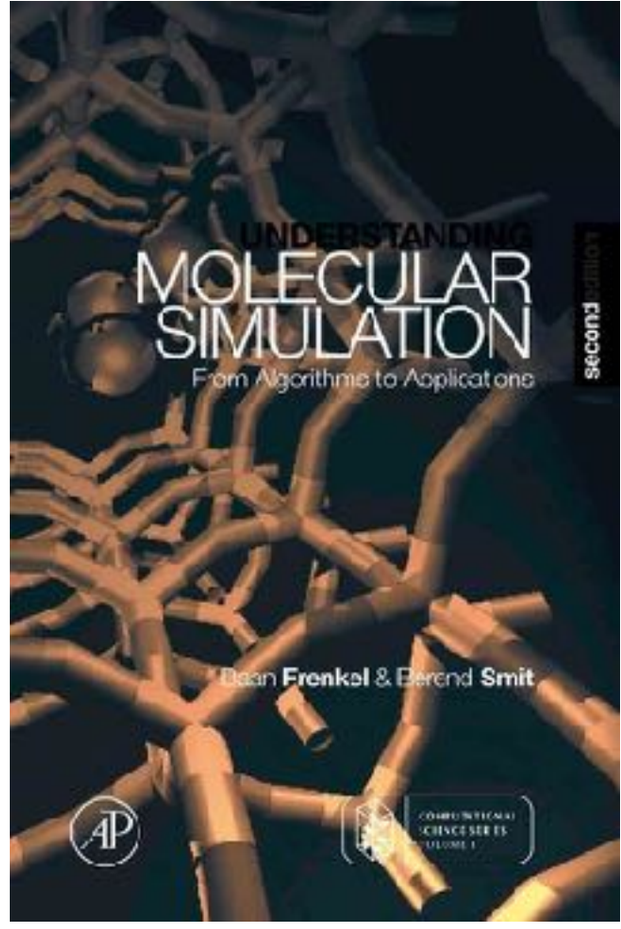
Simulation and Thermodynamics of Adsorption (part 2)



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
4. Calculation of the Chemical Potential
5. Some Case Studies

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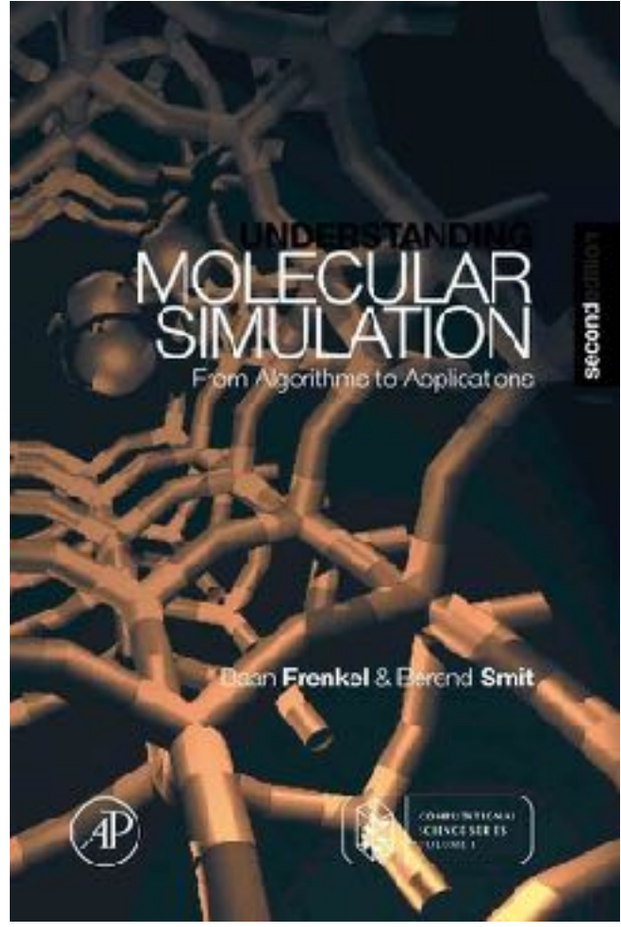
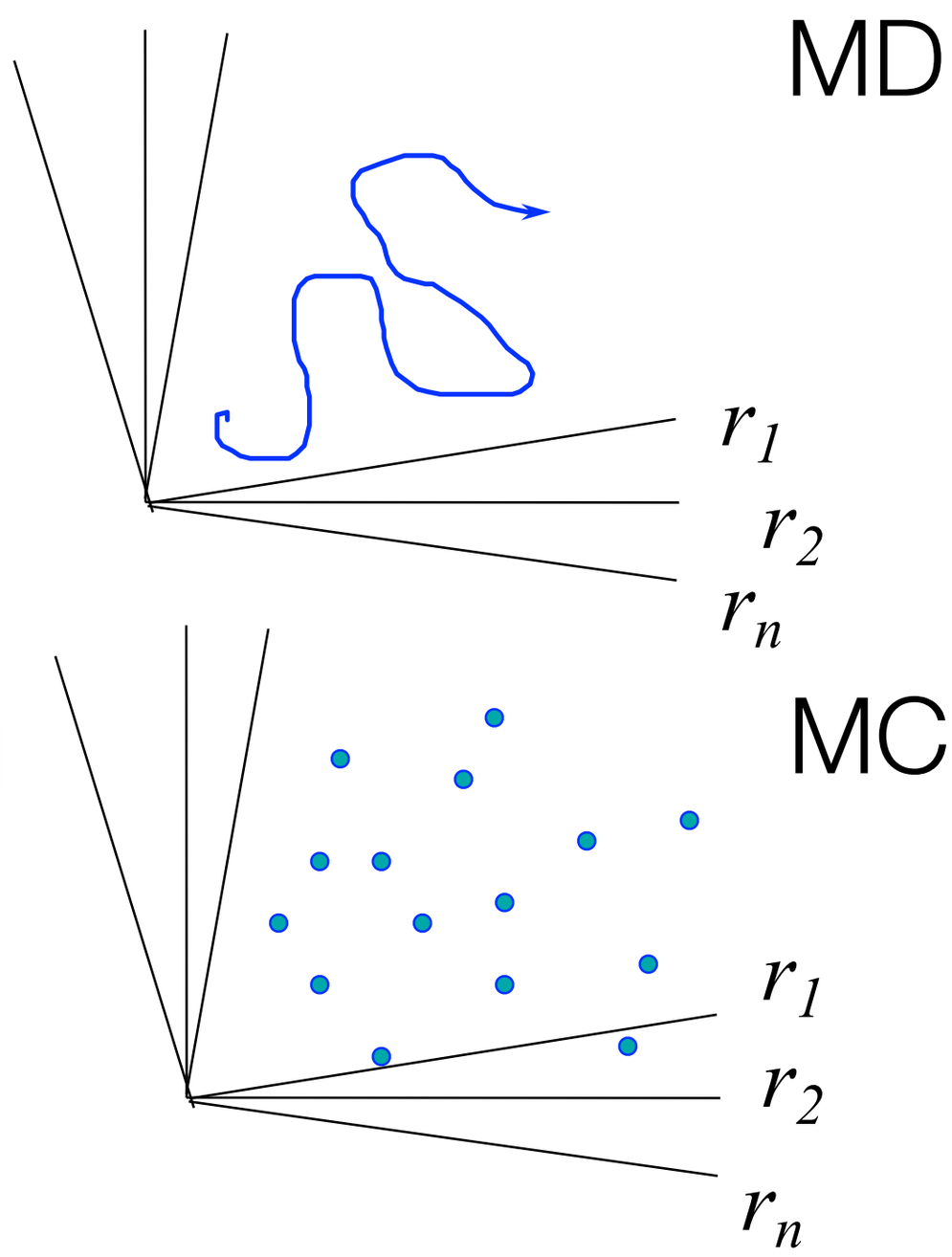


2.1 Introduction

Understanding Molecular Simulation

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 small

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
….

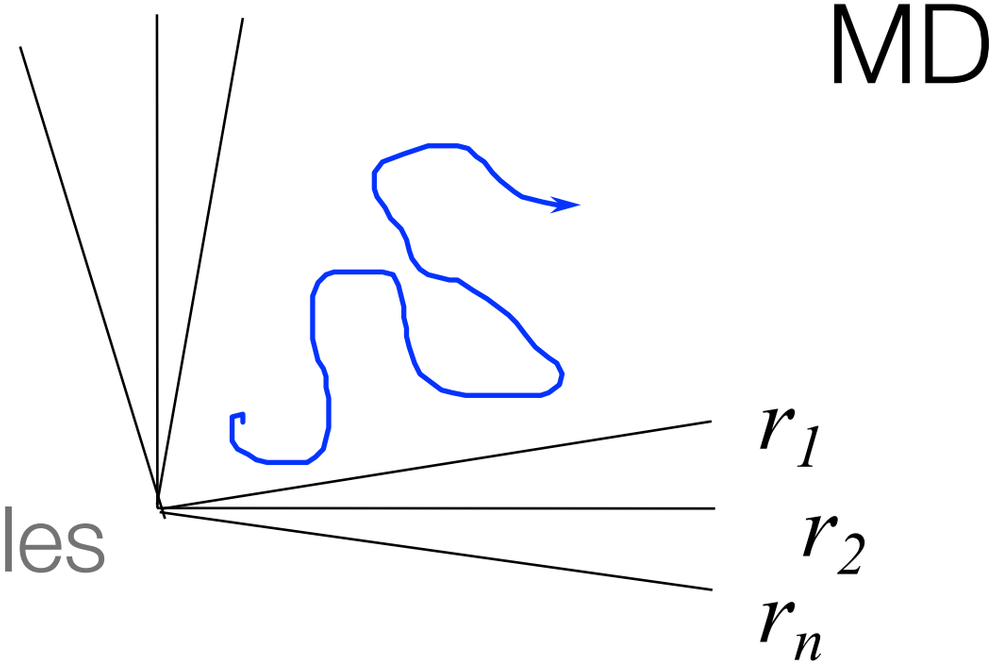
Diffusion coefficient
Viscosity
…

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



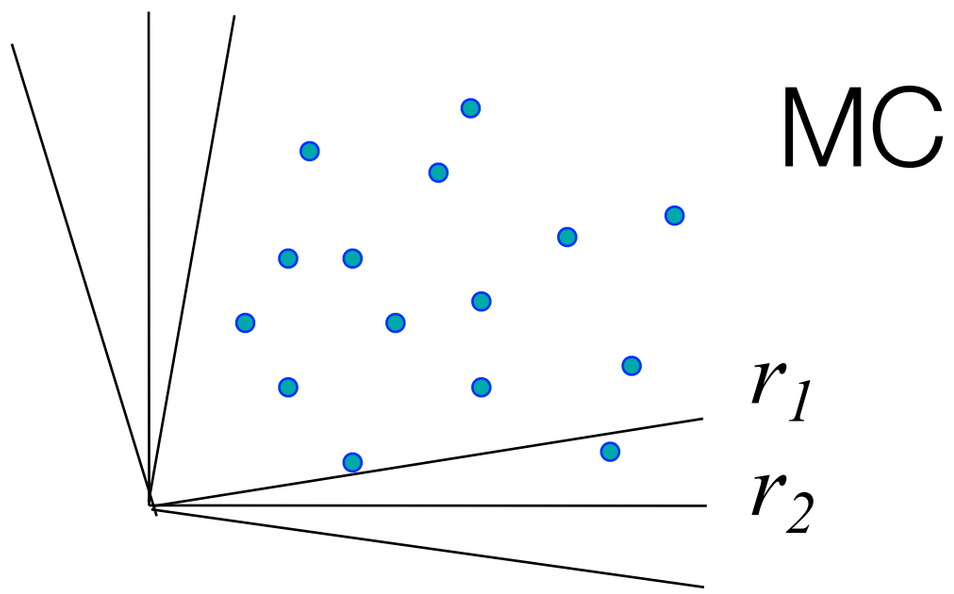
Monte Carlo

- 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



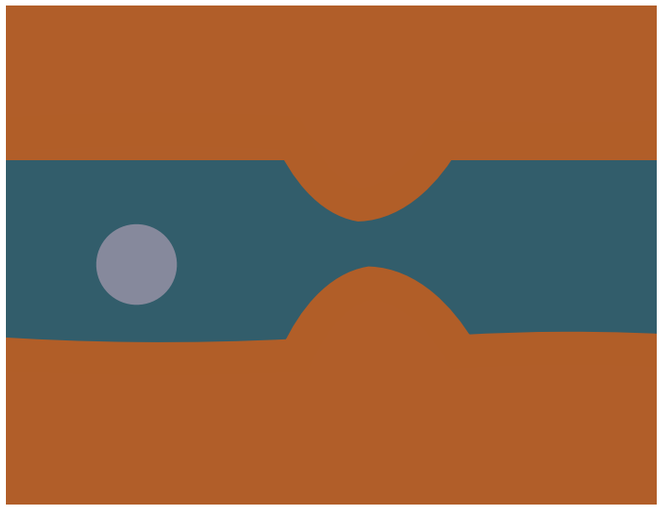
How do we know our simulation is correct?

