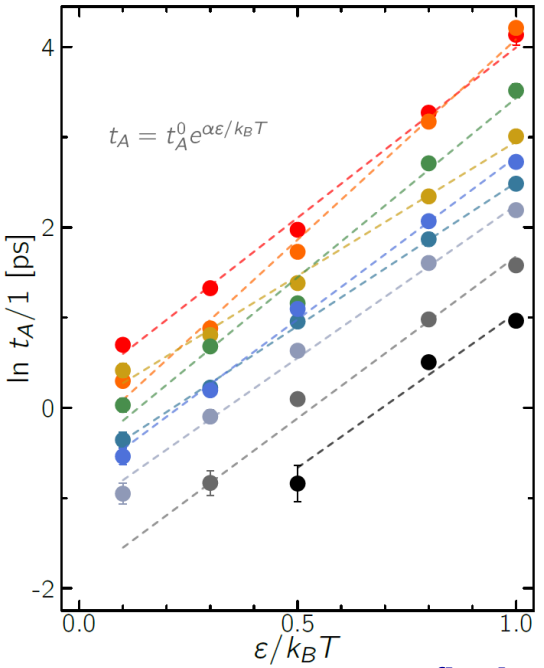
For a given porous matrix ρ and fluid/wall energy ε, there is a unique set of residence (t_A) and relocation (t_B) times for which the moleculard dynamics and random walk diffusivities match

$$t_A = t_A(d,\varepsilon) \qquad t_B = t_B(d,\varepsilon)$$

Bousige, Levitz, Coasne, Nature Comm. 2021

Residence Time t_A

- t_A increases with decreasing d because more severe confinement with decreased escape probability
- For a given structure, t_A increases with increasing ε/k_BT as a result of stronger fluid/surface interactions



confinement (decreasing pore size)

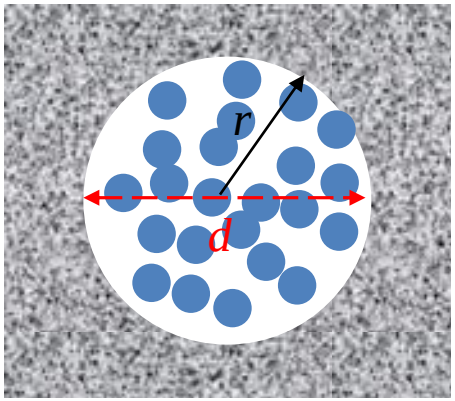
fluid/surface interaction

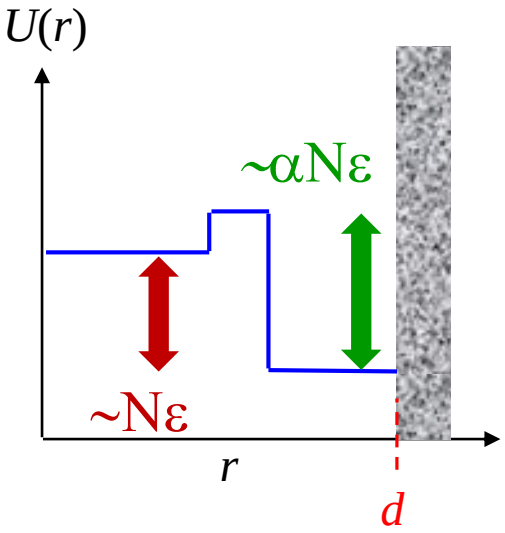
Quantitatively, our data follow a simple activation energy model involving an escape attempt frequency $t_A{}^0$ and an energy barrier $\sim \varepsilon$:

$$t_A \sim t_A{}^0(d) \times \exp[-\alpha N\varepsilon/kT]$$
with α a constant $\gtrsim 1$

