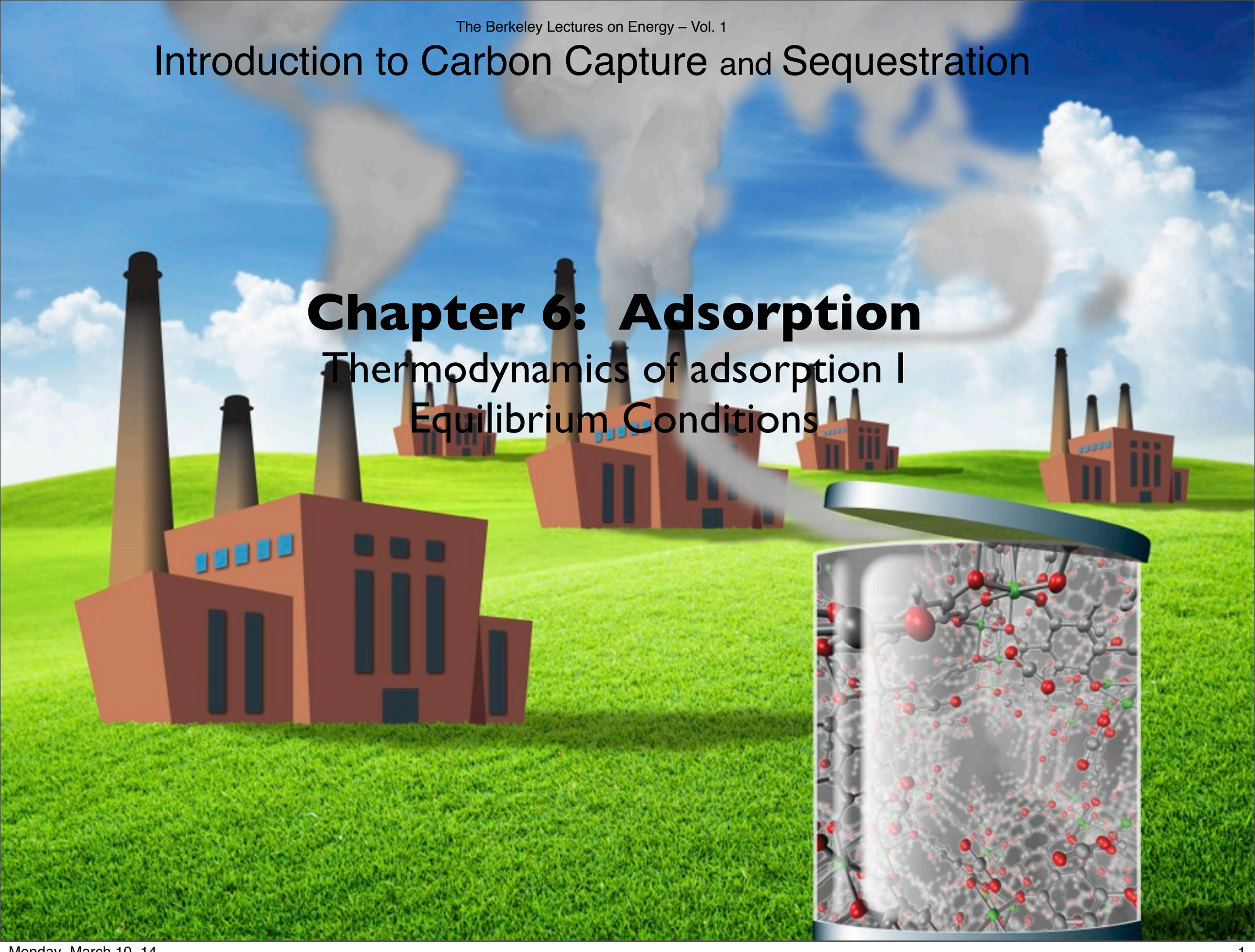
Introduction to Carbon Capture and Sequestration



