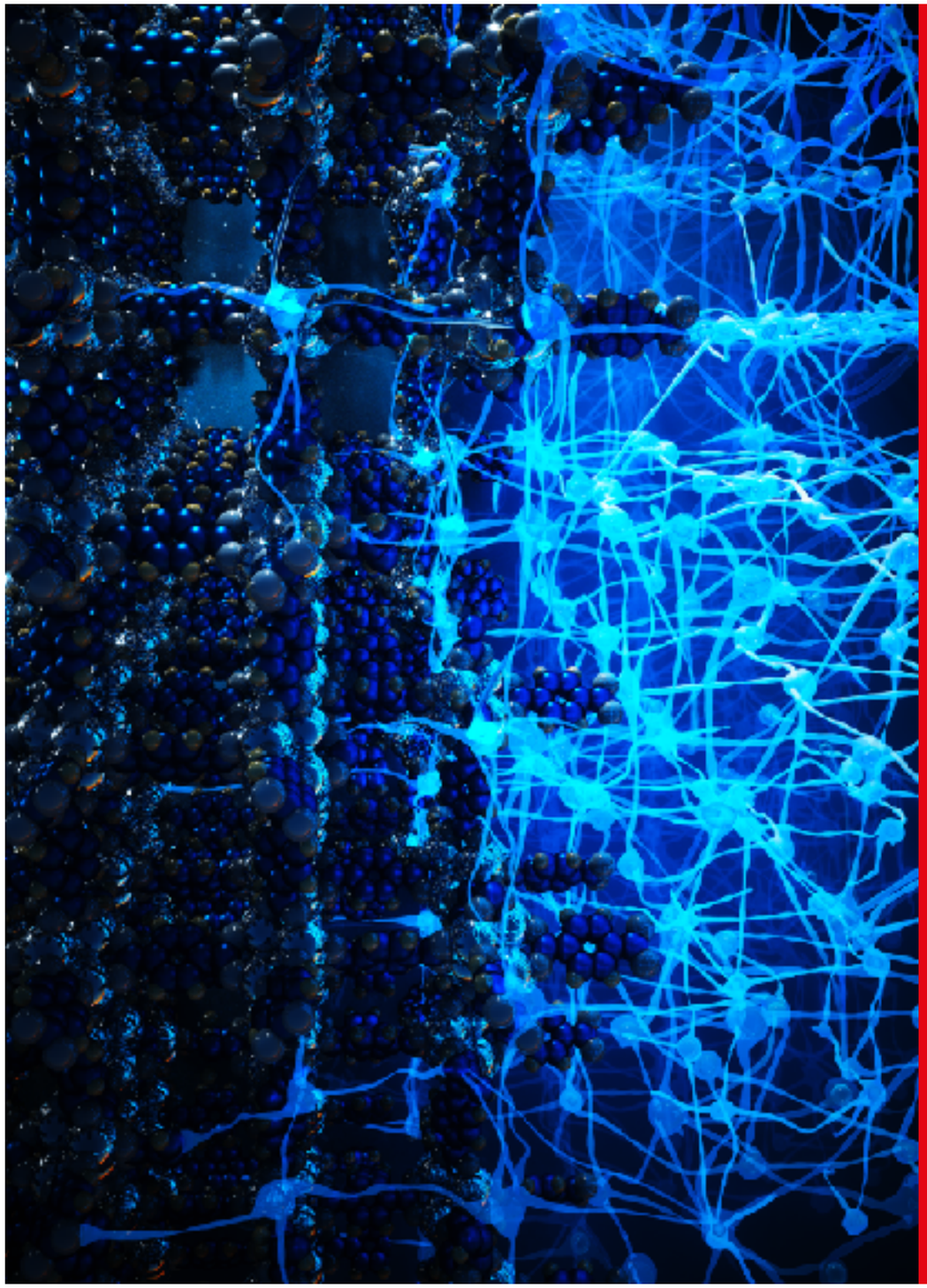


Modelling Lab

Course

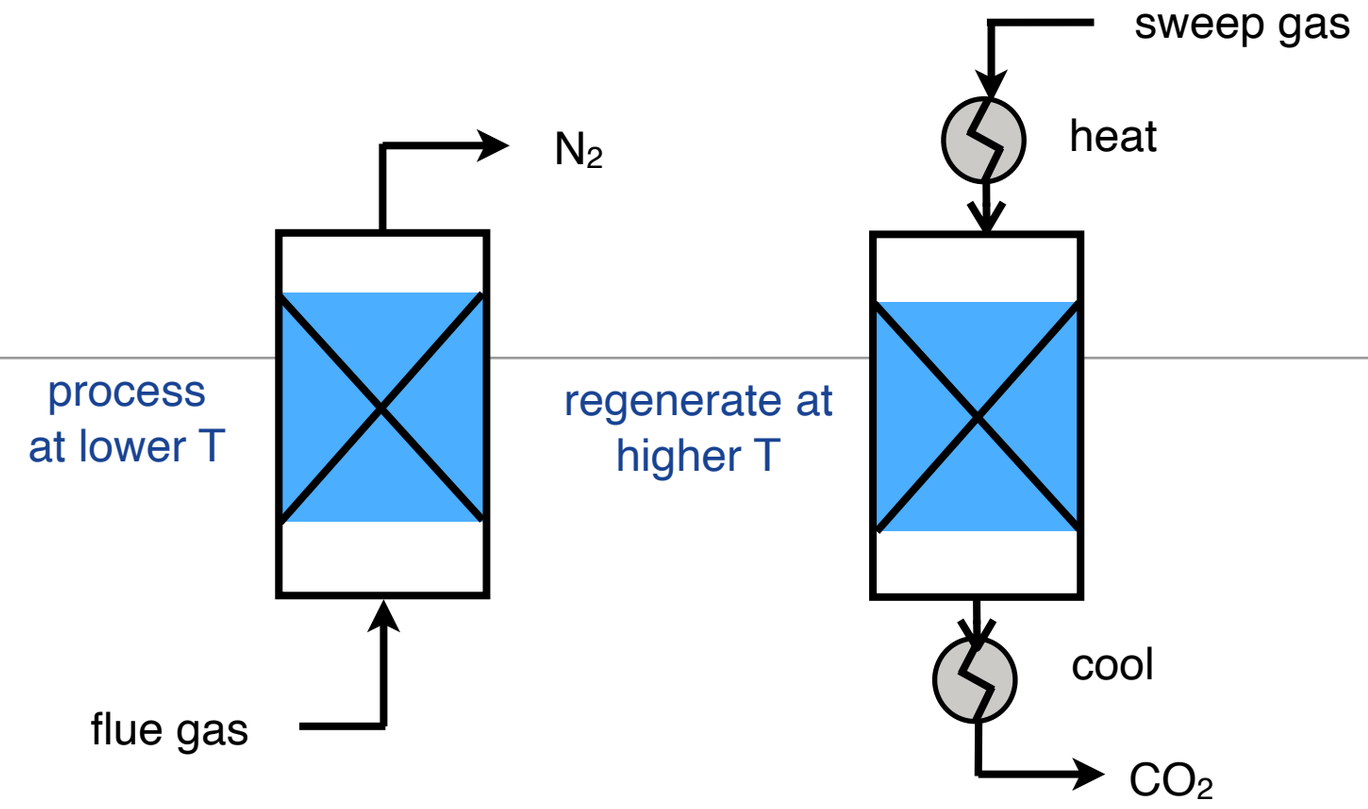
Modeling Lab

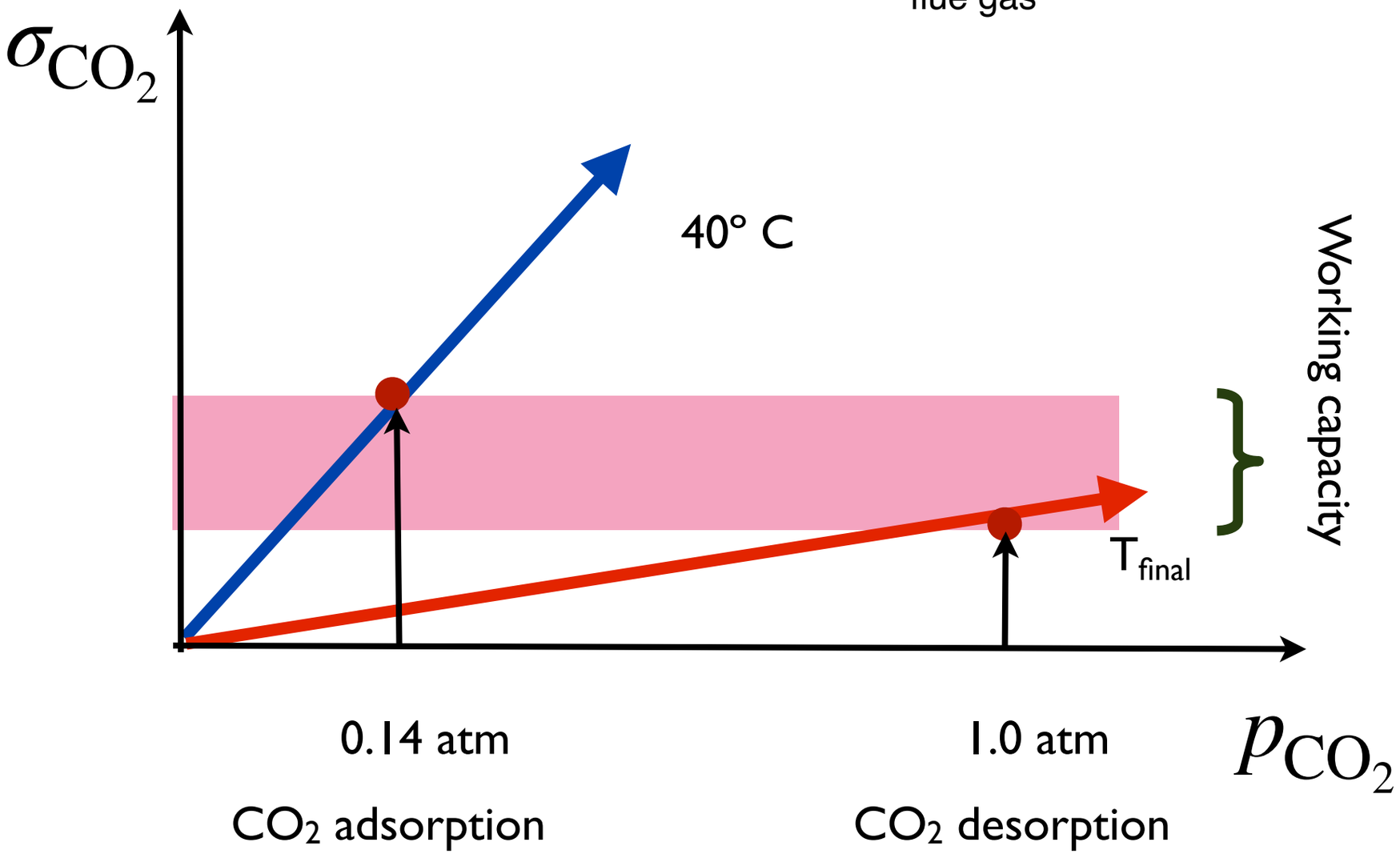
- **Skills for a wet chemical lab:**
  - Basic laboratory skills (working with glassware and balances. solution handling skills: making solutions, dilutions, pipetting, making calibration curves, safety, etc.)
  - Advanced laboratory skills (using analytical tools NMR, X-rays, IR, XPS, etc.)
  - Specialized skills (specific for each research group)
- **Skills for a computational lab:**
  - Basic skills: "Practical programming in chemistry" (2nd year)
  - This course:
    - More advanced skills, working in a computational laboratory
    - Tools for a specific computational study
    - Examples of how to do computational research

Adsorption

Thermodynamics

Temperature swing adsorption

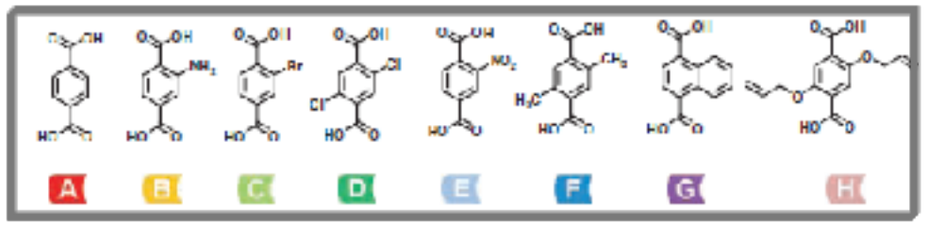




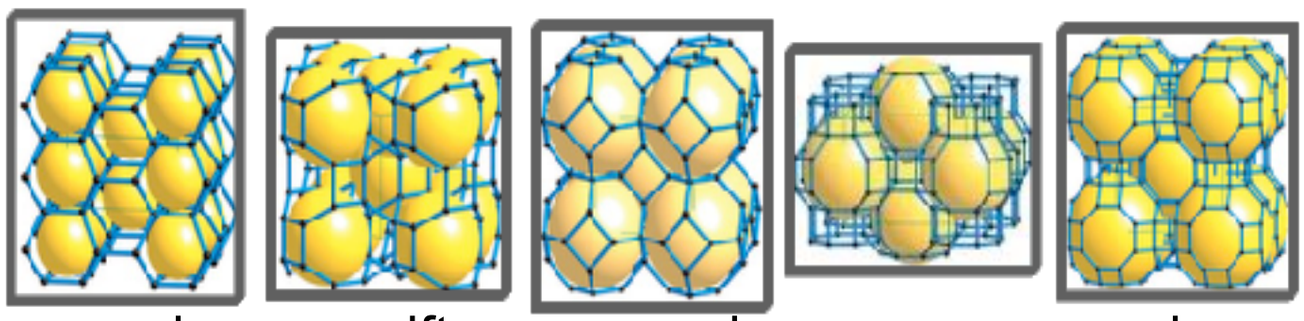
Metal-organic frameworks (MOFs)

Chemistry of MOFs:

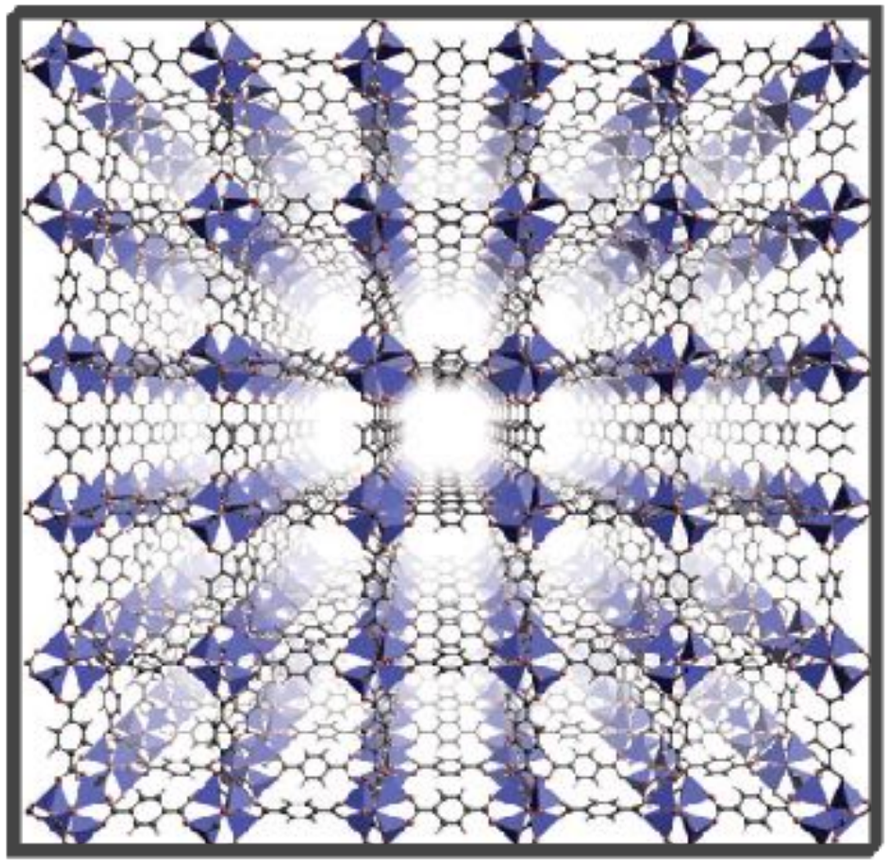
- We can change the metal: Fe, Mg, Ca, Zn, Cu, etc
- We can change the linker



- We can change the pore topology



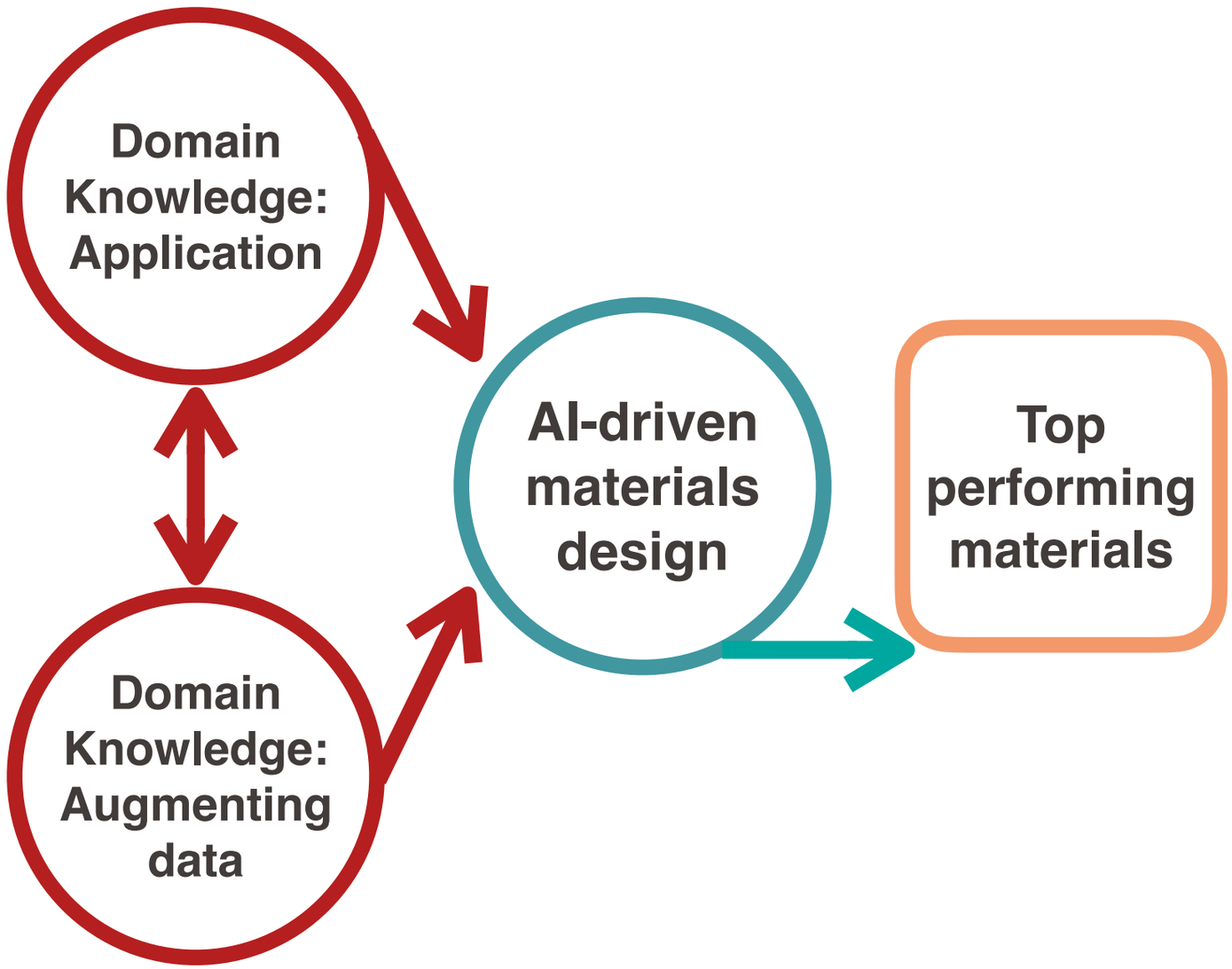
- Trillions of materials for many different applications (gas separation, storage, catalysis, sensing, metal removal, etc.)



