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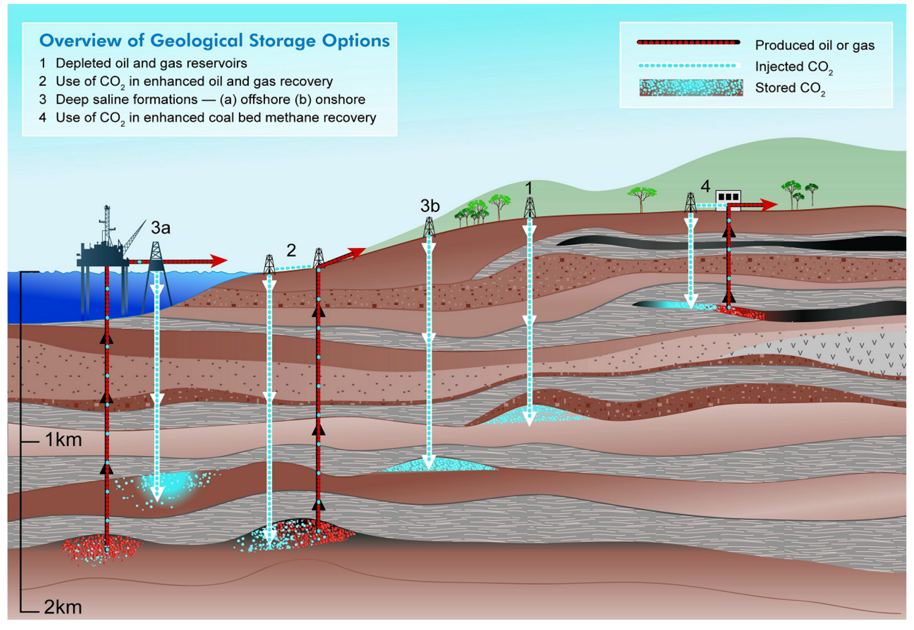
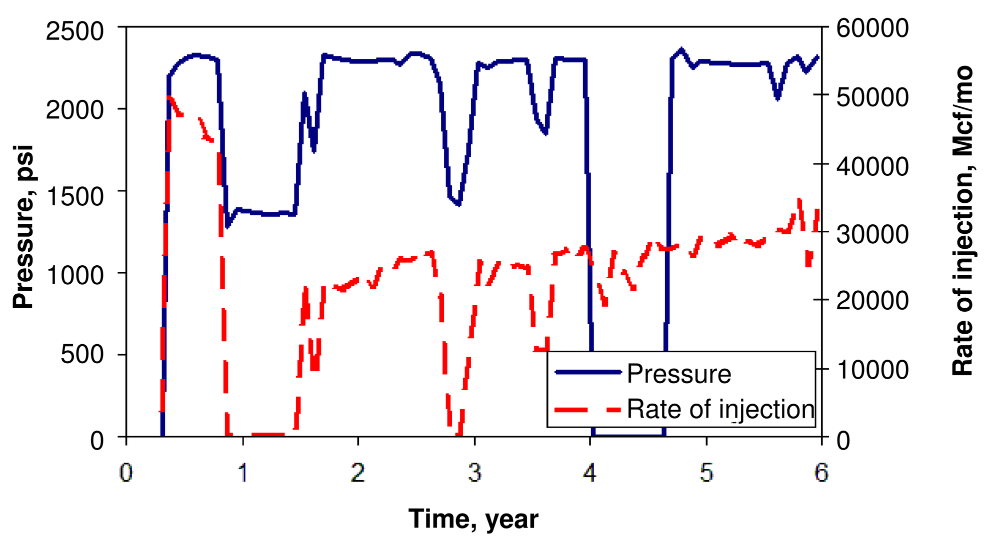
CONTEXT - CARBON SEQUESTRATION AND SWELLING OF COAL

In most scenarios for stabilization of atmospheric greenhouse gas concentrations [...] CCS contributes 15 - 55% to the cumulative mitigation effort worldwide

(From: IPCC report on Carbon Capture and Sequestration (2005))