- **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?

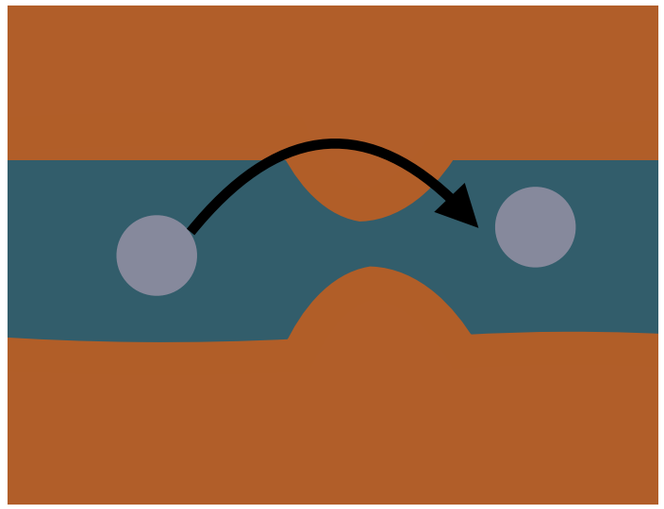
Statistical Thermodynamics

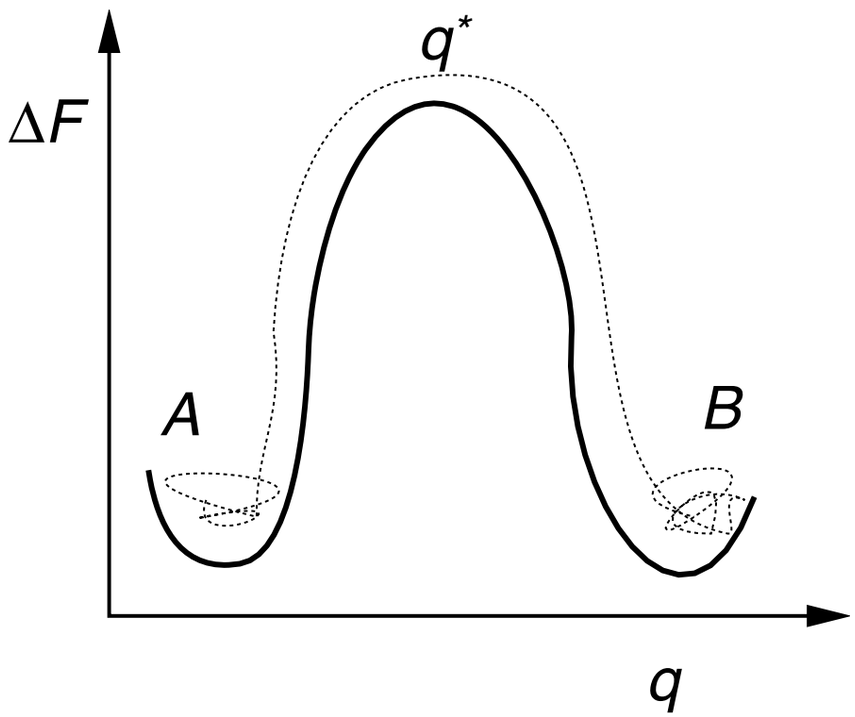
Monte Carlo versus Molecular Dynamics

molecular dynamics



Monte Carlo

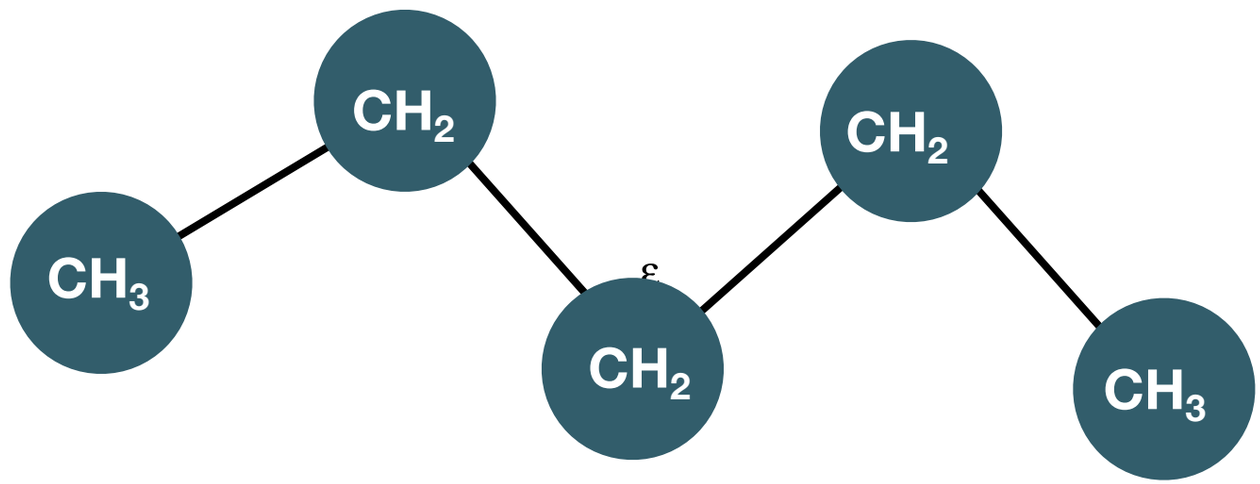




Intermolecular potential

United-atom model

- Fixed bond length
- Bond-bending
- Torsion



- Non-bonded: Lennard-Jones

$$u(r) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right]$$

- Point charges: Ions, Dipoles, Quadrupoles

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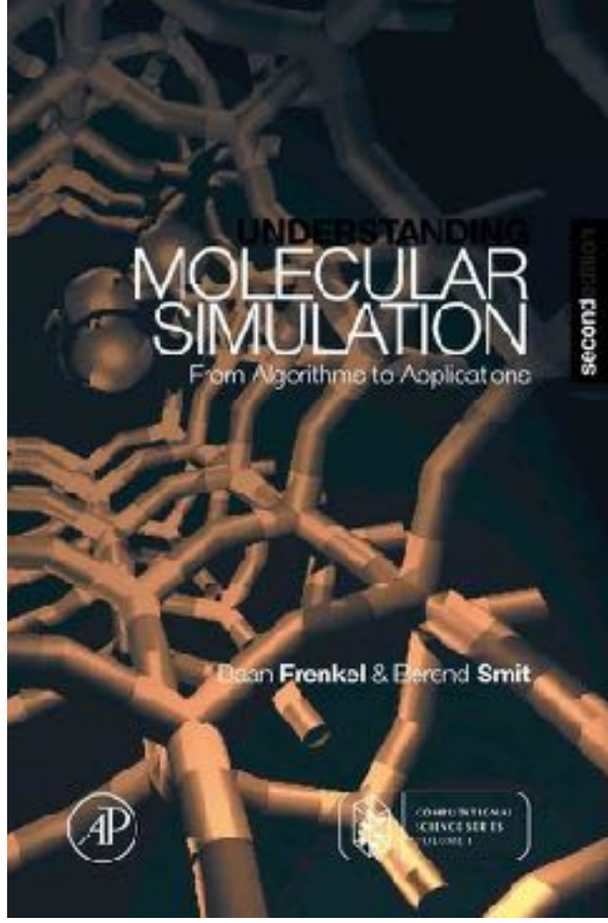


2.2.1 Statistical Thermodynamics: basics

Statistical Thermodynam

... but classical thermodynamics is based on laws

Basic Assumption:

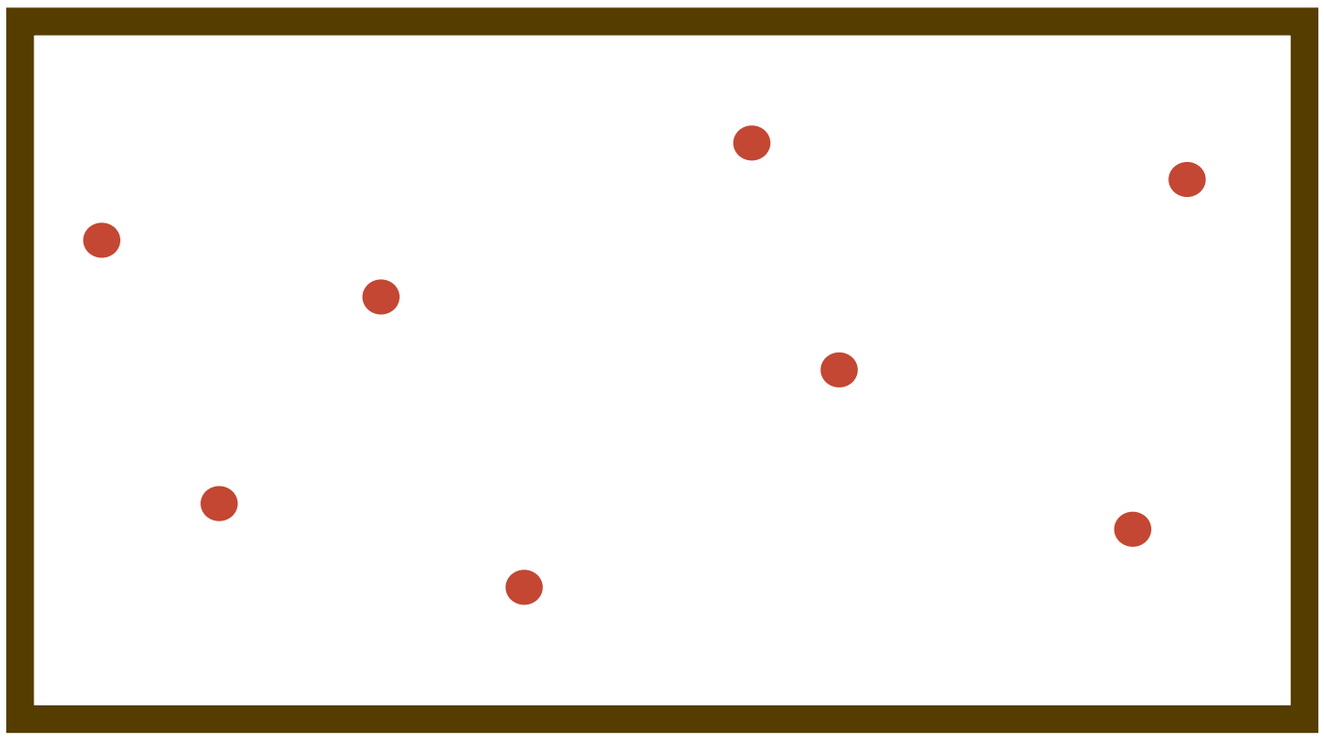
> For an isolated system any microscopic configuration is equally likely

Consequence:

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

Ideal gas - basic assumption

Let us make an ideal gas



We select:

(1) N particles,

(2) Volume V,

(3) initial velocities

+ positions

Basic Assumption:

> For an isolated system each microscopic configuration is equally likely

What is the probability to find this configuration?

