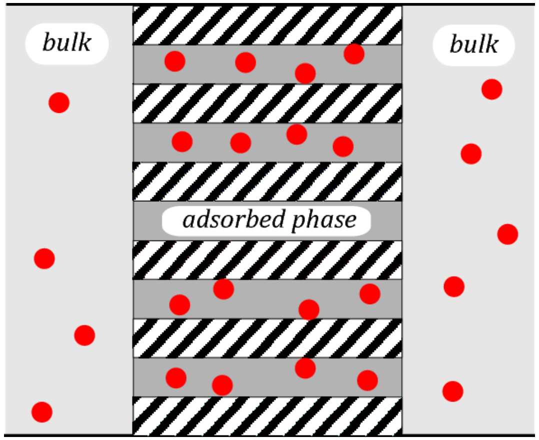
Phase transitions under constraints: from confinement to complex networks

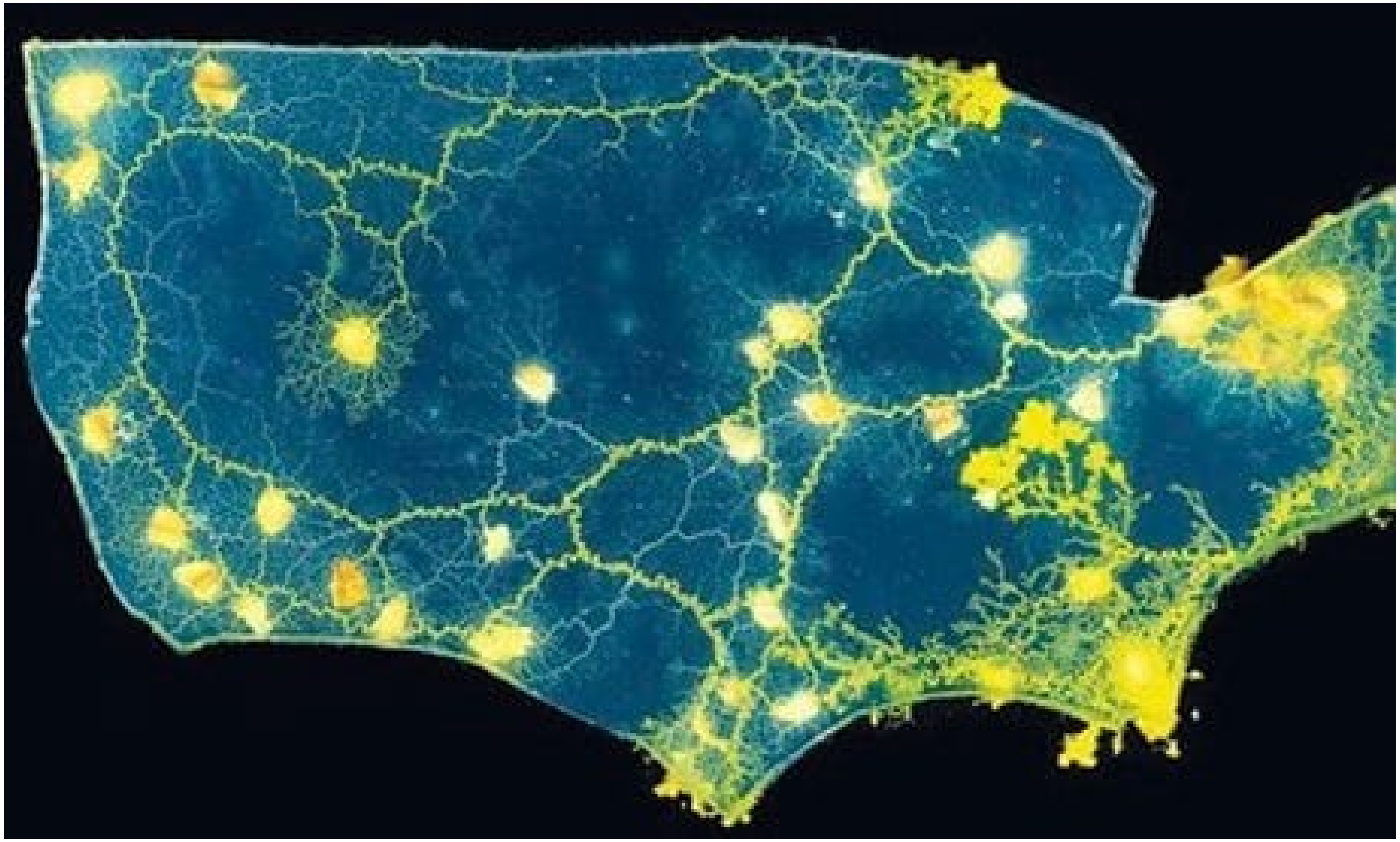


Kirill Glavatskiy

"Complexity, Criticality & Computation" (C3-2017)

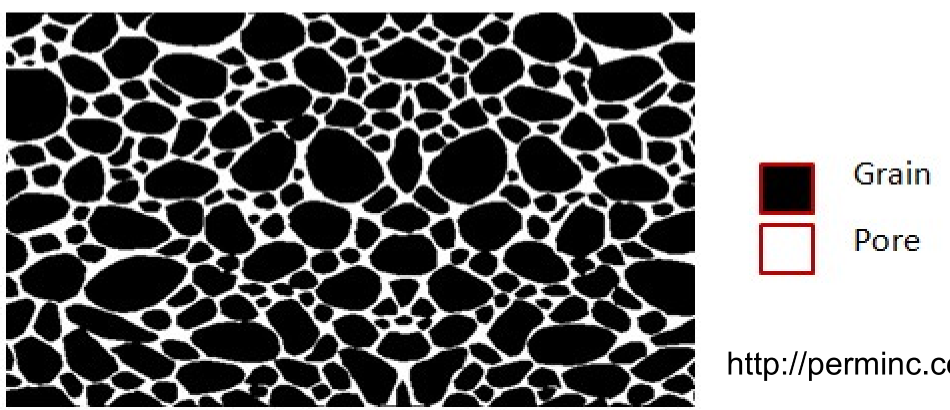
Sydney, 11-13 December 2017

THE UNIVERSITY OF SYDNEY



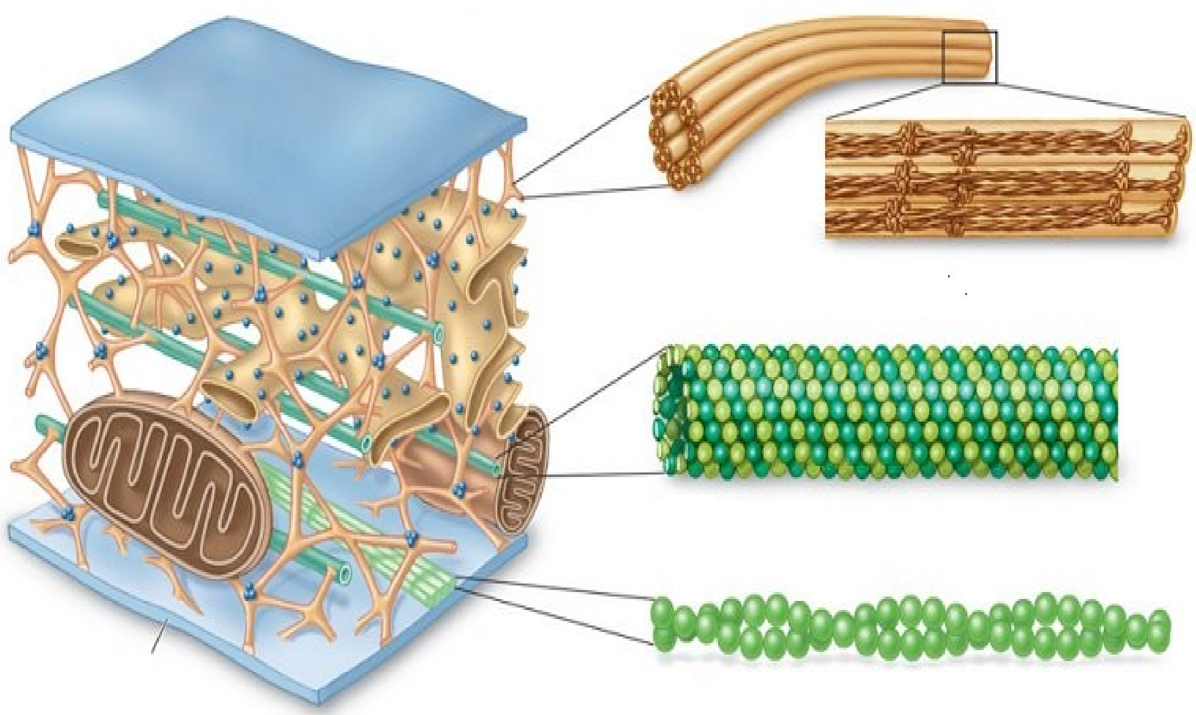
https://www.theguardian.com/cities/2014/feb/18/slime-mould-rail-road-transport-routes