Can we design the best material for carbon capture?

AI4Capture

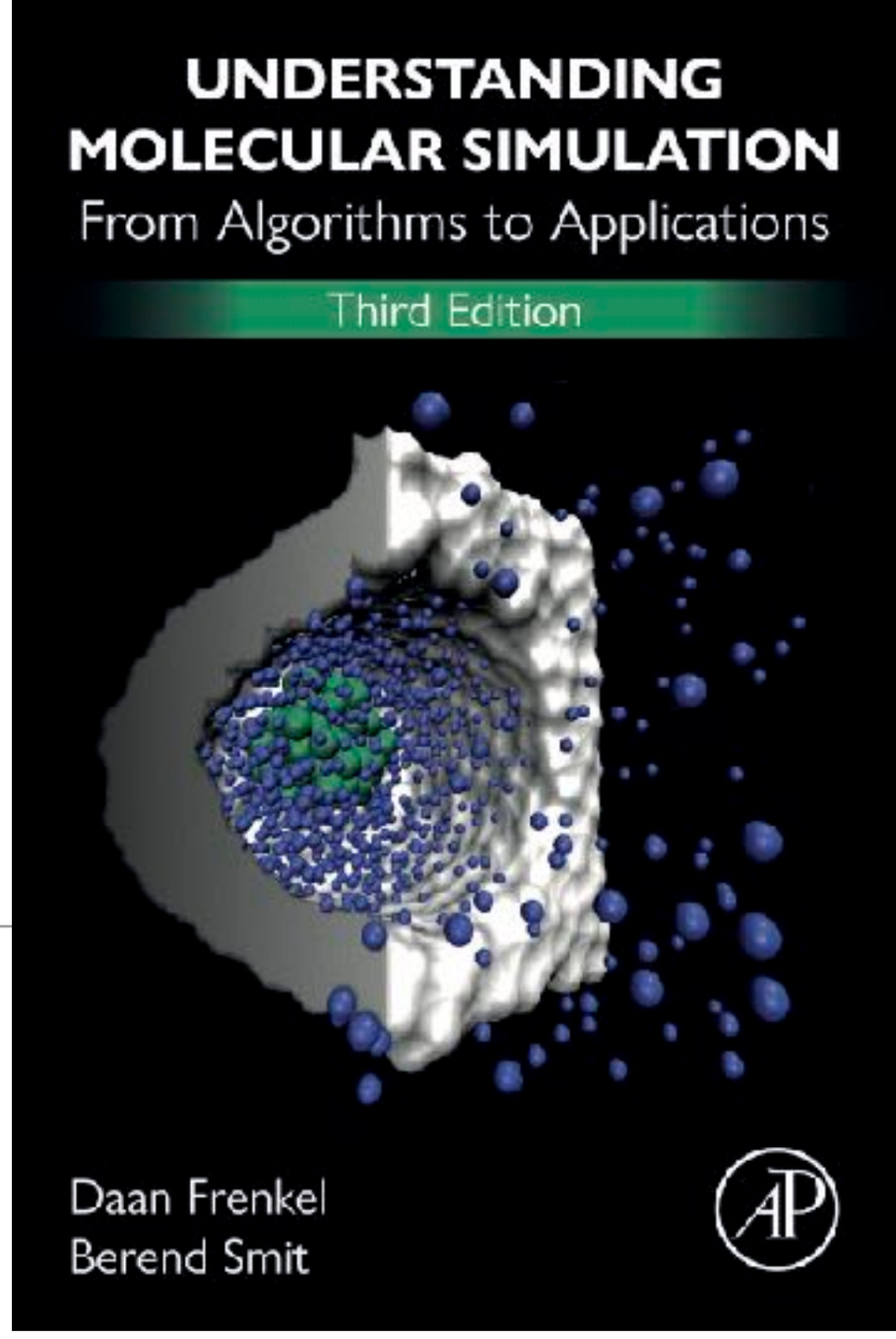
Use AI to design materials for carbon capture



Program

- Introduction to molecular simulations and adsorption thermodynamics
- **Assignment**:
  - The Langmuir isotherm
  - Statistical thermodynamics: NVT ensemble
- **Hands-on**: Adsorption Using AiiDAlab
  - How to predict an isotherm from the crystal structure
- **Project**: Rank a group of MOFs based on a proxy to measure performance in a capture process

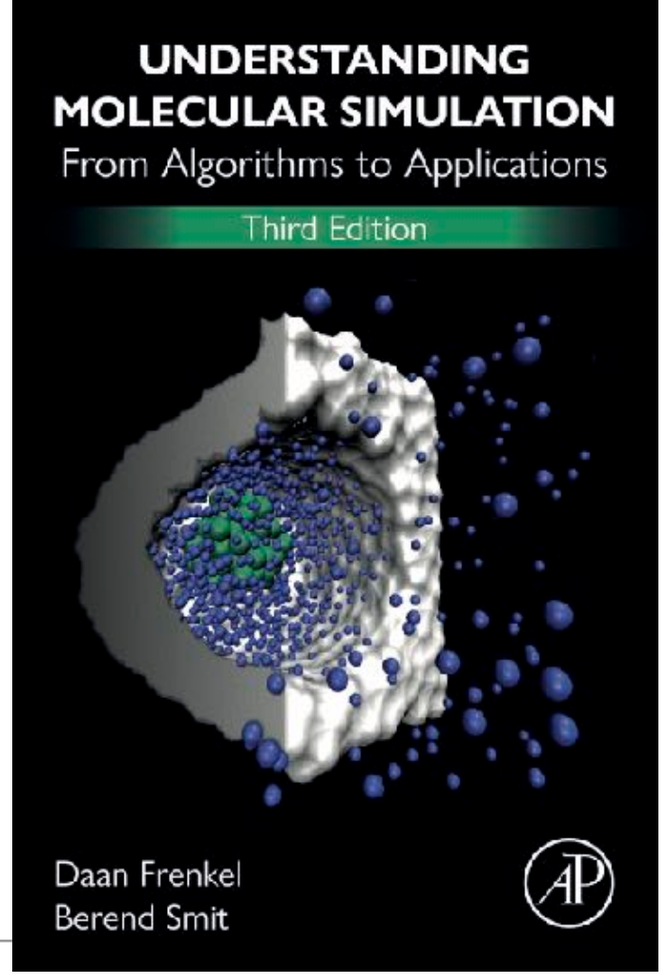
Molecular Simulation



Outline

1. Introduction to Molecular Simulations
2. Ensembles: Classical and Statistical Thermodynamics
   - micro-canonical ensemble (NVE)
   - canonical ensemble (NVT)
   - grand-canonical ensemble (μVT)
3. Monte Carlo Simulations
   - NVT ensemble
   - μVT ensemble

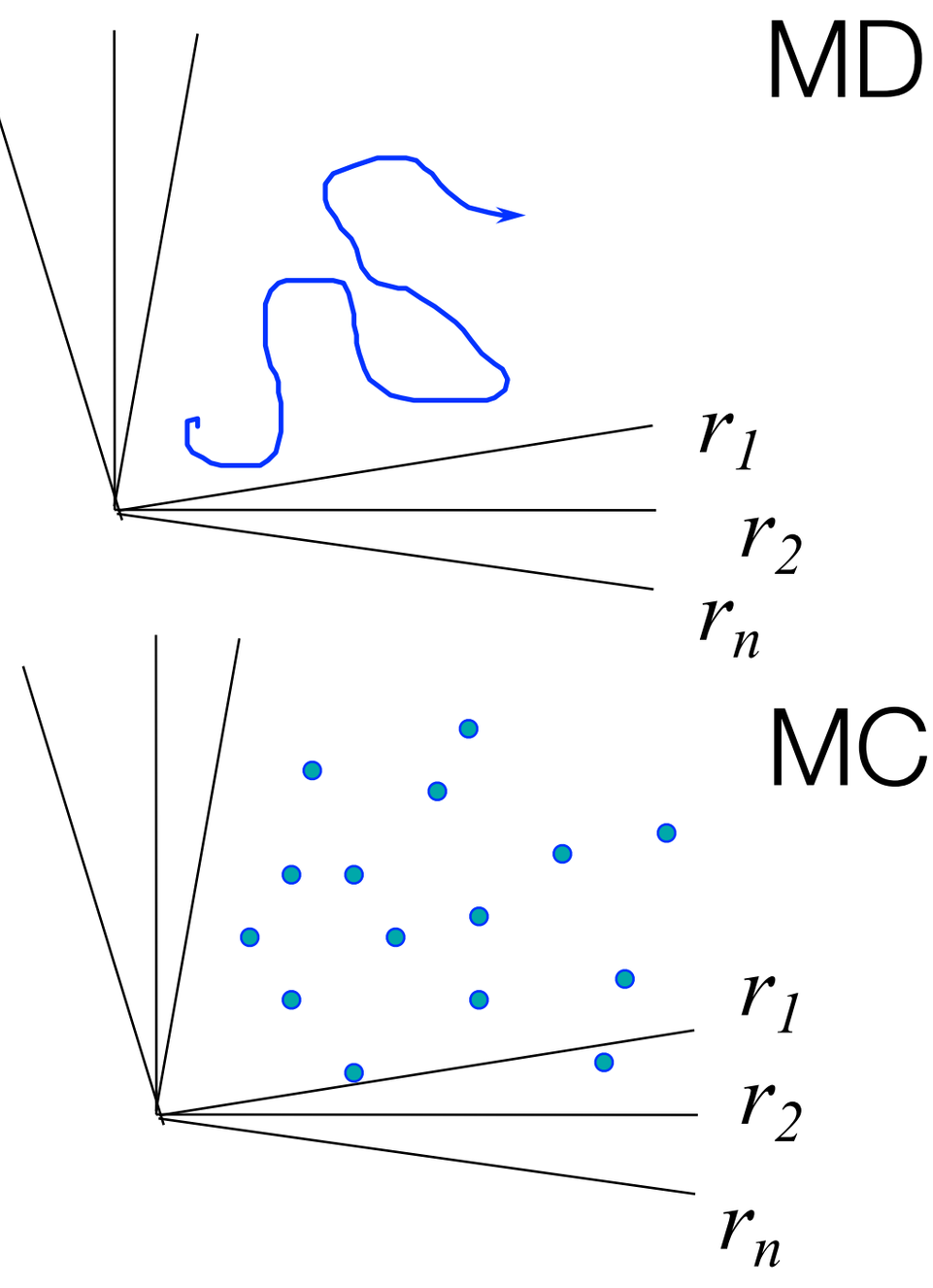
Simulation and Thermodynamics of Adsorption (part 2)



2.1 Introduction

Molecular Simulations

- **Molecular dynamics**: solve equations of motion
- **Monte Carlo**: importance sampling
- Calculate thermodynamic and transport properties for a given intermolecular potential



Uses of Molecular Simulations

We need to know the interactions between the atoms!

Exact= in the limit of infinitely long simulations the error bars can be made infinitely

The idea for a given *intermolecular potential* "*exactly*" compute the ***thermodynamic*** and ***transport*** properties of the ***system***

If one could envision an experimental system of these N particles that interact with the potential.

Pressure
Heat capacity
Heat of adsorption
Structure
….

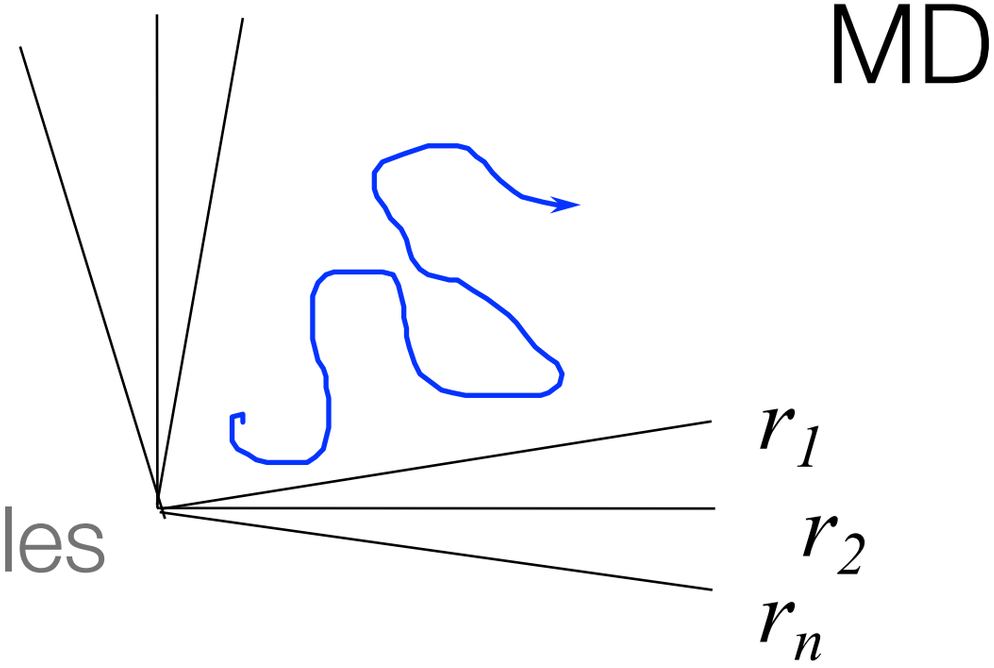
Diffusion coefficient
Viscosity
…

Molecular Dynamics

- Theory:

$$\mathbf{F} = m\frac{d^2\mathbf{r}}{dt^2}$$

- Compute the forces on the particles
- Solve the equations of motion
- Sample after some timesteps



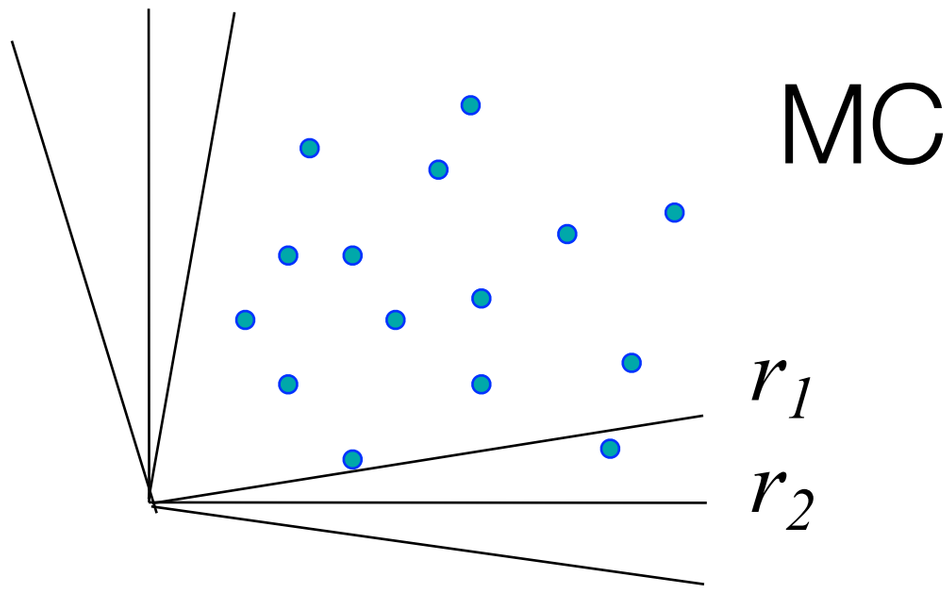
Monte Carlo

- Generate a set of configurations with the ***correct*** probability
- Compute the thermodynamic and transport properties as averages over all configurations

How to compute these properties from a simulation?

What is the correct probability?

Statistical Thermodynamics



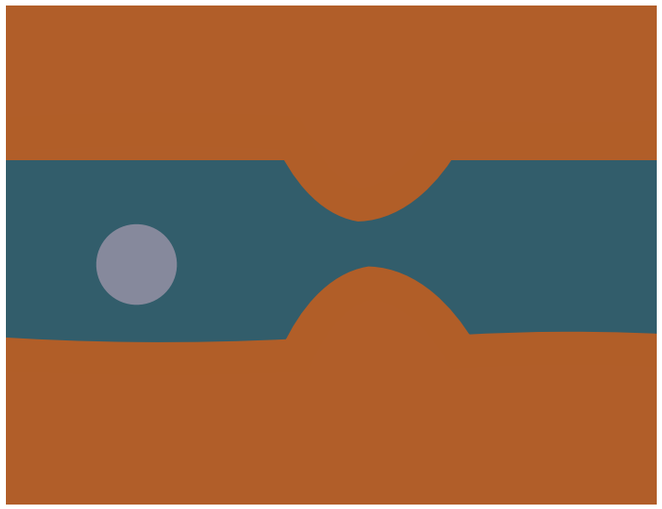
How do we know our simulation is correct?

- **Molecular Dynamics:**
  - if the force field is correct we follow the “real” dynamics of our system,
  - if we simulate sufficiently long, we can compute the properties of interest
- **Monte Carlo:**
  - what is the distribution we need to sample?
  - how do we sample this distribution?