The system has the same energy as the previous one!!

Our basis assumption states that this configuration is equally likely as any other configuration

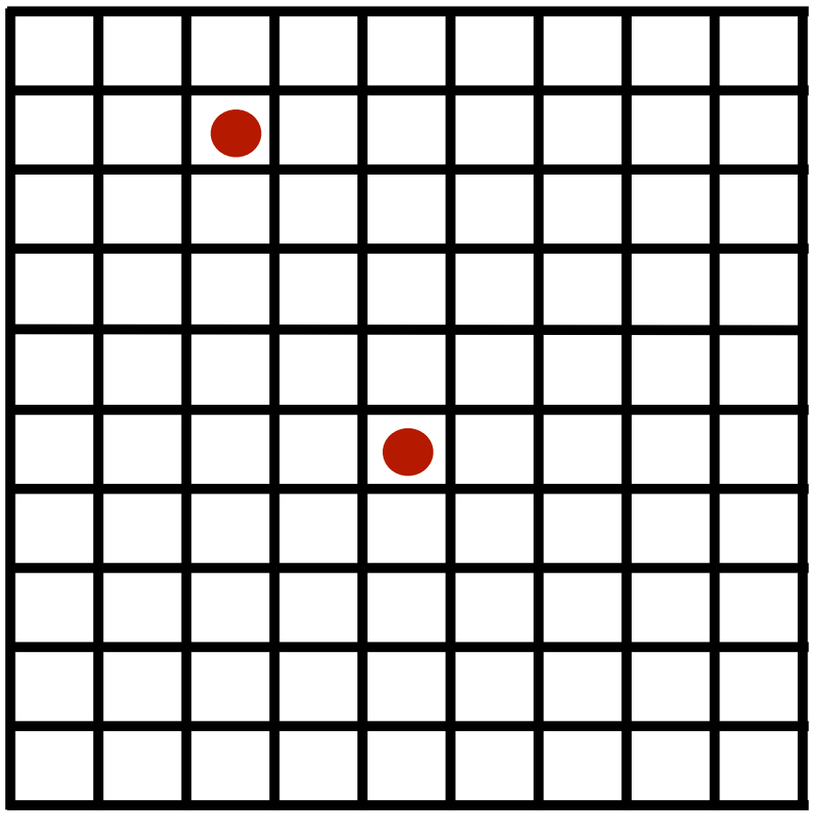
But having all atoms in the corner of our system seems to be very unlikely

…. and very dangerous

Our basic assumption must be seriously wrong!

Question: How to compute the probabilities of a particular configuration?

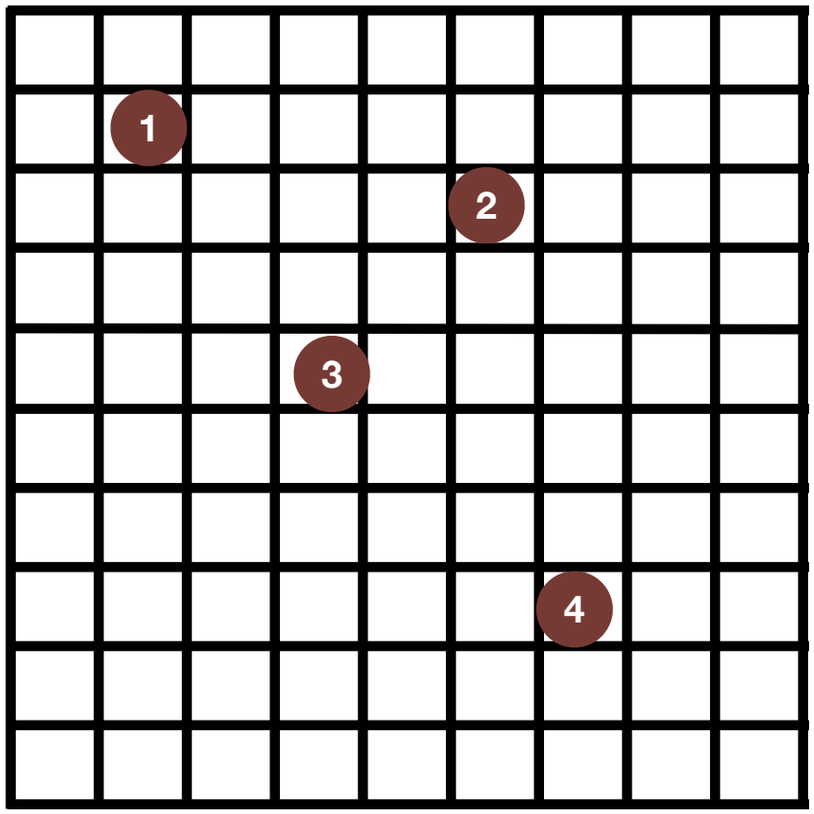
Use a lattice model to make the counting the number of possible confirmations easier



Assumptions:

- the position of a molecule is given by the lattice site
- there is no limit in the number of molecules per lattice site

Question: what is the probability of a given configuration?



Basic assumption:

$$P = \frac{1}{\text{Total \# of configurations}}$$

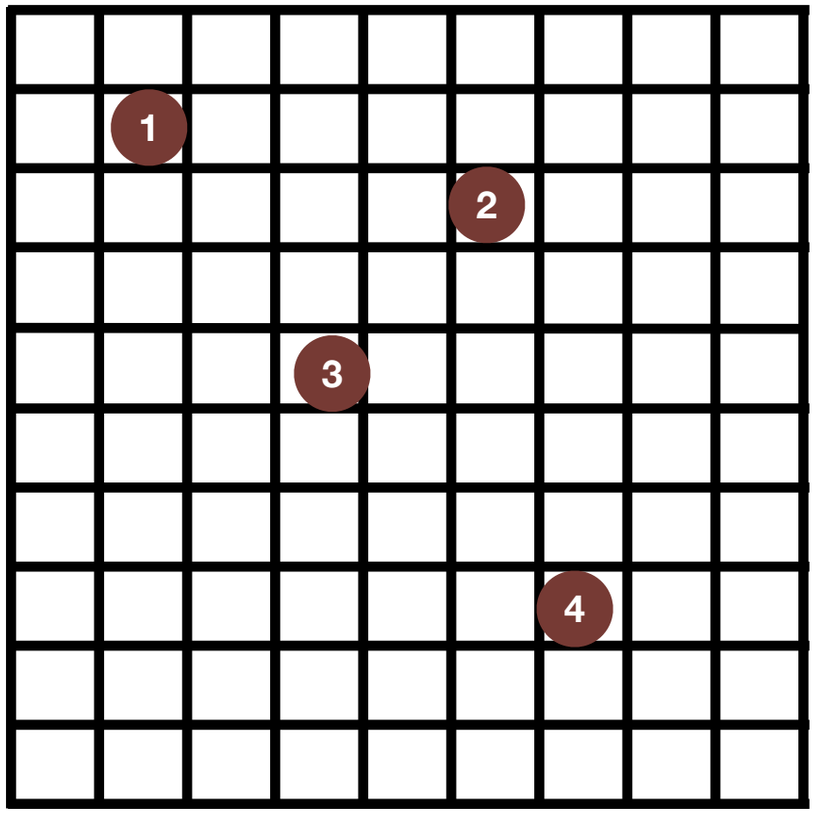
particle number 1 can be put in M positions, number 2 at M positions, etc.

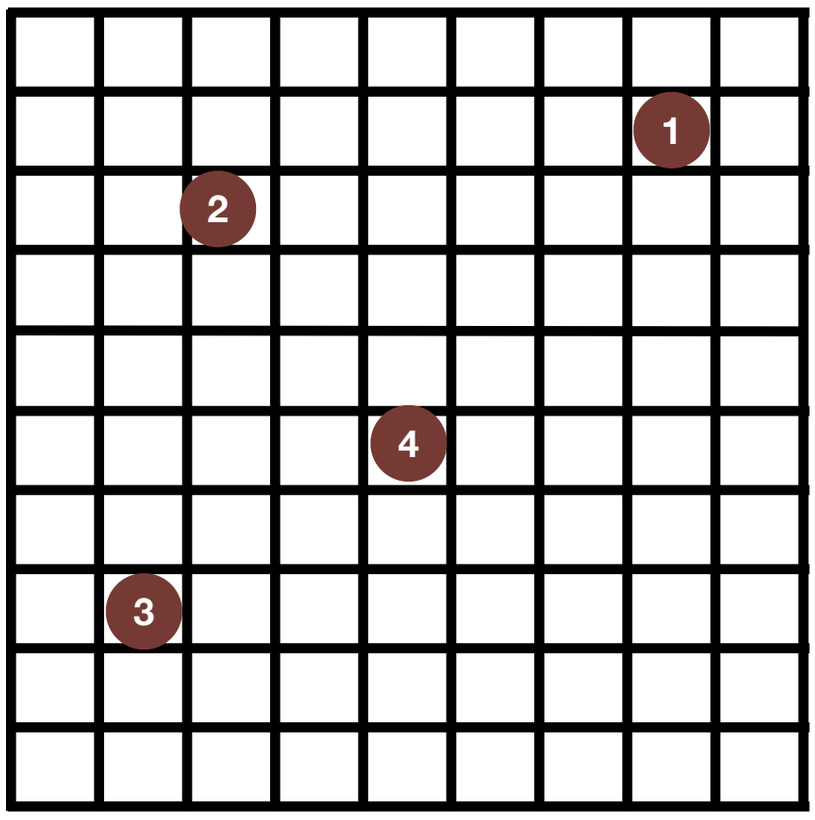
For N particle the total number of configurations is: M^N

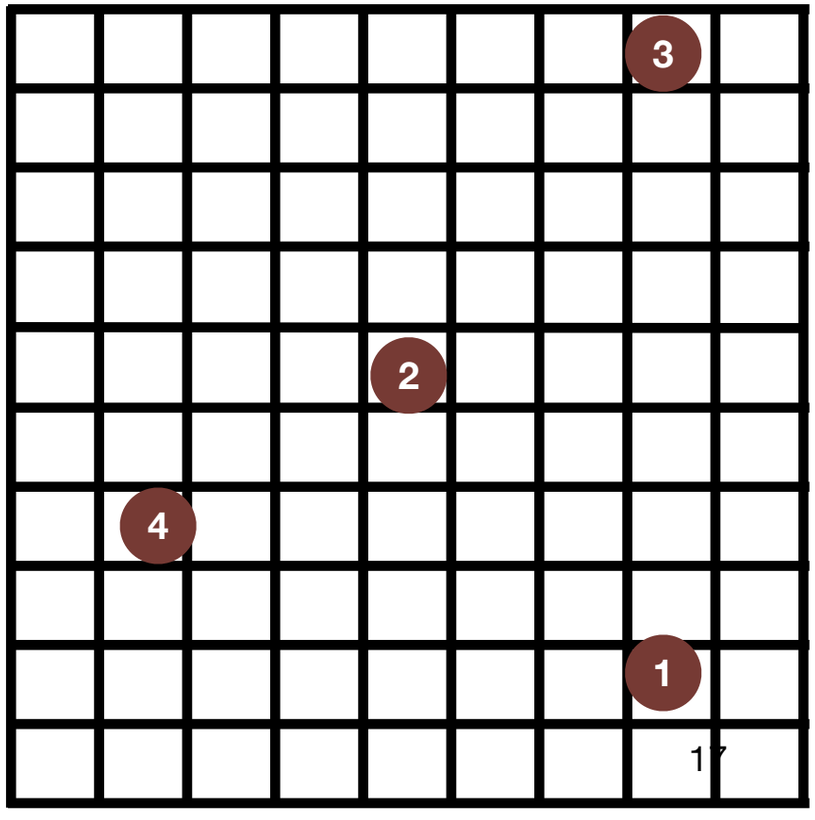
Hence the probability is: $P = \frac{1}{M^4}$

➡ **Question:** how does the statistics change if the particles are indistinguishable ?