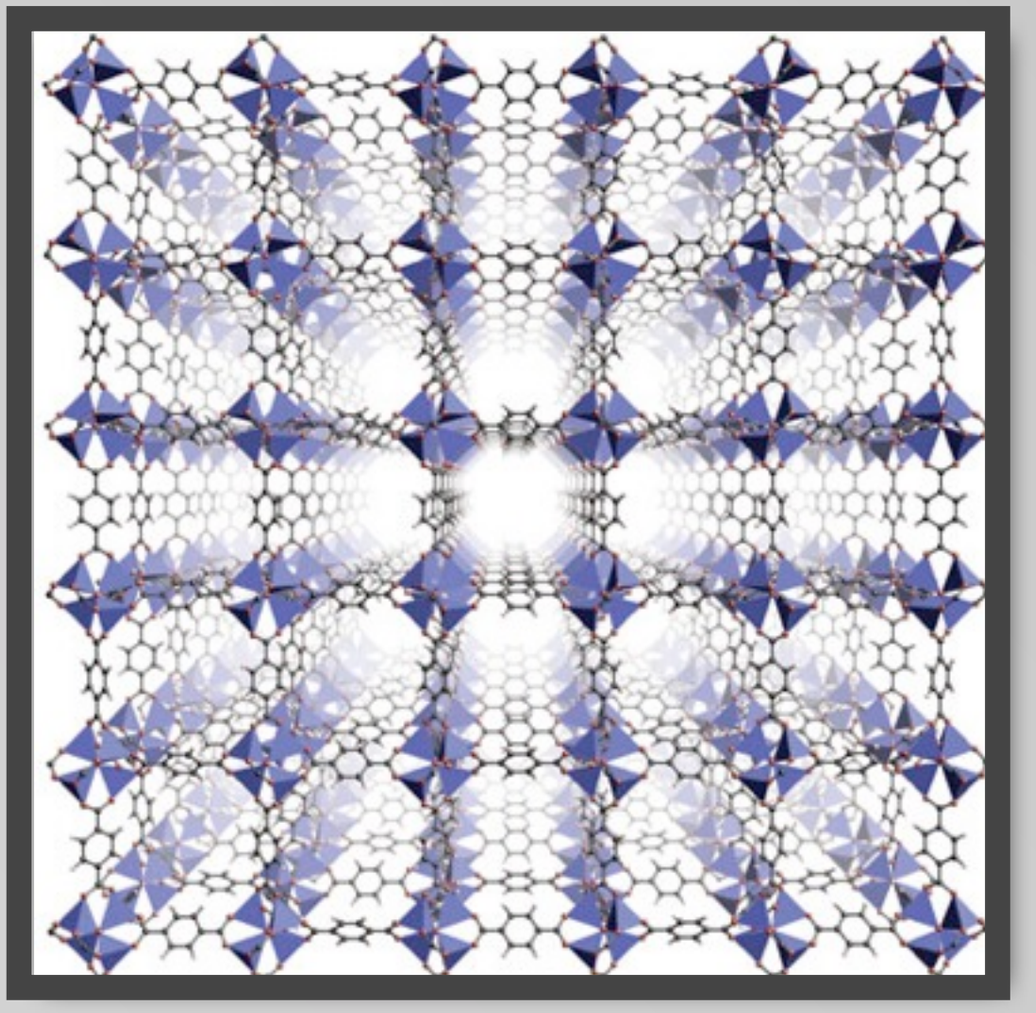
Chapter 6: Adsorption

Thermodynamics of adsorption I
Equilibrium Conditions

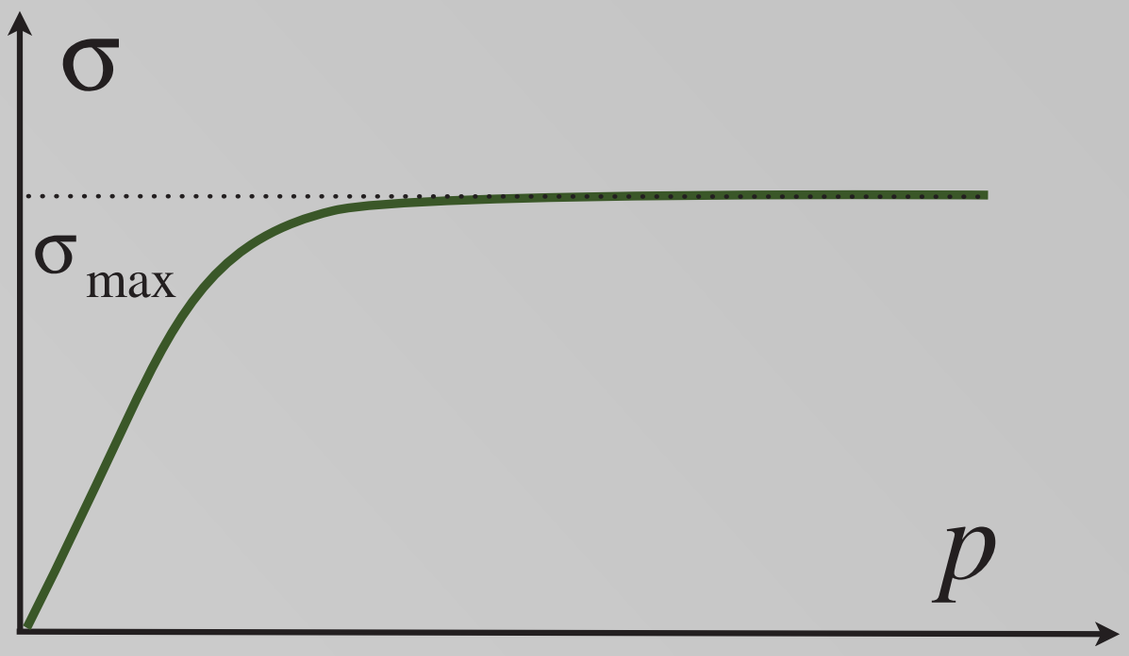
Chapter 6: Adsorption
Thermodynamics of Adsorption I (equilibrium conditions)

- Pressure in solids
- Equilibrium conditions
- Adsorption in rocks and nano-porous materials