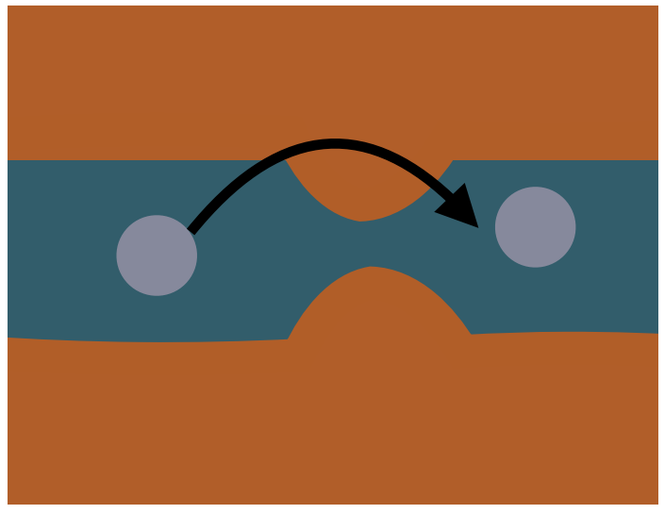
Statistical Thermodynamics

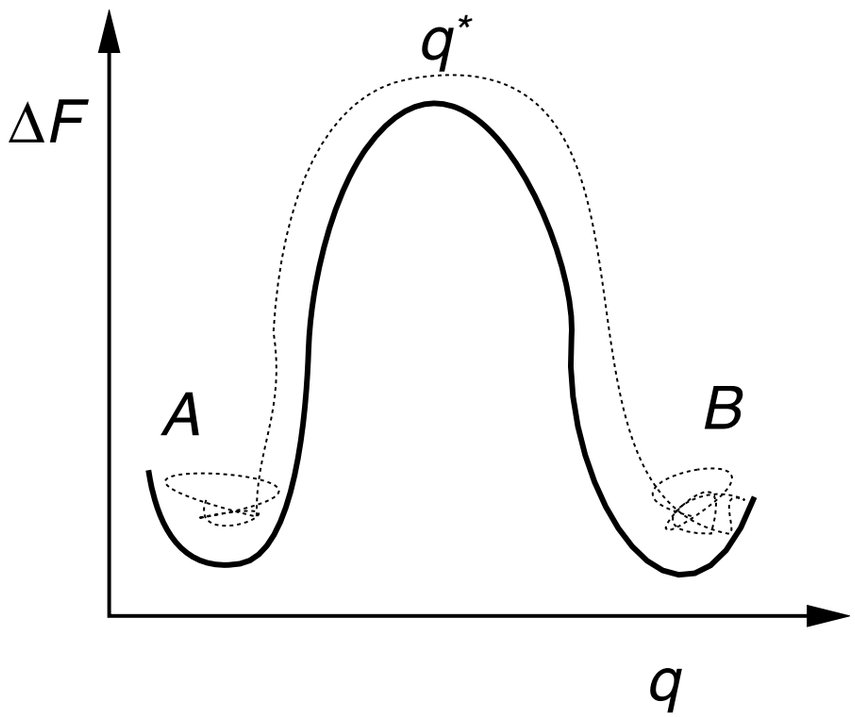
Monte Carlo versus Molecular Dynamics

molecular dynamics

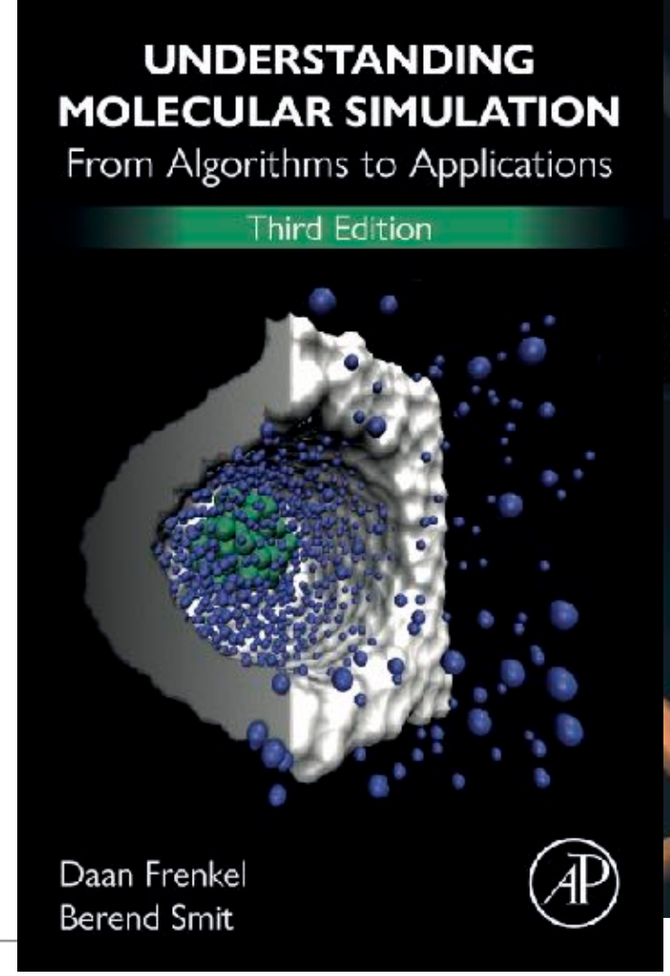


Monte Carlo





Simulation and Thermodynamics of Adsorption (part 2)



2.3.1 NVT ensemble - Statistical Thermo

Statistical Thermodynam

... but classical thermodynamics is based on laws

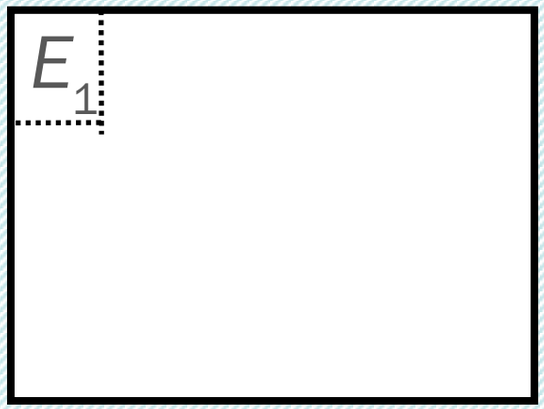
Basic Assumption:

> For an isolated system any microscopic configuration is equally likely

Consequence:

> **All** of statistical thermodynamics and equilibrium thermodynamics

Canonical ensemble: statistical mechanics



Consider a small system that can exchange energy with a big reservoir

$S=k_B \ln \Omega$

$=1/k_BT$

$$\ln\Omega\left(E_1, E-E_1\right) = \ln\Omega\left(E\right) - \left(\frac{\partial \ln\Omega}{\partial E}\right) E_1 + \cdots$$

If the reservoir is very big we can ignore the higher order terms:

$$\ln\left[\frac{\Omega\left(E_1, E-E_1\right)}{\Omega\left(E\right)}\right] = -\frac{E_1}{k_B T}$$

Hence, the probability to find E_1:

$$P\left(E_1\right) = \frac{\Omega\left(E_1, E-E_1\right)}{\sum_i \Omega\left(E_i, E-E_i\right)} = \frac{\Omega\left(E_1, E-E_1\right)/\Omega\left(E\right)}{\sum_i \Omega\left(E_i, E-E_i\right)/\Omega\left(E\right)} = C\frac{\Omega\left(E_1, E-E_1\right)}{\Omega\left(E\right)}$$

$$P\left(E_1\right) \propto \exp\left[-\frac{E_1}{k_B T}\right] \propto \exp\left[-\beta E_1\right]$$

$\beta=1/k_BT$

Summary: Canonical ensemble (N,V,T)

Partition function:

$$Q_{N,V,T} = \frac{1}{\Lambda^{3N} N!} \int e^{-\frac{U(r)}{k_B T}} dr^{3N}$$

Probability to find a particular configuration:

$$P\left(R^N\right) \propto e^{-\frac{U\left(R^N\right)}{k_B T}}$$

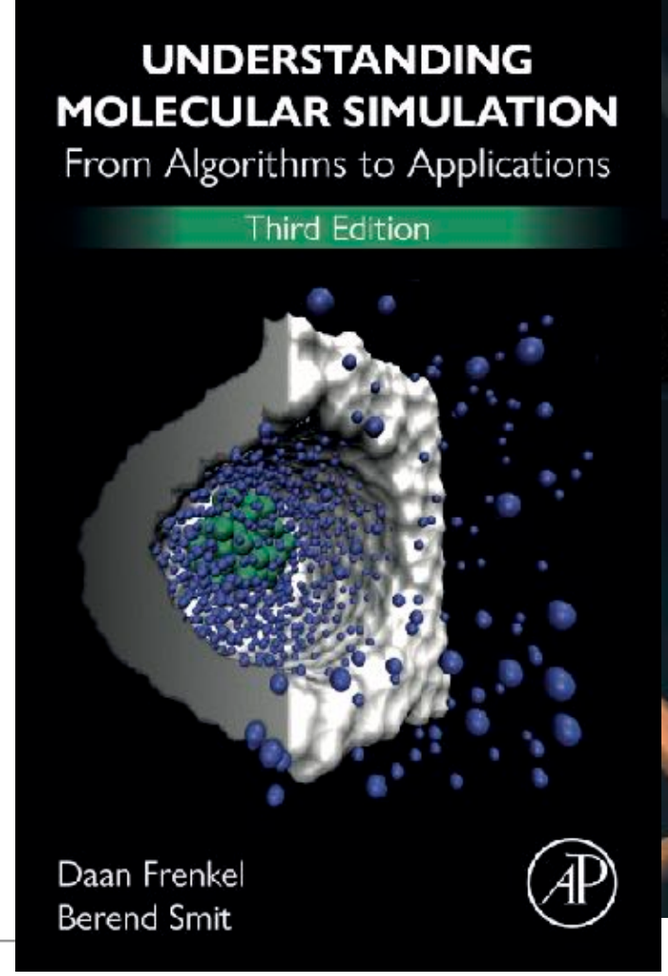
Ensemble average:

$$\left\langle A \right\rangle_{N,V,T} = \frac{\frac{1}{\Lambda^{3N} N!} \int A(r) e^{-\frac{U(r)}{k_B T}} dr^{3N}}{Q_{N,V,T}} = \frac{\int A(r) e^{-\beta U(r)} dr^{3N}}{\int e^{-\beta U(r)} dr^{3N}}$$

Free energy:

$$\beta F = -\ln Q_{NVT}$$

Simulation and Thermodynamics of Adsorption (part 2)



2.3.2 NVT ensemble - Molecular Simulation

Canonical ensemble (N,V,T)

Distribution we need to sample:

$$P\left(r^N\right) \propto e^{-\beta U\left(r^N\right)}$$

Moves:

- select a particle at random
- give this particle a random displacement

Acceptance rule: detailed balance

Algorithm 2 (Attempt to Displace a Particle)

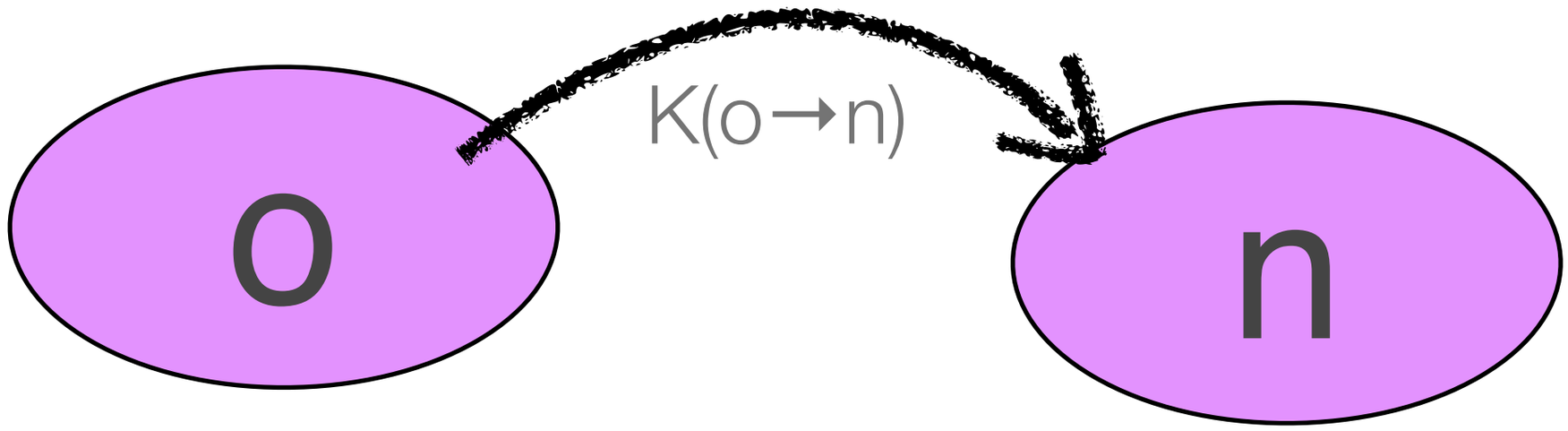
```
  SUBROUTINE mcmove                    attempts to displace a particle

  o=int(ranf()*npart)+1                select a particle at random
  call ener(x(o),eno)                  energy old configuration
  xn=x(o)+(ranf()-0.5)*delx            give particle random displacement
  call ener(xn,enn)                    energy new configuration
  if (ranf().lt.exp(-beta              acceptance rule (2.2.1)
 +    *(enn-eno)) x(o)=xn              accepted: replace x(o) by xn
  return
  end
```

Comments to this algorithm:

1. *Subroutine* `ener` *calculates the energy of a particle at the given position.*
2. *Note that, if a configuration is rejected, the old configuration is retained.*
3. *The* `ranf()` *is a random number uniform in* $[0, 1]$.

Detailed Balance

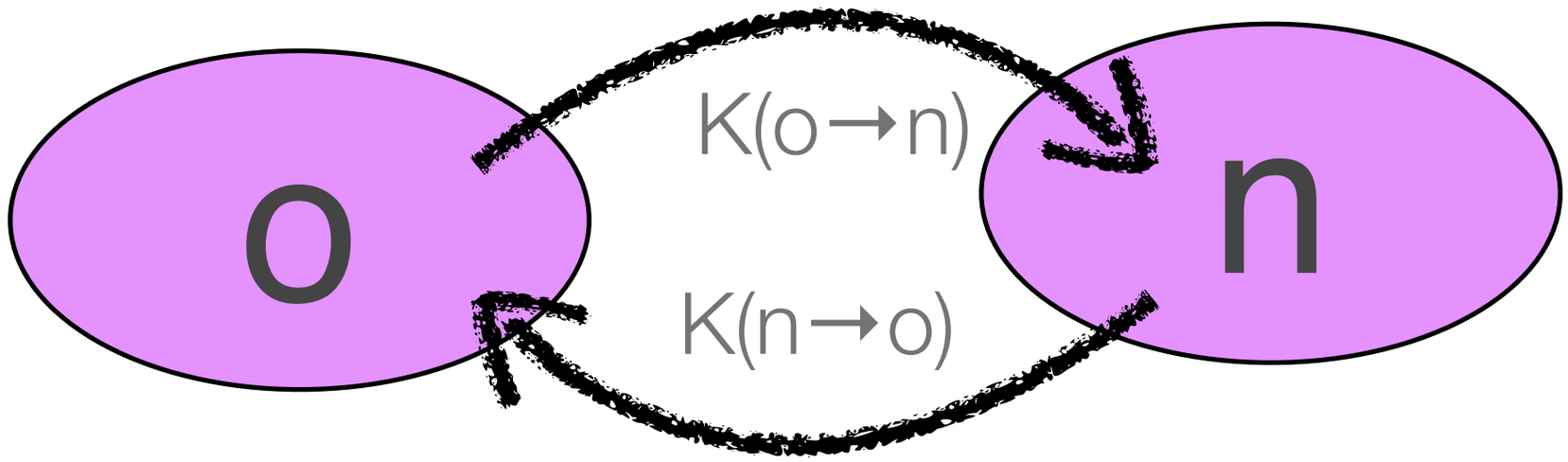


K(o → n): total number of systems in our ensemble that move *o* → *n*

$$K(o \to n) = N(o) \times \alpha(o \to n) \times \mathrm{acc}(o \to n)$$

- *N(o)* : total number of systems in our ensemble in state o
- *α(o → n)*: a priori probability to generate a move *o* → *n*
- *acc(o → n)*: probability to accept the move *o* → *n*

Acceptance rule: Detailed Balance



Condition of detailed balance:

$$K(o \to n) = K(n \to o)$$

$$K(o \to n) = N(o) \times \alpha(o \to n) \times \mathrm{acc}(o \to n)$$

$$K(n \to o) = N(n) \times \alpha(n \to o) \times \mathrm{acc}(n \to o)$$

$$\frac{\mathrm{acc}(o \to n)}{\mathrm{acc}(n \to o)} = \frac{N(n) \times \alpha(n \to o)}{N(o) \times \alpha(o \to n)}$$

Acceptance rule

Distribution we need to sample: $P(n) \propto e^{-\beta U(n)}$

Moves:

- a priori probability is independent of the configuration: $\alpha(o \to n) = \alpha(n \to o)$

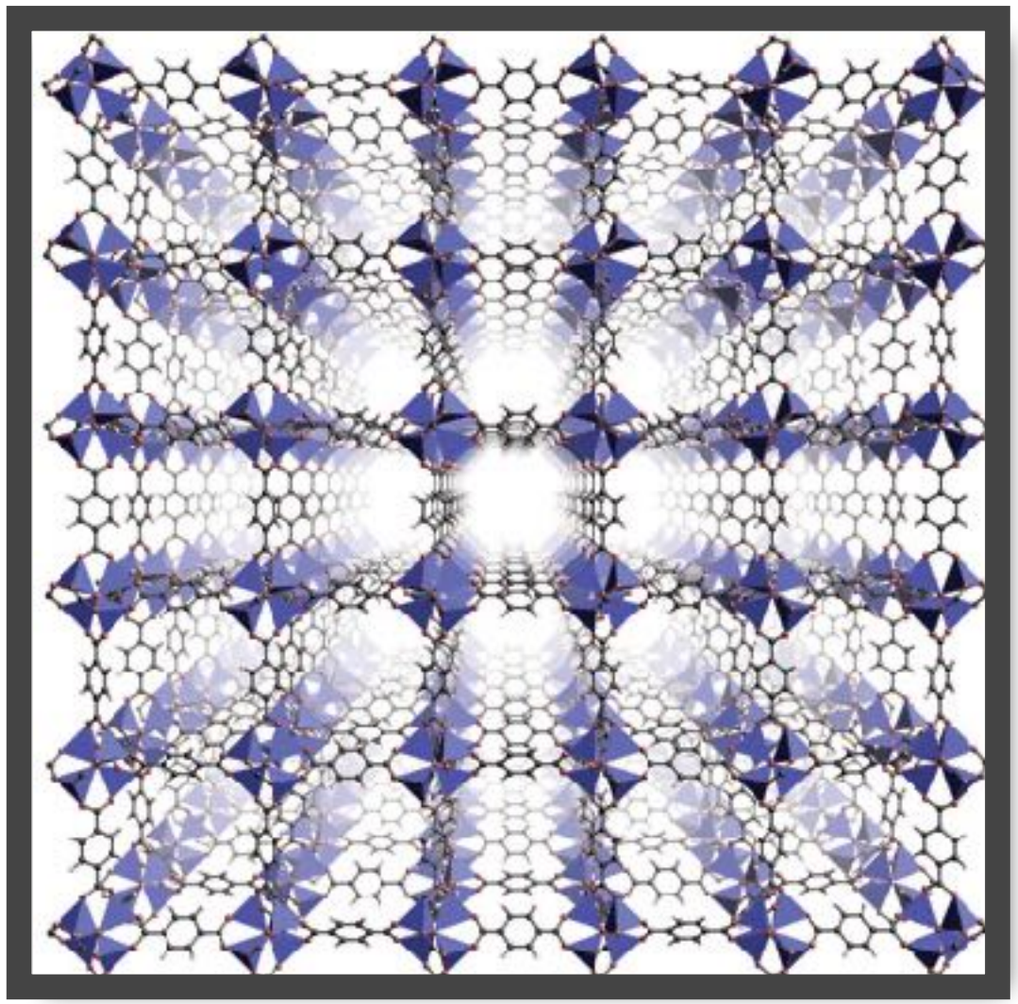
$$\frac{\mathrm{acc}(o \to n)}{\mathrm{acc}(n \to o)} = \frac{N(n) \times \alpha(n \to o)}{N(o) \times \alpha(o \to n)} = \frac{N(n)}{N(o)}$$

$$\frac{\mathrm{acc}(o \to n)}{\mathrm{acc}(n \to o)} = e^{-\beta[U(n) - U(o)]}$$