Residence Time t_A

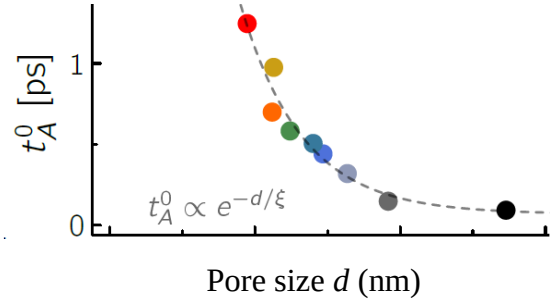
Activation energy model





$t_A \sim t_A^0(d) \times \exp[-\alpha N\varepsilon/kT]$
with α a constant $\gtrsim 1$

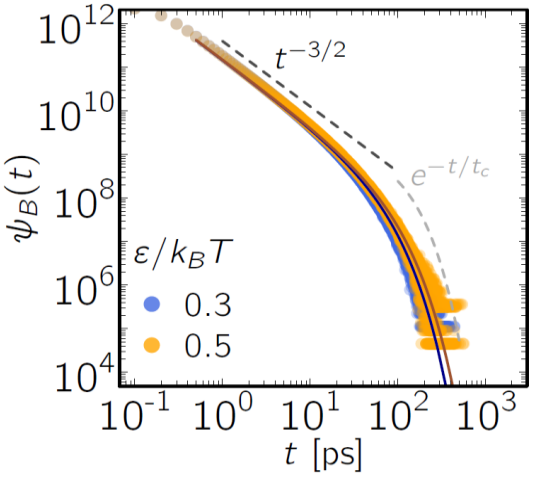
Time constant t_A^0 decreases with increasing d because local curvature decreases escape attempt frequency



Relocation Time t_B

- *Short time*
  Gaussian propagator corresponding to random walk diffusion:

$$\Longrightarrow \quad \Psi_B(t) \sim 1/[4\pi D_s^{\,p}\, t^3]^{1/2}$$



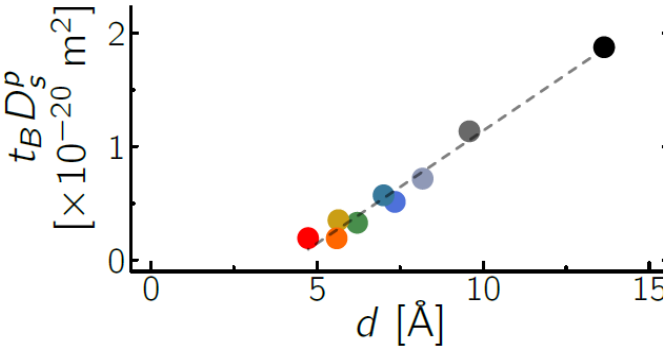
- *Long time*
  Cutoff in relocation as all molecules eventually reach the surface again (finite pore volume):

$$\Longrightarrow \quad \Psi_B(t) \sim 1/[4\pi D_s^{\,p}\, t^3]^{1/2} \times \exp[-t/t_C] \quad \text{where } t_C \sim d^2/D_s^{\,p}$$

$$t_B = \int_0^\infty t\psi_B(t)\mathrm{d}t$$

$$t_B \sim \mathrm{d}/D_s^{\,p}$$

~~$t_B \sim d^2/D_s^{\,p}$~~



Conclusion

- Simple physical models – relying on available parameters – are available to describe adsorption and transport in nanoporous media
- Adsorption in nanoporous media conforms the classical view of capillarity in porous solids. Yet, a apparent shift in the fluid critical point is observed upon confinement.
- Diffusion in nanoporous materials – even when complex solids are considered – can be described using simple statistical mechanics models such as a free volume theory or the intermittent Brownian motion
- Such simple physical models allow predicting the thermodynamics and long-time dynamics of fluids confined in ultraconfining materials using simple parameters available experimentally

Acknowledgments: C. Bousige, K. Falk, A. Schlaich, L. Bocquet, P. Levitz

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