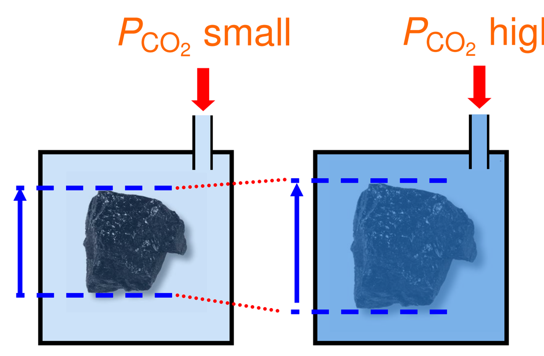


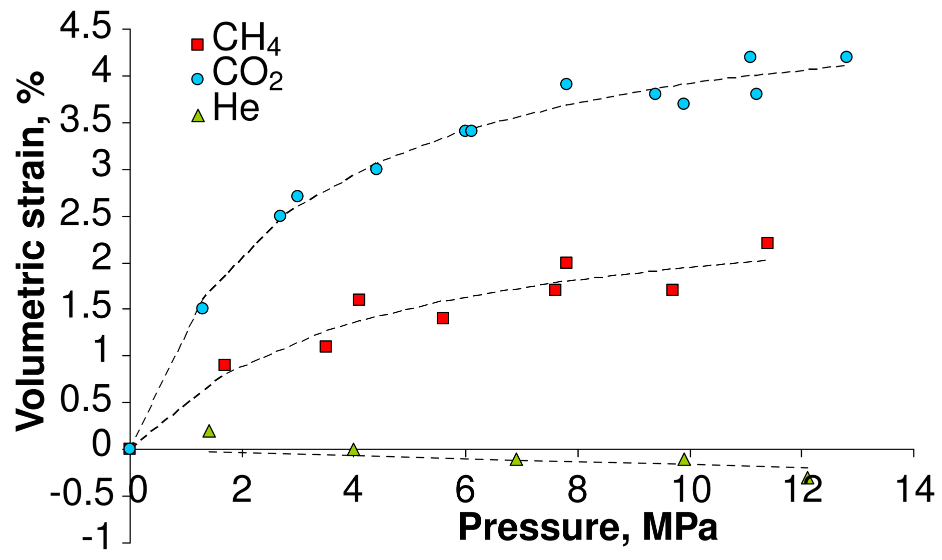
(adapted from Pekot & Reeves (2002))

Sequestration in coalbeds is promising (long term storage is safe and natural gas can be recovered, which improves the financial viability), but it is affected by a permeability issue. The injection pilots have encountered an important loss of permeability of the reservoir, after a few months of injection. Left: case of the Allison Unit, San Juan Basin (NM), US DOE.

Cause: coal swells more in a CO_2 atmosphere than in a CH_4 atmosphere

Experiment: inject either CO_2 or CH_4 in a coal sample free of stress





(adapted from Ottiger et al. (2008))

Conventional poromechanics fails to explain the swelling

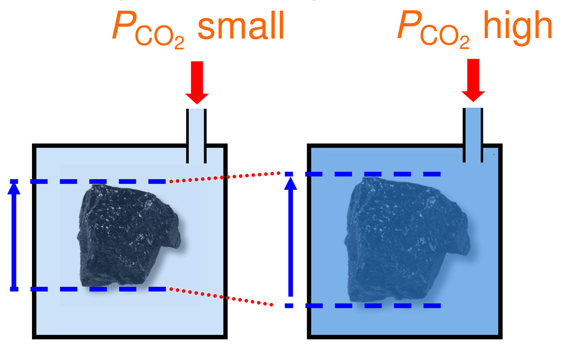
Helmholtz free energy of the solid matrix of a saturated isotropic porous medium:

$$f_{solid} = \frac{1}{2}\left(K + b^2 N\right)\epsilon^2 - bN\epsilon\varphi + \frac{N}{2}\varphi^2 + \sum_{i,j\in\{1,2,3\}} \frac{G}{2}e_{ij}^2$$

where:

- ϵ is the volumetric strain,
- φ the change of porosity,
- G the shear modulus,
- and N the Biot modulus.
- e_{ij} the deviatoric strains,
- K the bulk modulus,
- b the Biot coefficient,

Unjacketed experiment:



The volumetric stress is obtained with the state equation:

$$\sigma = \left.\frac{\partial f_{solid}}{\partial \epsilon}\right|_{\varphi, e_{ij}} = K\epsilon - bP$$

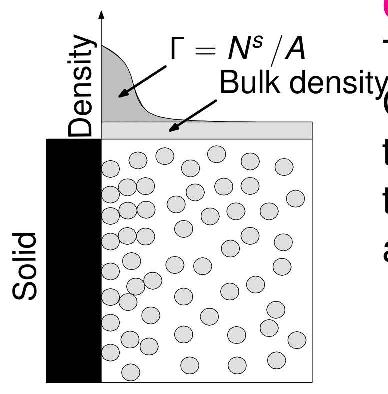
(Coussy (2010))

Conventional poromechanics predicts a shrinkage, and the same whatever the gas!