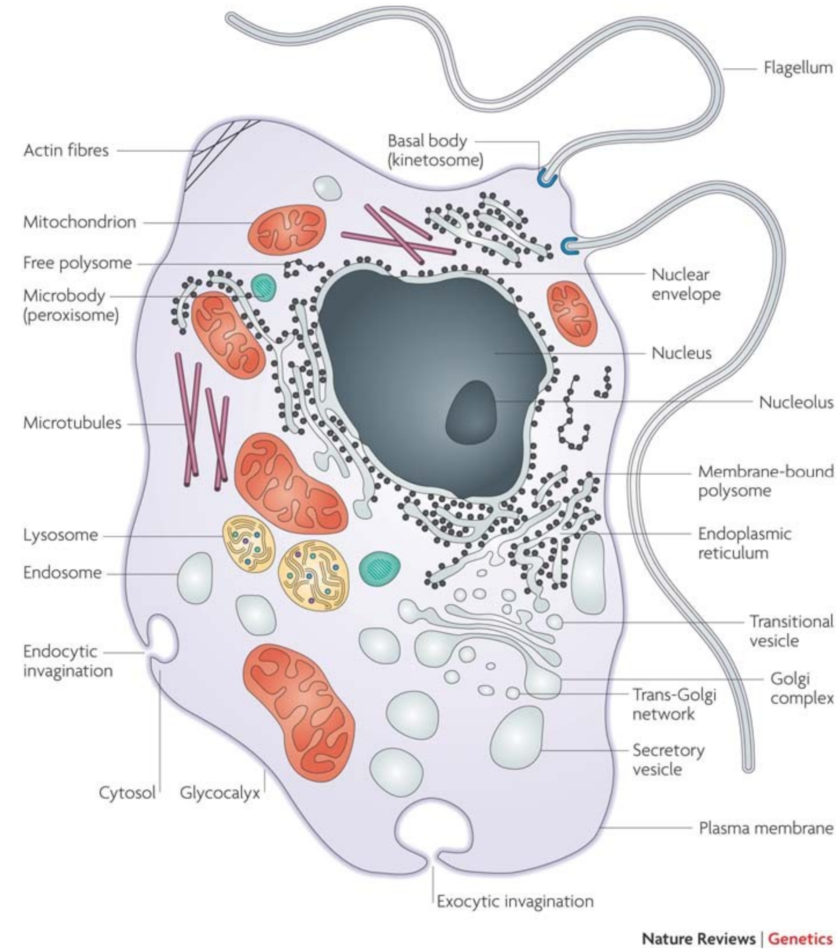
Porous rocks



http://perminc.com

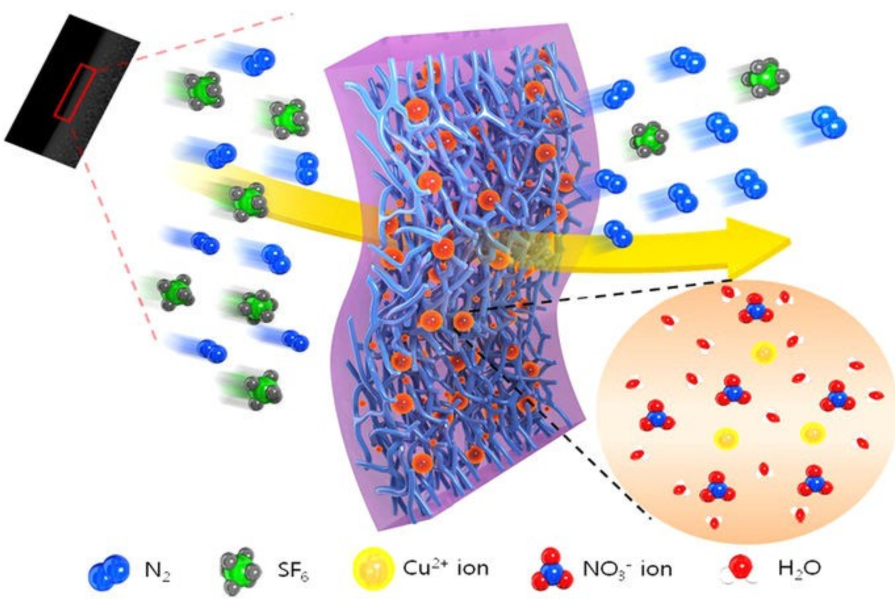
Membranes in biology



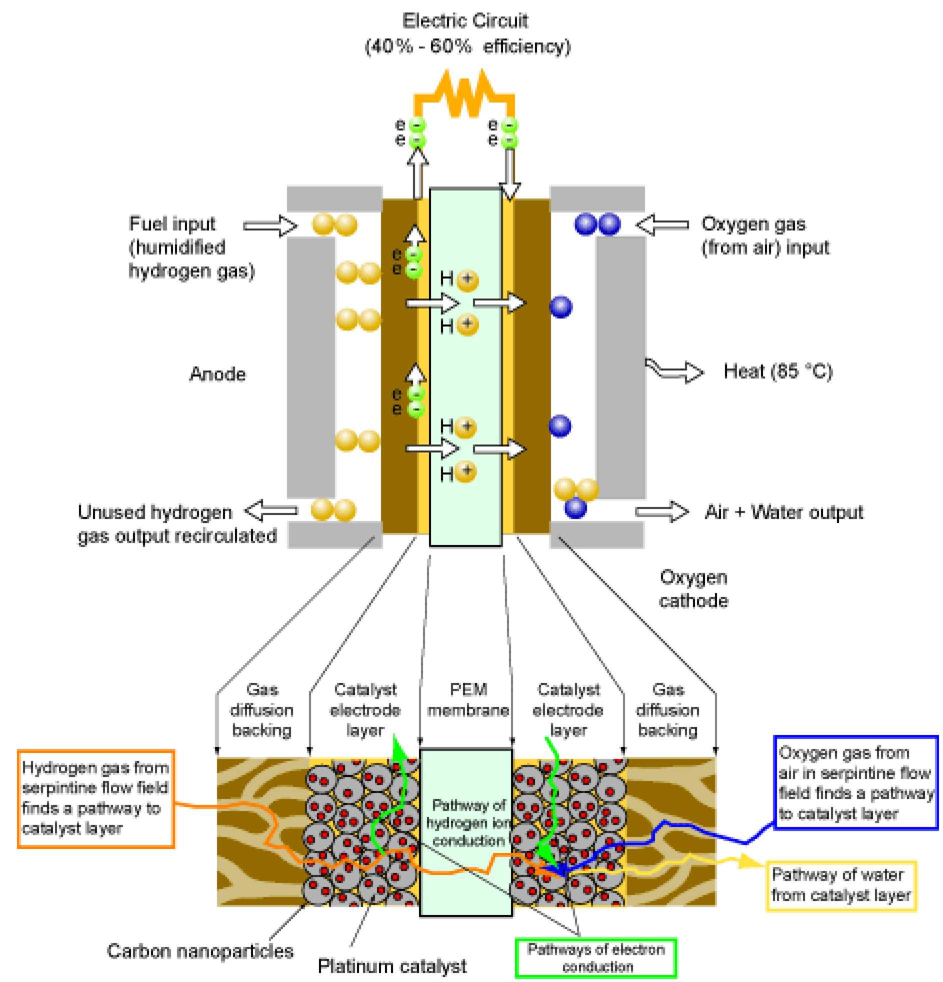


Membranes in chemistry

- Gas separation and filtration
- Fuel cells



Scientific Reports 6, 20430 (2016)

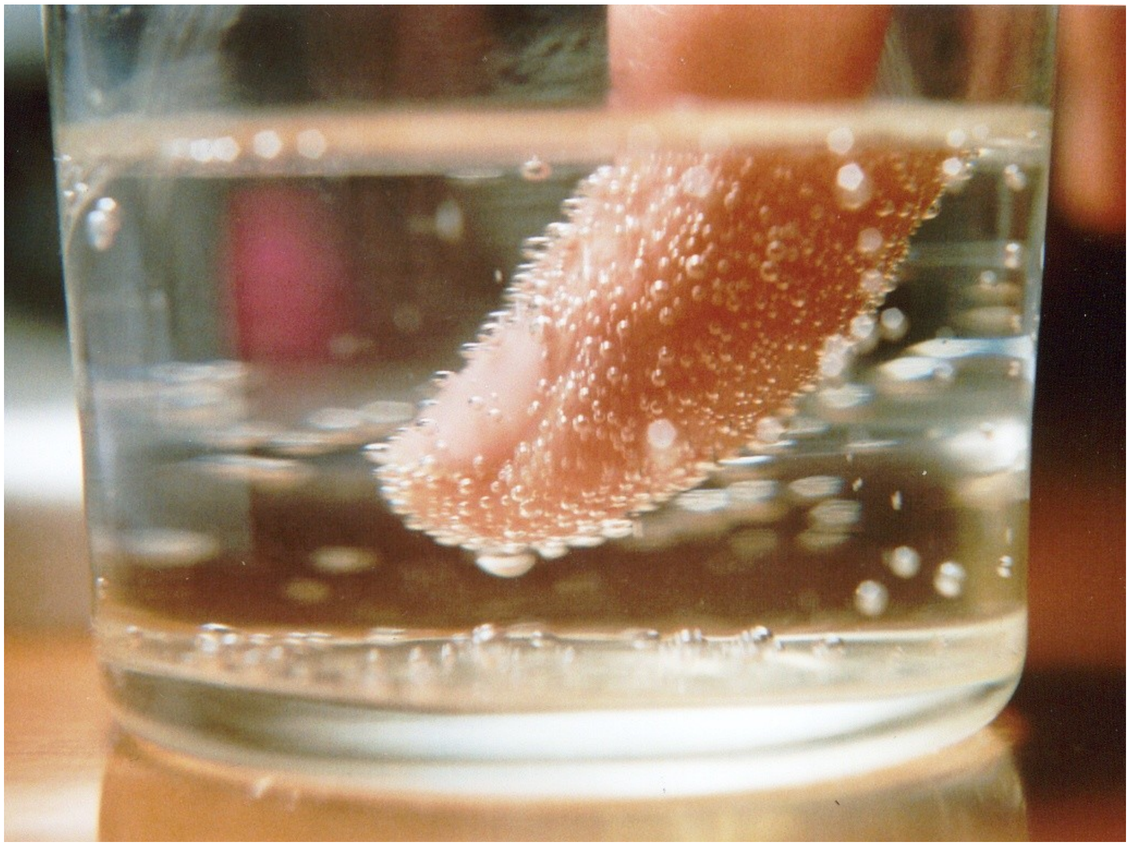


https://physics.nist.gov/MajResFac/NIF/pemFuelCells.html

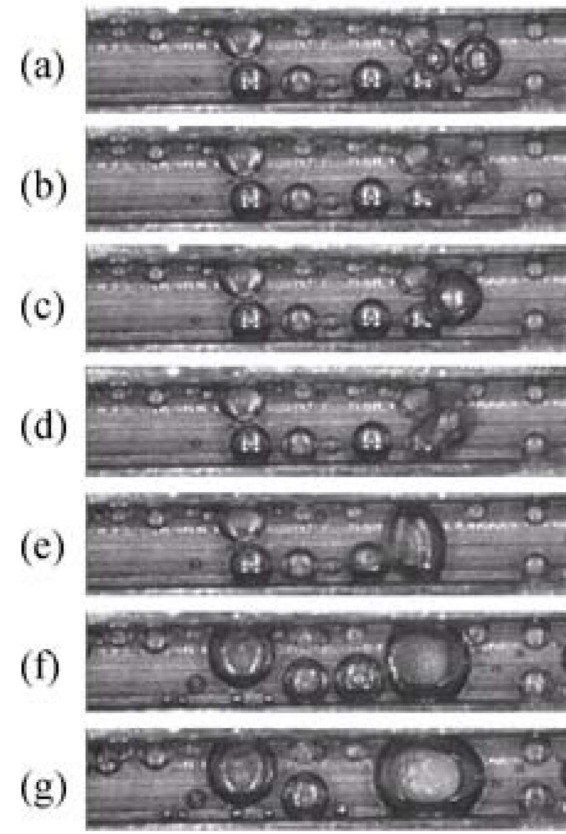
Phase transitions under constraints: from confinement to complex networks

- Phase transitions of confined fluids
- Fluid transport in channels

Nucleation



Wikipedia: nucleation

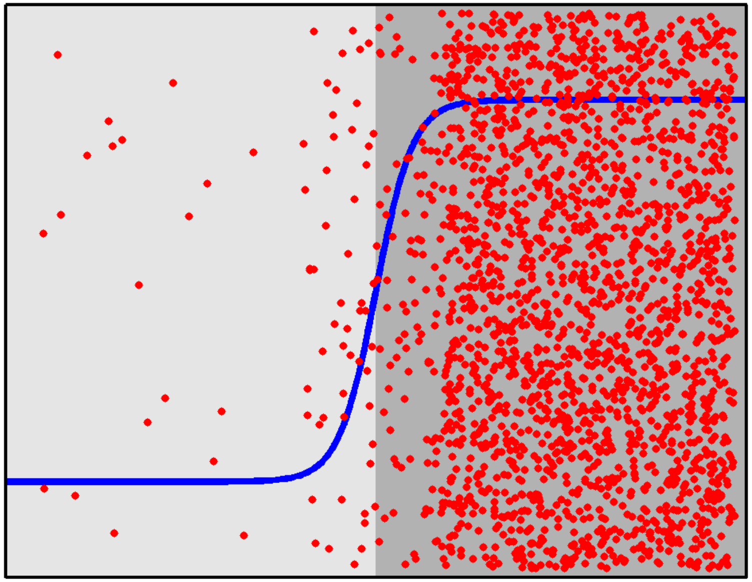


Journal of Thermal Science (2012), 21

Modelling the interface

- Current methodology

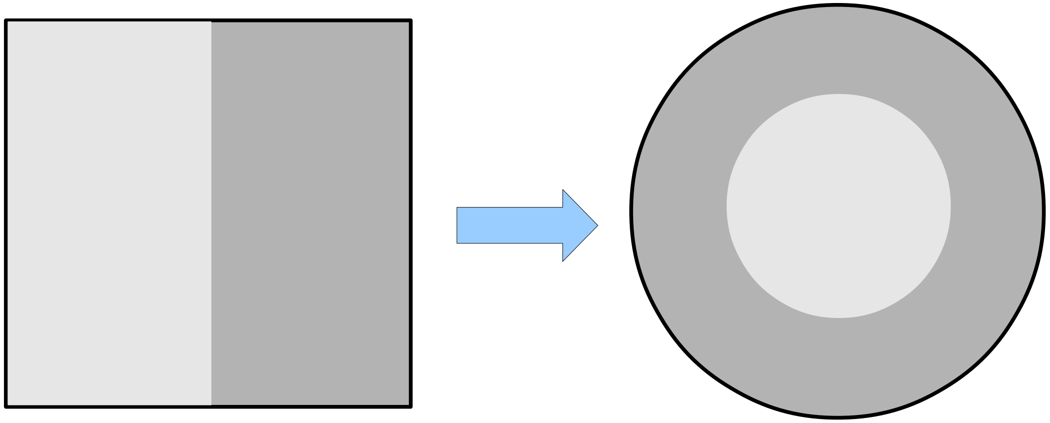
density profile is a result of free energy minimization, assuming smooth variables