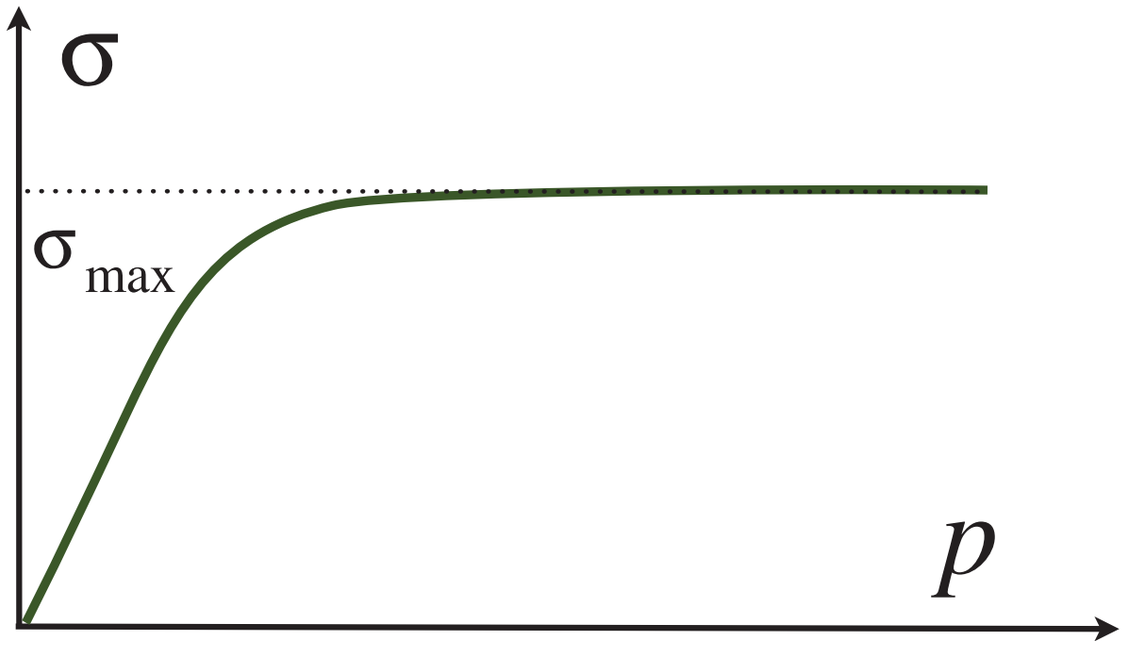
Adsorption Thermodynamics

- Equilibrium conditions
- Langmuir Isotherms
- Henry coefficients of some materials

Thermodynamics of adsorption

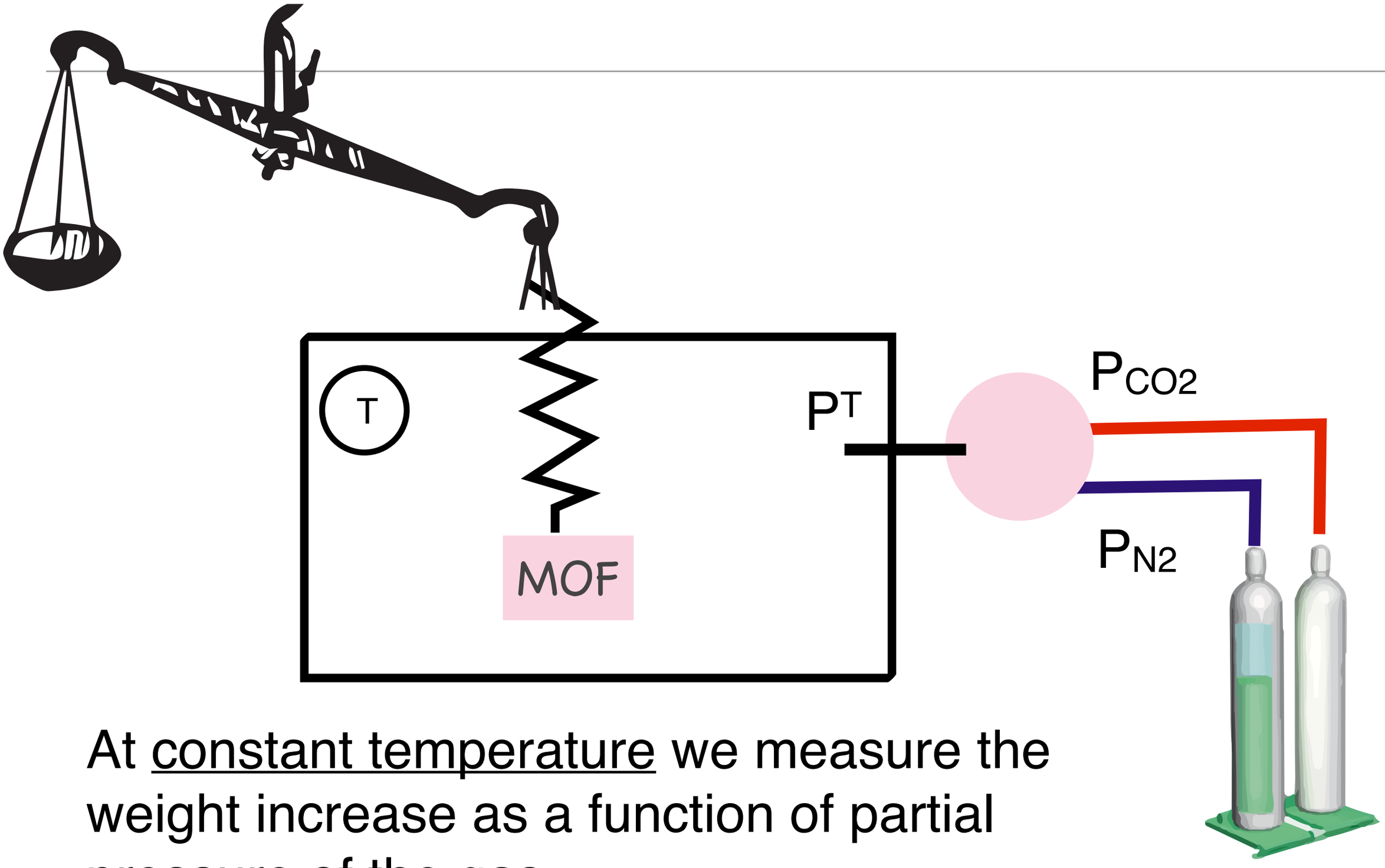


Metal Organic Framework



What are the appropriate thermodynamic variables?

Experimental setup

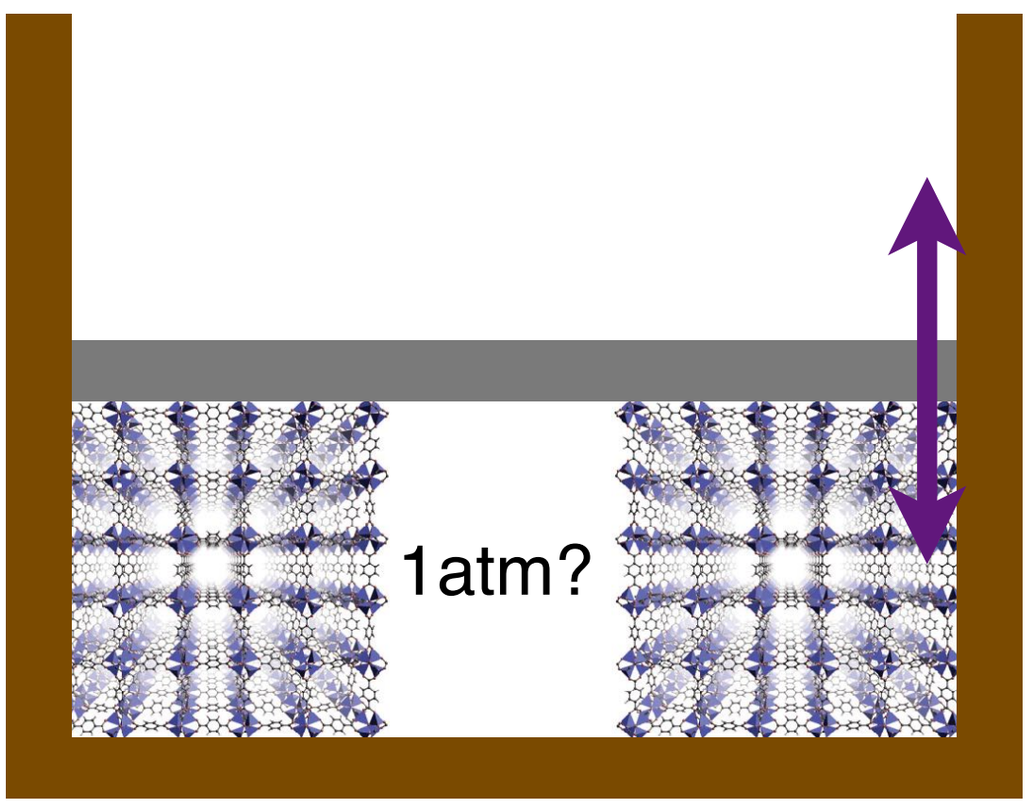


At <u>constant temperature</u> we measure the weight increase as a function of partial pressure of the gas

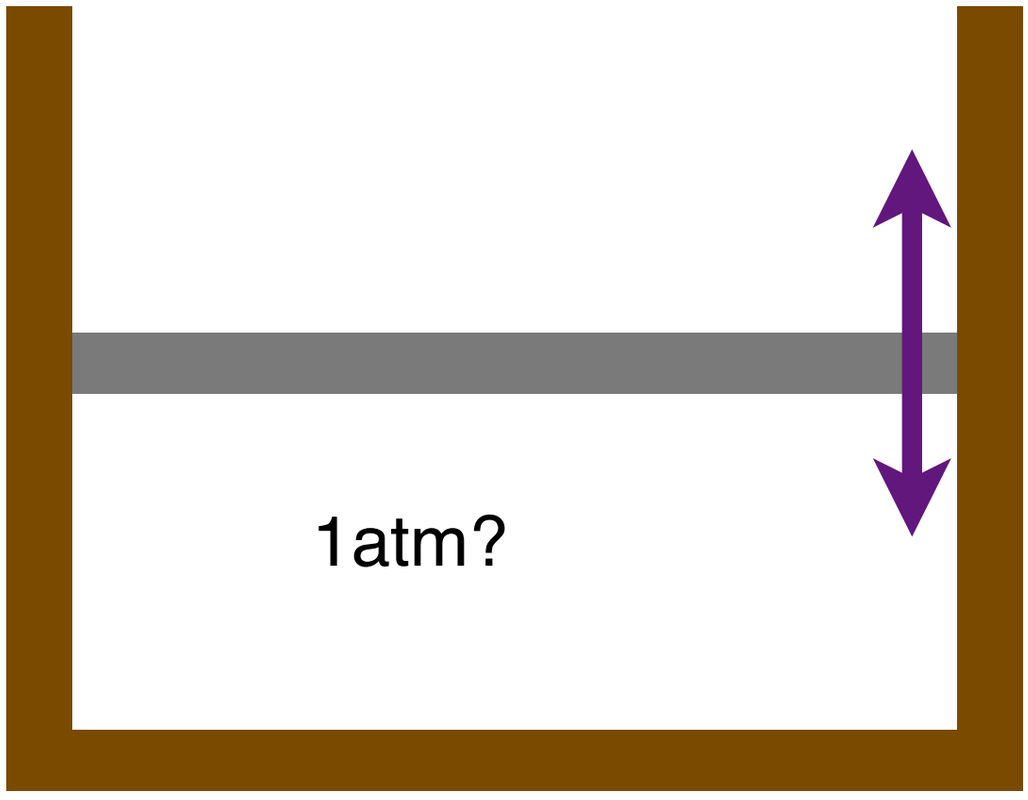
Pressure in Solids

How do we look at pressure in a solid?

Is pressure in a solid defined?



Gas + solid

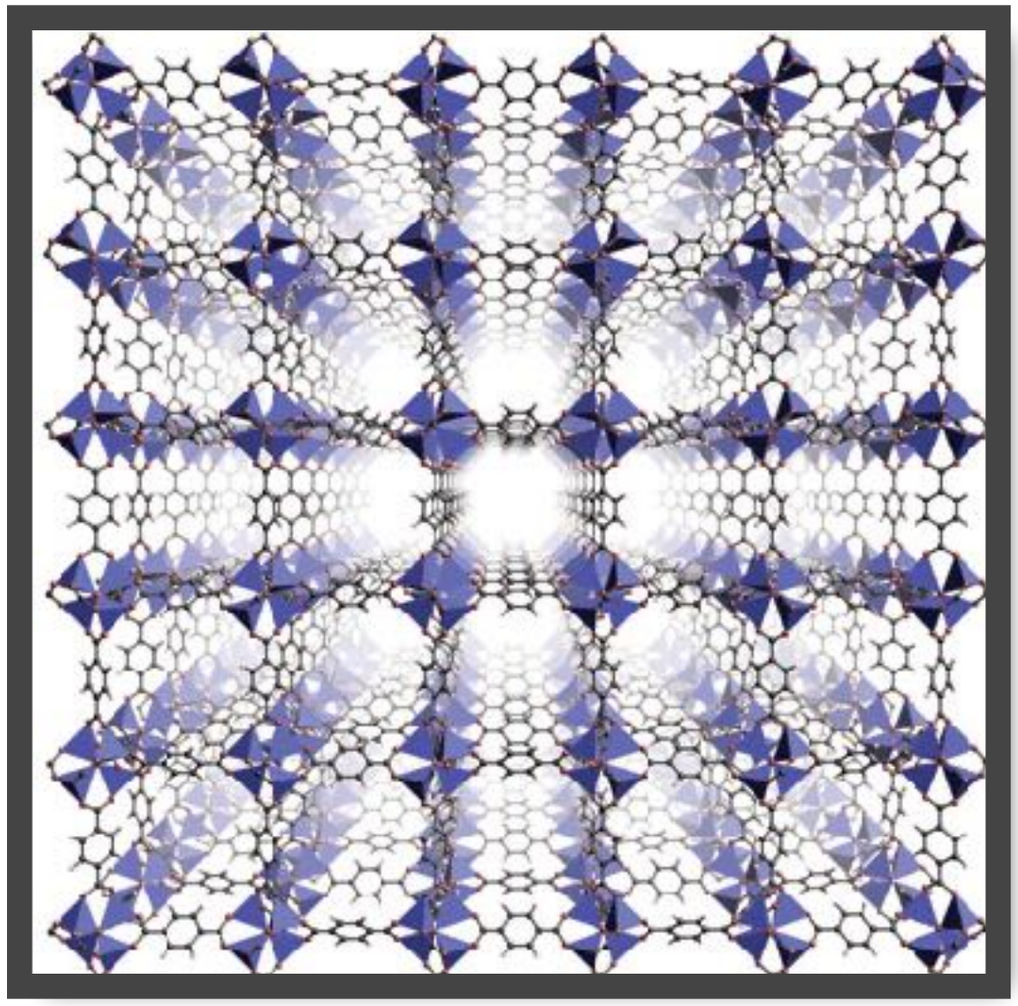


Gas

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

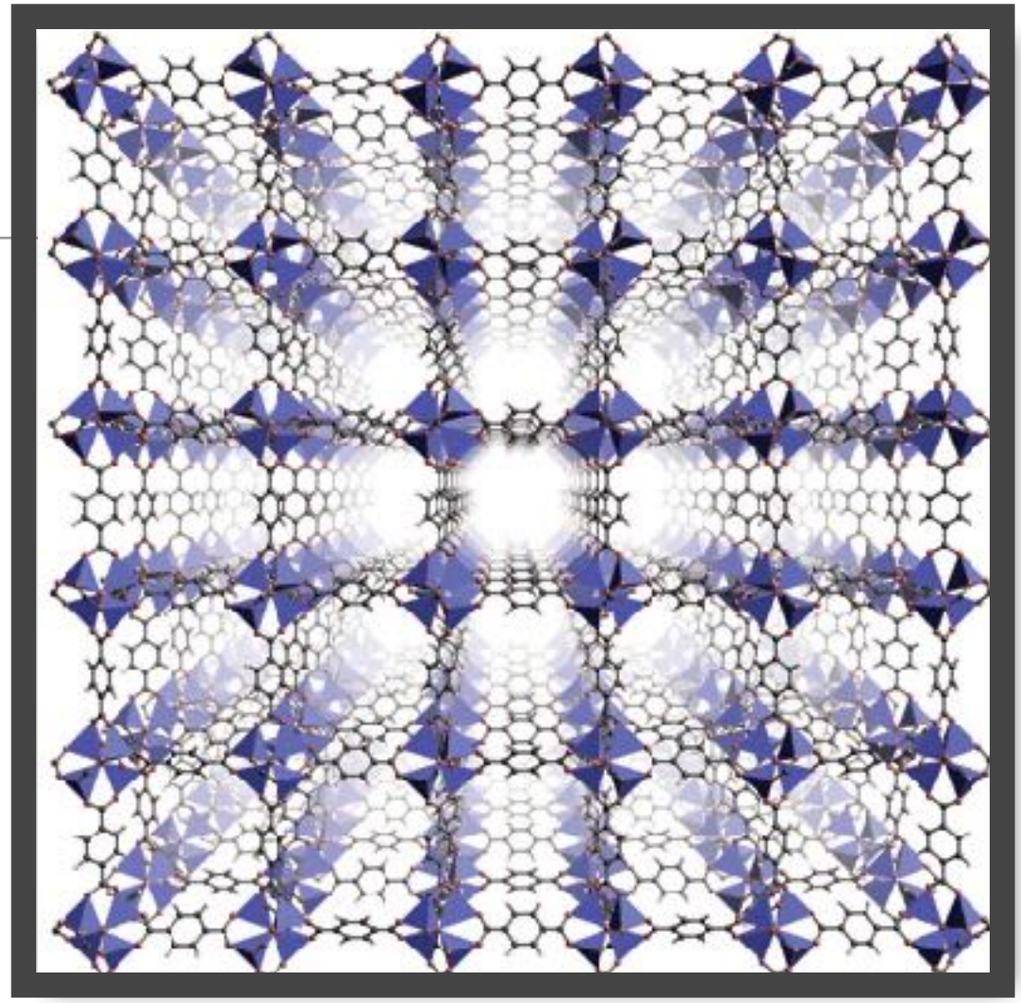
Does the adsorption isotherm of a brick change if we stand on it?