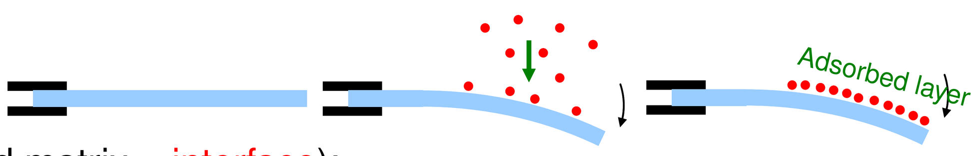
$$\sigma = -P \Rightarrow \epsilon = -\frac{1-b}{K}P < 0$$

Objective: Understand the physics of swelling and predict the permeability loss

CONVENTIONAL POROMECHANICS EXTENDED TO SURFACE EFFECTS



Contrary to CO_2 and CH_4, helium behaves as predicted by poromechanics. The difference stems from the adsorption (low for Helium, high for CO_2 and CH_4) which may have an impact on the mechanics of a solid, since it modifies the fluid-solid interface energy γ_{FS} (Gibbs adsorption equation, at fixed temperature and interface area): $d\gamma_{FS} = -\Gamma d\mu$. The mechanical impact of adsorption can be sketched in the case of a thin plate:



Helmholtz free energy of the (solid matrix + interface):

$$f_{solid} = \frac{1}{2}\left(K + b^2 N\right)\epsilon^2 - bN\epsilon\varphi + \frac{N}{2}\varphi^2 + \sum_{i,j\in\{1,2,3\}} \frac{G}{2}e_{ij}^2 + \gamma s$$

- s the specific surface.,
- and γ_{FS} the fluid-solid interface energy.

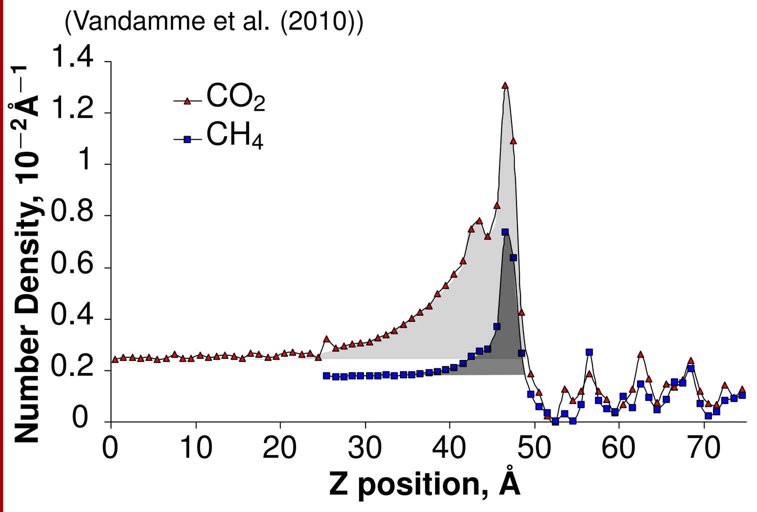
$$\sigma = K\epsilon - bP + \tilde{\sigma}_s \left.\frac{\partial s}{\partial \epsilon}\right|_P \text{ where } \tilde{\sigma}_s = \gamma + s\frac{\partial \gamma}{\partial s} \text{ is the interface stress.}$$

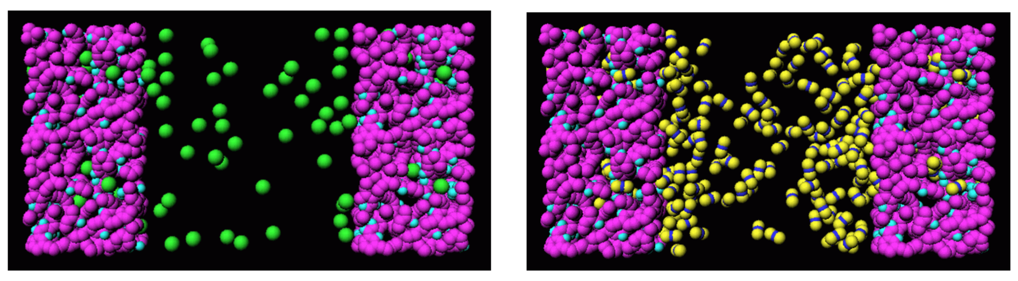
(Vandamme et al. (2010))