- surface tension is derived from density variation

- Challenge

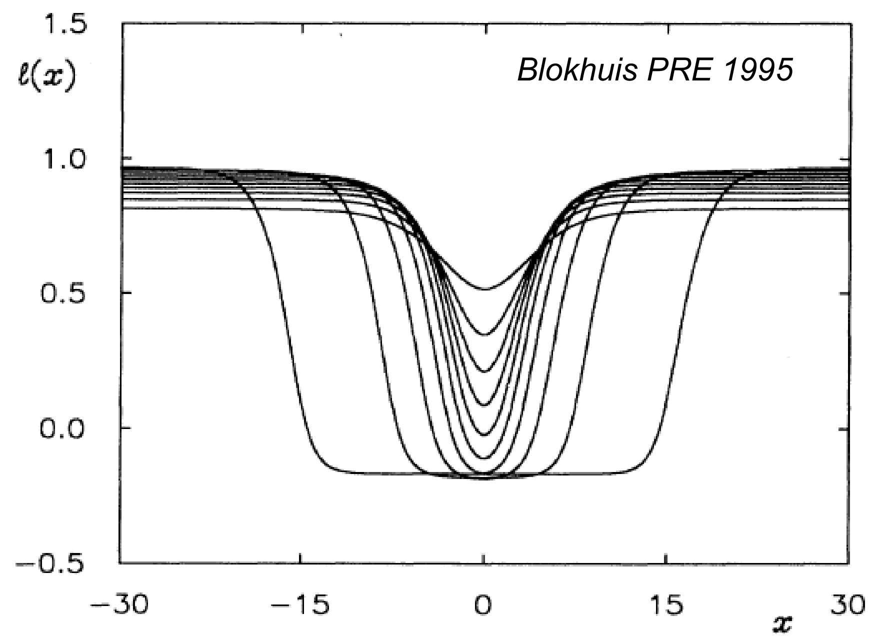
apply methodology of planar interface to spherical interface



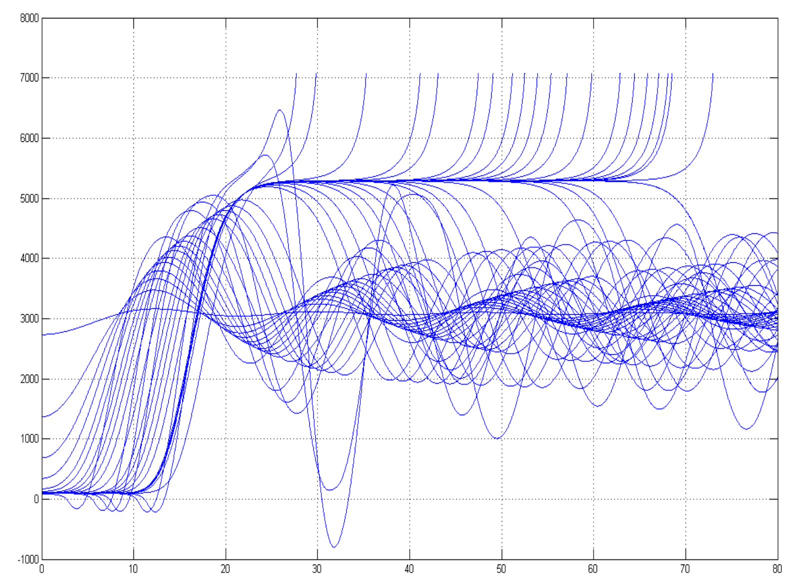
- problem of singularity
- varying surface area

Density profile

- What we may expect:



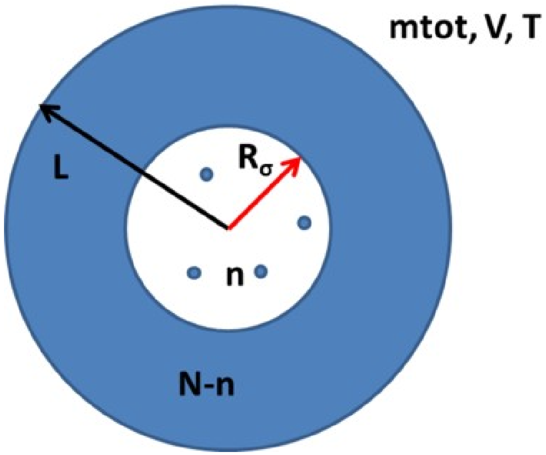
- What we actually see:



small bubble is not stable?

small bubble is not stable!

- Closed system
  - *fixed amount of molecules,*
    which can be in either of two phases: gas or liquid
- Commpressible fluid
  - *density may be adjusted*

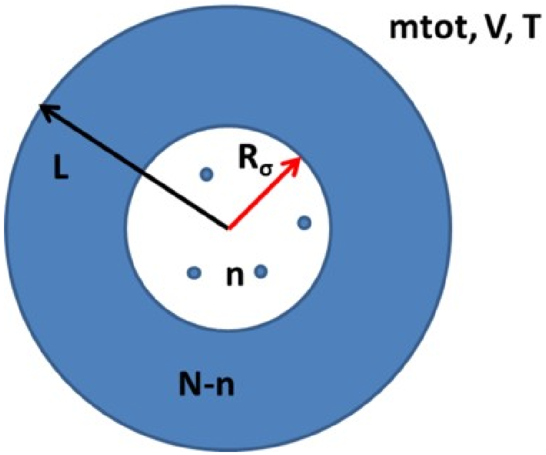


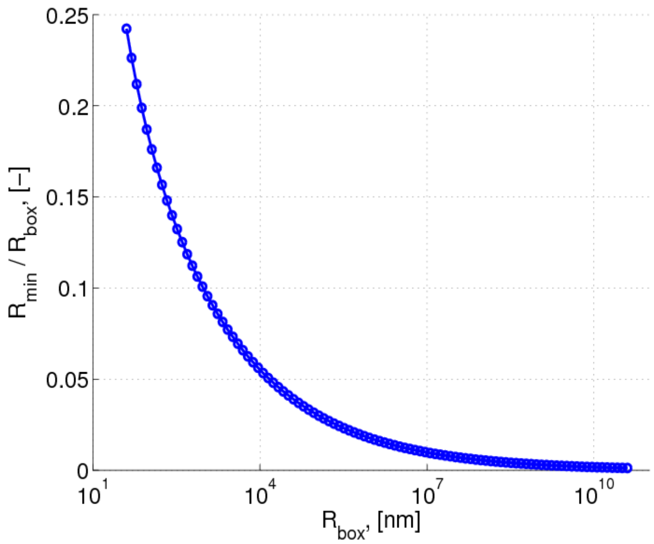
- fix N (or m_{tot})
- obtain n and R_s

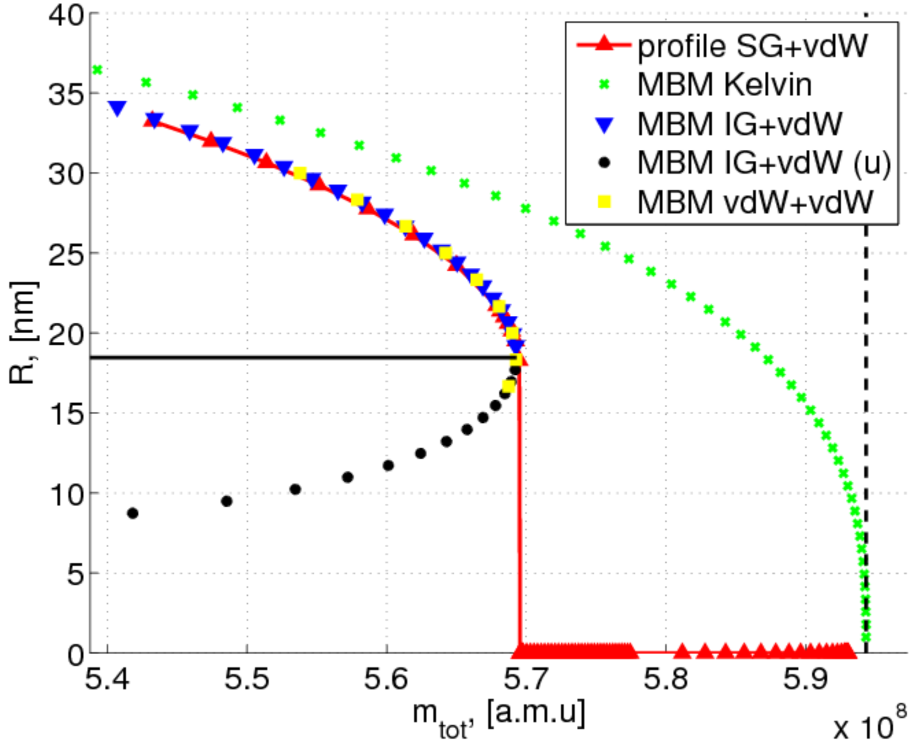
Thermodynamics: $$T\,dS = dU + p\,dV - \mu\,dN$$

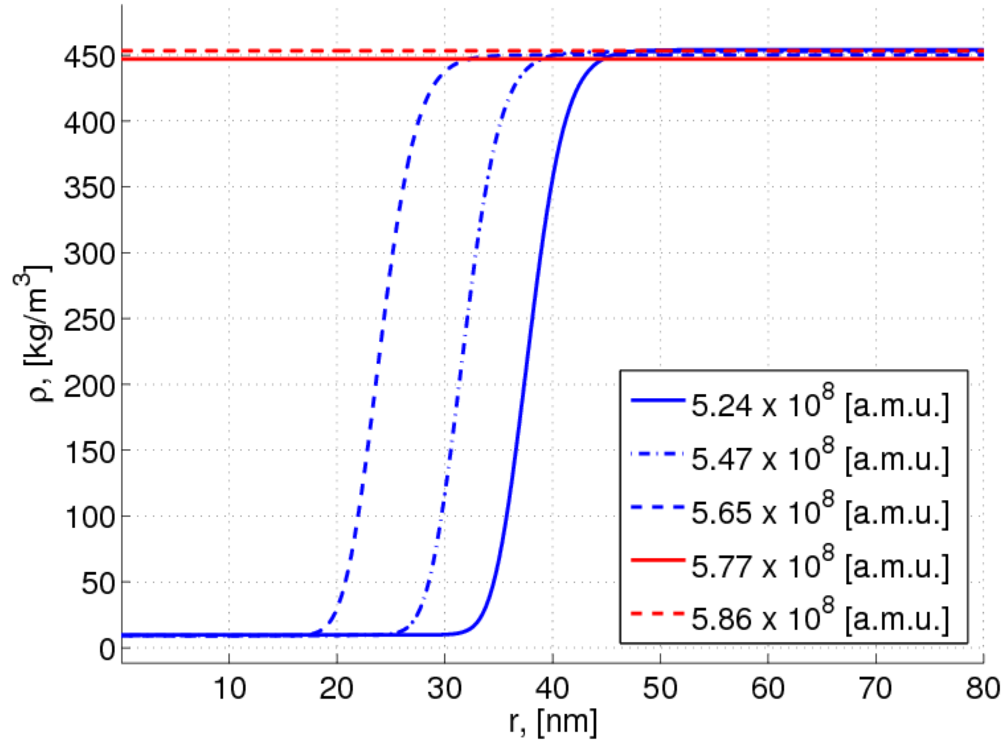
Equilibrium:
$$\mu_{in}(p_{in}, T) = \mu_{out}(p_{out}, T)$$
$$p_{in} - p_{out} = \frac{2\sigma}{R}$$