Pressure in a solid

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

Hence,

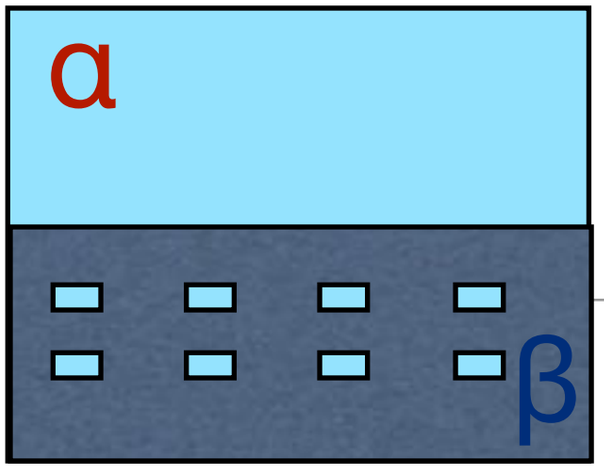
$$\left(\frac{\partial F}{\partial V}\right)_{T,N} = \infty$$



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

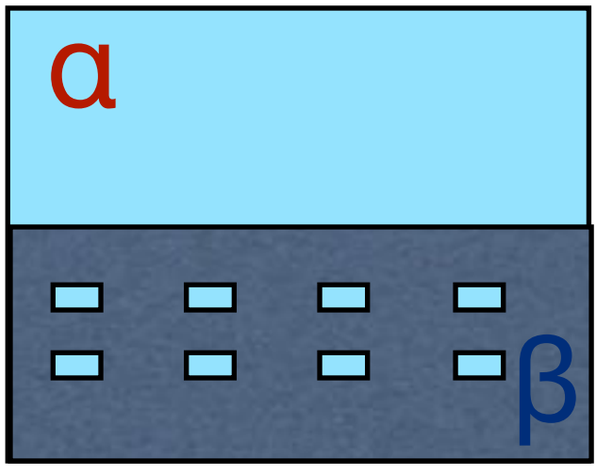
Question: When are these two systems in equilibrium?

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**

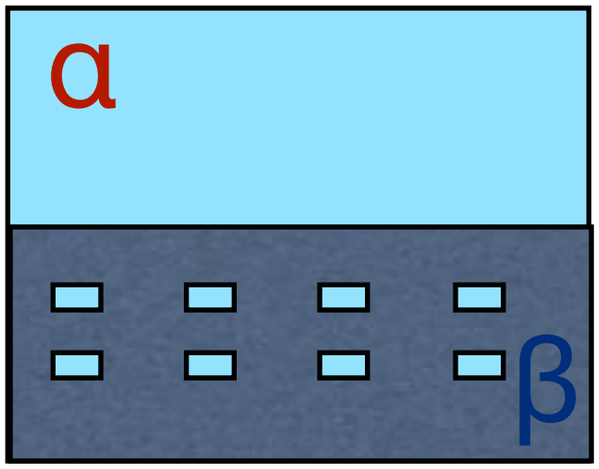
$$dS = dS_\alpha + dS_\beta \geq 0$$

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

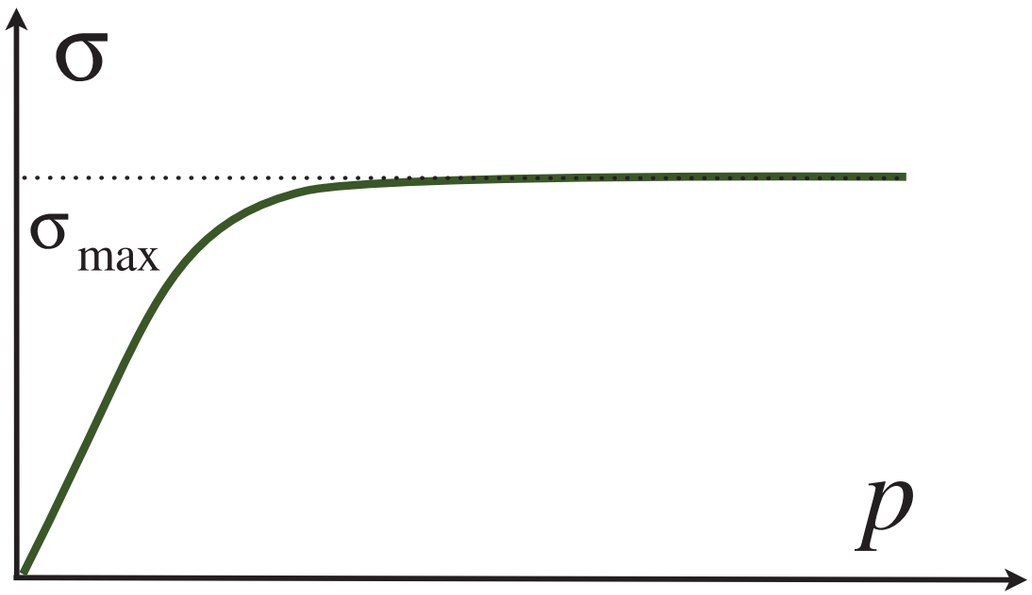
Adsorption Thermodynamics

- Equilibrium conditions
- Langmuir Isotherms
- Henry coefficients of some materials

The simplest description of an adsorption isotherm is the **Langmuir adsorption isotherm**

Langmuir

$$\theta = \frac{\sigma}{\sigma_{\max}} = \frac{bp}{1 + bp}$$



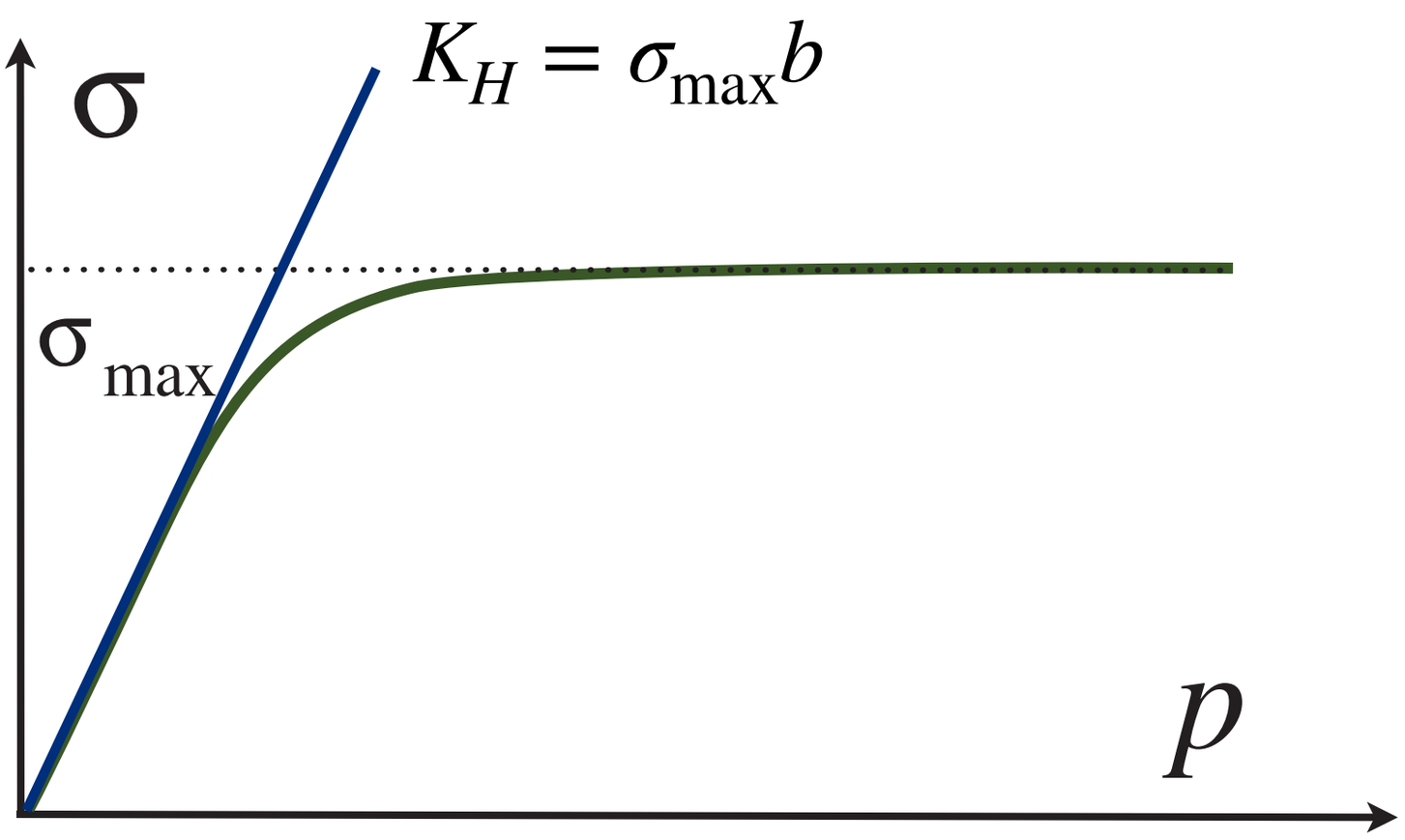
where θ is the fractional coverage and p is the bulk pressure

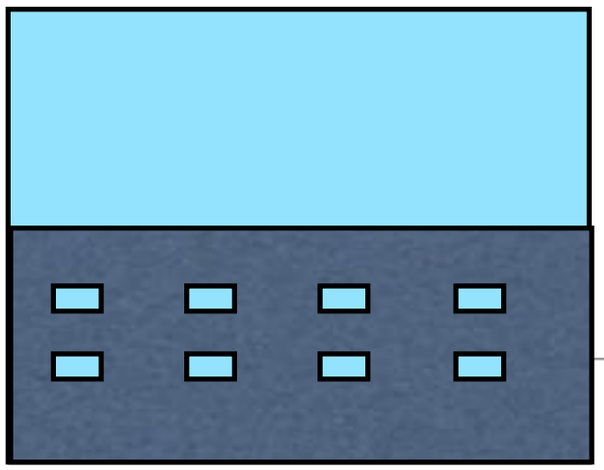
the Langmuir adsorption isotherm

Consider the limit p → 0

Henry coefficient:

$$K_H = \lim_{p\to 0} \frac{\sigma}{p} = \lim_{p\to 0} \sigma_{\max} \frac{b}{1+bp} = \sigma_{\max} b$$





Thermodynamics

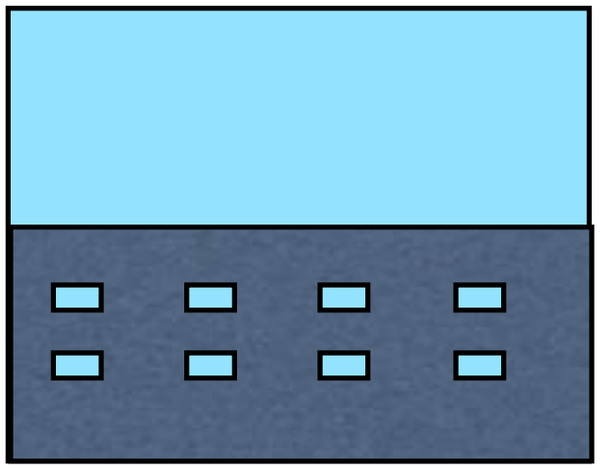
Equilibrium of the CO_2 between the gas and the adsorbed phase:

$$T^{\text{gas}} = T^{\text{ads}} = T$$

$$\mu^{\text{gas}}(T, p) = \mu^{\text{ads}}(T, \sigma)$$

(equal chemical potential and equal temperature)

We need an expression for the chemical potential of a molecule in the gas phase and in the adsorbed phase



Let us assume that the gas is an **ideal gas**:

Chemical potential of an ideal gas:

$$\mu^{\mathrm{gas}}(T,\rho) = \mu^{0}(T) + k_B T \ln(\rho)$$

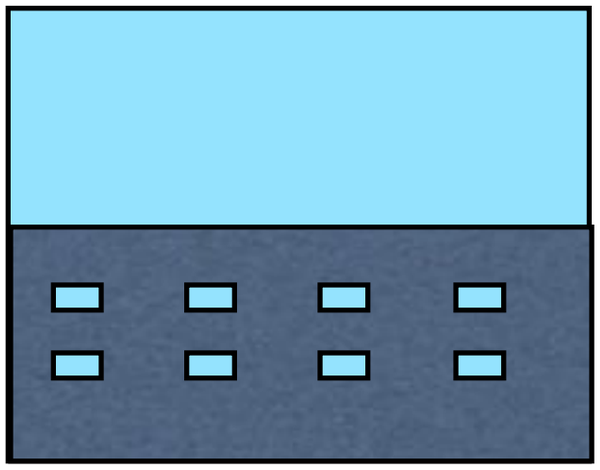
Boltzmann's constant

density

reference chemical potential

With the ideal gas law:

$$\mu^{\mathrm{IG}}(T,P) = \mu^{0}(T) + k_B T \ln\left(\frac{p}{k_B T}\right)$$



loading: number of adsorbed molecules per unit volume

ideal gas chemical potential

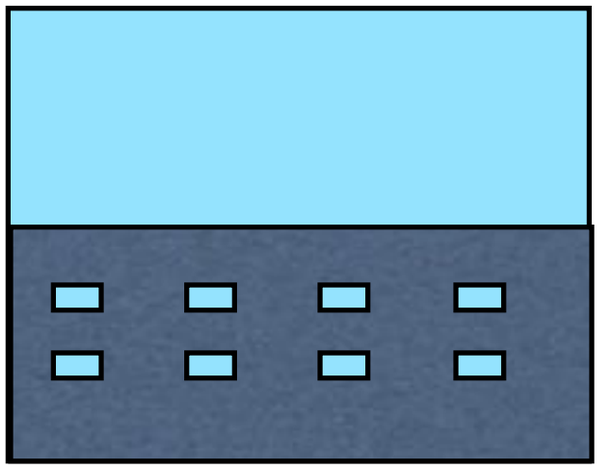
excess chemical potential

For the absorbent:

$$\mu^{\mathrm{ads}}(T,\sigma) = \mu^{\mathrm{IG}}(T,\sigma) + \mu^{\mathrm{ex}}(T,\sigma)$$

If we use the expression for the ideal gas chemical potential:

$$\mu^{\mathrm{ads}}(T,\sigma) = \mu^{0}(T) + k_B T \ln\left(\rho\right) + \mu^{\mathrm{ex}}(T,\sigma)$$



Equilibrium: $$T^{\text{gas}} = T^{\text{ads}} = T$$

$$\mu^{\text{gas}}(T,p) = \mu^{\text{ads}}(T,\sigma)$$

Gas phase:

$$\mu^{\text{IG}}(T,P) = \mu^{0}(T) + k_B T \ln\left(\frac{p}{k_B T}\right)$$

For the absorbent:

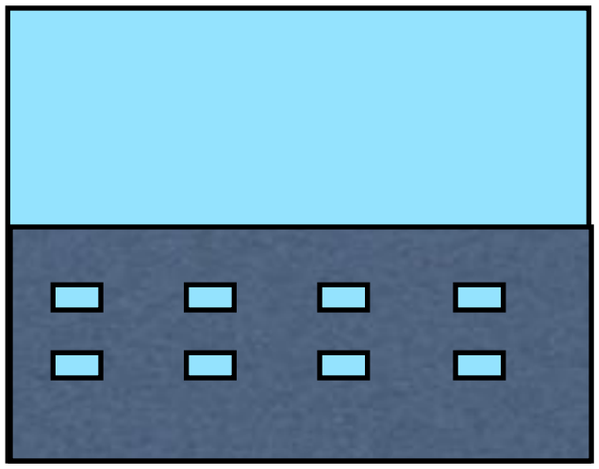
$$\mu^{\text{ads}}(T,\sigma) = \mu^{0}(T) + k_B T \ln(\sigma) + \mu^{\text{ex}}(T,\sigma)$$

Equilibrium:

$$\ln\left(\frac{p}{k_B T}\right) = \ln\sigma + \frac{\mu^{\text{ex}}(T,\sigma)}{k_B T}$$

or

$$\sigma = \frac{p}{k_B T}\exp\left(-\frac{\mu^{\text{ex}}(T,\sigma)}{k_B T}\right)$$

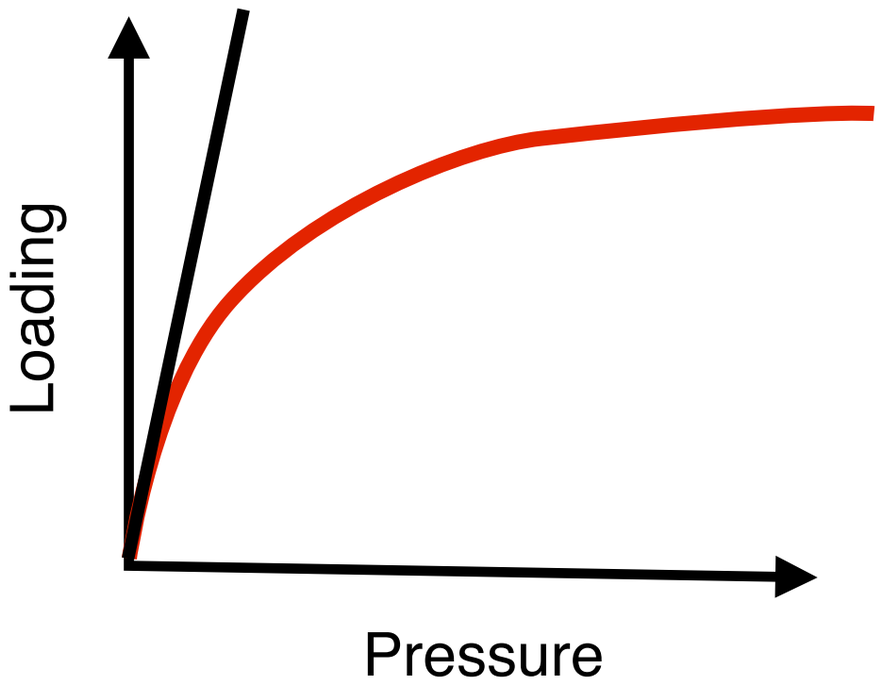


$$\sigma = \frac{p}{k_B T} \exp\left(-\frac{\mu^{\mathrm{ex}}(T,\sigma)}{k_B T}\right)$$