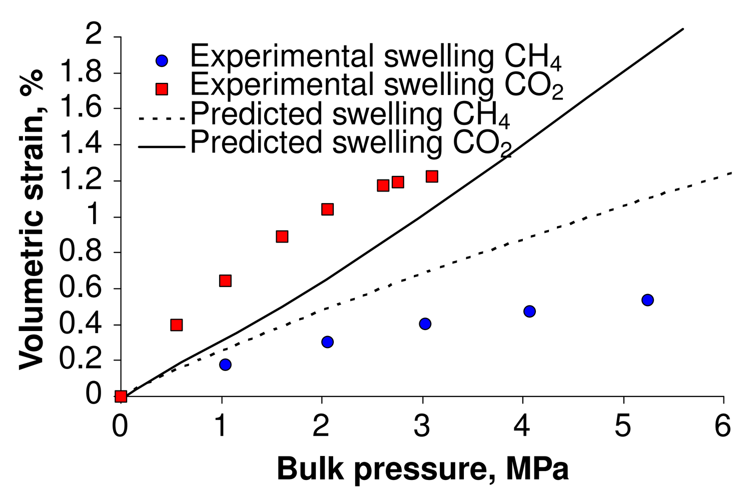
Predicts a possible swelling, specific to each fluid:

$$\epsilon = -\frac{1-b}{K}P - \frac{\Delta\tilde{\sigma}_s}{K}\left.\frac{\partial s}{\partial \epsilon}\right|_P \quad (1)$$

with $\Delta\gamma = -\int_{\mu_0}^{\mu}\left(\frac{N^{Ex}}{A}d\mu\right)$ and $\Delta\tilde{\sigma}_s = \Delta\gamma + s\frac{\partial \Delta\gamma}{\partial s}$







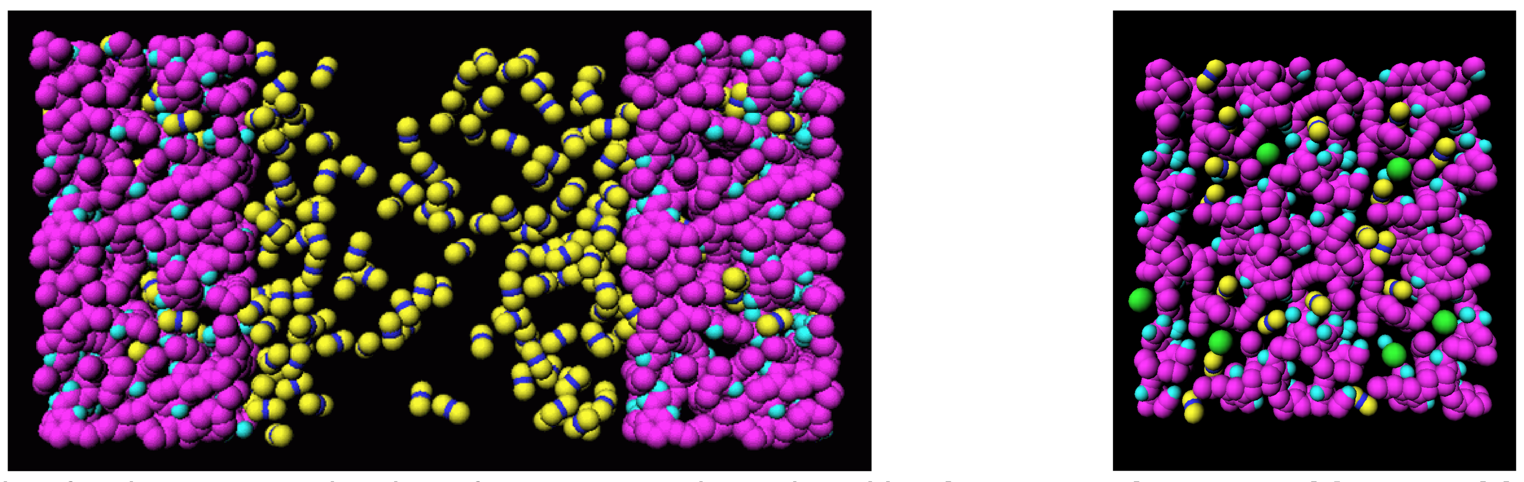
CO_2 and CH_4 density profiles on the surface of coal matrix were obtained by molecular simulation.The swelling predicted by the model (Equation 1) is compared to the experimental swelling.

The model does not capture the experimental swelling

(Experimental data from Levine (1996))

POROMECHANICS OF NANOPORE ADSORPTION

Explanation: Adsorption occurs also in the nanopores of the solid matrix.