Capillary model

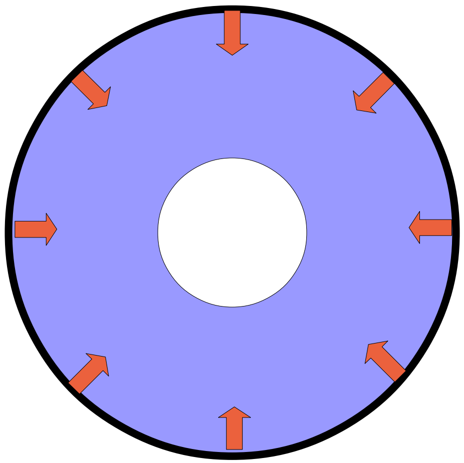


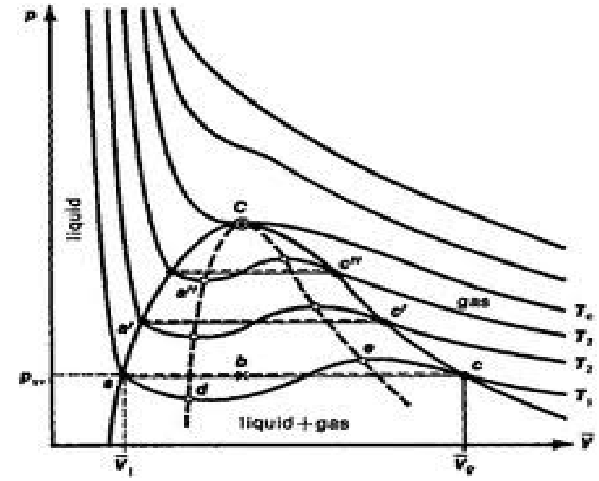






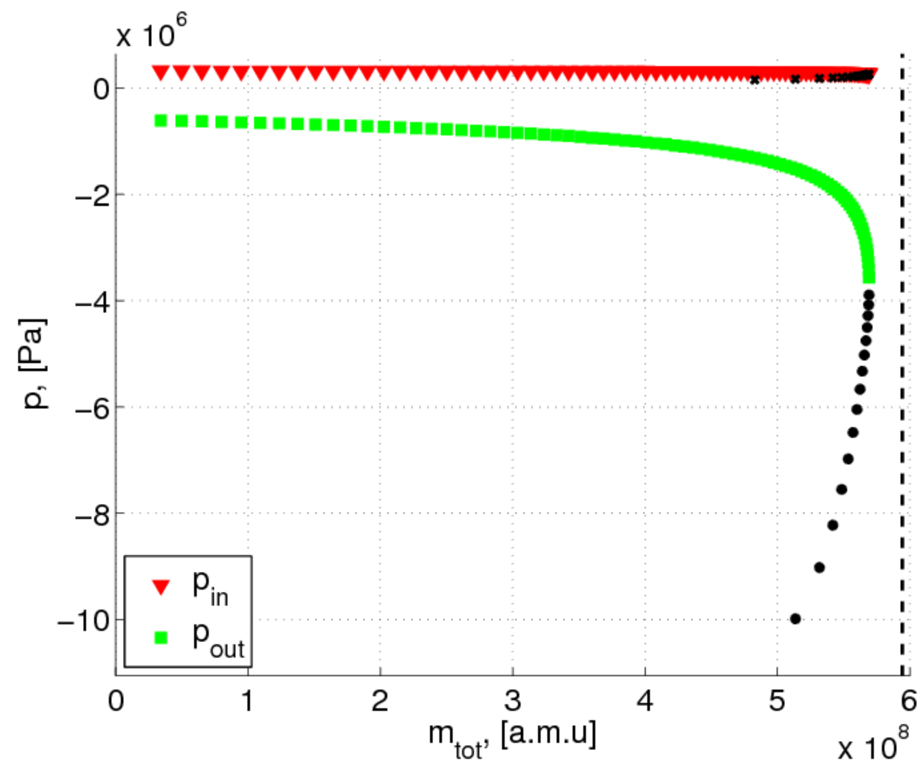
Phase diagram





large negative pressure
leads to stretching of the liquid

resulting fluid density is lower
than the coexistence one
- «metastable» region

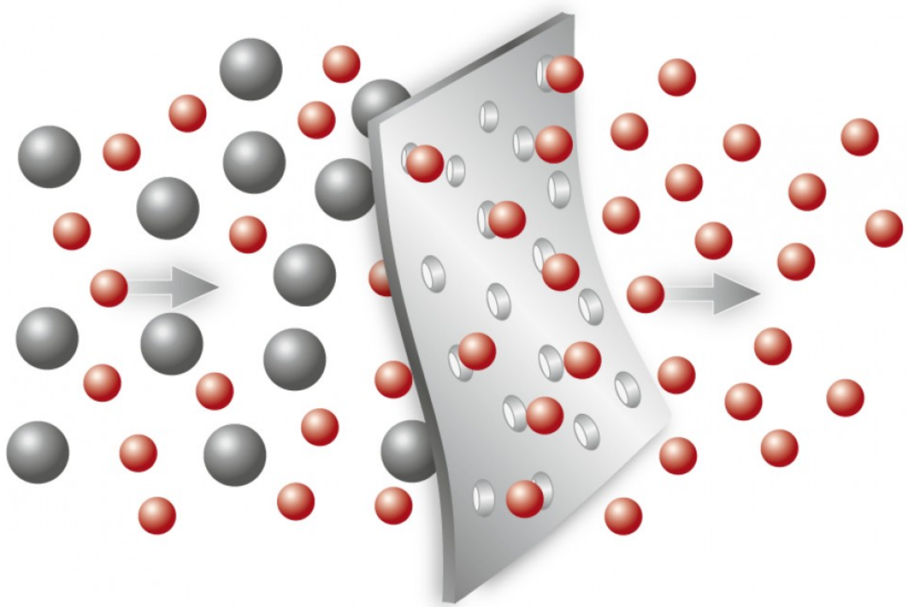


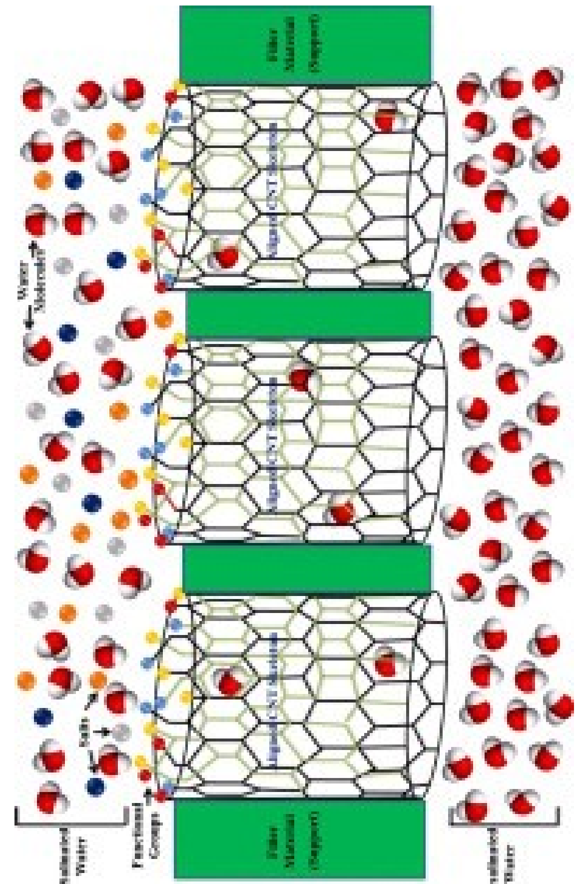
Summary: nucleation

- Confinement:
  - energy redistribution under constraints
- Altered phase diagram
  - closed system + compressible fluid
- Effect is larger for smaller system

- Apparent negative compressibility
- Restrictions on cluster size

Porous transport

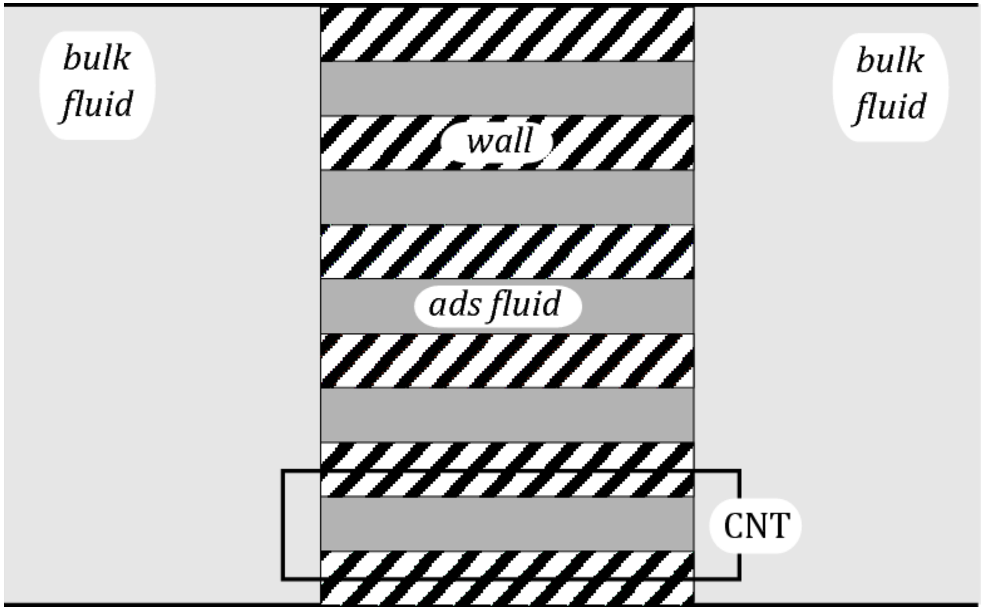




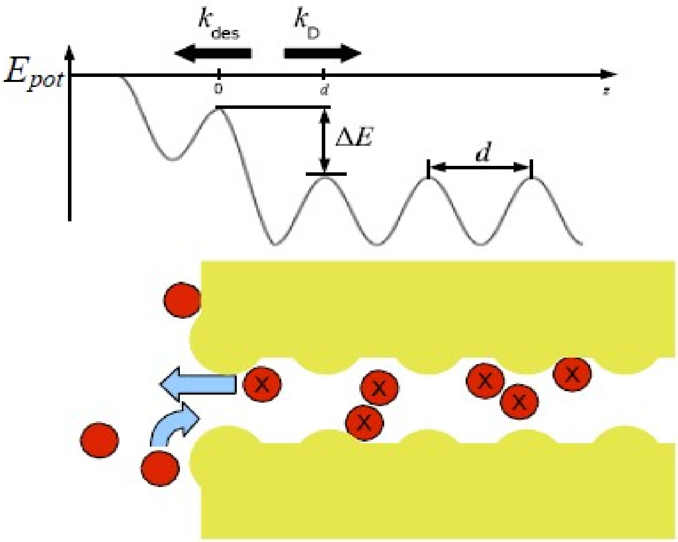
Desalination 336, 97-109, (2014)