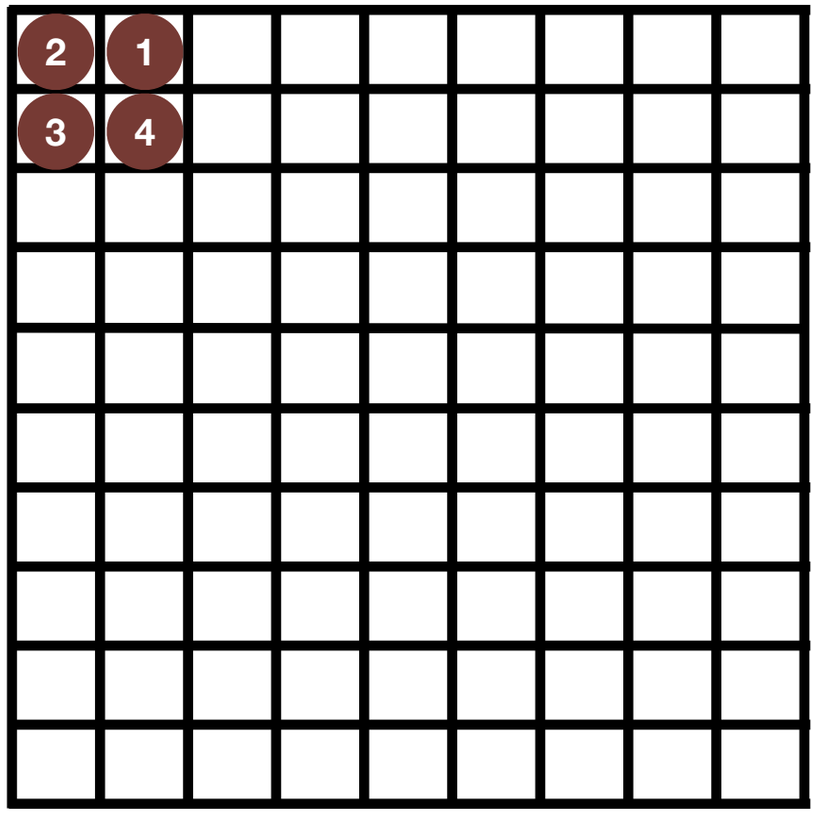
➡ **Question:** What are the probabilities of these configurations ?







➡ … and this one ?



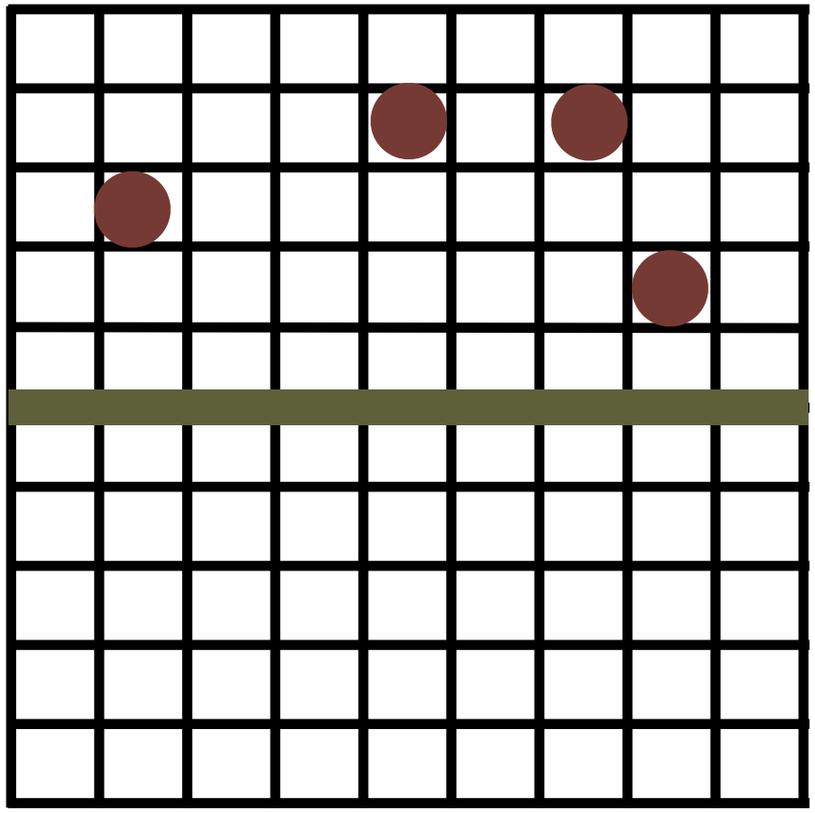
Is there a real danger that all the oxygen atoms are all in one part of the room?

Are we asking the right question?

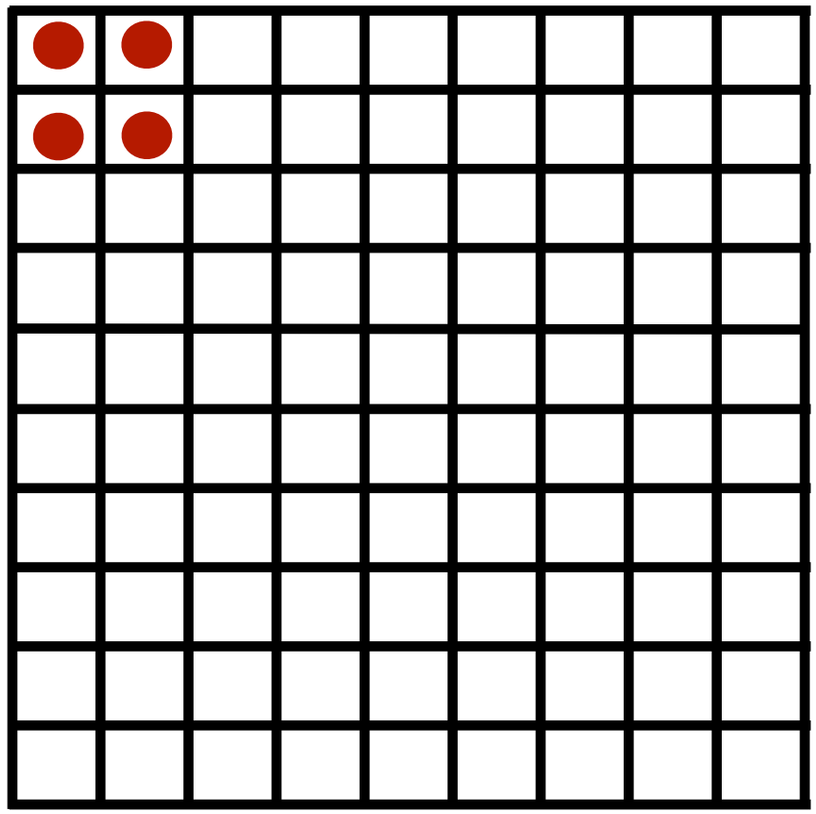
Thermodynamic is about **macroscopic properties**:

These are averages over many configurations

Measure densities: what is the probability that we have all our *N* gas particle in the upper half?



N	P(empty)
1	0.5
2	0.5 x 0.5
1. 3	1. 0.5 x 0.5 x 0.5
1000	10^{-301}



What is the probability to find this configuration?

exactly equal as to any other configuration!!!!!!

This is reflecting the microscopic reversibility of Newton's equations of motion. A microscopic system has no "sense" of the direction of time

Summary

- On a **microscopic level** all configurations are equally likely
- On a **macroscopic level**; as the number of particles is extremely large, the probability that we have a fluctuation from the average value is **extremely** low
- Let us now quantify this

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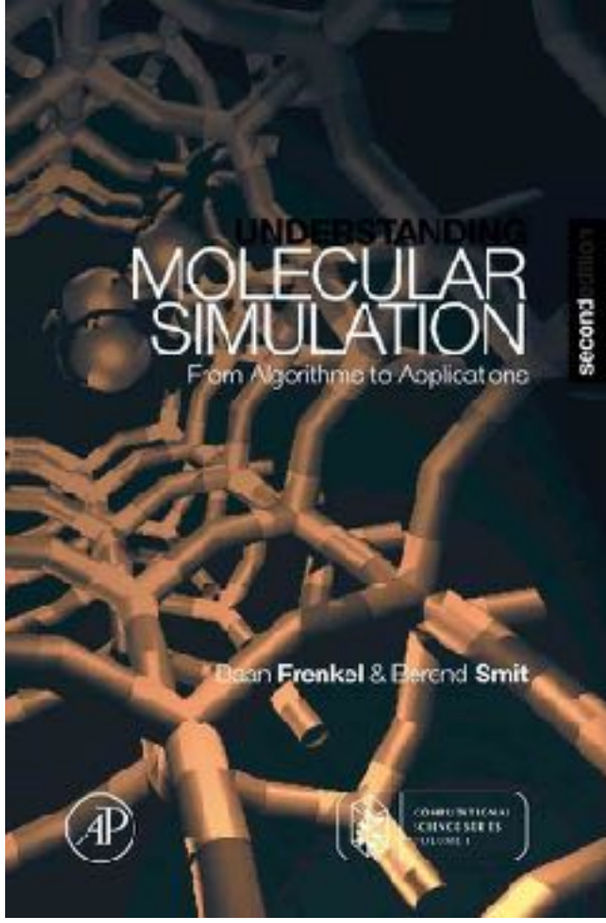
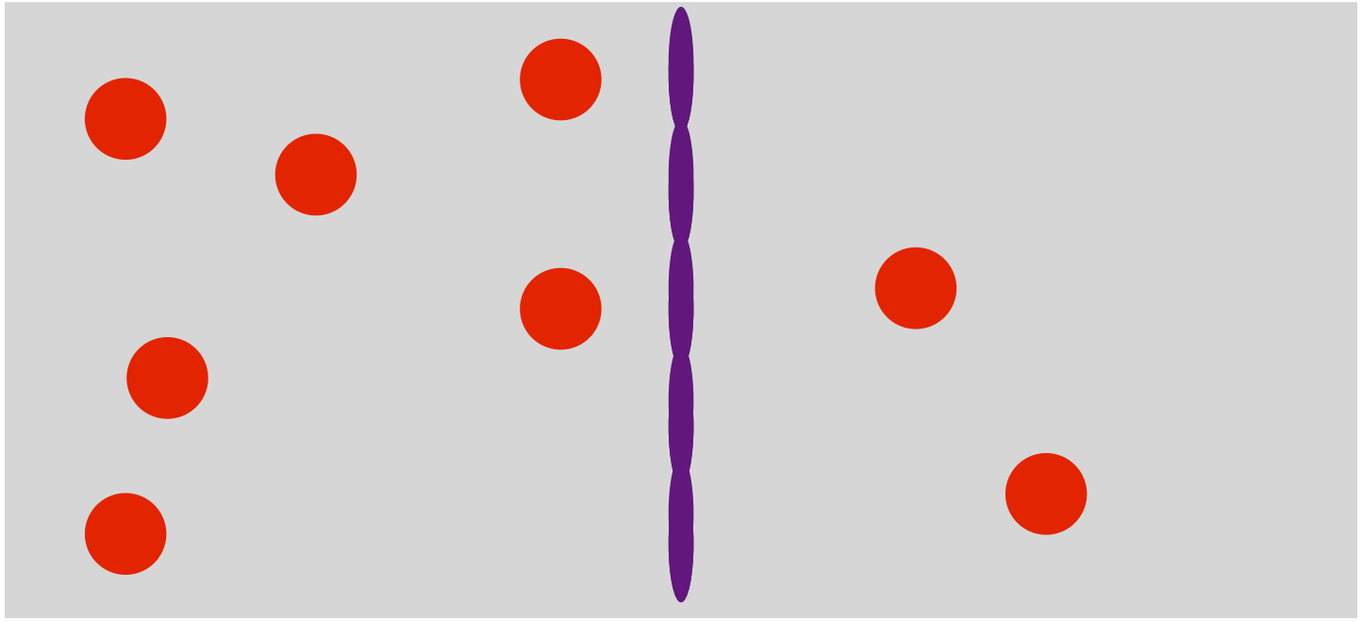