Guideline for the poromechanics of nanopore adsorption: Use **known and measurable quantities only**. Questionable quantities (porosity, specific surface) should not intervene.

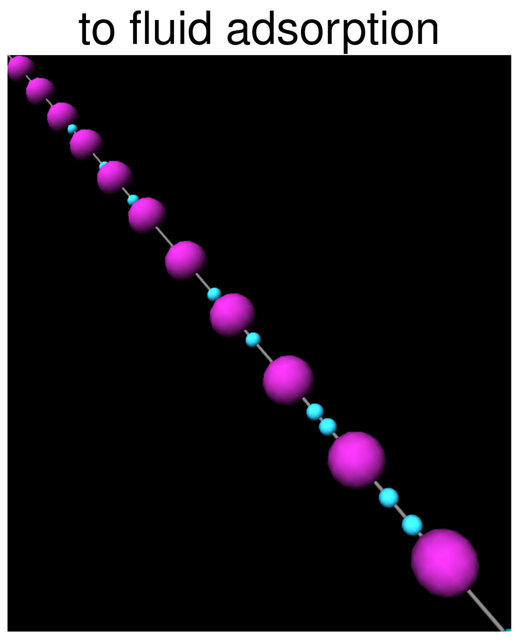
Behavior law of a porous solid subjected to a fluid under any form (bulk, surface adsorption, nanopore adsorption...)

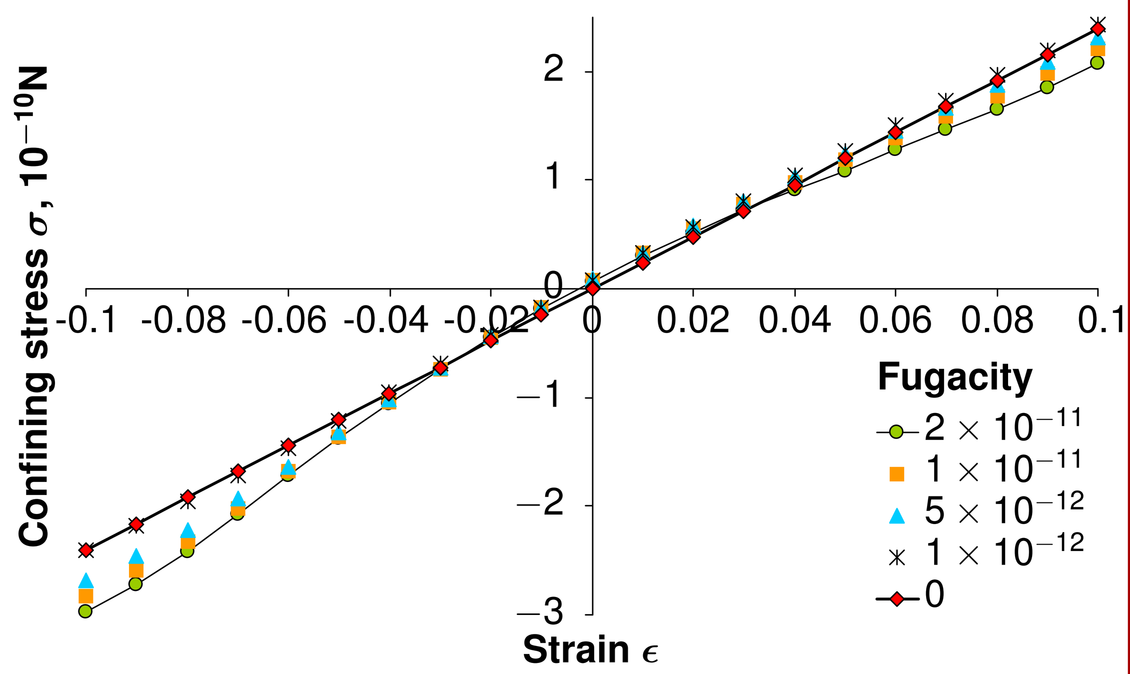
$$\sigma = \frac{df_S}{d\epsilon} - \left.\frac{\partial}{\partial \epsilon}\left(\int_{-\infty}^{\mu}\frac{N}{V_0}d\mu\right)\right|_{\mu} \quad (2)$$

- V_0 is the volume of the porous solid under unstressed conditions,
- N is the number of fluid molecules whatever their state (adsorbed in nanopores, on surfaces, bulk...).
- $f_S = F_S/V_0$ and F_S is the free energy of the sole solid, that is when there is no fluid molecule in the pores. $f_S = \frac{1}{2}K\epsilon^2$ for an elastic solid.