Carbon nanotube membrane

- Membrane model

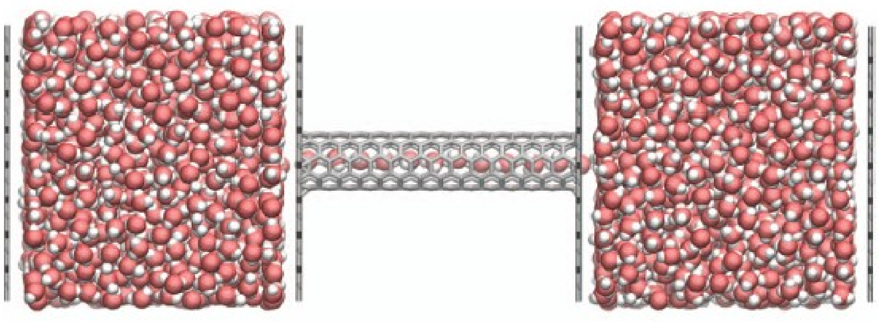


- Energy profile at CNT entrance

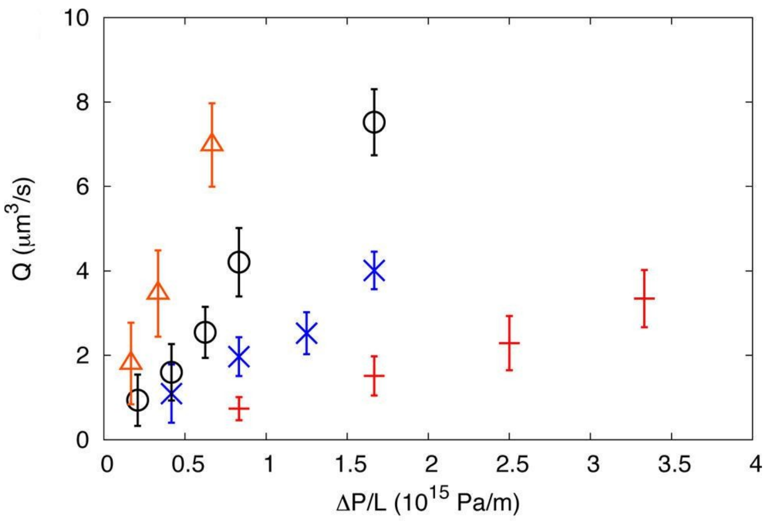


(Gulín-González et al., 2006)

Gravelle et al, J Chem Phys (2014)



Walther et al, Nano Lett (2013)

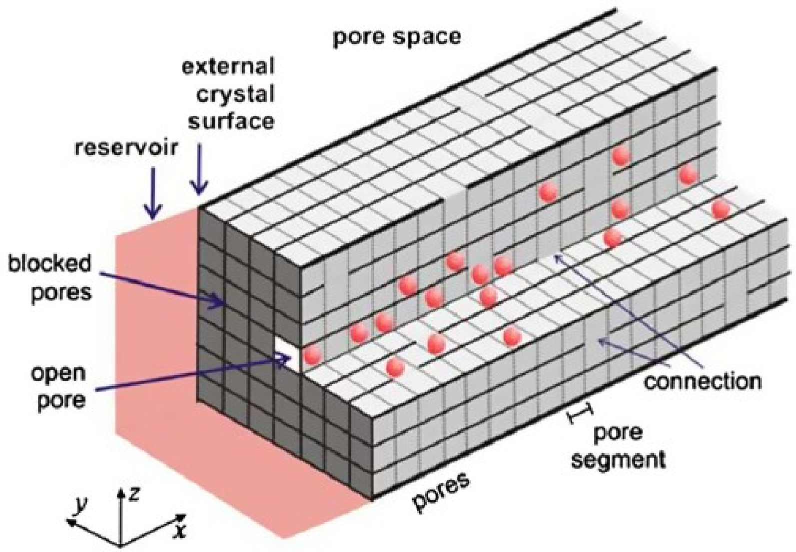


- Pore entry $$\Delta_S P = Q C \eta \left(\frac{1}{r_a^3} - \frac{1}{r_b^3} \right)$$
- Poiseuille $$\frac{\Delta_P P}{L} = Q \frac{8\eta}{\pi r^4 + 4\pi r^3 s}$$
- Bernoully $$\Delta_B P = \frac{Q^2}{2\pi\rho_b} \left(\frac{1}{r_a^2} - \frac{1}{r_b^2} \right)$$

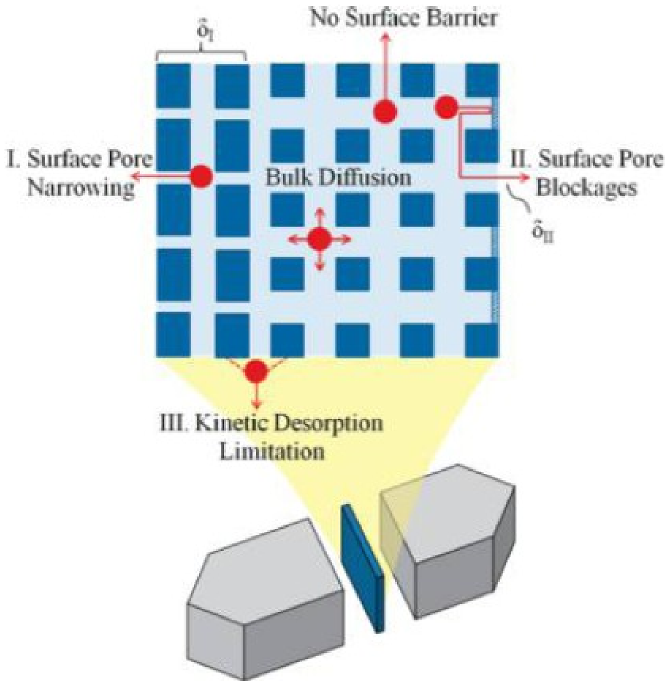
ΔP	pressure drop
Q	flow rate
r	pore radius
L	pore length

Pore blockage

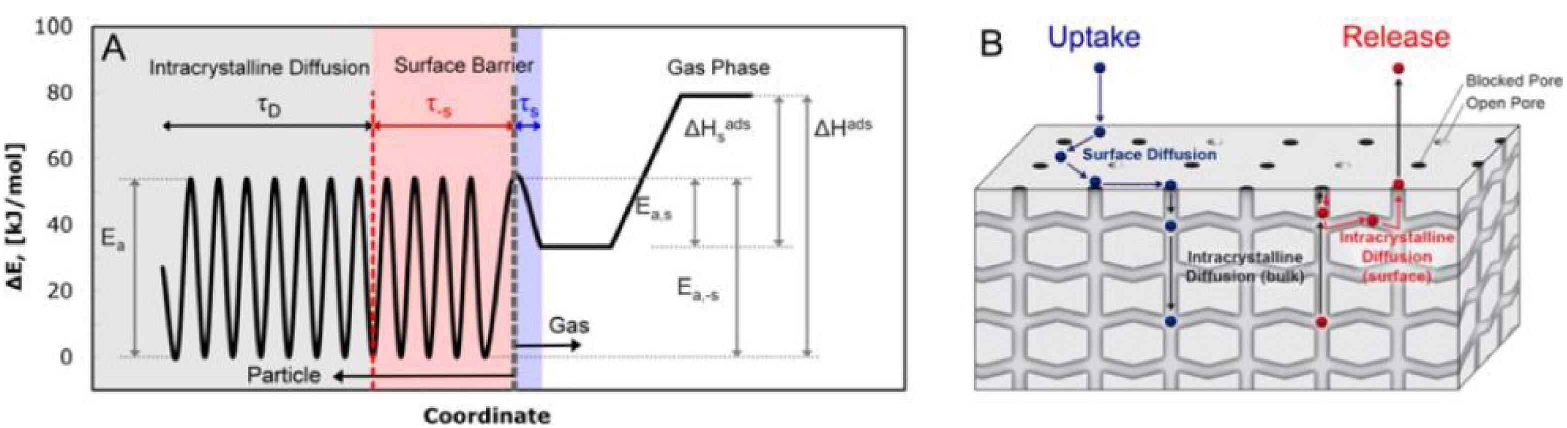
Heinke & Karger, Phys Rev Lett (2011)



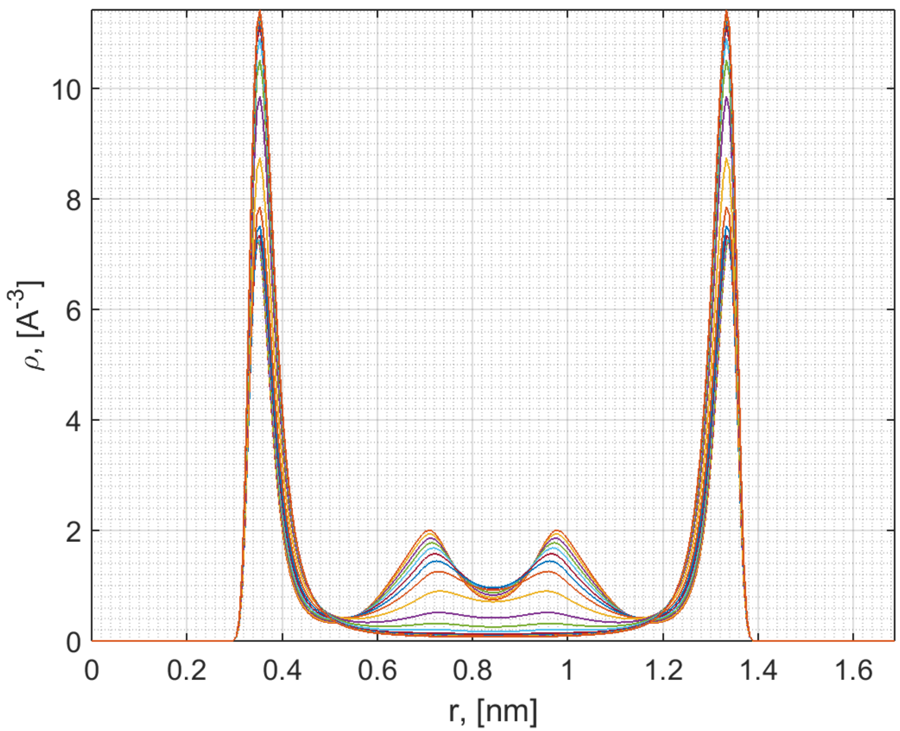
Teixeira et al, J Phys Chem C (2013)



Teixeira et al, J Phys Chem C (2014)