2.2.2 Equilibrium

Understanding Molecular Simulation

Question



If all configurations are equally likely what will be then the energy we will observe in the two boxes?

or this one

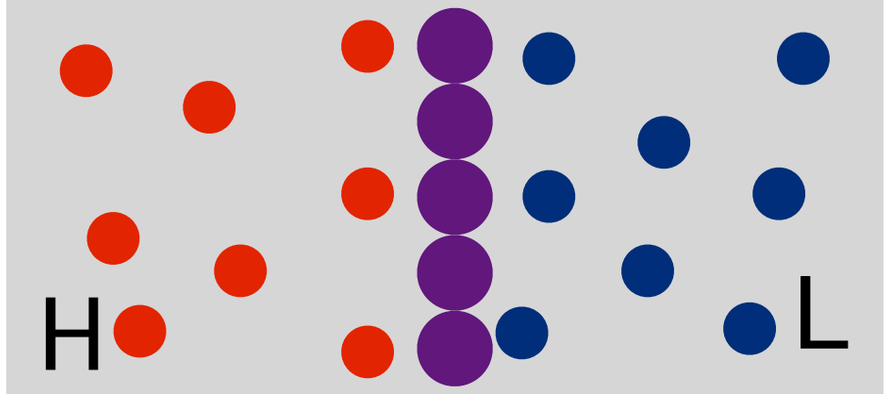
We have a closed and isolated system

Basic Assumption: every configuration is equally likely

Classical Thermodynamics

- 1st law of Thermodynamics
  - Energy is conserved
- 2nd law of Thermodynamics
  - Heat spontaneously flows from hot to cold (entropy increases)

Equilibrium



Let us look at the very initial stage

dq is so small that the temperatures of the two systems do not change

For system H $$dS_H = -\frac{dq}{T_H}$$

For system L $$dS_L = \frac{dq}{T_L}$$

Hence, for the total system:

$$dS = dS_L + dS_H = dq\left(\frac{1}{T_L} - \frac{1}{T_H}\right)$$

Heat goes from warm to cold: or if dq > 0 then $T_H > T_L$

This gives for the entropy change:

$$dS \geq 0$$

Hence, the entropy increases until the two temperatures are equal

Discussion: equilibrium (2)

We have a closed and isolated system, but heat can flow between system 1 and 2

Basic Assumption: every configuration is equally likely:

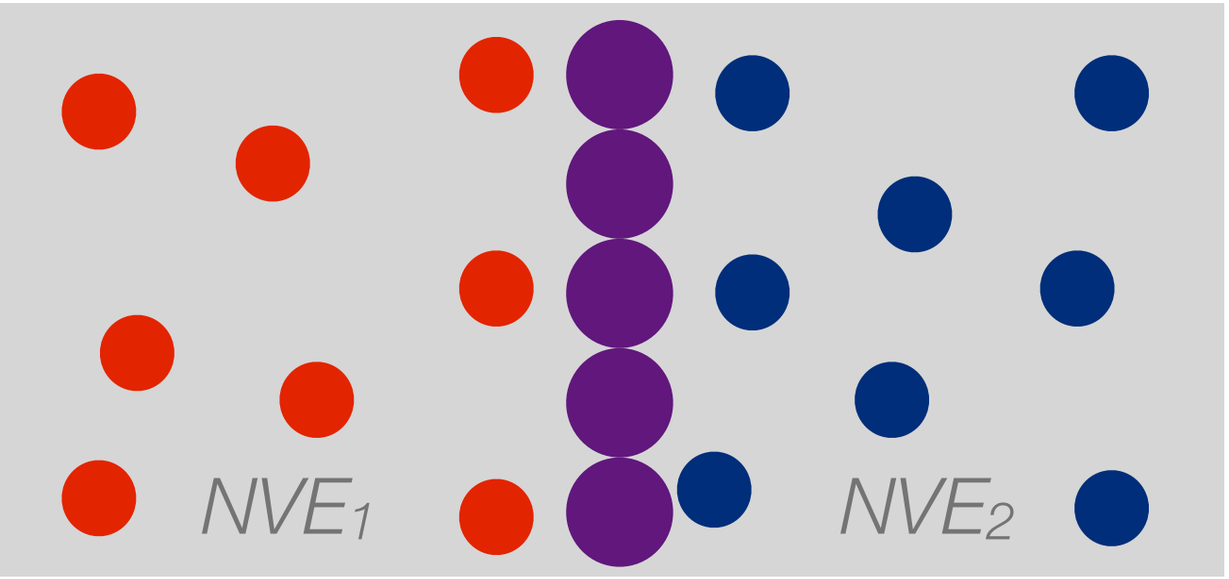
- **Questions:**
  - How do we know the system is in equilibrium?
  - how does this tell us what will what will be the macroscopic properties (e.g., temperature) of the two systems?

Solution:

All micro states **are** equally likely!

... but the number of micro states that give an particular density or energy distribution over the 2 systems **are not** ...

Macroscopically we will observe the most likely one



$P(E_1,E_2)$ The probability to find E_1 in volume 1 and E_2 in volume 2

$N_1(E_1)$ The number of configurations that result in an energy E_1 in volume 1.

$E_2 = E - E_1$ The total energy E is constant

$$P(E_1,E_2) = \frac{N_1(E_1)N_2(E-E_1)}{\sum_{E_1=0}^{E_1=E} N_1(E_1)N_2(E-E_1)} = CN_1(E_1)N_2(E-E_1)$$

Experimentally we will observe the most likeley configuration; which is given by the maximum

We need to find:

$$\frac{dP(E_1,E_2)}{dE_1} = 0$$

Finding:

$$\frac{dP\left(E_1,E_2\right)}{dE_1}=0$$

with:

$$P\left(E_1,E_2\right)=CN_1\left(E_1\right)N_2\left(E-E_1\right)$$

Is equivalent in finding:

$$\frac{d\ln\left(P\left(E_1,E_2\right)\right)}{dE_1}=0$$

or:

$$\frac{d\ln\left(N_1\left(E_1\right)\right)}{dE_1}+\frac{d\ln\left(N_2\left(E-E_1\right)\right)}{dE_1}=0$$

with $E_2=E-E_1$

$$\frac{d\ln\left(N_1\left(E_1\right)\right)}{dE_1}-\frac{d\ln\left(N_2\left(E-E_1\right)\right)}{dE_2}=0$$

The solution of this equation gives the energies in volume 1 and 2 that are most likely, i.e., the largest number of configurations have these energies

Let us define a property (almost S, but not quite) :

$$S^* = \ln\left(N\left(E\right)\right)$$

Equilibrium if:

$$\frac{d\ln\left(N_1\left(E_1\right)\right)}{dE_1} = \frac{d\ln\left(N_2\left(E-E_1\right)\right)}{dE_2}$$

or

$$\left(\frac{\partial S_1^*}{\partial E_1}\right)_{N_1,V_1} = \left(\frac{\partial S_2^*}{\partial E_2}\right)_{N_2,V_2}$$

And for the total system:

$$S^* = S_1^* + S_2^*$$

For a system at constant energy, volume and number of particles S* increases until it has reached its maximum value at equilibrium

What is this magic property S*?

Defined a property S^* (that is almost S):

$$S^*\left(E_1, E - E_1\right) = \ln\left(N\left(E_1, E - E_1\right)\right)$$

Question 1: Why is maximising S^* the same as maximising N?

Answer: The logarithm is a monotonically increasing function.

Question 2: Why is the logarithm a convenient function?

Answer: makes S* additive! Leads to extensivity.

Question 3: Why is S^* not quite entropy?

Answer: Units! The logarithm is just a unitless quantity.

$$S = k_B S^* = k_B \ln\left(N\left(E\right)\right)$$

For a partitioning of E between 1 and 2, the number of configuration is maximized when:

$$\left(\frac{\partial S_1^*}{\partial E_1}\right)_{N_1,V_1} = \left(\frac{\partial S_2^*}{\partial E_2}\right)_{N_2,V_2}$$

What do these partial derivatives relate to?

$$dE = TdS - pdV + \sum_{i=1}^{i=M} \mu_i dN_i$$

Temperature

$$T = \left(\frac{\partial E}{\partial S}\right)_{N_i,V} \quad \text{or} \quad \frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N_i,V}$$

Thermal equilibrium → equal temperature of system 1 and 2!

$$S = k_B S^* = k_B \ln\left(N\left(E\right)\right)$$

Question: How large is N(E) for a glass of water?

How to estimate N(E)

- Number of molecules of the order 10^{23}
- Make a grid of 10^6 cells (100x100x100)

$$N(E) \gg \left(10^6\right)^{10^{23}}$$

Summary:

- For macroscopic systems N(E) is super-astronomically large
- Macroscopic deviations from the second law of thermodynamics are not forbidden, but they are extremely unlikely.