Let us take the limit
p→0, or σ→0

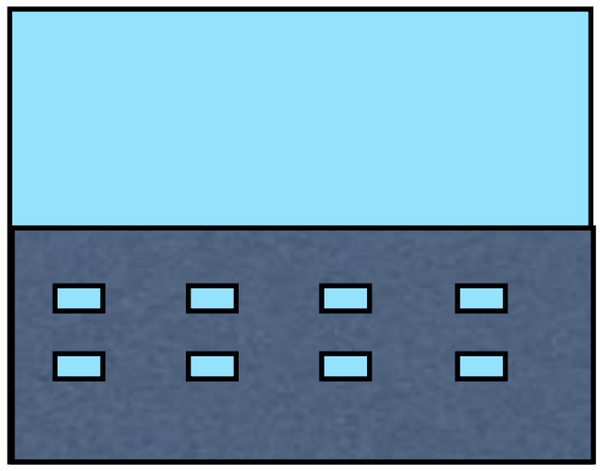
$$\sigma = \frac{p}{k_B T} \exp\left(-\frac{\mu^{\mathrm{ex}}(T,0)}{k_B T}\right) = K_H p$$

This defines the Henry coefficient K_H



$$K_H = \frac{1}{k_B T} \exp\left(-\frac{\mu^{\mathrm{ex}}(T,0)}{k_B T}\right)$$

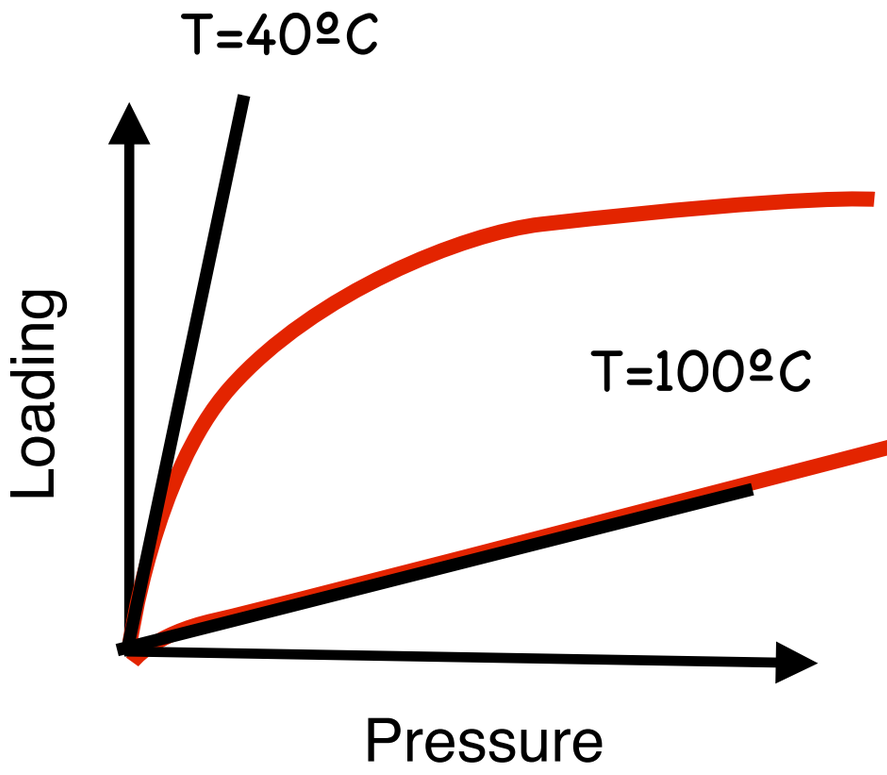
At **low pressures** this gives a good approximation

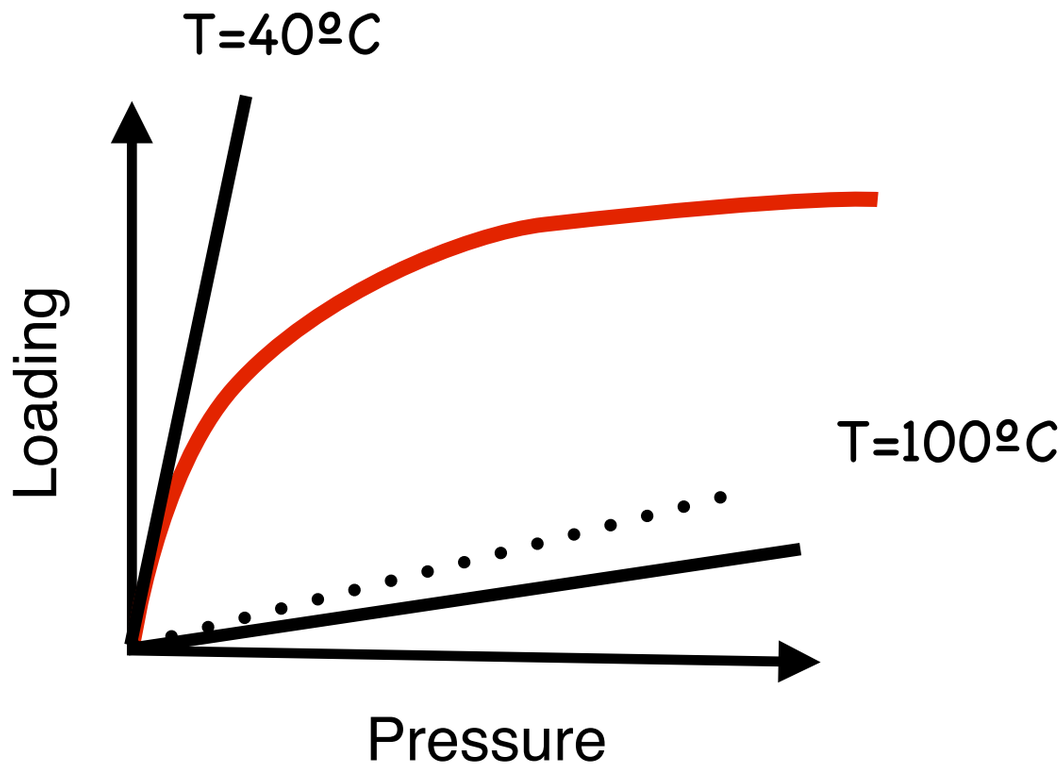


$$K = K_0 \exp\left(-\frac{q_{ad}}{k_B T}\right)$$

Van 't Hoff equation

Higher heat of adsorption





... larger difference between the Henry coefficients at high and low temperatures!

Thermodynamics II

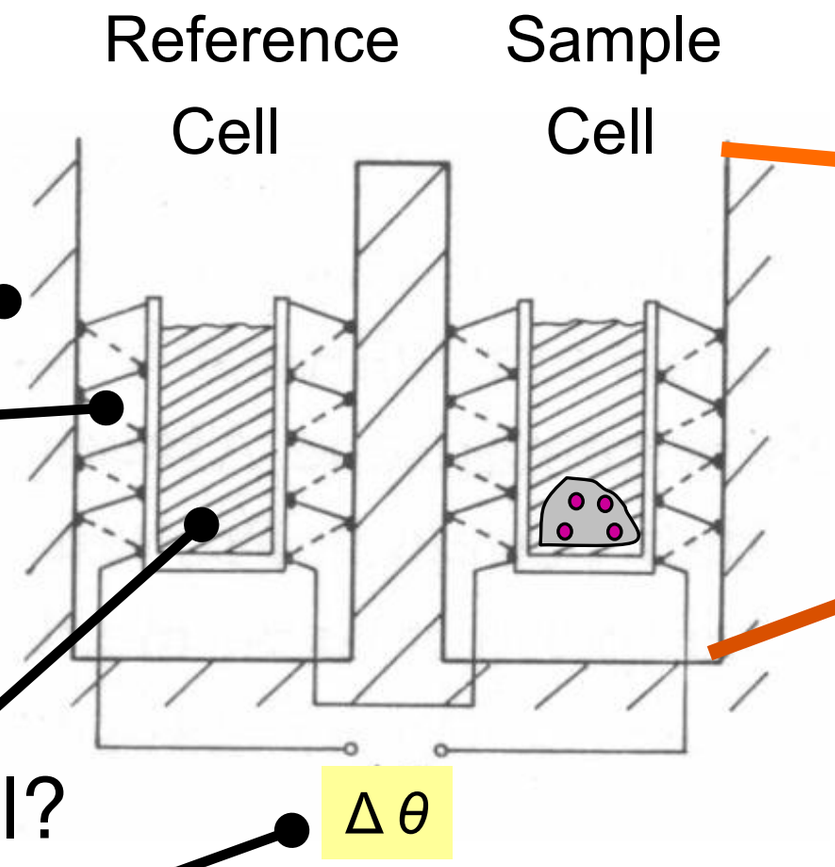
- Equilibrium conditions
- Langmuir Isotherms
- Henry coefficients of some materials
- Temperature dependence
- Temperature dependence Henry coefficient
- **Experimental: heat of adsorption**

Experiment: microcalorimetry

kept at constant temperature

thermo couples

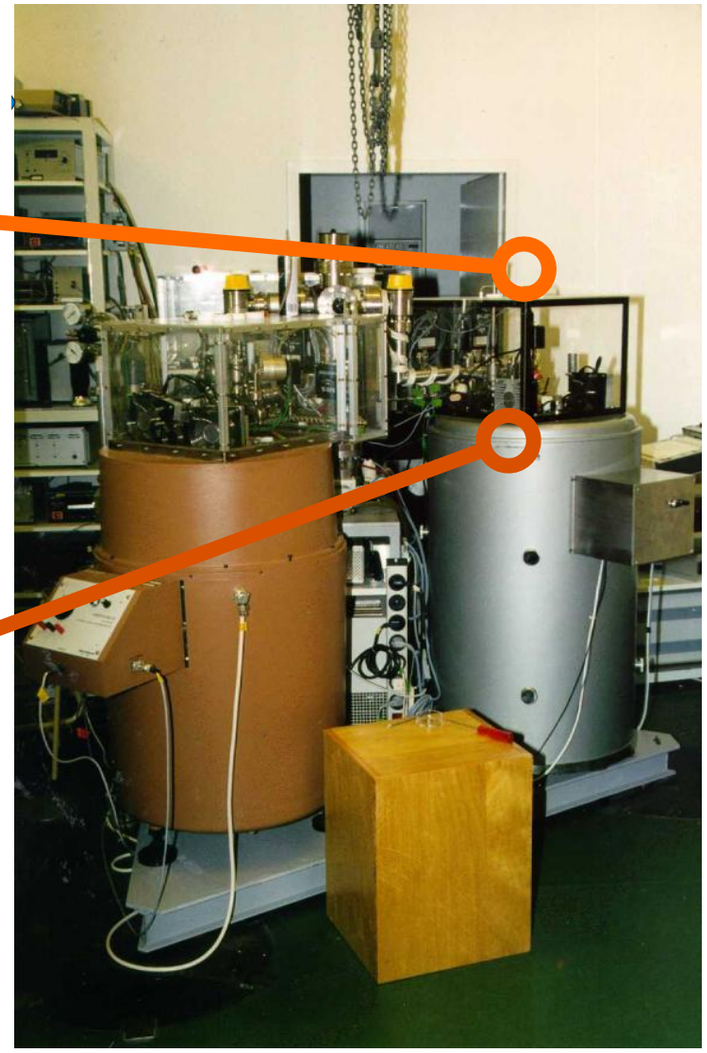
why a reference cell?



Setup according to Tian and Calvet

measure the difference in current generated by the thermo couples

Adsorptive Microcalorimetry

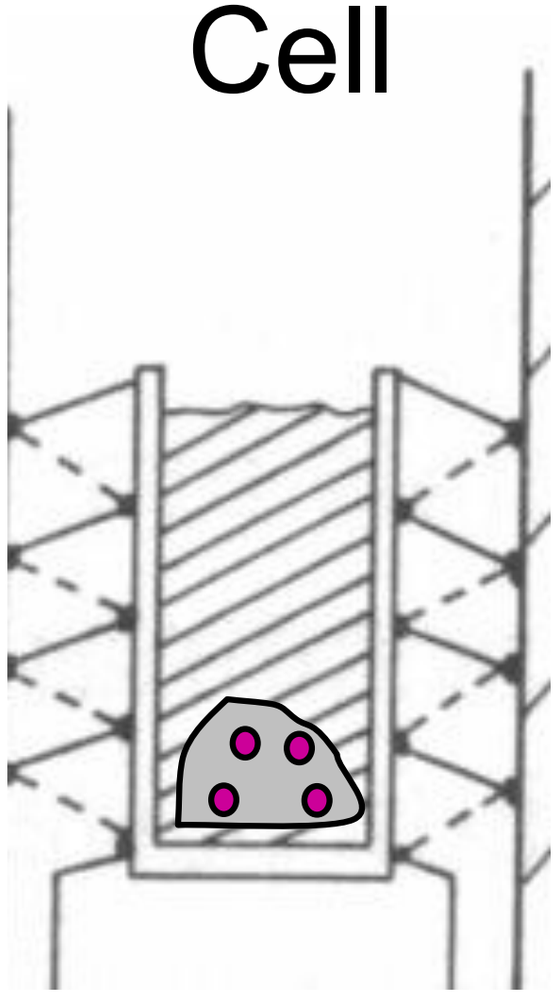


MS 70 Tian-Calvet calorimeter of SETARAM combined with a custom-designed high vacuum and gas dosing apparatus.

Karge, H.G. etal., J. Phys. Chem. 98, 1994, 8053.

Experiment: What do we measure?

Sample Cell



Begin: gas + empty sample

End: some gas in sample + heat

In the Google we find:

- differential heat of adsorption
- isosteric heat of adsorption

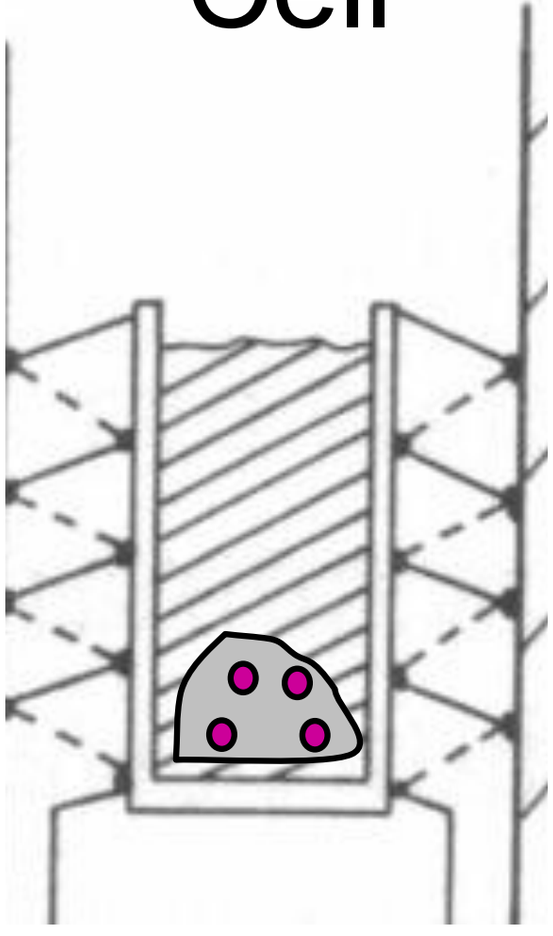
Which one do we measure?

Why are there these differences?

Rule 1 of thermodynamics: Never think you understand it

Rule 2 of thermodynamics: Understand the boundary conditions of the experiment

Sample Cell



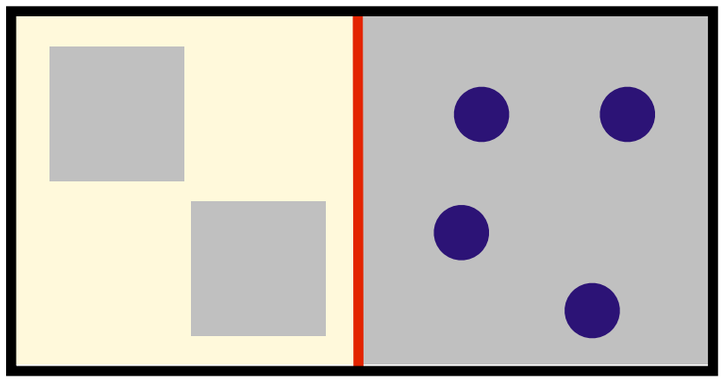
Boundary conditions (which variables are kept constant)

- volume and temperature
  - ----> differential heat of adsorption
- pressure and temperature
  - ----> isosteric heat of adsorption

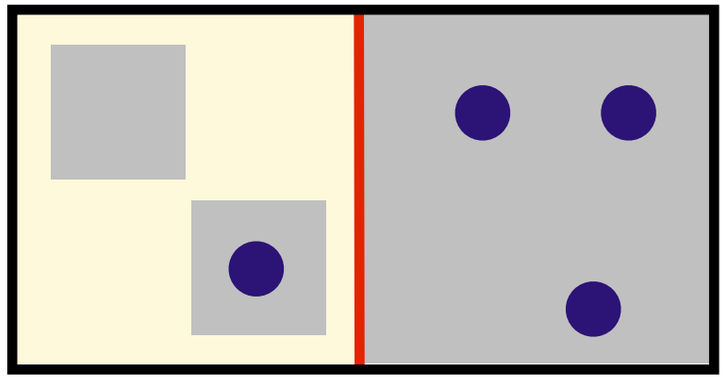
Rule 2 of thermodynamics:

Understand the boundary conditions of the experiment

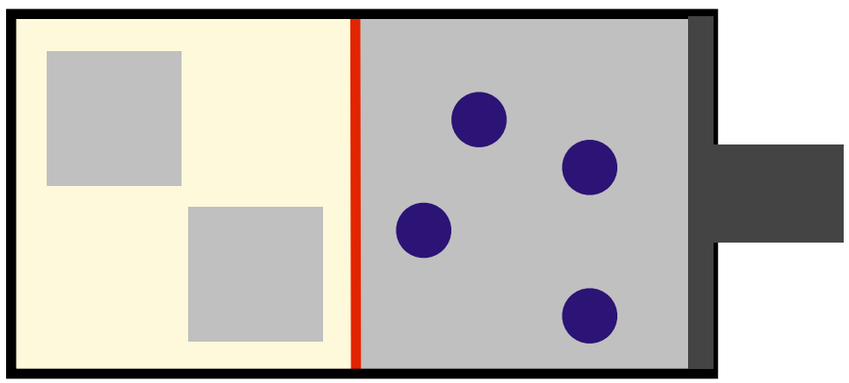
Before

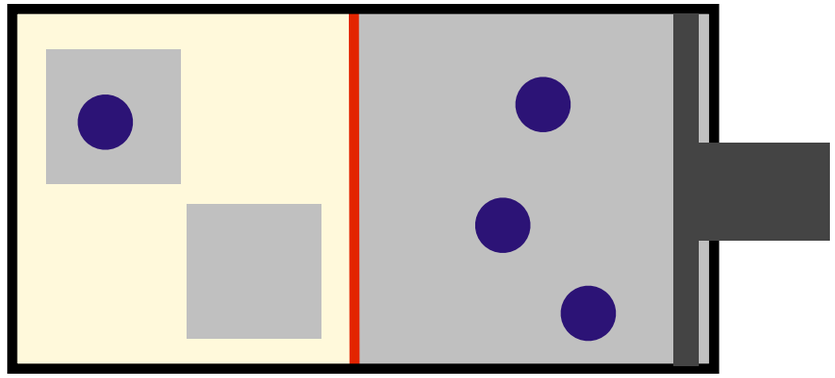


After

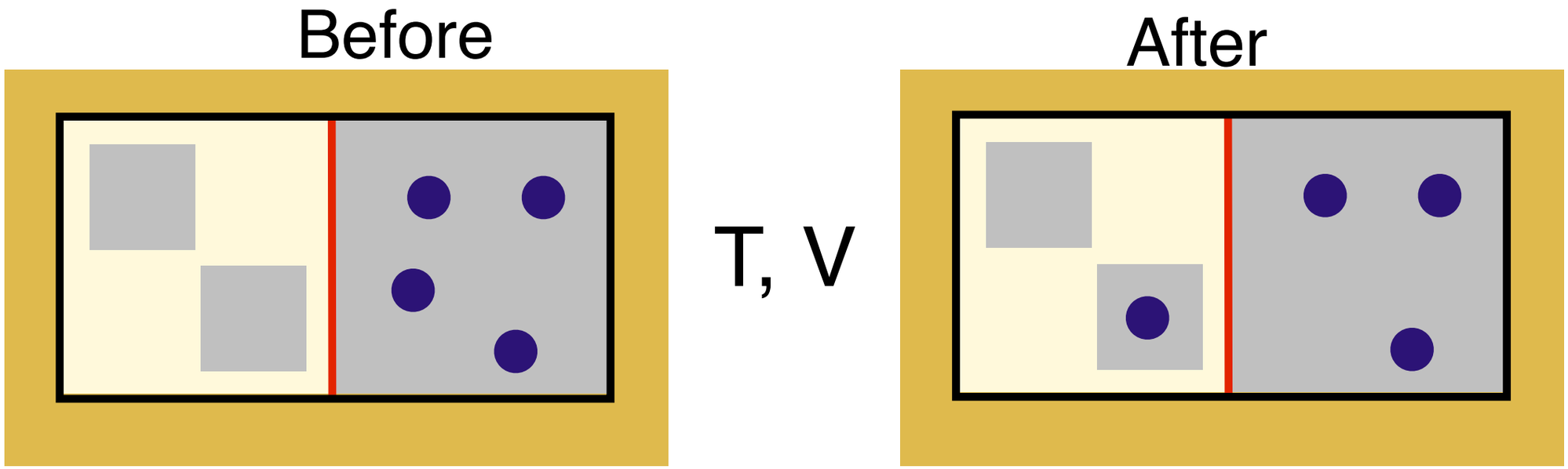


T, V





T, P



Total system is at constant temperature and constant volume

Experiment:

- We start with an empty adsorbate and a gas
- We open the separation and let the system equilibrate
- We measure the heat that is released Q^{isoTV}
- We measure the number of molecules that adsorb: n^A

First law:

$$dU = \delta Q + \delta W$$

Volume is constant: no work!

$$\Delta U = -Q^{\mathrm{iso}_{TV}}$$

Why the - ?

First law:

$$\Delta U = U^{After} - U^{Before} = -Q^{isoTV}$$

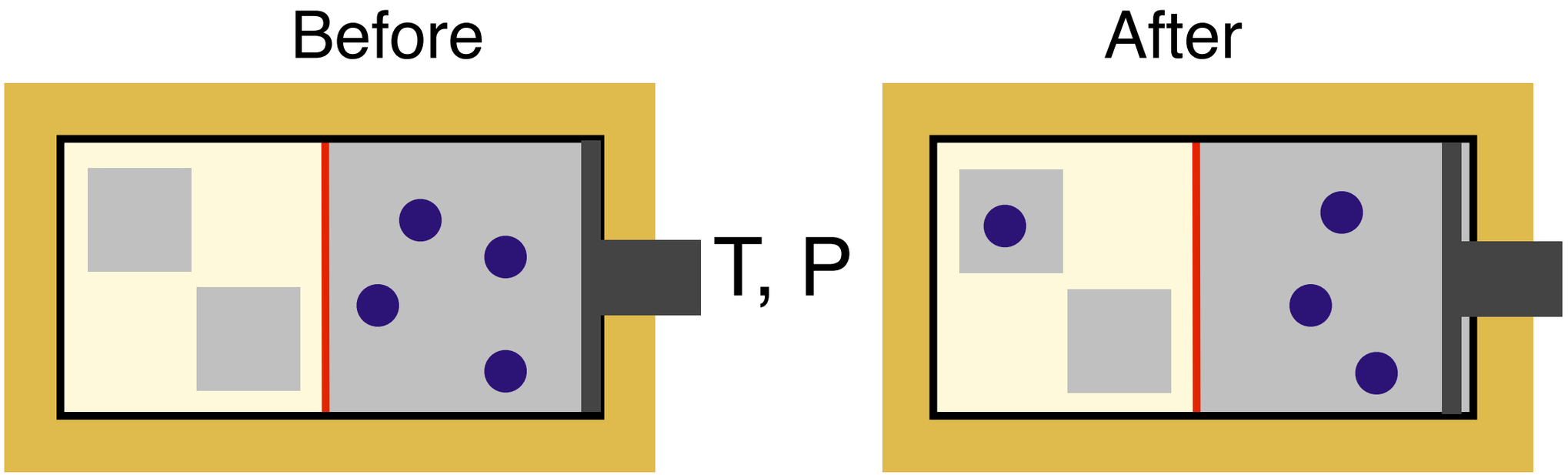
$$\Delta U^{A} + \Delta U^{G} = -Q^{isoTV}$$

$$\Delta U^{A} = n^{A}\left(\Delta u^{A} - \Delta u^{G}\right) = -Q^{isoTV}$$

$$-q^{isoTV} = \frac{-Q^{isoTV}}{n^{A}} = \Delta u^{A} - \Delta u^{G}$$

$$-q^{isoTV} = \Delta u^{A} - \Delta u^{G}$$

Hence **differential heat of adsorption** measures the change in the internal energy if a molecule moves from the gas phase to the adsorbed phase



Total system is at constant temperature and constant pressure

Experiment:

- We start with an empty adsorbate and a gas
- We open the separation and let the system equilibrate, keeping the **pressure constant**
- We measure the heat that is released Q^{iso}
- We measure the number of molecules that adsorb: n^A

First law:

$$dU = \delta Q + \delta W$$

$$\Delta U + p\Delta V = -Q^{iso}$$

Volume is **not** constant: work!

First law:

$$-Q^{iso} = \Delta U + p\Delta V = \left(U^{After} - U^{Before}\right) + p\left(V^{After} - V^{Before}\right)$$

$$p\Delta V = pV^{After} - pV^{Before} \approx \left(n - n^{A}\right)k_B T - nk_B T$$

Ideal gas

$$p\Delta V = -n^{A} RT$$

Enthalpy:

$$H \equiv U + pV$$

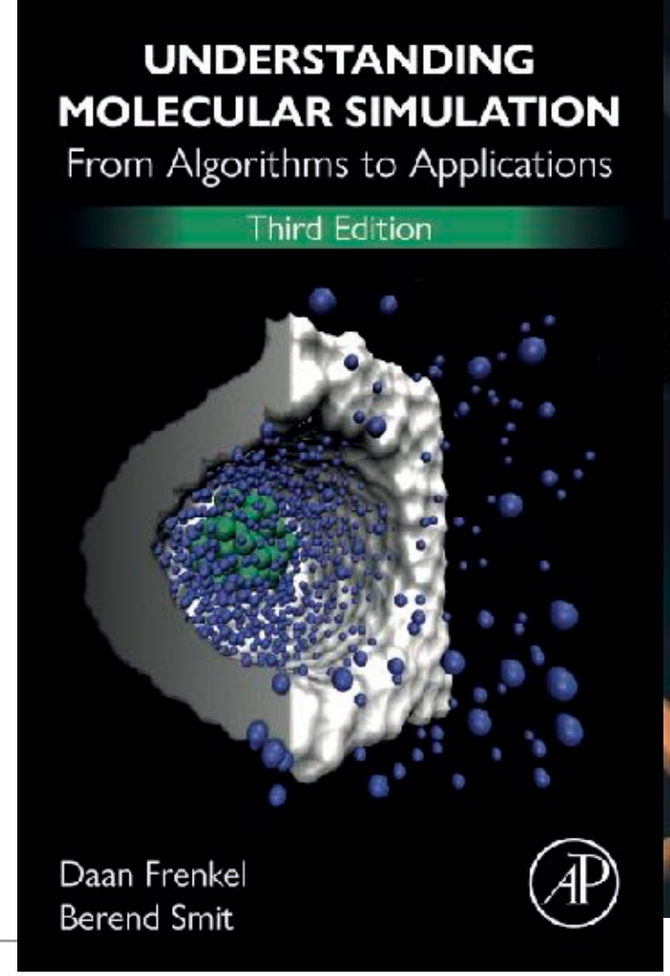
$$\Delta H = -Q^{iso}$$

$$-q^{iso} = \frac{-Q^{iso}}{n^{A}} = \Delta h^{A} - \Delta h^{G} \approx \left(\Delta u^{A} - \Delta u^{G}\right) + k_B T$$

Hence **isosteric heat of adsorption** measures the change in the enthalpy if a molecule moves from the gas phase to the adsorbed phase

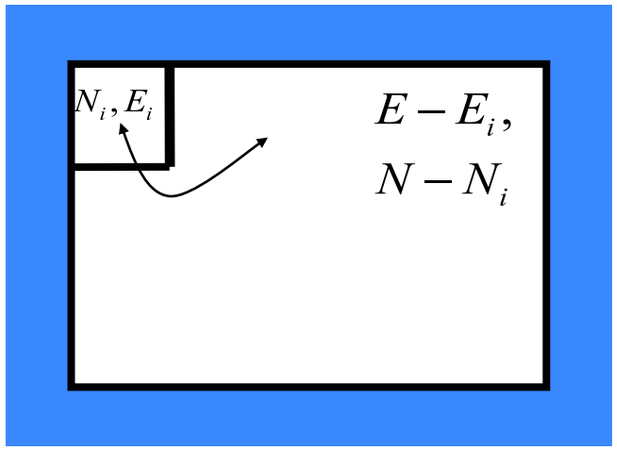
We have seen how the heat of adsorption is measured and why different experiments give different heats of adsorption.

Simulation and Thermodynamics of Adsorption (part 2)



2.3.3 μVT ensemble - Thermodynamics

μ, V, T ensemble



Consider a small system that can exchange *particles* and energy with a big reservoir

$$\ln\Omega\left(N-N_1, E-E_1\right) = \ln\Omega\left(N,E\right) - \left(\frac{\partial \ln\Omega}{\partial E}\right)E_1 - \left(\frac{\partial \ln\Omega}{\partial N}\right)N_1 + \cdots$$

The terms in the expansion follow from the connection with Thermodynamics: $S = k_B \ln\Omega$

Giving:

$$dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dN$$

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T} \qquad \text{and} \qquad \left(\frac{\partial S}{\partial N}\right)_{V,T} = -\frac{\mu}{T}$$

$$\ln\Omega\left(N-N_1,E-E_1\right)=\ln\Omega\left(N,E\right)-\left(\frac{\partial\ln\Omega}{\partial E}\right)E_1-\left(\frac{\partial\ln\Omega}{\partial N}\right)N_1+\cdots$$

$$\ln\Omega\left(N-N_1,E-E_1\right)=\ln\Omega\left(N,E\right)-\frac{E_1}{k_BT}+\frac{\mu N_1}{k_BT}+\cdots$$

$$\ln\left[\frac{\Omega\left(N-N_1,E-E_1\right)}{\Omega\left(N,E\right)}\right]=-\frac{1}{k_BT}\left(E_1-\mu N_1\right)$$

Hence, the probability to find E_1,N_1:

$$P\left(N_1,E_1\right)=\frac{\Omega\left(N-N_1,E-E_1\right)}{\sum_{i,j}\Omega\left(N-N_i,E-E_j\right)}=\frac{\Omega\left(N-N_1,E-E_1\right)/\Omega\left(N,E\right)}{\sum_{i,j}\Omega\left(N-N_i,E-E_j\right)/\Omega\left(N,E\right)}=Ce^{-\frac{1}{k_BT}\left(E_1-\mu N_1\right)}$$

$$P\left(N,E\right)\propto Ce^{-\beta\left(E-\mu N\right)}$$

In the classical limit, the partition function becomes

$$Q\left(\mu,V,T\right)=\sum_{N=0}^{\infty}\frac{e^{\beta\mu N}}{\Lambda^{3N}N!}\int dr^{N}e^{-\beta U\left(r^{N}\right)}$$

The probability to find a particular configuration:

$$P\left(N,r^{N}\right)\propto e^{-\beta\left[U\left(r^{N}\right)-\mu N\right]}$$

Statistical thermodynamics: μ, V, T ensemble

The partition function:

$$Q\left(\mu,V,T\right)=\sum_{N=0}^{\infty}\frac{e^{\beta\mu N}}{\Lambda^{3N}N!}\int dr^{N}e^{-\beta U\left(r^{N}\right)}$$

It is convenient to introduce scale coordinates:

$$s\equiv\frac{r}{L}$$

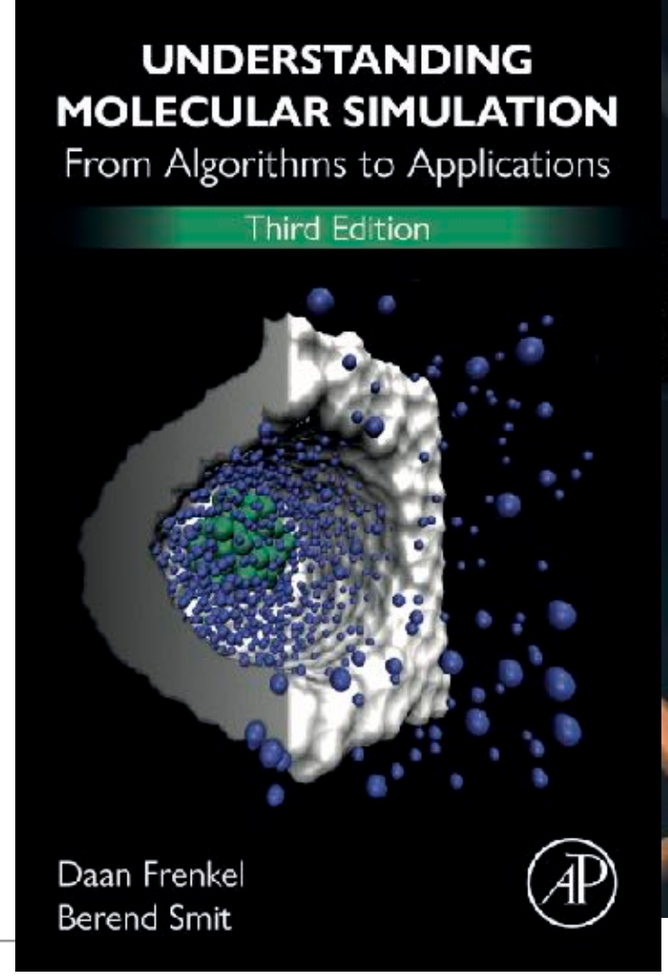
which gives

$$Q\left(\mu,V,T\right)=\sum_{N=0}^{\infty}\frac{V^{N}e^{\beta\mu N}}{\Lambda^{3N}N!}\int ds^{N}e^{-\beta U\left(r^{N}\right)}$$

The probability to find a particular configuration:

$$P\left(N,r^{N}\right)\propto\frac{V^{N}}{N!}e^{-\beta\left[U\left(r^{N}\right)-\mu N\right]}$$

Simulation and Thermodynamics of Adsorption (part 2)



2.3.4 μVT ensemble - Molecular Simulation

Grand-canonical ensemble (μ,,T)

Distribution we need to sample:

$$P\left(N,r^N\right) \propto \frac{V^N}{N!} e^{-\beta\left[U\left(r^N\right)-\mu N\right]}$$

Moves:

- select a particle at random: give this particle a random displacement
- add/remove a particle

Acceptance rule: detailed balance

Acceptance rules (μ,V,T)

Distribution we need to sample:

$$P\left(N,r^N\right) \propto \frac{V^N}{N!} e^{-\beta\left[U\left(r^N\right)-\mu N\right]}$$

Detailed balance:

$$\frac{\mathrm{acc}\left(o \to n\right)}{\mathrm{acc}\left(n \to o\right)} = \frac{N\left(n\right)}{N\left(o\right)}$$

Move: displacement of a randomly selected particle

$$P\left(n\right) \propto \frac{V^N}{N!} e^{-\beta\left[U\left(n\right)-\mu N\right]}$$

$$P\left(o\right) \propto \frac{V^N}{N!} e^{-\beta\left[U\left(o\right)-\mu N\right]}$$

$$\frac{\mathrm{acc}\left(o \to n\right)}{\mathrm{acc}\left(n \to o\right)} = \frac{\frac{V^N}{N!} e^{-\beta\left[U\left(n\right)-\mu N\right]}}{\frac{V^N}{N!} e^{-\beta\left[U\left(o\right)-\mu N\right]}} = e^{-\beta\left[U\left(n\right)-U\left(o\right)\right]}$$

Acceptance rules (μ,V,T)

Distribution we need to sample:

$$P\left(N,r^N\right) \propto \frac{V^N}{N!} e^{-\beta\left[U\left(r^N\right)-\mu N\right]}$$

Detailed balance:

$$\frac{\mathrm{acc}\left(o \to n\right)}{\mathrm{acc}\left(n \to o\right)} = \frac{N\left(n\right)}{N\left(o\right)}$$

Move: add or remove a particle

$$P\left(n\right) \propto \frac{V^{N_n}}{N_n!} e^{-\beta\left[U\left(n\right)-\mu N_n\right]} \qquad P\left(o\right) \propto \frac{V^{N_o}}{N_o!} e^{-\beta\left[U\left(o\right)-\mu N_o\right]}$$

$$\frac{\mathrm{acc}\left(o \to n\right)}{\mathrm{acc}\left(n \to o\right)} = \frac{\frac{V^{N_n}}{N_n!} e^{-\beta\left[U\left(n\right)-\mu N_n\right]}}{\frac{V^{N_o}}{N_o!} e^{-\beta\left[U\left(o\right)-\mu N_n\right]}} = \frac{N_n!}{N_o!} V^{\left(N_n-N_o\right)} e^{-\beta\left[U\left(n\right)-U\left(o\right)-\mu\left(N_n-N_o\right)\right]}$$