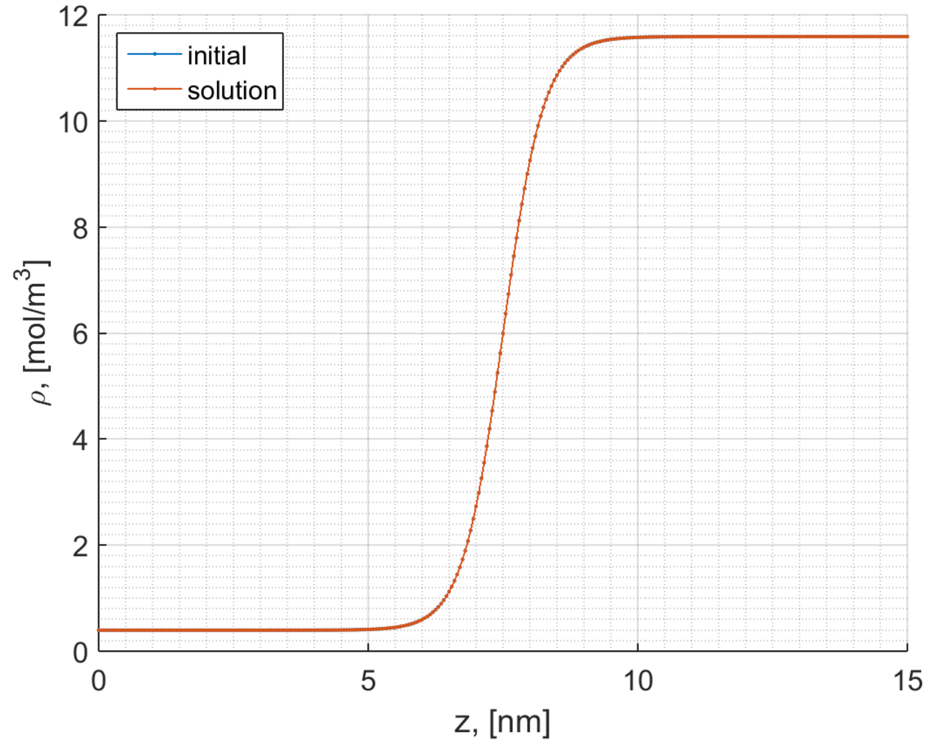


Fluid structure



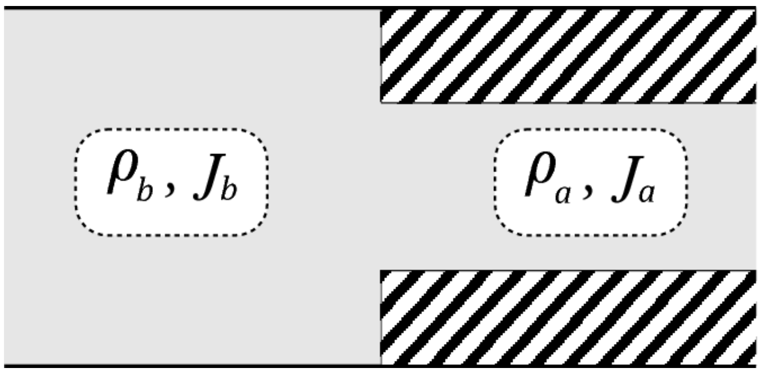
density inside the pore

$$\rho(x) \Rightarrow \rho_a$$



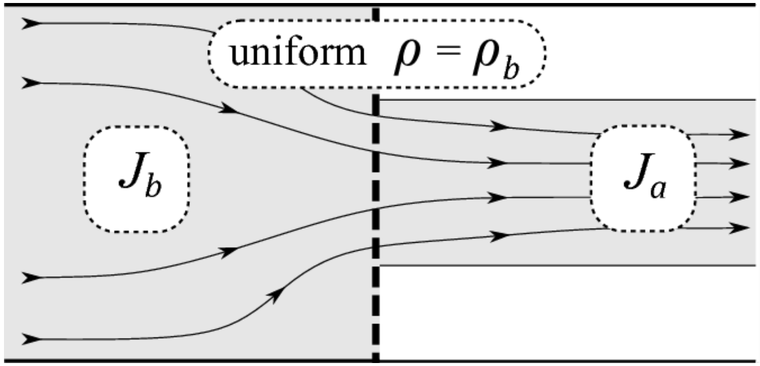
density across the interface

$$\rho(x, z) \Rightarrow \rho(z)$$



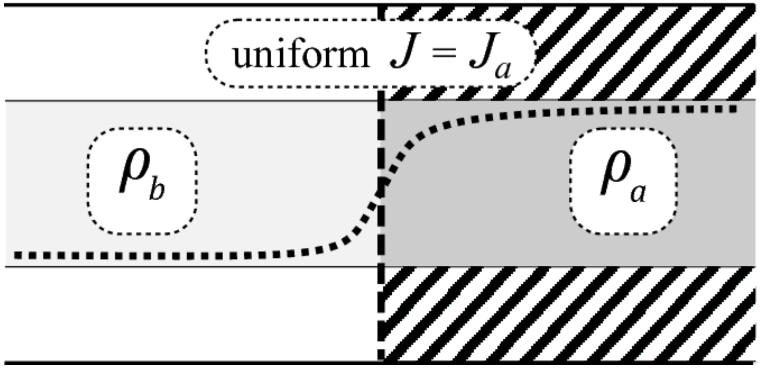
- Hydrodynamic resistance:

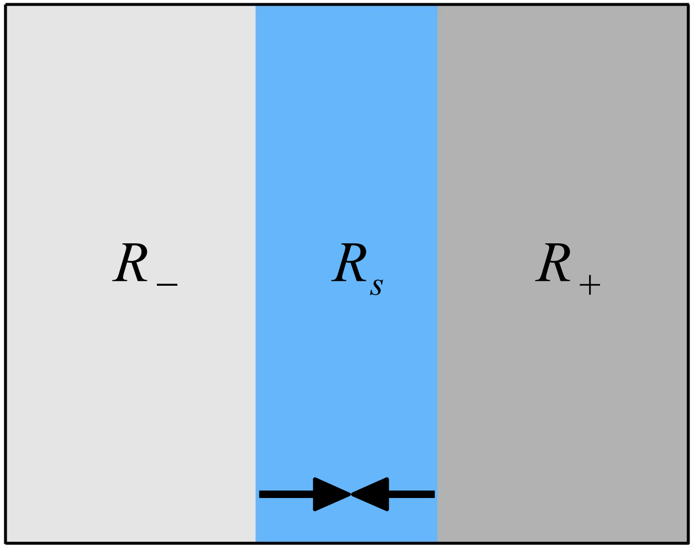
  bending of the flow lamina
  at a geometrical obstacle

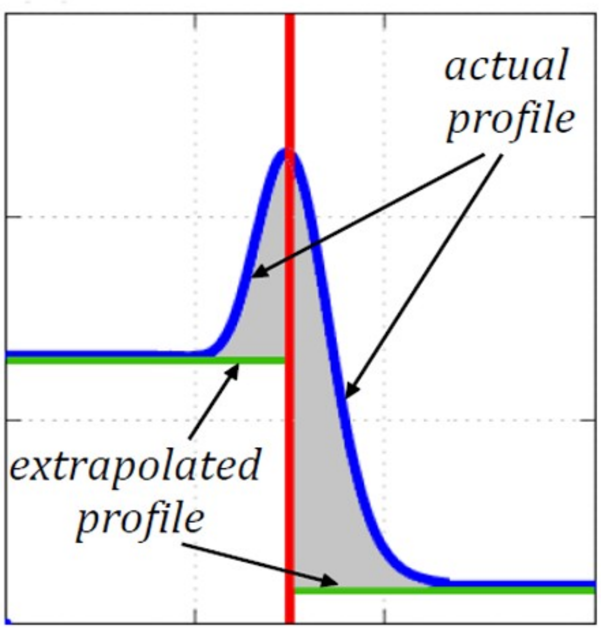


- Thermodynamic resistance:

  phase difference between
  inside and outside the membrane



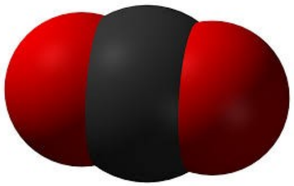


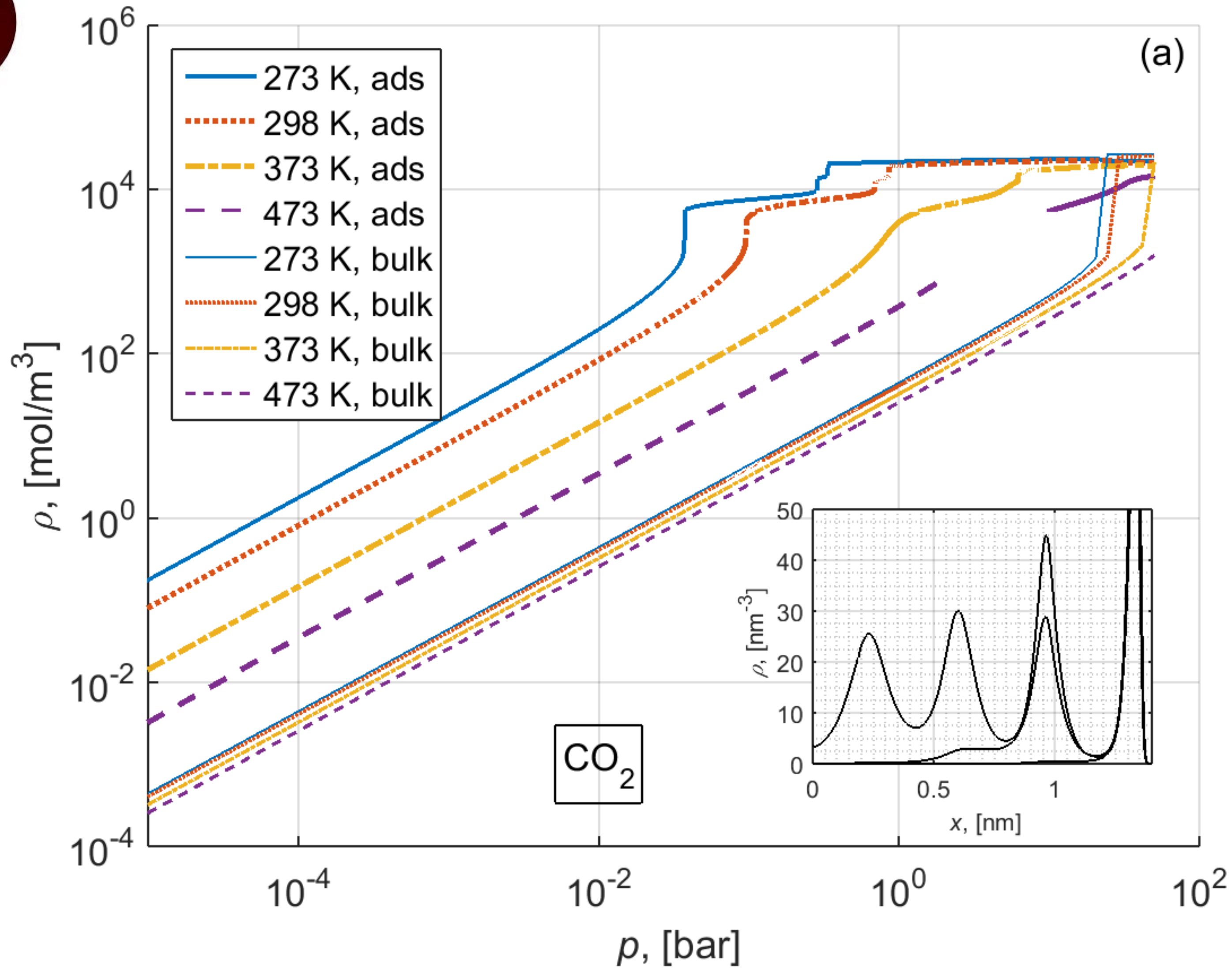


- Excess resistance

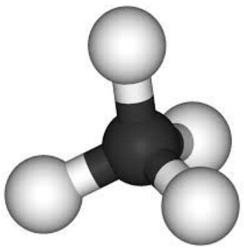
$$R_s = \int_{z_-}^{z_+} r(z)\,dz - r_-(z_s - z_-) - r_+(z_+ - z_s)$$