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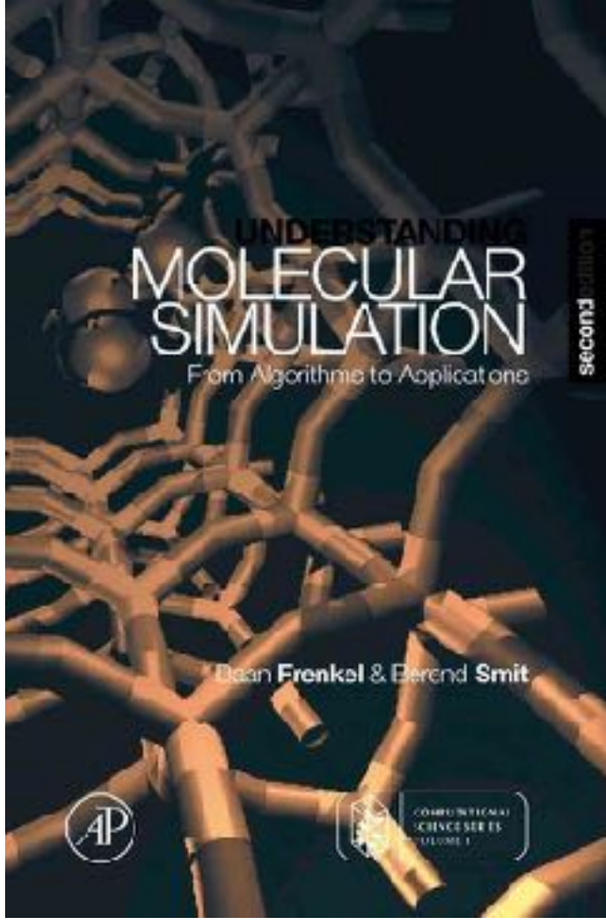
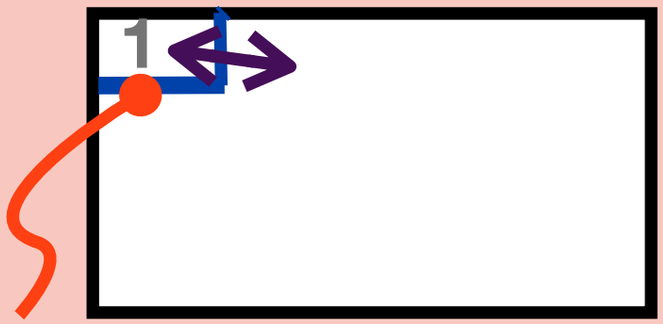


2.3.1 NVT ensemble - Statistical Thermo

Understanding Molecular Simulation

Canonical ensemble: classical thermodynamics



fixed volume but can exchange energy

Our entire system is isolated (NVE), but our subsystems (box 1 and bath) can exchange energy

First law $dU = TdS - pdV$

Second law $dS \geq 0$

Box 1: *constant volume and temperature*

1st law: $dU = dU_1 + dU_b = 0$ or $dU_1 = -dU_b$

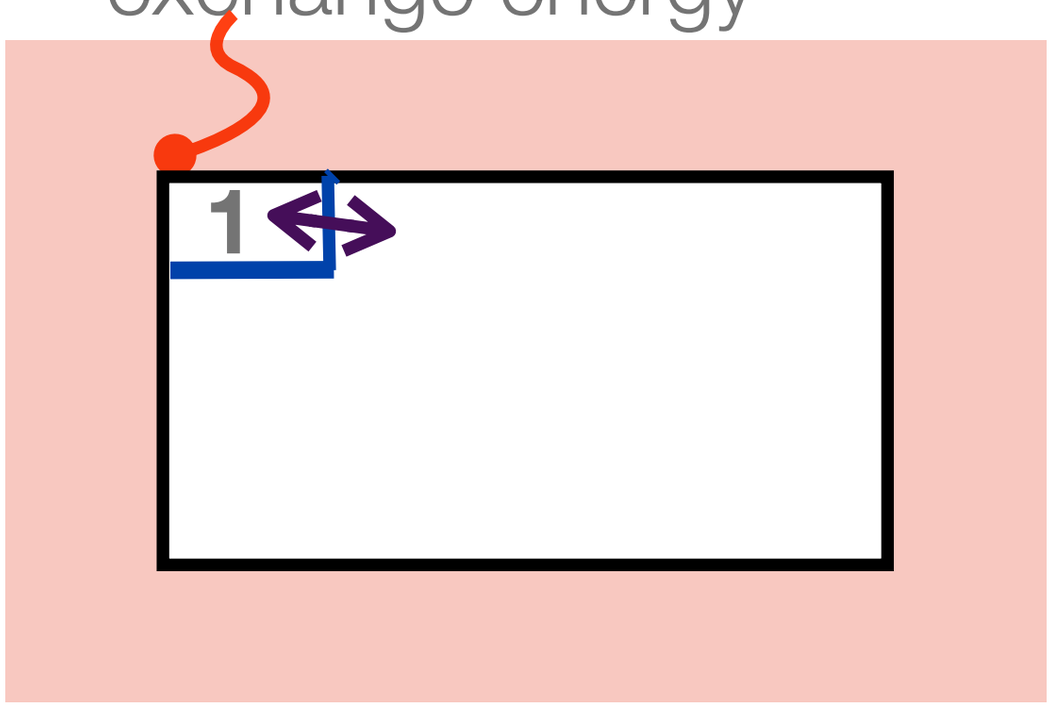
The bath is so large that the heat flow does not influence the temperature of the bath + the process is reversible

2nd law: $dS = dS_1 + dS_b \geq 0$ or $dS_1 + dS_b = dS_1 + \frac{dU_b}{T} = dS_1 - \frac{dU_1}{T} \geq 0$

Giving: $TdS_1 - dU_1 \geq 0$

we have a criteria that only depends on box 1

fixed volume but can exchange energy



Total system is isolated and the volume is constant

Box 1: *constant volume and temperature*

2nd law: $TdS_1 - dU_1 \geq 0$

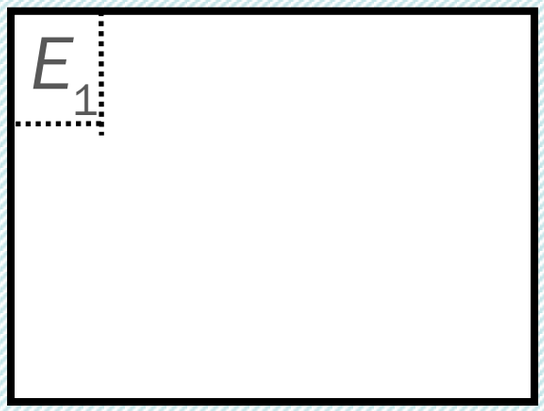
$$d\left(U_1 - TS_1\right) \leq 0$$

Let us define the Helmholtz free energy (*F*): $F \equiv U - TS$

For box 1 we can write: $dF_1 \leq 0$

Hence, for a system at *constant temperature and volume* the Helmholtz free energy decreases and takes its minimum value at equilibrium

Canonical ensemble: statistical mechanics



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

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

$=1/k_BT$

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

Hence, the probability to find E_1:

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

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

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

$\beta=1/k_BT$

Partition function: $$q = \sum_{n=1}^{\infty} e^{-\frac{E_n}{k_B T}} = \int_0^{\infty} e^{-\frac{E_n}{k_B T}} dn$$

we assume that the potential energy does **not** depend on the velocity

Hamiltonian: $$H = U_{\text{kin}} + U_{\text{pot}} = \sum_{i=i}^{N} \frac{p_i^2}{2m} + U_{\text{pot}}\left(r^N\right)$$

one atom:

$$Z_{1,V,T} = C\iint e^{-\frac{H}{k_B T}} dp^3 dr^3 = C\int e^{-\frac{p^2}{2mk_B T}} dp^3 \int e^{-\frac{U_{\text{pot}}(r)}{k_B T}} dr^3$$

one ideal gas atom: $U_p(r)=0$

$$Z_{1,V,T}^{\text{ideal gas}} = C\int e^{-\frac{p^2}{2mk_B T}} dp^3 \int 1 dr^3 = CV\int e^{-\frac{p^2}{2mk_B T}} dp^3 = CV\left(2\pi mk_B T\right)^{\frac{3}{2}}$$

Compare:

$$q_{\text{translational}} = \left(\frac{2\pi mk_B T}{h^2}\right)^{3/2} V = \frac{V}{\Lambda^3}$$

if we define $C=1/h^3$

$$Z_{1,V,T}^{\text{ideal gas}} = CV\left(2\pi mk_B T\right)^{\frac{3}{2}} = \frac{V}{\Lambda^3}$$

N gas molecules:

$$Z_{N,V,T} = \frac{1}{h^{3N}} \iint e^{-\frac{H}{k_B T}} dp^{3N} dr^{3N}$$

wrong: particles are indistinguishable

if we swap the position of two particles we do not have a new configuration!

$$Z_{N,V,T} = \frac{1}{h^{3N} N!} \iint e^{-\frac{H}{k_B T}} dp^{3N} dr^{3N}$$

Configurational part of the partition function:

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

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:

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

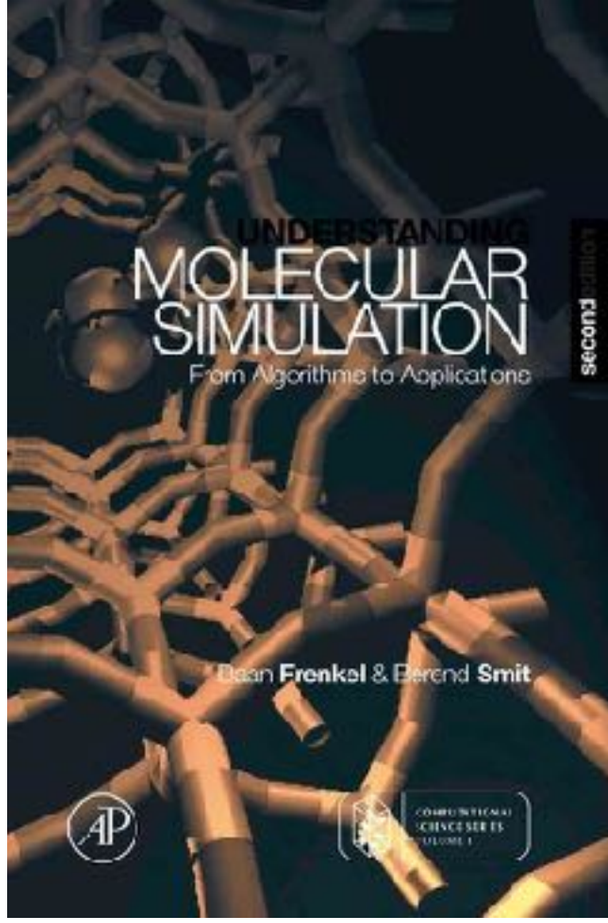
Ensemble average:

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

Free energy:

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

Simulation and Thermodynamics of Adsorption (part 2)



2.3.2 NVT ensemble - Molecular Simulation

Understanding 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 1 (Basic Metropolis Algorithm)

```
 PROGRAM mc                                  basic Metropolis algorithm

 do icycl=1,ncycl                            perform ncycl MC cycles
   call mcmove                               displace a particle
   if (mod(icycl,nsamp).eq.0)
+    call sample                            sample averages
 enddo
 end
```

Comments to this algorithm:

1. *Subroutine* `mcmove` *attempts to displace a randomly selected particle (see Algorithm 2).*
2. *Subroutine* `sample` *samples quantities every* `nsamp`*th cycle.*

Algorithm 2 (Attempt to Displace a Particle)