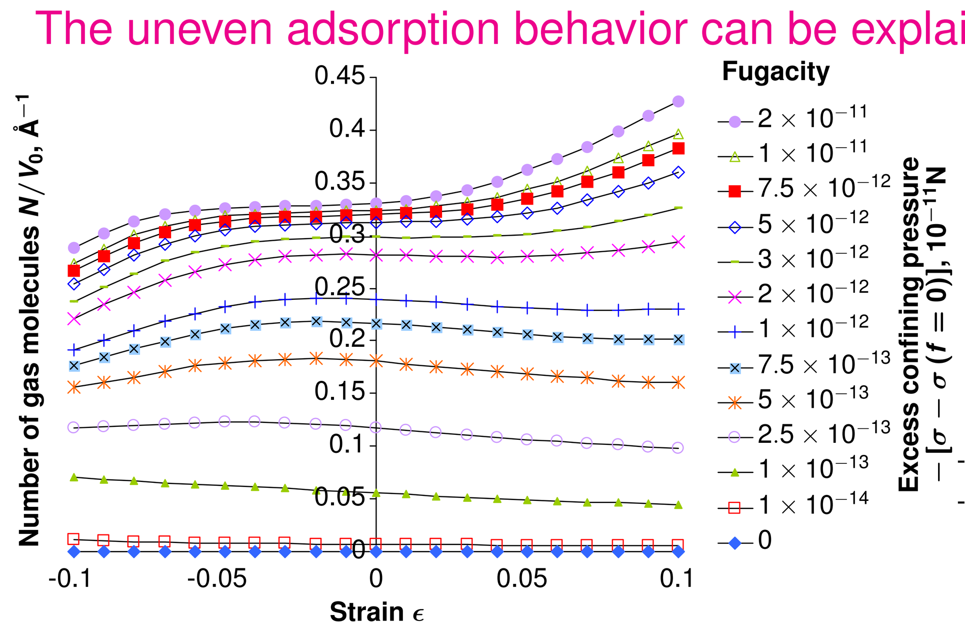
Requires to know the adsorbed amount as a function of both μ and ϵ.

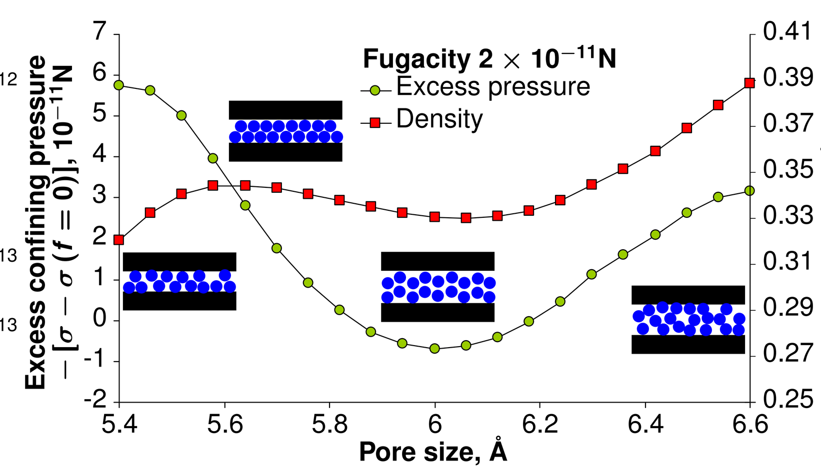
Case of a 1D chain subjected to fluid adsorption





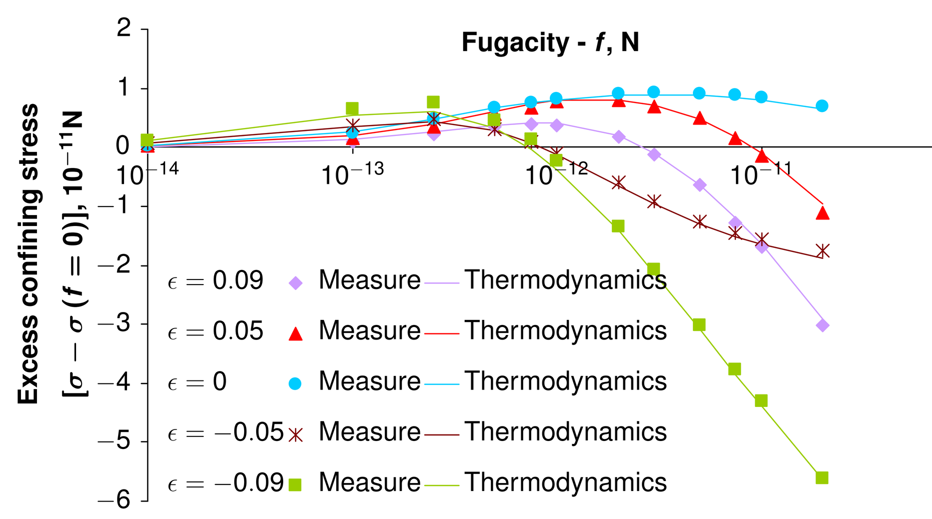
The uneven adsorption behavior can be explained by the pore commensurability