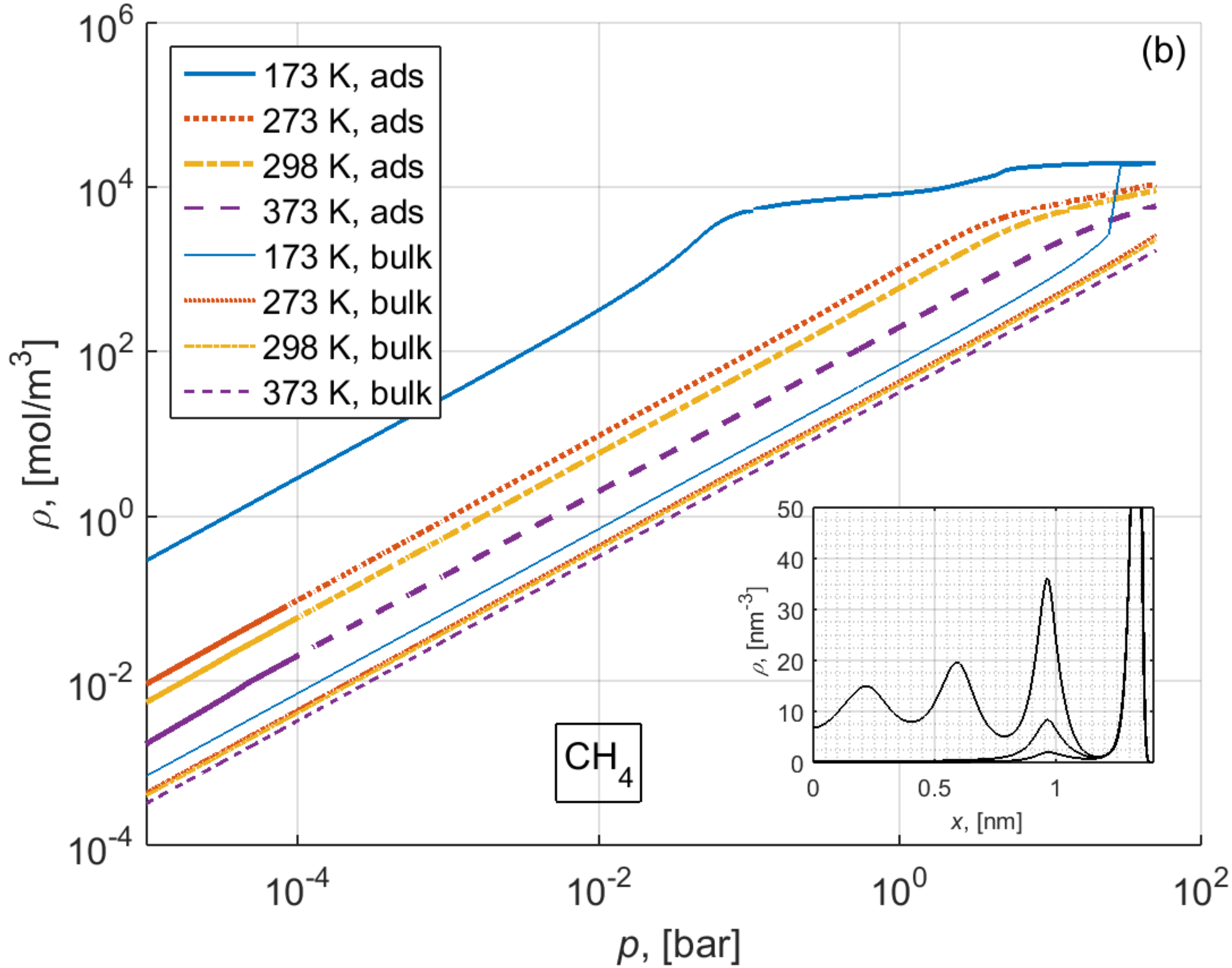
Adsorption isotherms: temperature



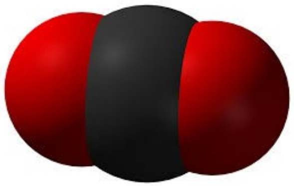


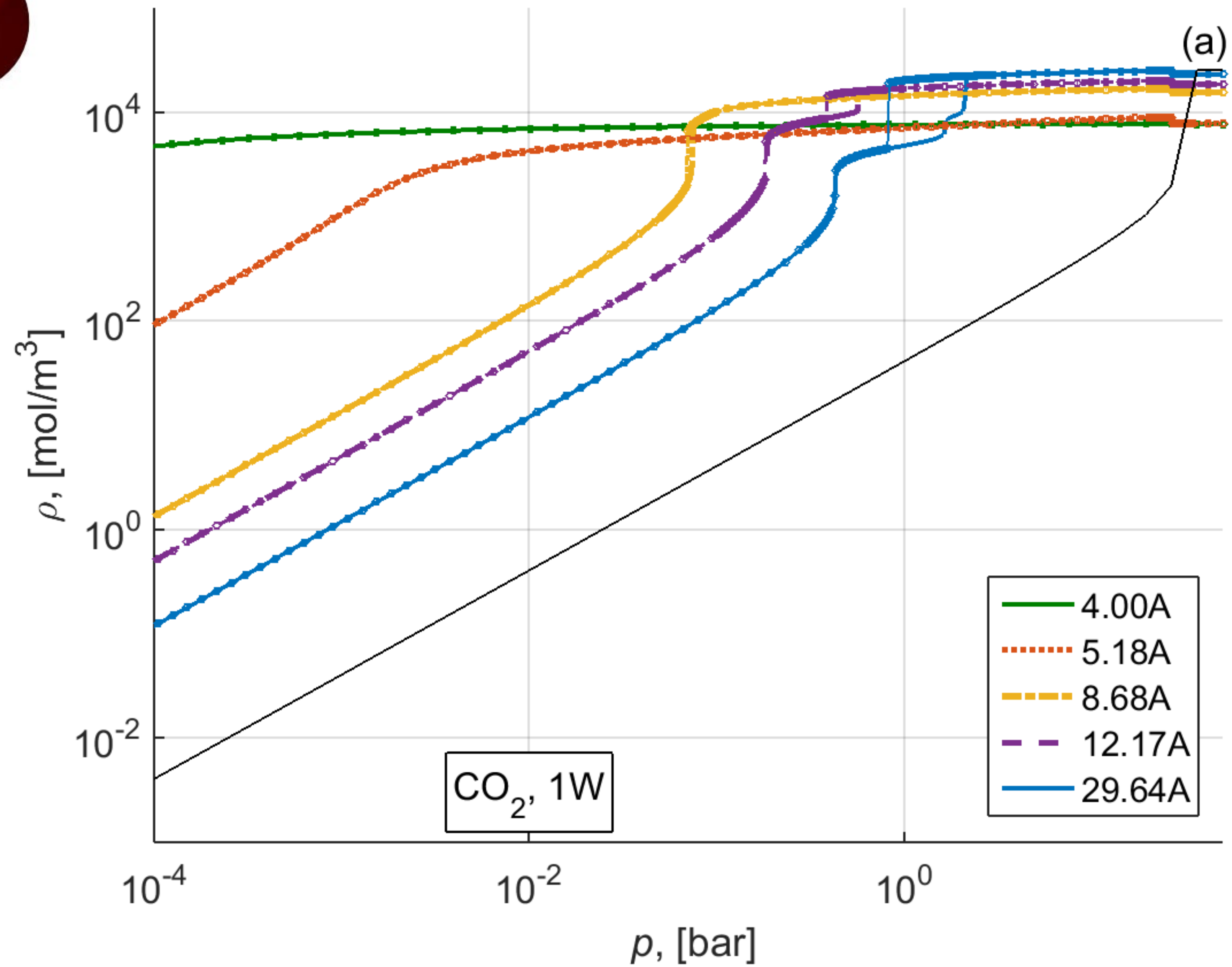
Adsorption isotherms: temperature



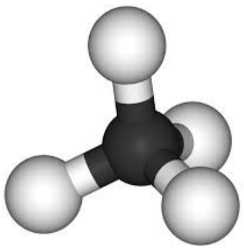


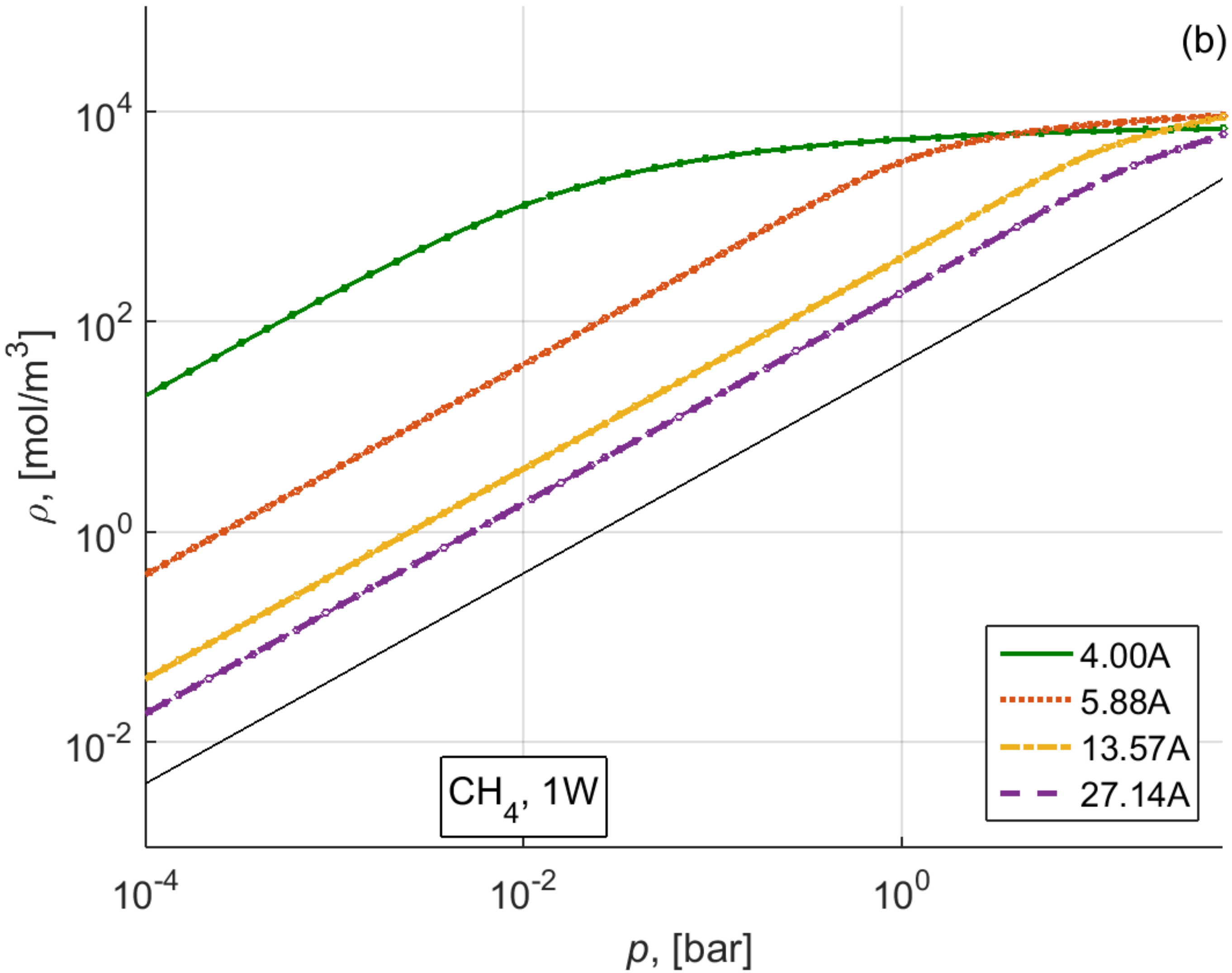
Adsorption isotherm: pore size



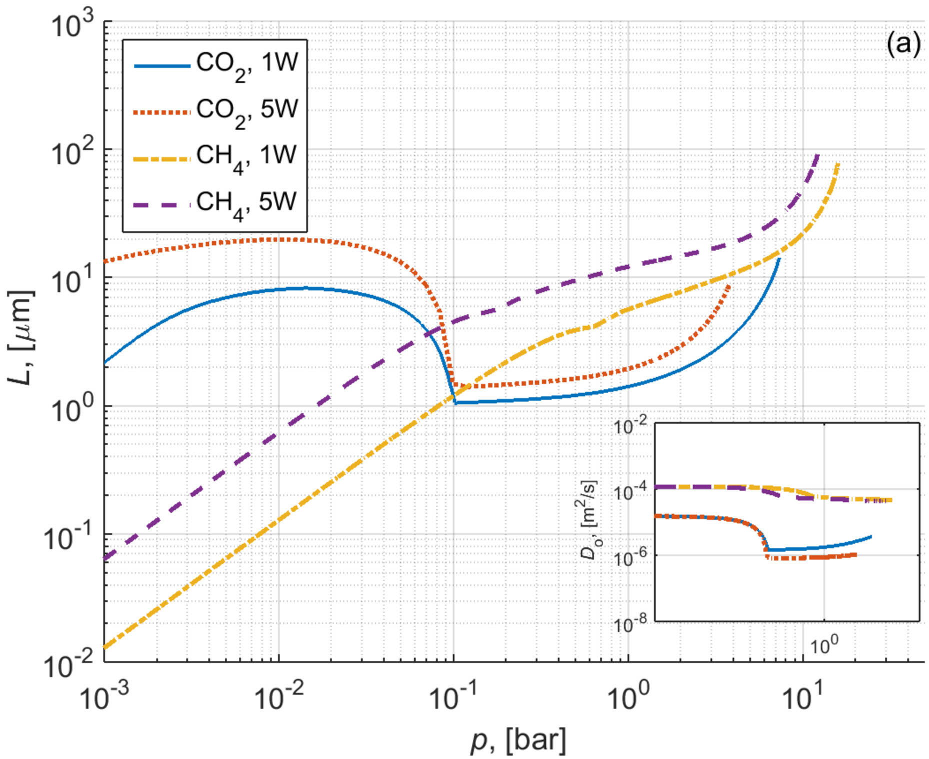


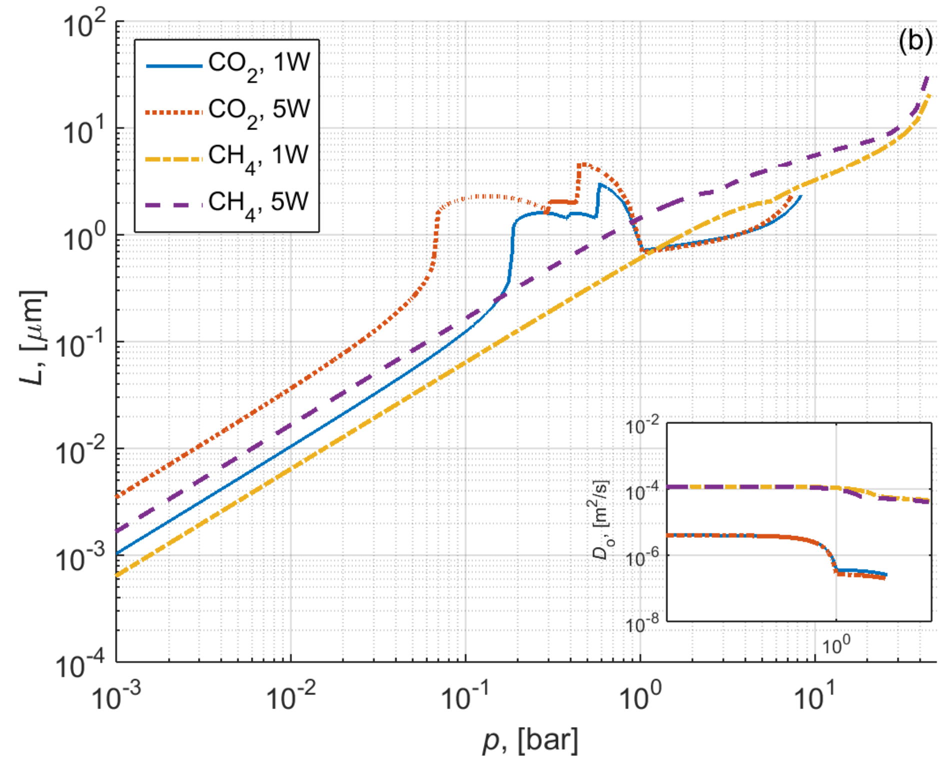
Adsorption isotherm: pore size





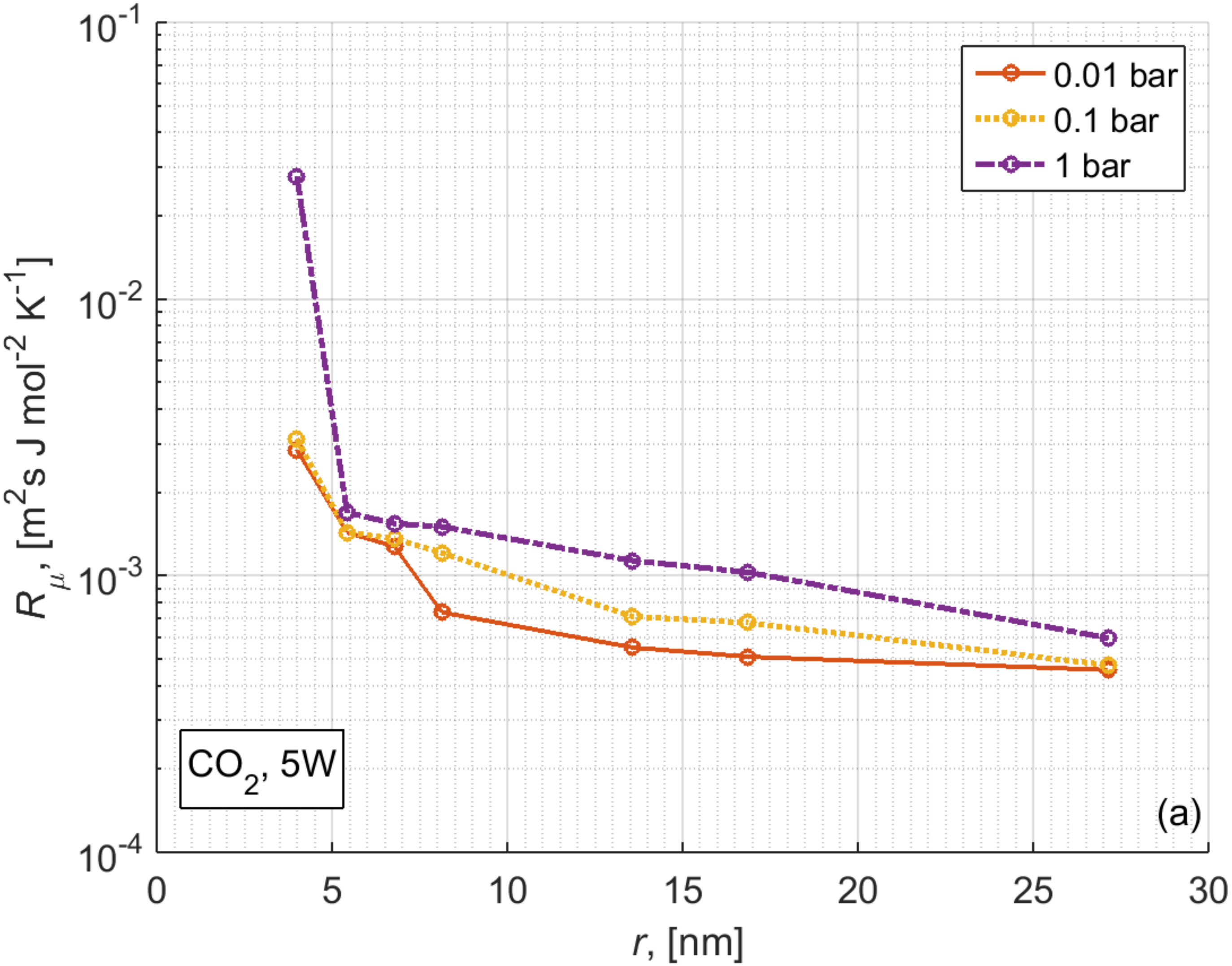
- 5 Å
- 13 Å



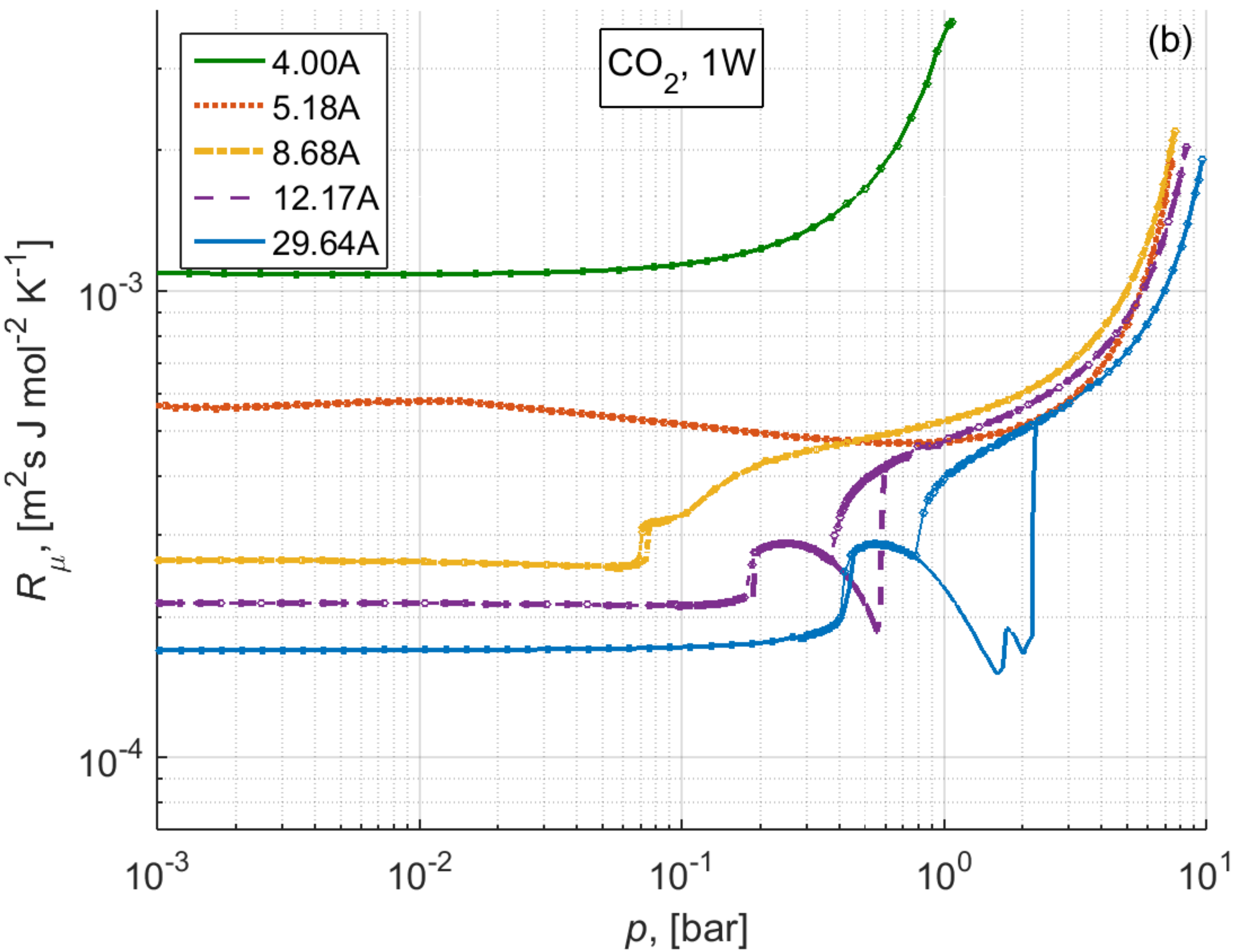


Length of the nanotube, which has the same internal resistance as the interfacial resistance

Resistance vs pore size



Resistance vs pressure



Summary: porous transport

- Confinement:
  - energy redistribution under constraints
- Altered phase diagram
  - closed system + compressible fluid
- Effect is larger for smaller system

- Phase transition leads to extra resistance
- Interactions with network are relevant

Acknowledgments

- *Thanks to*
  - David Reguera
  - Dick Bedeaux
  - Suresh Bhatia
  - Peter Daivis

VISTA

Det Norske Videnskaps-Akademi

Statoil

Australian Government

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- *J. Chemical Physics 138*, 204708 (2013)
- *Langmuir* 32, 3400 (2016)
- *J. Membrane Science* 524, 738-745 (2017)