Thermodynamics of adsorption

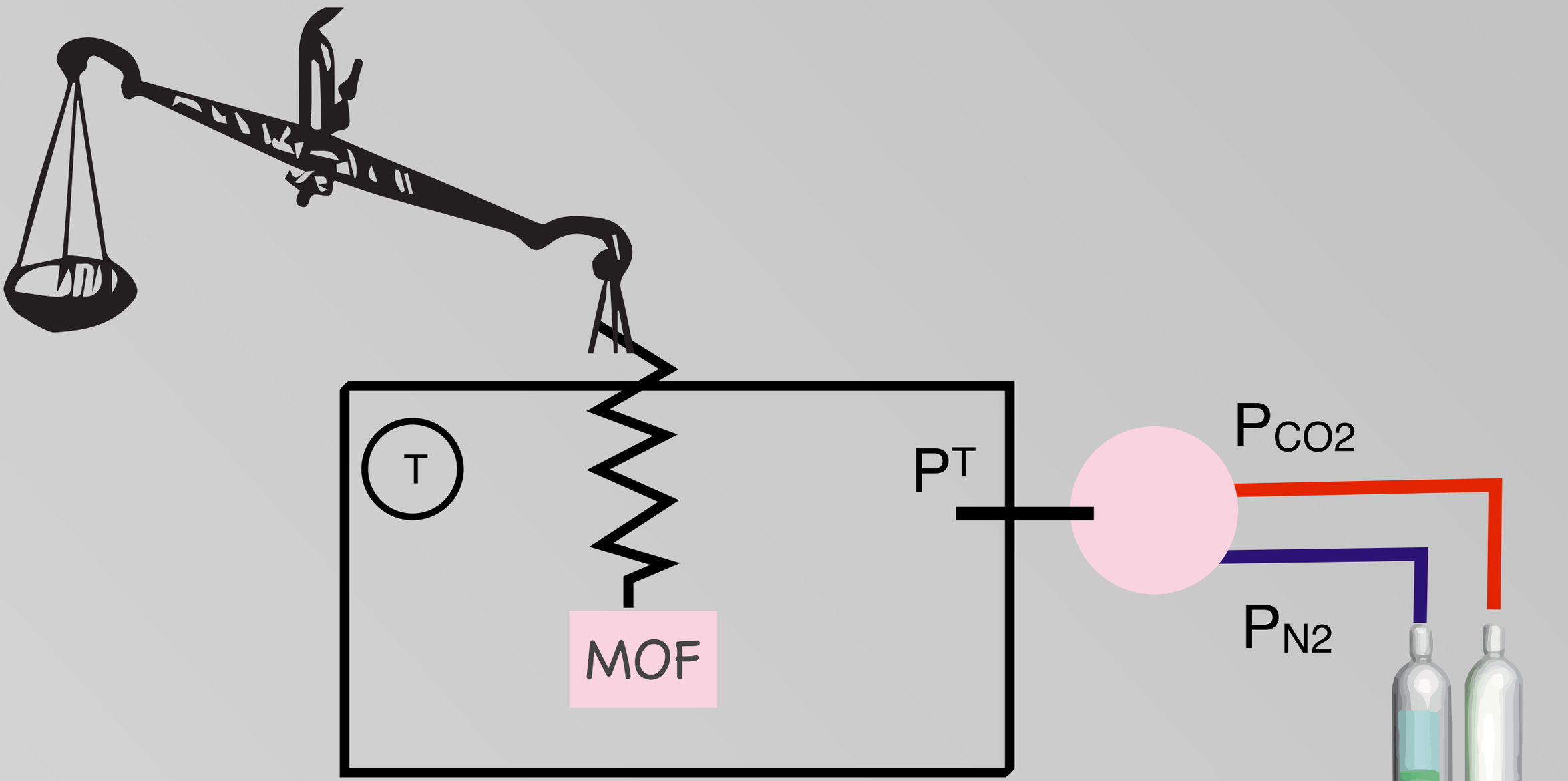


Metal Organic Framework



What are the appropriate thermodynamic variables?

Experimental setup



At <u>constant temperature</u> we measure the weight increase as a function of partial pressure of the gas

Thermodynamics of adsorption

What is the thermodynamic language of adsorption?

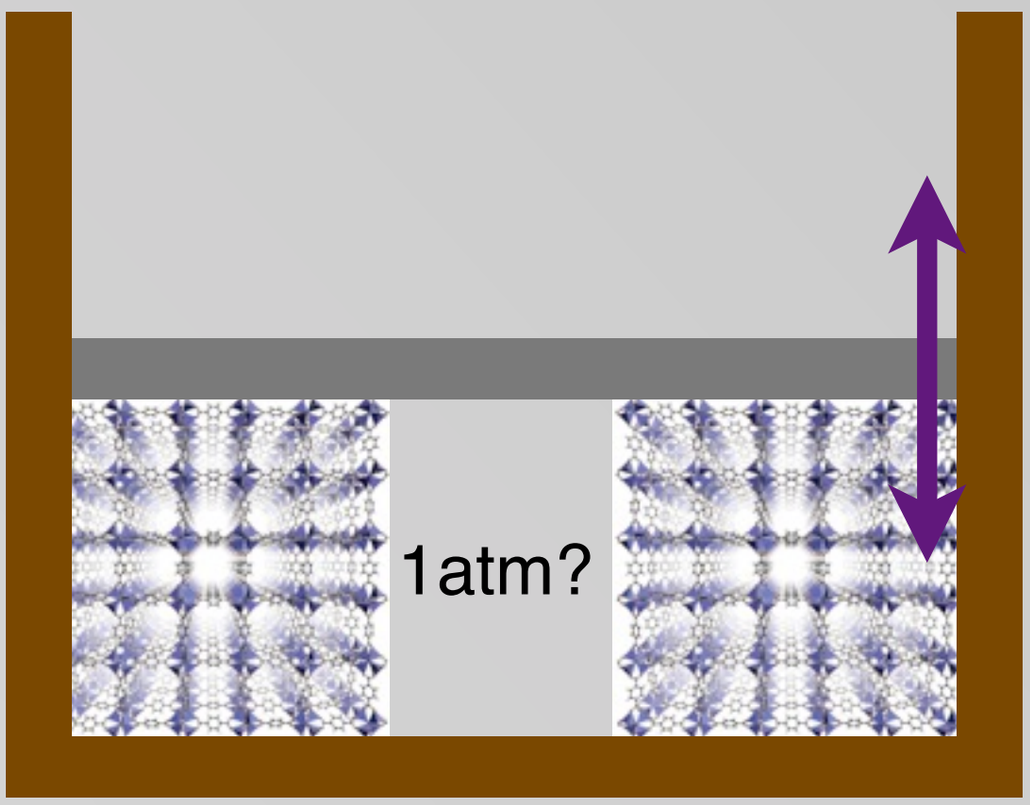
What are the equilibrium conditions?

Can we make a molecular model of adsorption?