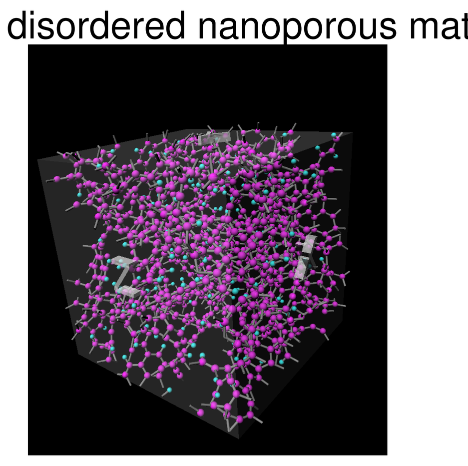


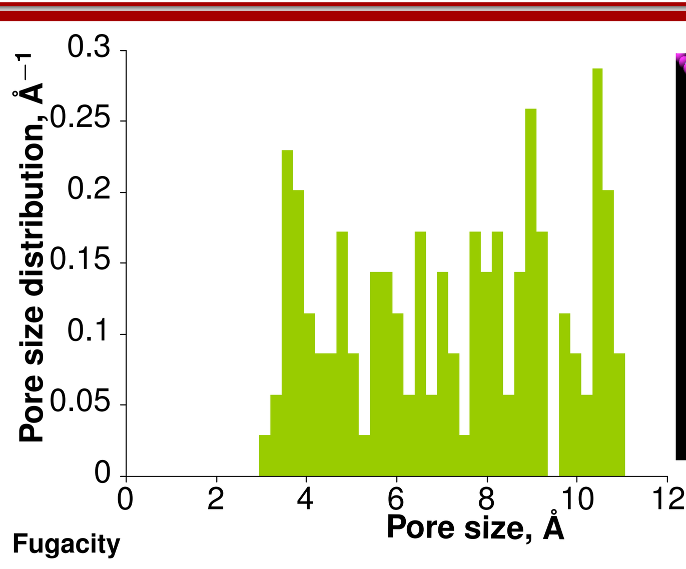
The excess stress directly computed (virial estimate) and the excess stress predicted by the proposed thermodynamics (Equation 2) are consistent.

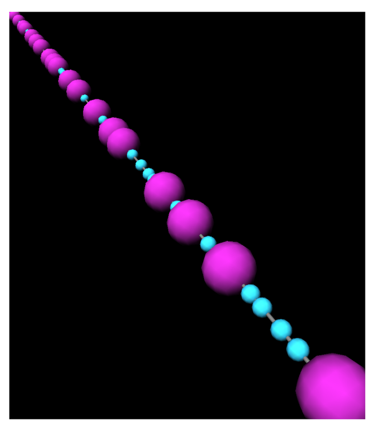
$$\sigma - \sigma(f=0) = -\left.\frac{\partial}{\partial \epsilon}\left(\int_{-\infty}^{\mu}\frac{N}{V_0}d\mu\right)\right|_{\mu}$$