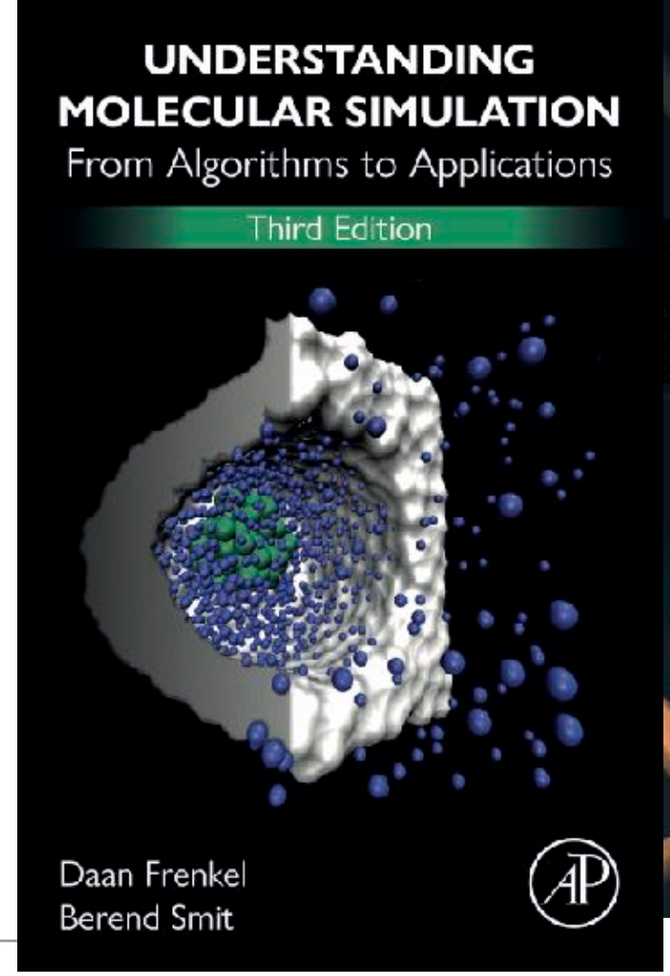
Algorithm 12 (Basic Grand-Canonical Ensemble Simulation)

```
PROGRAM mc_gc                                  basic μVT ensemble
                                               simulation
do icycl=1,ncycl                               perform ncycl MC cycles
 ran=int(ranf()*(npav+nexc))+1
 if (ran.le.npart) then
   call mcmove                                 displace a particle
 else
   call mcexc                                  exchange a particle
  endif                                        with the reservoir
  if (mod(icycl,nsamp).eq.0)
+   call sample                                sample averages
 enddo
 end
```

Algorithm 13 (Attempt to Exchange a Particle with a Reservoir)

```
 SUBROUTINE mcexc                      attempt to exchange a particle
                                       with a reservoir
 if (ranf().lt.0.5) then               decide to remove or add a particle
   if (npart.eq.0) return              test whether there is a particle
   o=int(npart*ranf())+1               select a particle to be removed
   call ener(x(o),eno)                 energy particle o
   arg=npart*exp(beta*eno)             acceptance rule (5.6.9)
+       /(zz*vol)
   if (ranf().lt.arg) then
     x(o)=x(npart)                     accepted: remove particle o
     npart=npart-1
   endif
 else
   xn=ranf()*box                       new particle at a random position
   call ener(xn,enn)                   energy new particle
   arg=zz*vol*exp(-beta*enn)           acceptance rule (5.6.8)
+       /(npart+1)
   if (ranf().lt.arg) then
     x(npart+1)=xn                     accepted: add new particle
     npart=npart+1
   endif
 endif
 return
 end
```

Simulation and Thermodynamics of Adsorption (part 2)

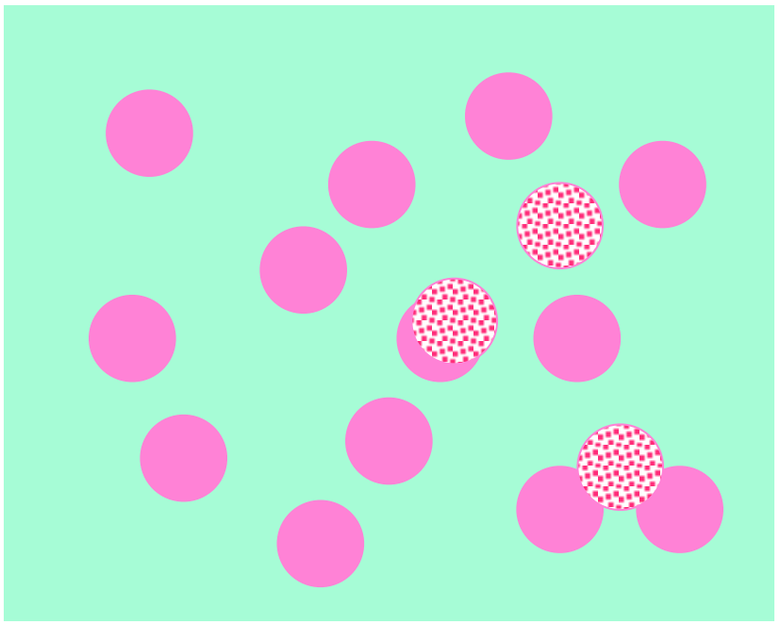


2.4 Chemical potential: Widom's test particle method

Hard spheres

For the chemical potential we have

$$\beta\mu^{ex} = -\ln\left(\int \mathrm{ds}_{N+1} \left\langle \exp\left[-\beta\Delta U^{+}\right]\right\rangle_{NVT}\right)$$



The hard sphere potential:

$$U(r) = \begin{cases} \infty & r \le \sigma \\ 0 & r > \sigma \end{cases}$$

If we insert a particle, we have

$$\left\langle \exp\left[-\beta\Delta U^{+}\right]\right\rangle = \begin{cases} 0 & \text{if overlap} \\ 1 & \text{no overlap} \end{cases}$$

Probability to insert a test particle!

Adsorption Thermodynamics

- Equilibrium conditions
- Langmuir Isotherms
- Henry coefficients of some materials

Henry coefficient:

$$K_H = \frac{1}{k_B T} \exp\left(-\frac{\mu^{\mathrm{ex}}(T,0)}{k_B T}\right)$$

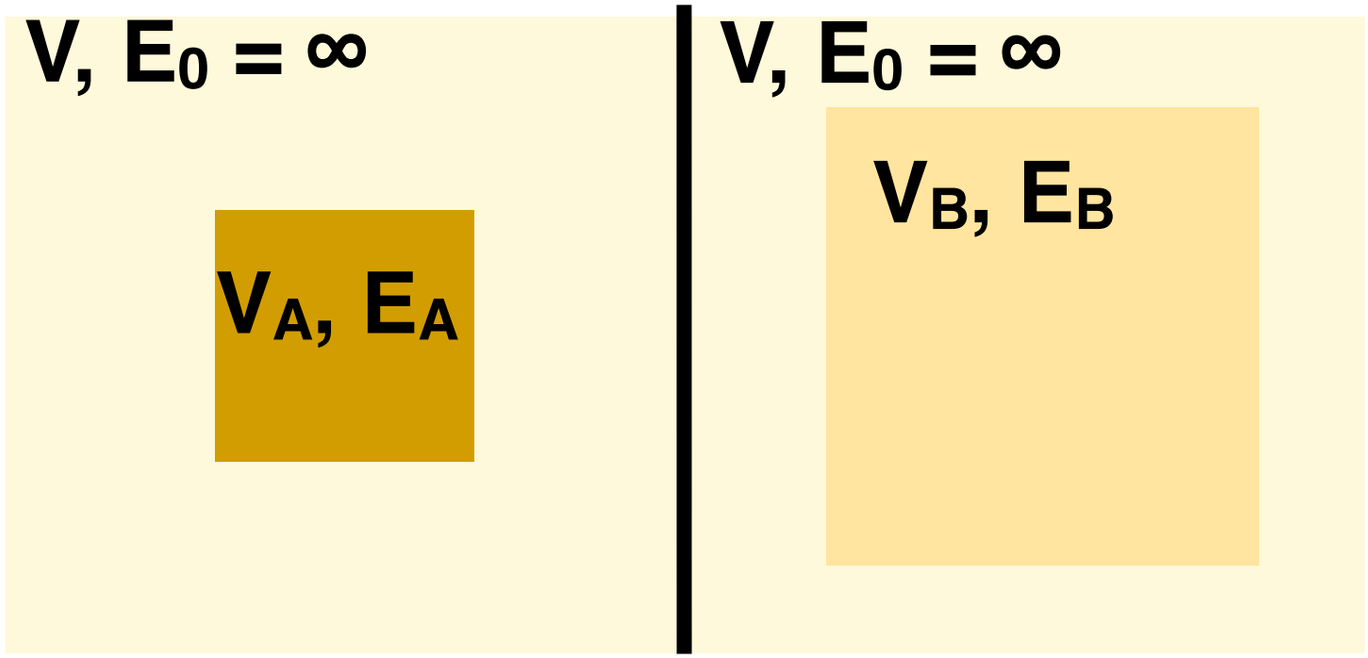
Statistical Mechanics:

The average energy of a CO_2 inserted in a random position in the adsorbent

$$\exp\left(-\frac{\mu^{\mathrm{ex}}(T,0)}{k_B T}\right) = \left\langle \exp\left(-\frac{U_{\mathrm{CO_2}}}{k_B T}\right)\right\rangle_{\mathrm{ads}}$$

$$K_H = \frac{1}{k_B T}\left\langle \exp\left(-\frac{U_{\mathrm{CO_2}}}{k_B T}\right)\right\rangle_{\mathrm{ads}}$$

Model adsorbent:



$V = 2V_B = 8V_A$

$E_A = E_B = 0$

Model adsorbate: Ideal gas molecules that feel energy E_i in the pores

Question:

- Which material has the highest Henry coefficient?

V, $E_0 = \infty$

V_A, $E_A = 0$

$$K_H = \frac{1}{k_B T} \left\langle \exp\left(-\frac{U_{CO_2}}{k_B T} \right) \right\rangle_{\text{ads}}$$

$$K_H = \frac{1}{k_B T} \left[\frac{V_A}{V} e^{(0)} + \frac{V - V_A}{V} e^{(-\infty)} \right] = \frac{1}{k_B T} \frac{V_A}{V}$$

Let us look at the limit $V_A \rightarrow V$:

$$K_H = \frac{1}{k_B T}$$

Loading:

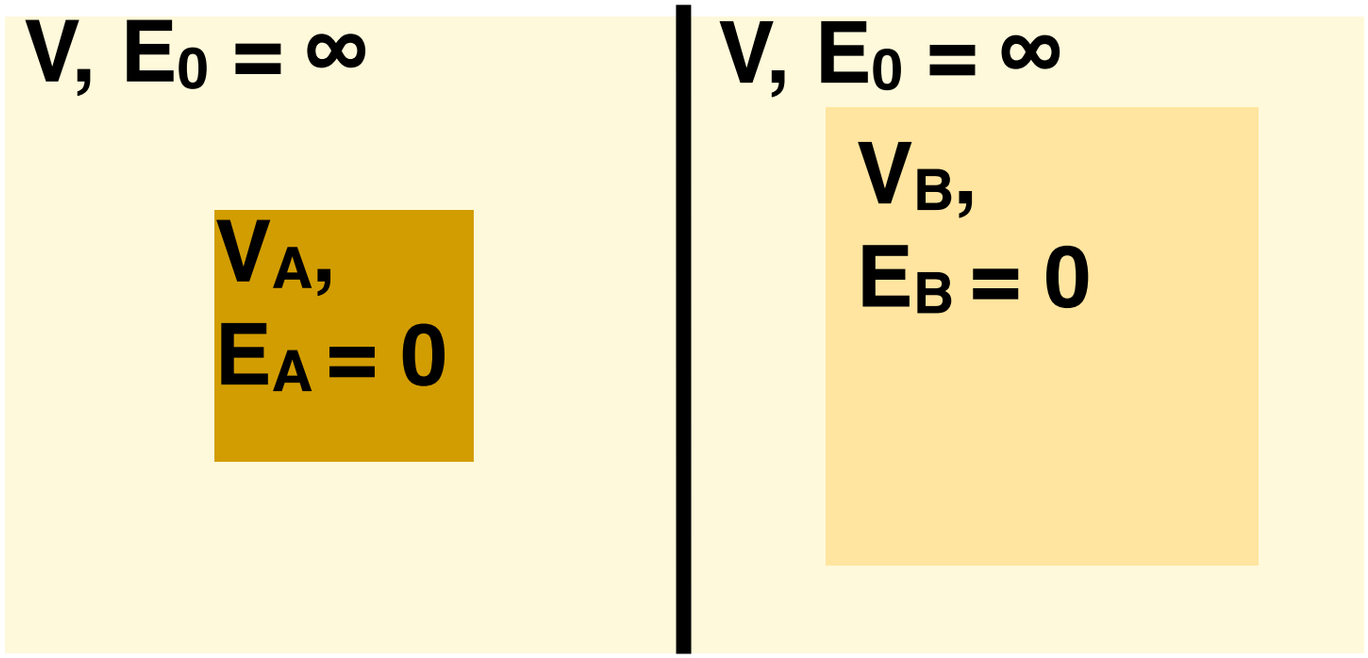
ideal gas

$$\sigma = K_H p = \frac{p}{k_B T}$$

For $V_A < V$, the loading is:

Entropy loss

$$\sigma = K_H p = \frac{p}{k_B T} \frac{V_A}{V}$$



Pore A:

$$K_H^A = \frac{1}{k_B T}\left[\frac{V_A}{V}e^{(0)} + \frac{V - V_A}{V}e^{(-\infty)}\right] = \frac{1}{k_B T}\frac{V_A}{V}$$

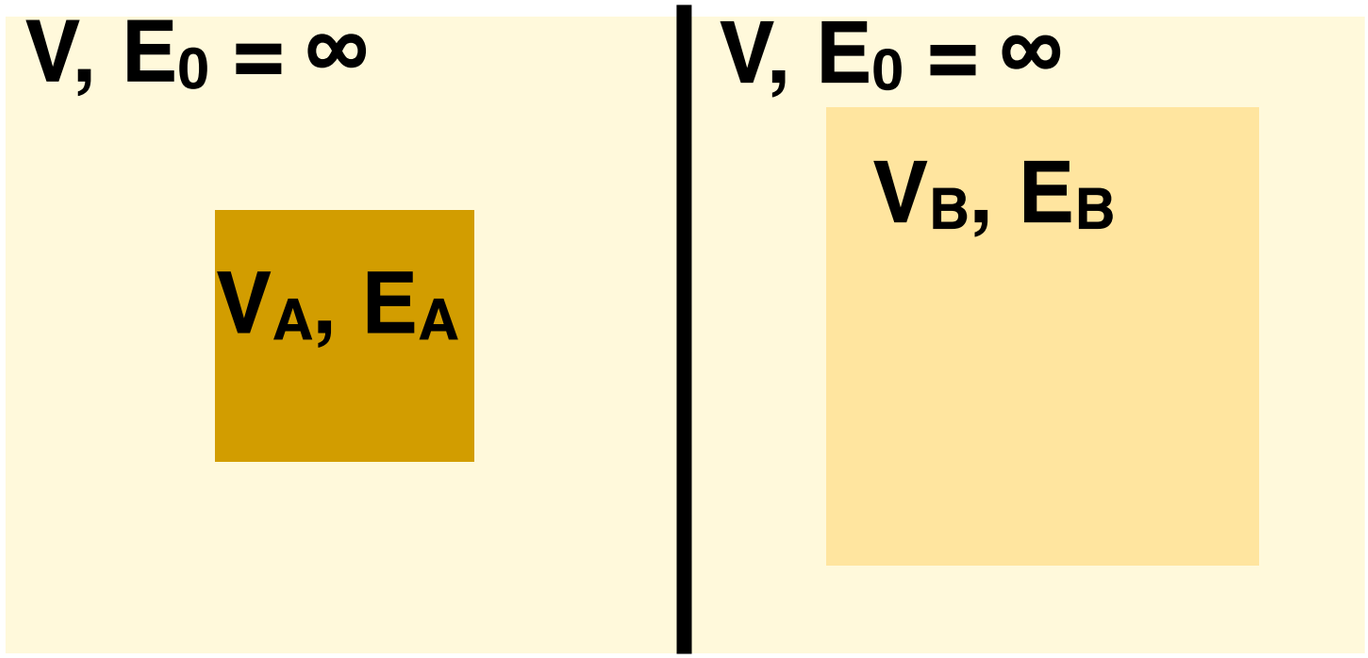
Pore B:

$$K_H^B = \frac{1}{k_B T}\left[\frac{V_B}{V}e^{(0)} + \frac{V - V_B}{V}e^{(-\infty)}\right] = \frac{1}{k_B T}\frac{V_B}{V}$$

Ratio of the Henry coefficients:

$$\frac{K_H^A}{K_H^B} = \frac{V_A}{V_B}$$

Model adsorbent:



$V = 2V_B = 8V_A$

$E_A = 2E_B = -20$ kJ/mole

Questions:

- At T=0 which material has the highest Henry coefficient?
- At T>> which material has the highest Henry coefficient
- For which temperature the Henry coefficients of the two materials are equal?

V, $E_0 = \infty$

V_A, E_A

$V = 2V_B = 8V_A$

$E_A = 2E_B = -20$ kJ/mole

$$K_H = \frac{1}{k_B T}\left\langle \exp\left(-\frac{U_{CO_2}}{k_B T}\right)\right\rangle_{ads}$$

Material A:

$$K_H^A = \frac{1}{k_B T}\left[\frac{V_A}{V}e^{(-E_A/k_B T)} + \frac{V - V_A}{V}e^{(-\infty)}\right]$$

$$K_H^A = \frac{1}{k_B T}\frac{V_A}{V}e^{(-E_A/k_B T)}$$

Energy gain

Entropy loss

$$\ln(k_B T K_H^A) = \frac{-E_A}{k_B T} + \ln\left(\frac{V_A}{V}\right)$$

Henry coefficient: balance between the entropy loss caused by the confinement and the energy gain caused by the interactions with the wall

Workflow hands-on

- Characterize the MOF: Zeo++
  - Density,
  - Pore volume: probe radius
  - Inaccessible pore blocking
- Compute the Henry coefficient (test particle insertion)
- Compute the CO_2 and N_2 pure component isotherms
- Use Ideal Adsorbed Solution Theory (IAST) to predict mixture isotherms:
  - Investigate selectivity