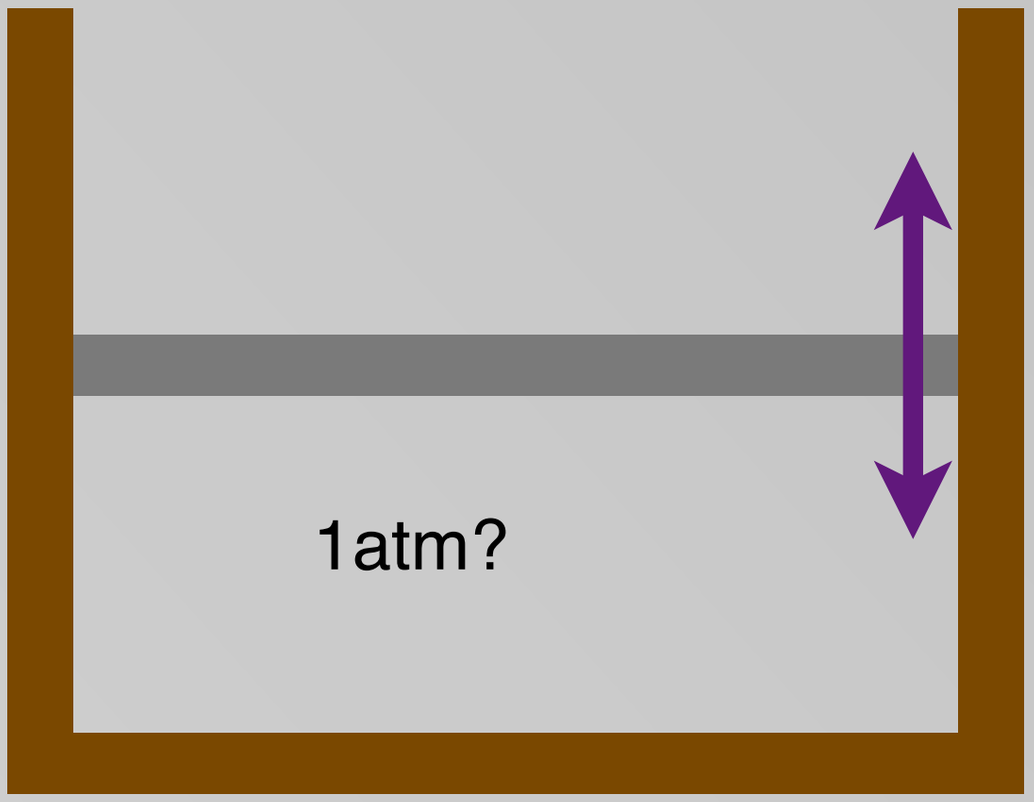
Pressure in Solids

How do we look at pressure in a solid?

Is pressure in a solid defined?