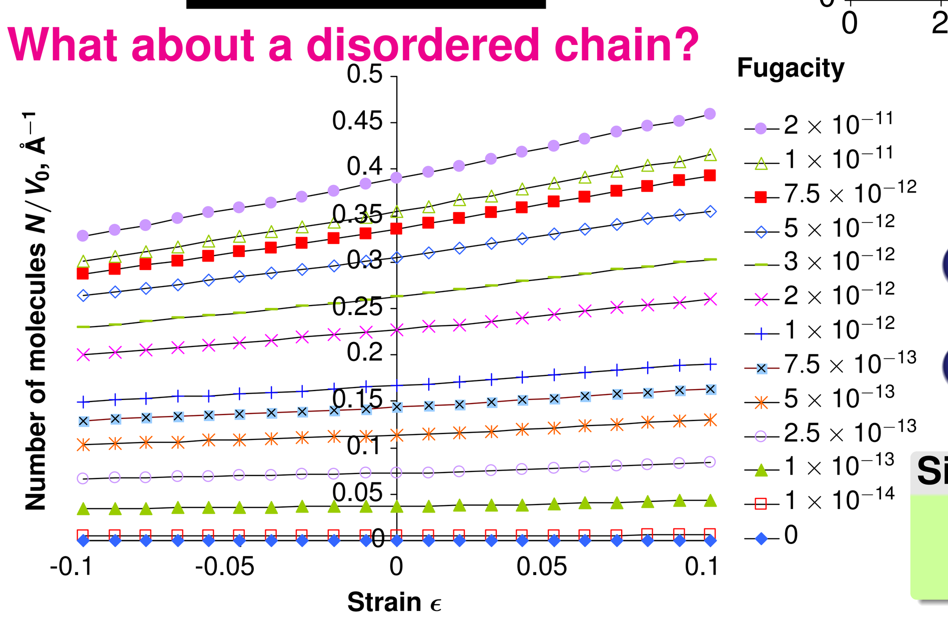
Coal is a disordered nanoporous matrix.







What about a disordered chain?



The adsorption behavior in the disordered chain is ordered!

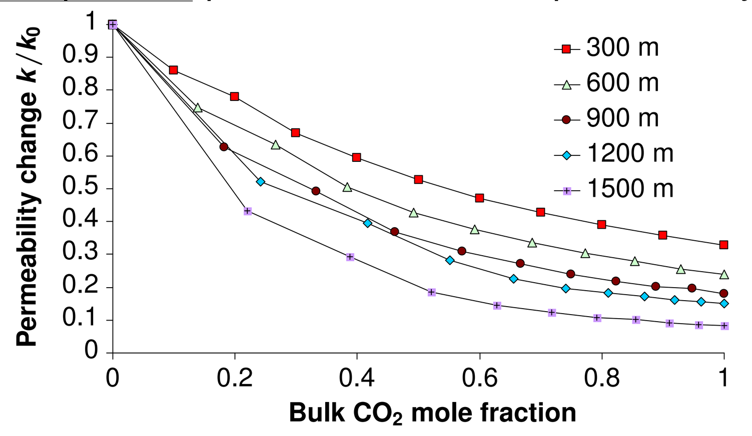
1. The amount adsorbed is a linear function of strain,
2. and the slope is proportional to the number of fluid atoms.

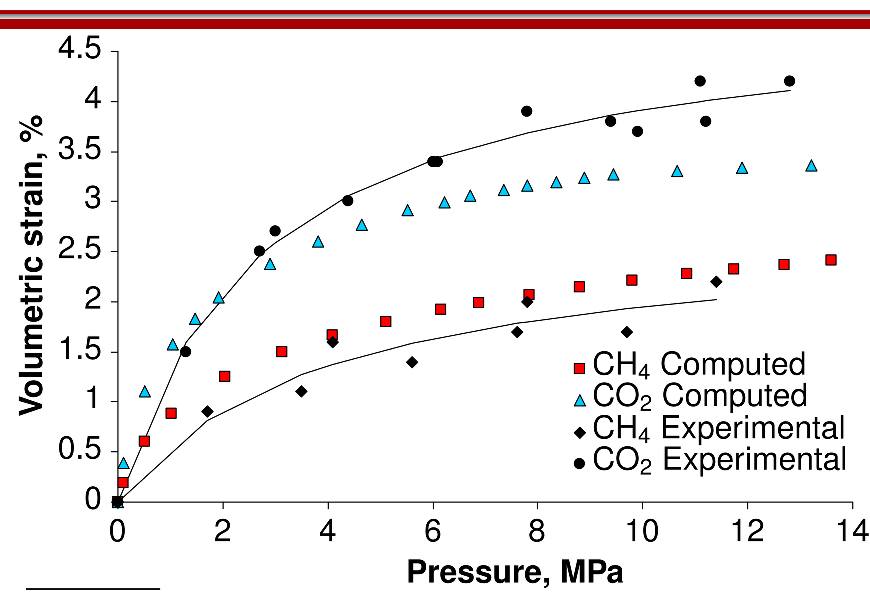
Simplified model

$$\sigma = \frac{df_S}{d\epsilon} - C\int_{-\infty}^{\mu}\frac{N(\epsilon = 0, \mu)}{V_0}d\mu$$

Swellings predicted with the simplified model are satisfying.

Perspective: predict the reservoir permeability





(Experimental results from Ottiger et al. (2008))