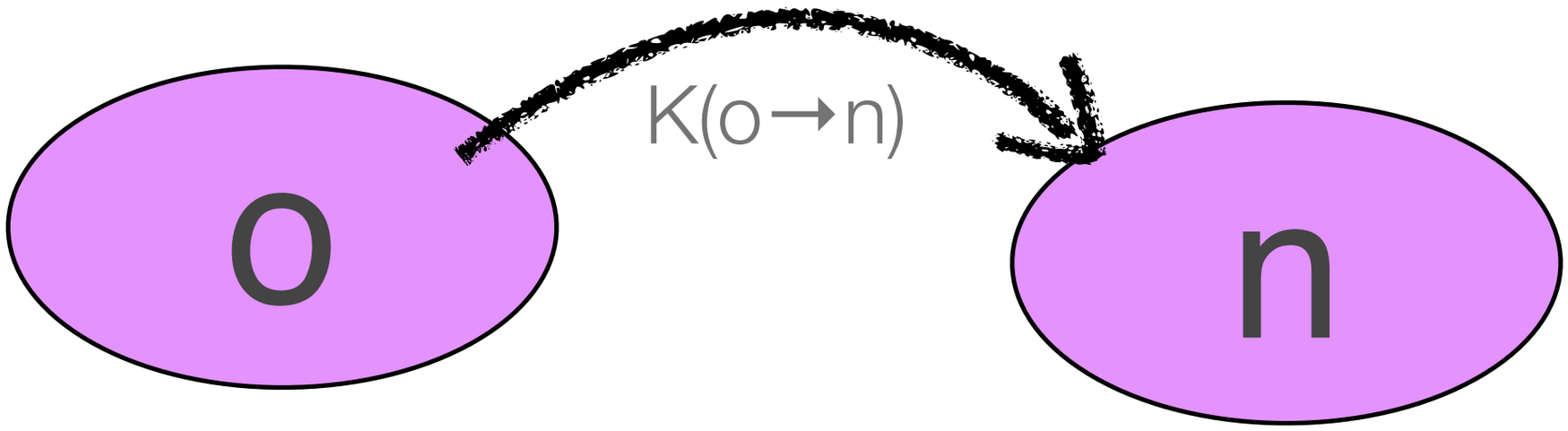
```
 SUBROUTINE mcmove                    attempts to displace a particle

 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

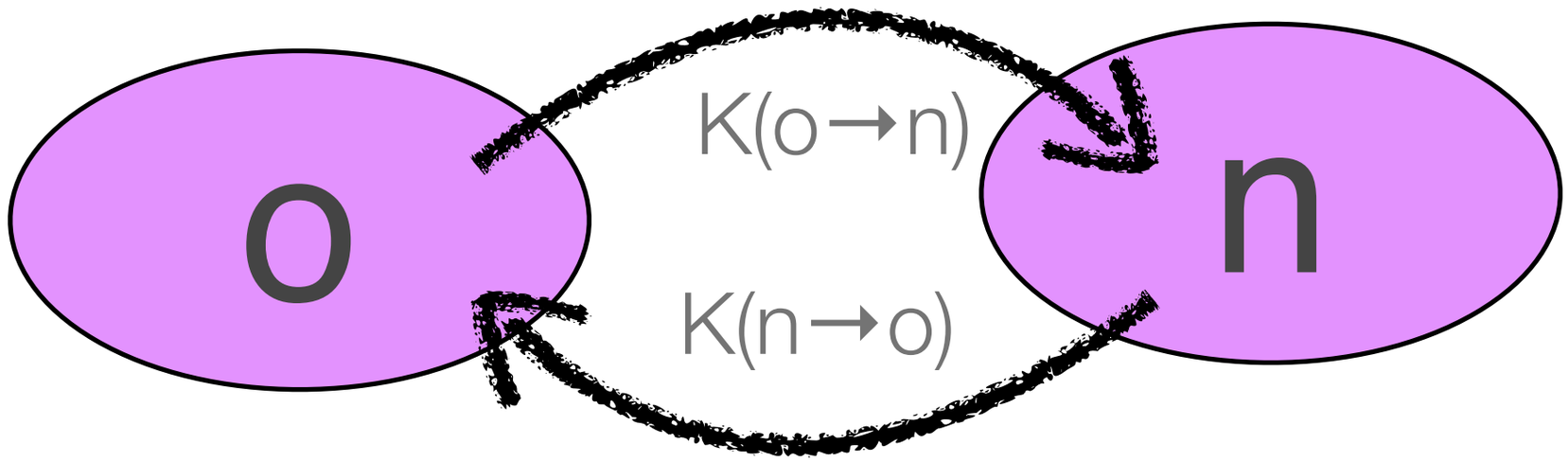


K(o → n): total number of systems in our ensemble that move *o* → *n*

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

- *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: $P(n) \propto e^{-\beta U(n)}$

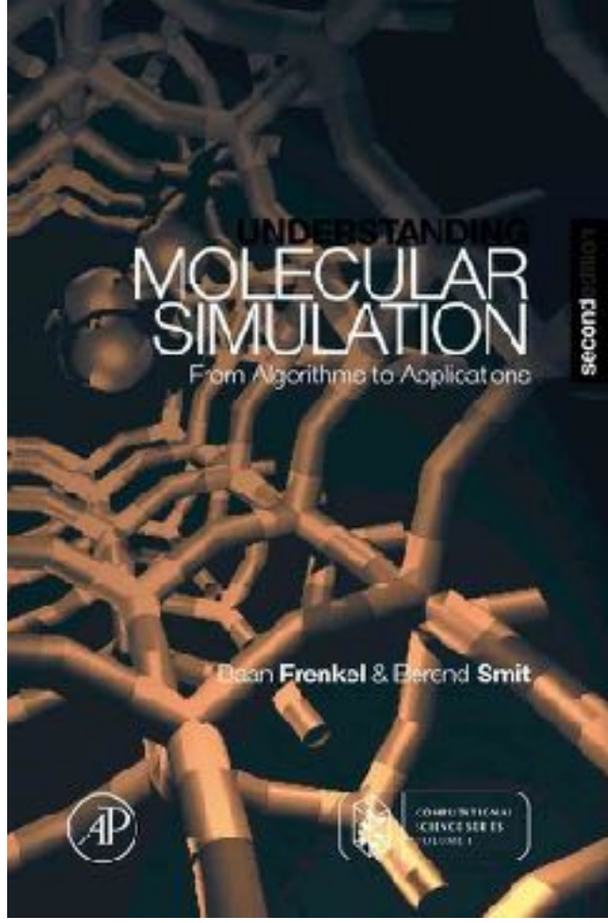
Moves:

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

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

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

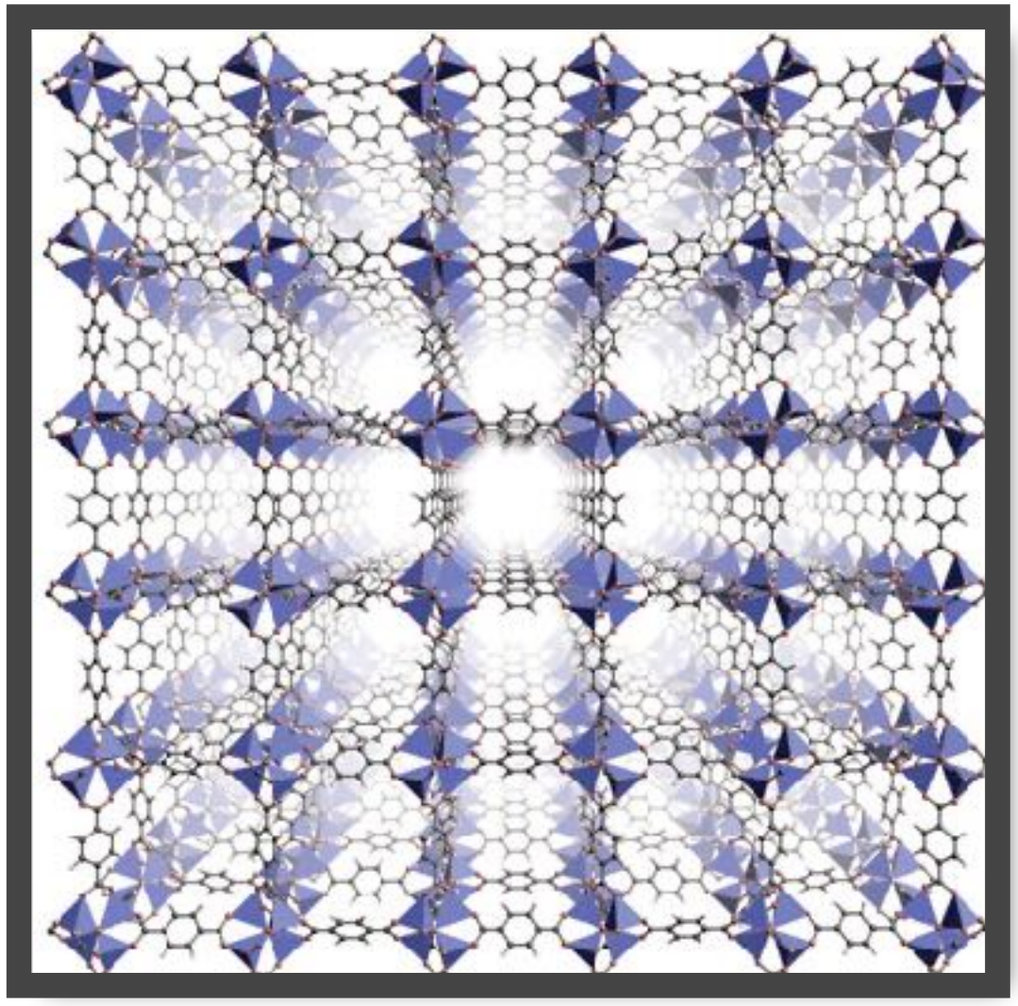
Simulation and Thermodynamics of Adsorption (part 2)



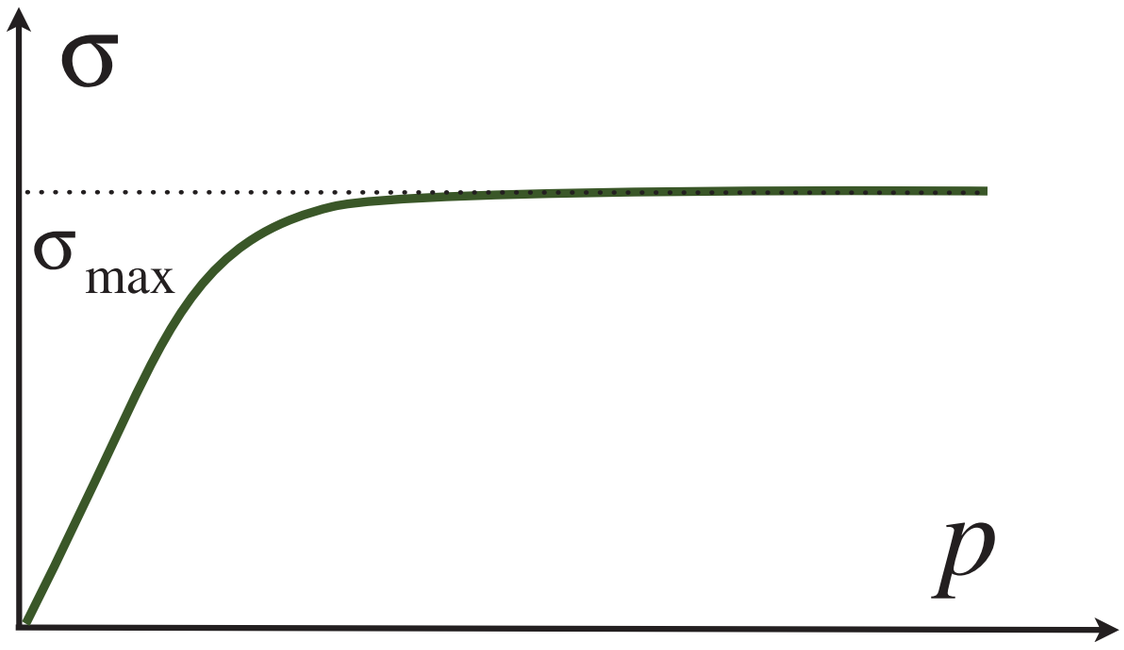
2.3.3 μVT ensemble - Thermodynamics

Understanding Molecular Simulation

Thermodynamics of adsorption

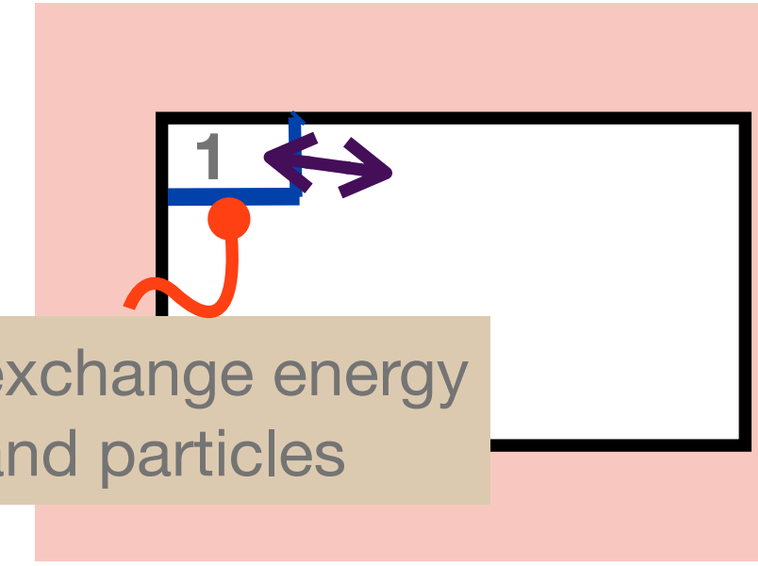


Metal Organic Framework



What are the appropriate thermodynamic variables?

Constant: T and μ



Total system is isolated and the volume is constant

First law $dU = TdS - pdV + \mu dN = 0$

Second law $dS \geq 0$

Box 1: *constant chemical potential and temperature*

1st law: $dU_1 + dU_b = 0$ or $dU_1 = -dU_b$

$dN_1 + dN_b = 0$ or $dN_1 = -dN_b$

The bath is very large and the small changes do not change μ or T; in addition the process is reversible

2nd law:

$$dS = dS_1 + dS_b = dS_1 + \left[\frac{dU_b}{T} - \mu \frac{dN_b}{T} \right] \geq 0$$

$$dS = dS_1 + dS_b = dS_1 + \left[\frac{dU_b}{T} - \mu \frac{dN_b}{T} \right] \geq 0$$

We can express the changes of the bath in terms of properties of the system

$$dS_1 + \left[-\frac{dU_1}{T} + \mu \frac{dN_1}{T} \right] \geq 0$$

$$d\left(TS_1 - U_1 + \mu N_1\right) \geq 0$$

$$d\left(U_1 - TS_1 - \mu N_1\right) \leq 0$$

For the Gibbs free energy we can write:

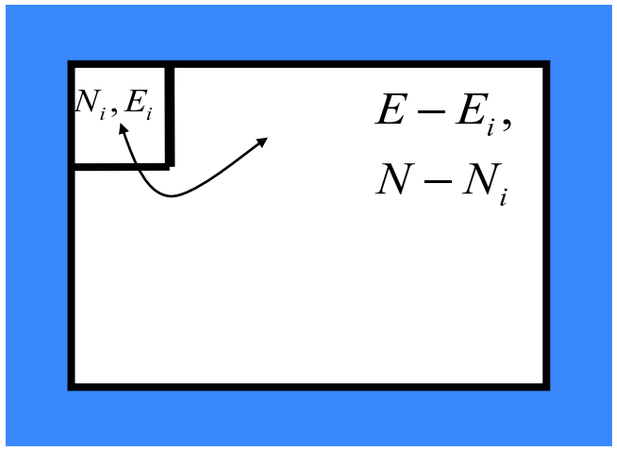
$$G \equiv U - TS + pV$$

$$G = \mu N \qquad \text{or} \qquad -pV = U - TS - \mu N$$

Giving: $d\left(-pV\right) \leq 0$ or $d\left(pV\right) \geq 0$

Hence, for a system at *constant temperature and chemical potential* pV increases and takes its maximum value at equilibrium

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:

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

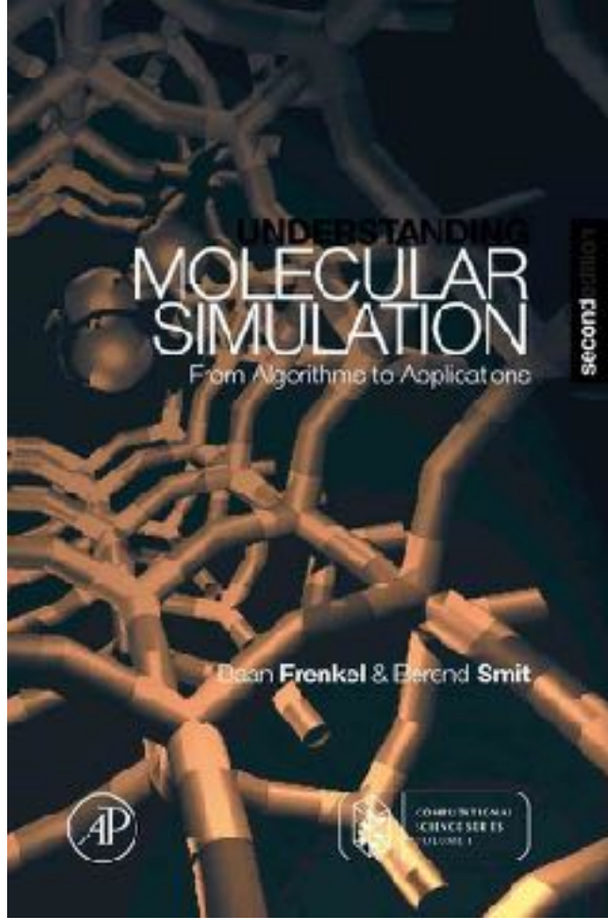
which gives

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

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

Understanding 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

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

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

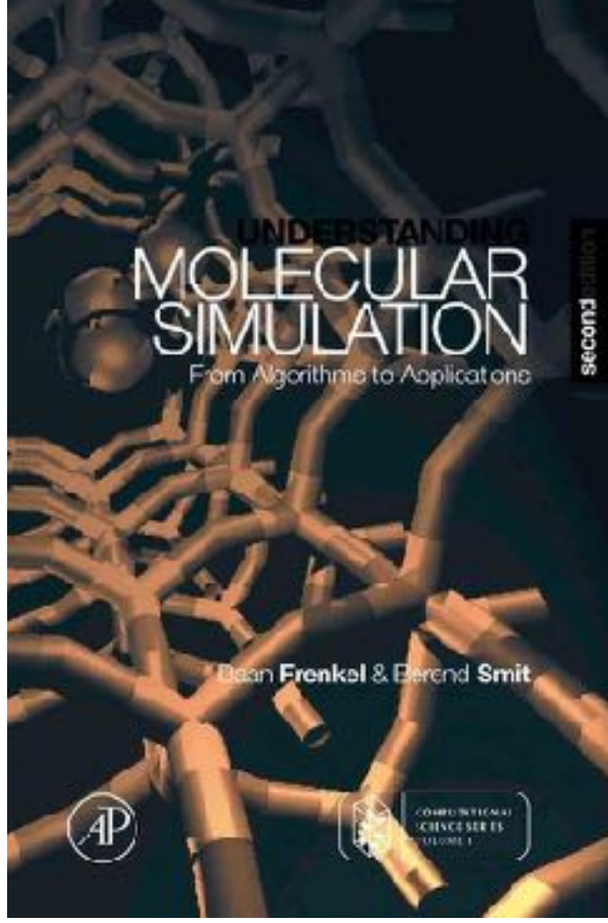
Algorithm 12 (Basic Grand-Canonical Ensemble Simulation)