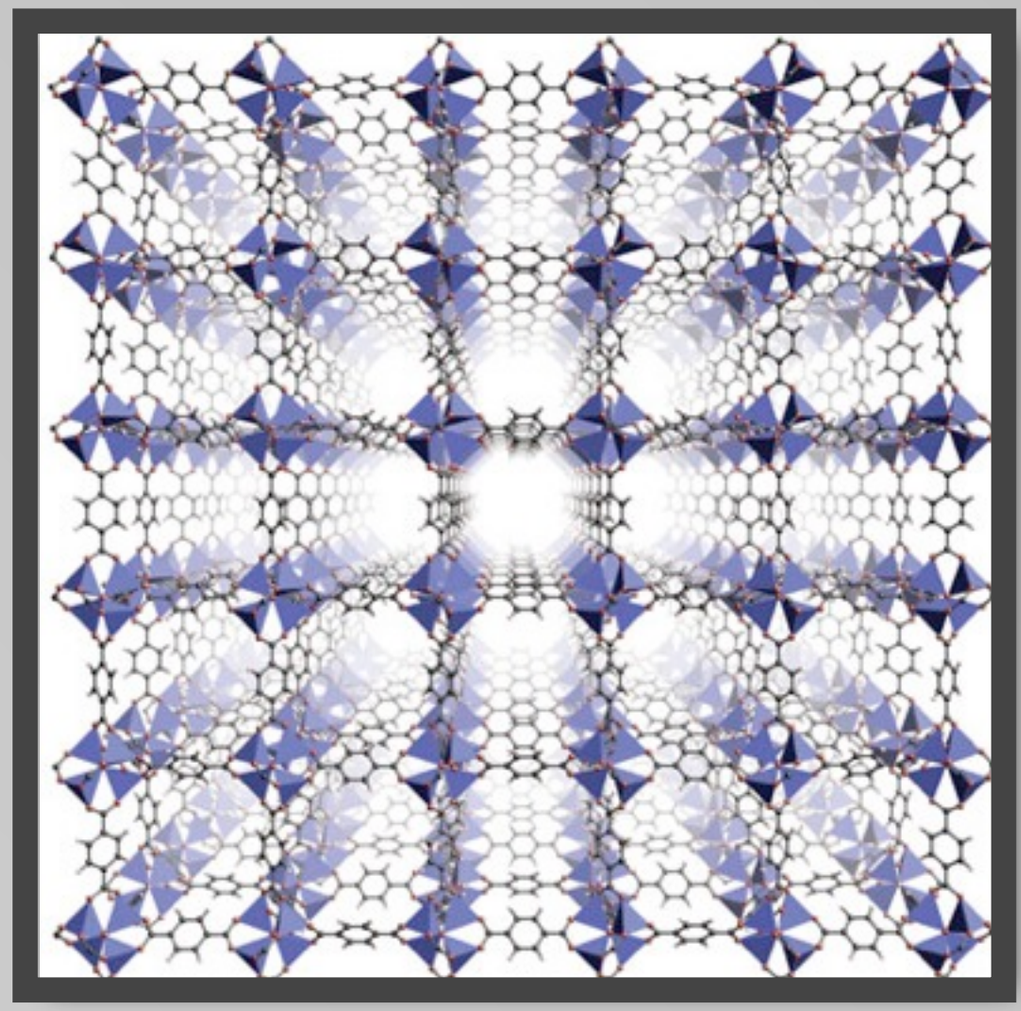
Gas + solid



Gas

Pressure

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$$



In a solid the free energy change to change the volume can be anisotropic

Is described by a **stress tensor**

Unlike a fluid a solid can resist strain; forces are much larger

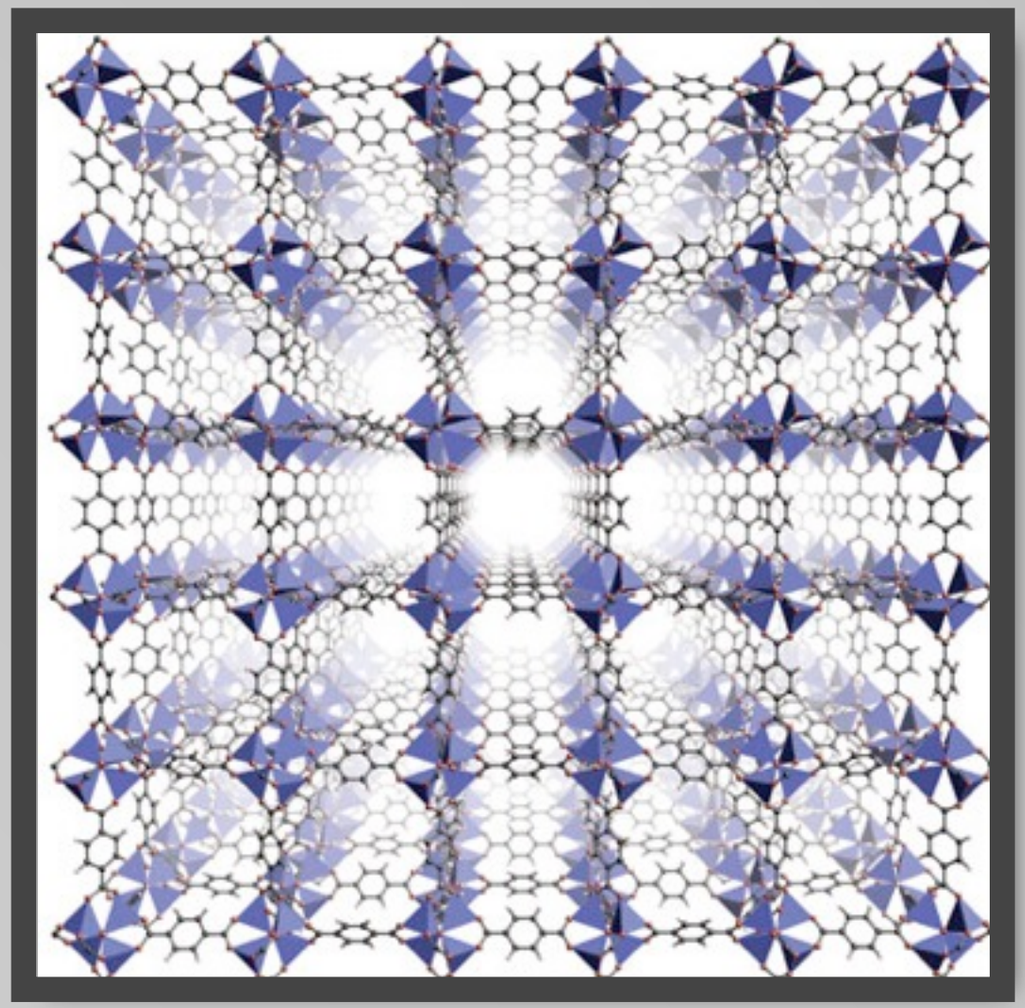
Does the adsorption isotherm of a brick change if we stand on it?

Pressure in a solid

Let us assume that in the pressure range of the isotherm the solid does not deform

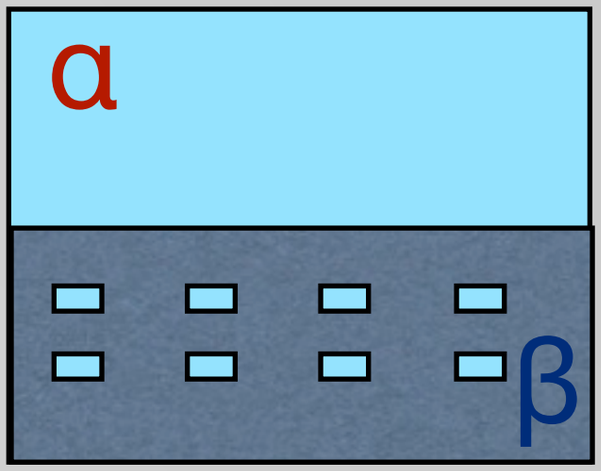
Hence,

$$\left(\frac{\partial F}{\partial V}\right)_{T,N} = \infty$$



We cannot change the **volume** of our solid; hence **pressure is not defined** inside the solid.

For these adsorption studies the pressure of the gas phase is not the preferred thermodynamic variable!



Equilibrium

A solid phase β and a large reservoir which is the fluid phase α

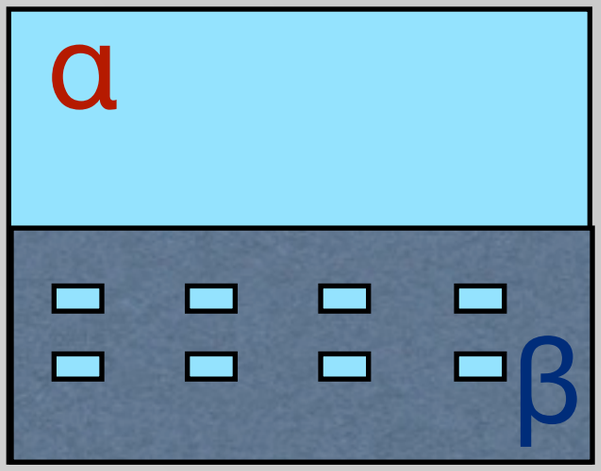
Question: When are these two systems in equilibrium?

Equilibrium: 2nd Law of Thermodynamics

For a system at constant energy U, number of particles N, and volume V: entropy is maximal

Total system NVU: **dS ≥ 0**

$$dS = dS_\alpha + dS_\beta \geq 0$$



Total system NVU: **dS ≥ 0**

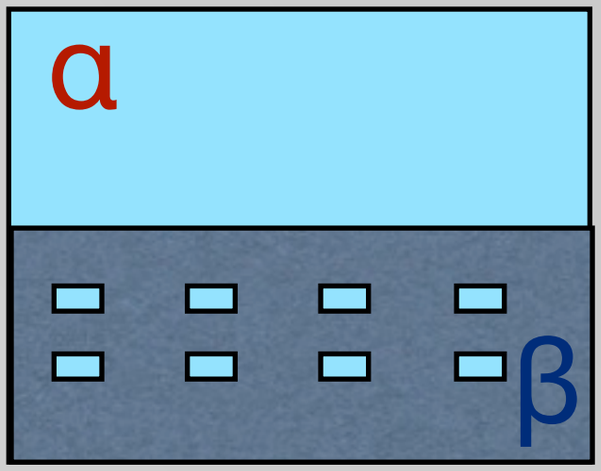
$$dS = dS_\alpha + dS_\beta \geq 0$$

1st Law of Thermodynamics:

$$dU = TdS - pdV + \sum_i \mu_i dN_i$$

Chemical potential of component i

the change in internal energy if we add a particle while keeping the entropy and volume constant



Total system NVU: **dS ≥ 0**

$$dS = dS_\alpha + dS_\beta \geq 0$$

$$dS_\beta = \frac{1}{T_\beta} dU_\beta + \cancel{\frac{p}{T_\beta} dV_\beta} - \sum_i \frac{\mu_i^\beta}{T_\beta} dN_i^\beta$$

As the total system is at constant *U* and *N:*

$$dU_\alpha + dU_\beta = 0$$

$$dN_\alpha + dN_\beta = 0$$

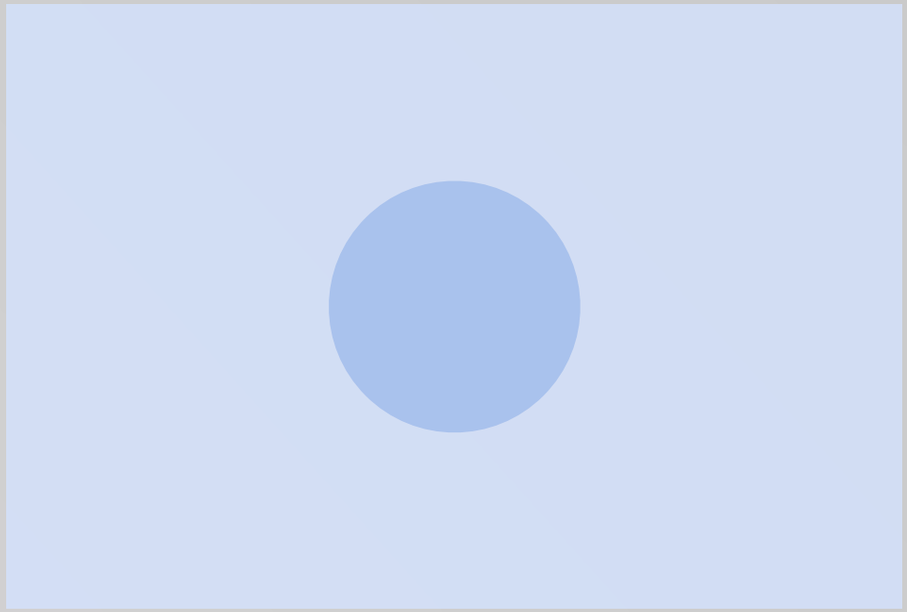
$$dS_\alpha + dS_\beta = \left(\frac{1}{T_\alpha} - \frac{1}{T_\beta} \right) dU_\alpha - \sum_i \left(\frac{\mu_i^\alpha}{T_\alpha} - \frac{\mu_i^\beta}{T_\beta} \right) dN_i^\alpha$$

Equilibrium:

$$T_\alpha = T_\beta \quad \wedge \quad \mu_i^\alpha = \mu_i^\beta$$

Equilibrium: the adsorbed gas has an equal temperature and chemical potential as the reservoir

Capillary Forces



What is the pressure difference between the inside and the outside of the bubble?

$$-\Delta p \delta V + \gamma \delta A = 0$$

$$A = 4\pi R^2$$

Hence,

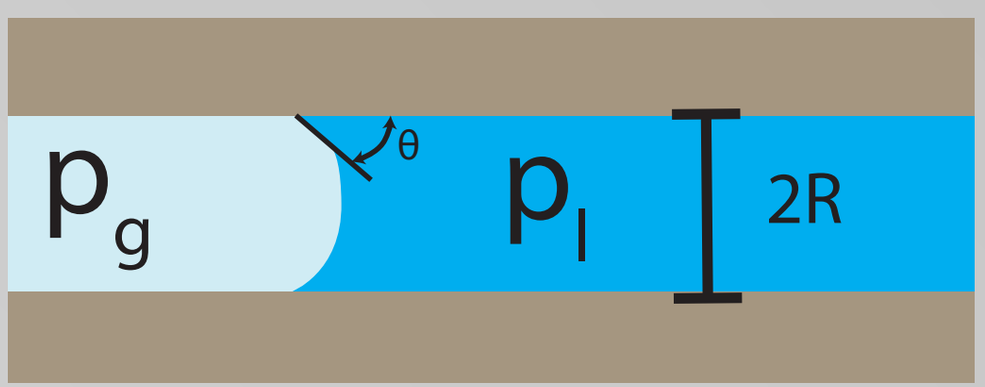
$$\Delta p = \frac{2\gamma}{R}$$

$$V = \frac{4}{3}\pi R^3$$

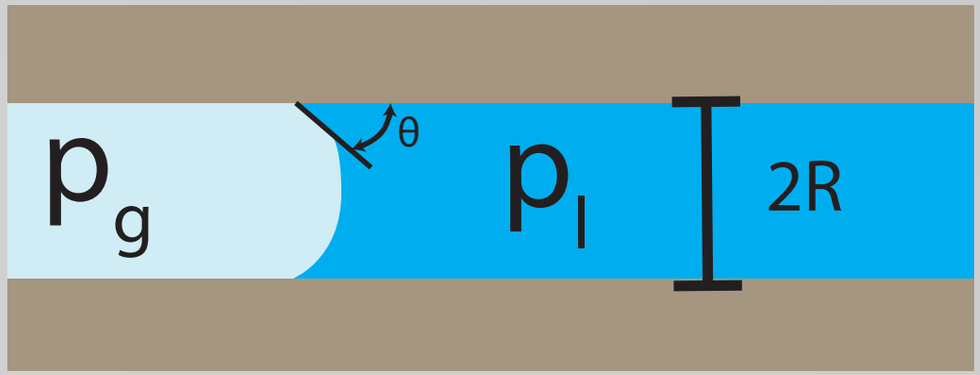
More general shape:

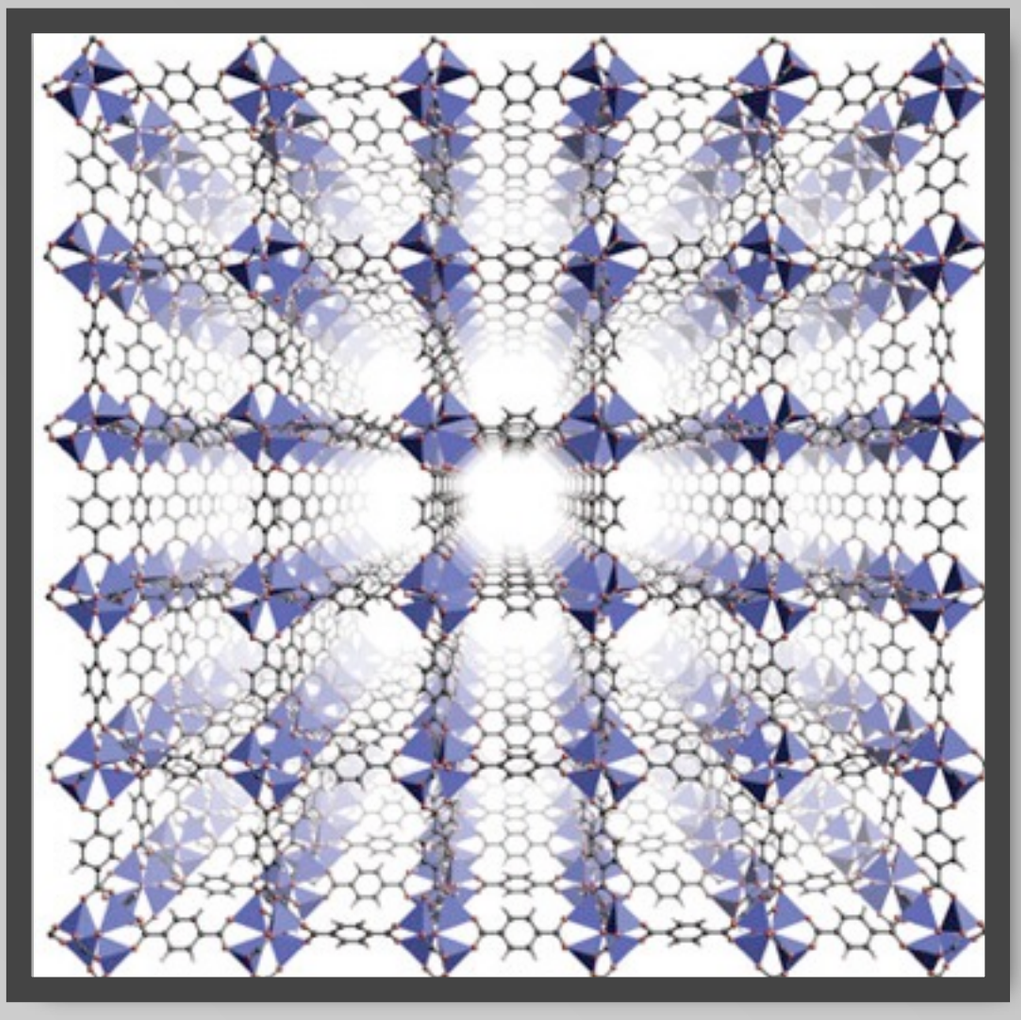
$$\Delta p = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$

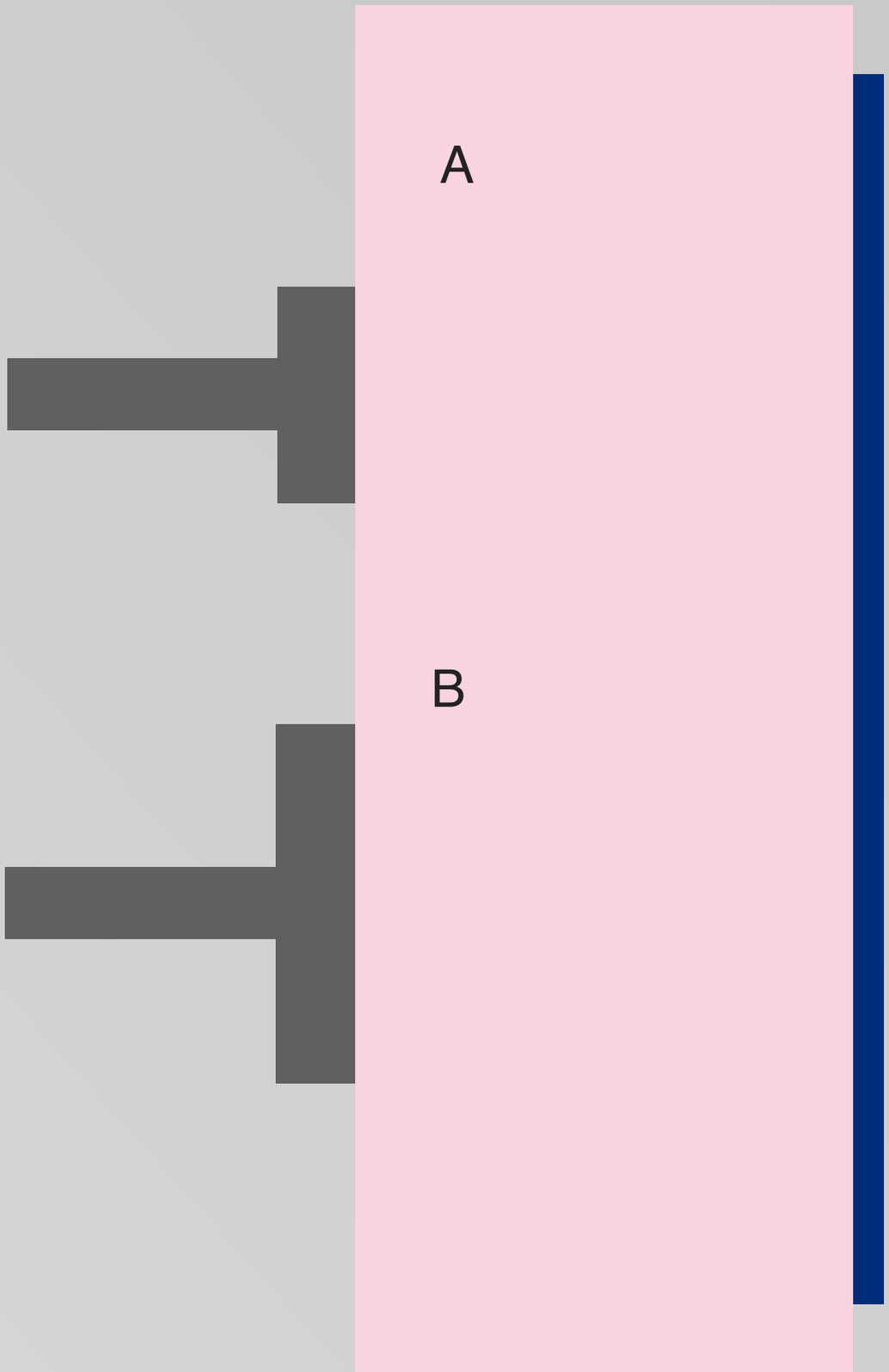
$$\frac{dA}{dV} = \frac{2}{R}$$



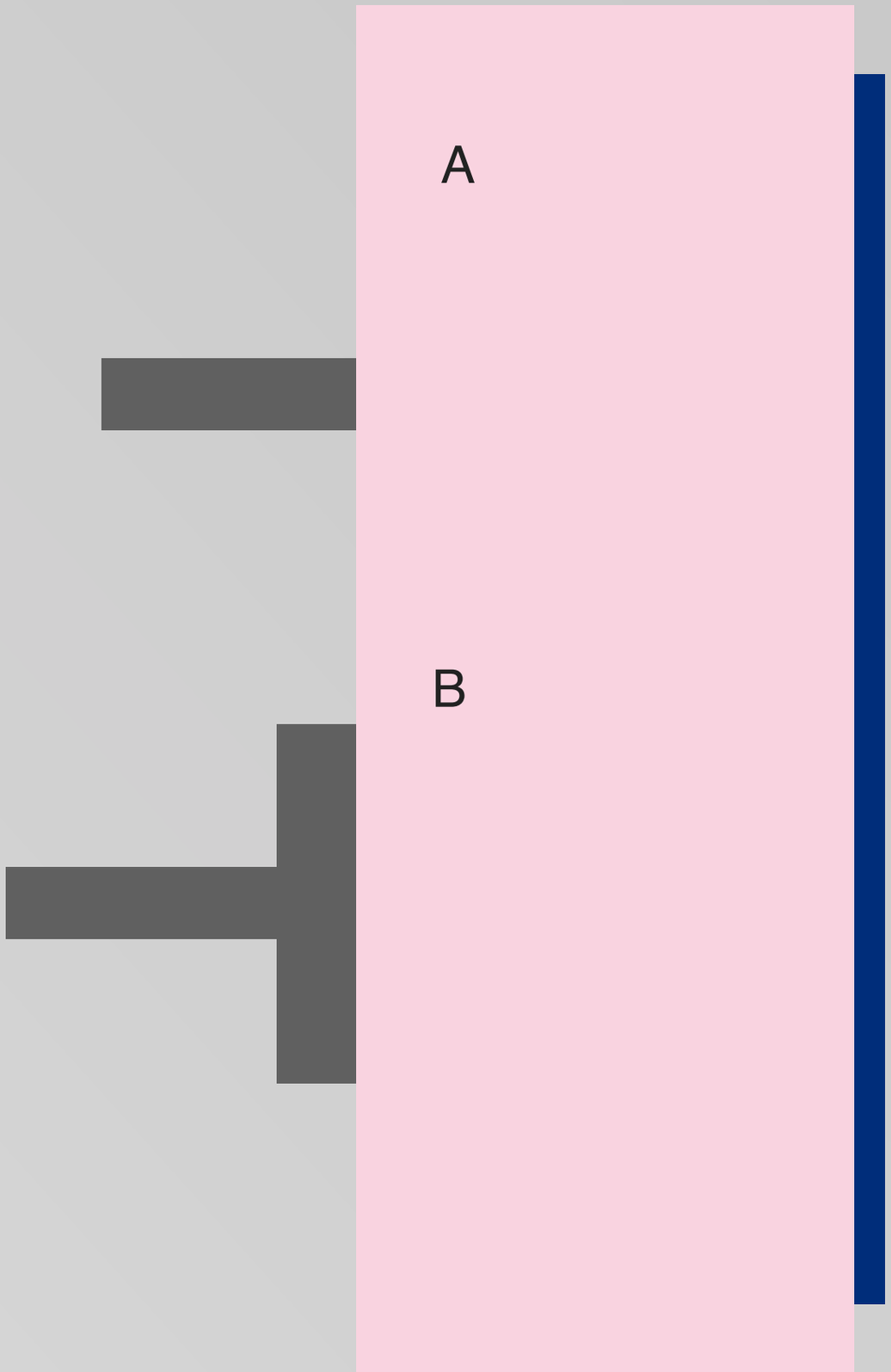
Pressure or no pressure







Pressure: we need to make a measurement in which we can change the volume



Pressure: we need to make a measurement in which we can change the volume

Experiment A: our piston is sufficiently small that we can the pore volume => we can measure pressure in the pore

Experiment B: our piston is too large, we cannot change the volume => we cannot measure the pressure in the pore

Summary

We discussed how to describe adsorption equilibria from a thermodynamic point of view