```
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

Chemical potential: Widom's test particle

We start with the partition function of the NVT ensemble

$$Q_{NVT} = \frac{1}{\Lambda^{3N} N!} \int \mathrm{d}\mathbf{r}^N \exp\left[-\beta U\left(\mathbf{r}^N\right)\right]$$

It is convenient to have the volume dependence explicitly; scaled coordinates: s=r/L

$$Q_{NVT} = \frac{V^N}{\Lambda^{3N} N!} \int \mathrm{d}\mathbf{s}^N \exp\left[-\beta U\left(\mathbf{s}^N; L\right)\right]$$

For the free energy we have

$$\beta F = -\ln\left(Q_{NVT}\right) = -\ln\left(\frac{V^N}{\Lambda^{3N} N!}\right) - \ln\left(\int \mathrm{d}\mathbf{s}^N \exp\left[-\beta U\left(\mathbf{s}^N; L\right)\right]\right)$$

$$= -N \ln\left(\frac{1}{\Lambda^3 \rho}\right) - \ln\left(\int \mathrm{d}\mathbf{s}^N \exp\left[-\beta U\left(\mathbf{s}^N; L\right)\right]\right)$$

Stirling's formula and ρ=N/V

For the free energy we have obtained

$$\beta F = -\ln\left(Q_{NVT}\right)$$

$$= -N\ln\left(\frac{1}{\Lambda^3\rho}\right) - \ln\left(\int \mathrm{d}s^N \exp\left[-\beta U\left(s^N; L\right)\right]\right)$$

It is convenient to split the free energy into an ideal gas contribution and the excess:

$$\beta F = \beta F^{IG} + \beta F^{ex}$$

The we can also do for the chemical potential

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

$$\beta\mu = \beta\mu^{IG} + \beta\mu^{ex}$$

Giving

$$\mu^{IG} \equiv \left(\frac{\partial F^{IG}}{\partial N}\right)_{V,T} \qquad \mu^{ex} \equiv \left(\frac{\partial F^{ex}}{\partial N}\right)_{V,T}$$

From the free energy $\beta\mu \equiv \left(\frac{\partial \beta F}{\partial N} \right)_{V,T}$

$$\beta\mu = \frac{\beta F\left(N+1\right) - \beta F\left(N\right)}{N+1-N} = -\ln \frac{Q\left(N+1\right)}{Q\left(N\right)}$$

$$= -\ln\left(\frac{\frac{V^{N+1}}{\Lambda^{3N+3}\left(N+1\right)!}}{\frac{V^{N}}{\Lambda^{3N}N!}} \right) - \ln\left(\frac{\int \mathrm{ds}^{N+1} \exp\left[-\beta U\left(\mathrm{s}^{N+1};L\right)\right]}{\int \mathrm{ds}^{N} \exp\left[-\beta U\left(\mathrm{s}^{N};L\right)\right]} \right)$$

Ideal gas part

$$= -\ln\left(\frac{V}{\Lambda^{3}\left(N+1\right)} \right) - \ln\left(\frac{\int \mathrm{ds}^{N+1} \exp\left[-\beta U\left(\mathrm{s}^{N+1};L\right)\right]}{\int \mathrm{ds}^{N} \exp\left[-\beta U\left(\mathrm{s}^{N};L\right)\right]} \right)$$

This gives us:

$$\beta\mu = \beta\mu^{IG} + \beta\mu^{ex}$$

$$\beta\mu^{ex} = -\ln\left(\frac{\int \mathrm{ds}^{N+1} \exp\left[-\beta U\left(\mathrm{s}^{N+1};L\right)\right]}{\int \mathrm{ds}^{N} \exp\left[-\beta U\left(\mathrm{s}^{N};L\right)\right]} \right)$$

For the excess chemical potential we have

$$\beta\mu^{ex} = -\ln\left(\frac{\int \mathrm{d}s^{N+1} \exp\left[-\beta U\left(s^{N+1};L\right)\right]}{\int \mathrm{d}s^{N} \exp\left[-\beta U\left(s^{N};L\right)\right]}\right)$$

For the interactions of particles N+1 we can write

$$U\left(s^{N+1};L\right) = \Delta U^{+} + U\left(s^{N};L\right)$$

which gives

$$\beta\mu^{ex} = -\ln\left(\frac{\int \mathrm{d}s^{N} \int \mathrm{d}s_{N+1} \exp\left[-\beta\left(\Delta U^{+} + U\left(s^{N};L\right)\right)\right]}{\int \mathrm{d}s^{N} \exp\left[-\beta U\left(s^{N};L\right)\right]}\right)$$

$$= -\ln\left(\frac{\int \mathrm{d}s_{N+1} \int \mathrm{d}s^{N} \left\{\exp\left[-\beta\Delta U^{+}\right]\right\} \exp\left[-\beta U\left(s^{N};L\right)\right]}{\int \mathrm{d}s^{N} \exp\left[-\beta U\left(s^{N};L\right)\right]}\right)$$

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

ghost particle

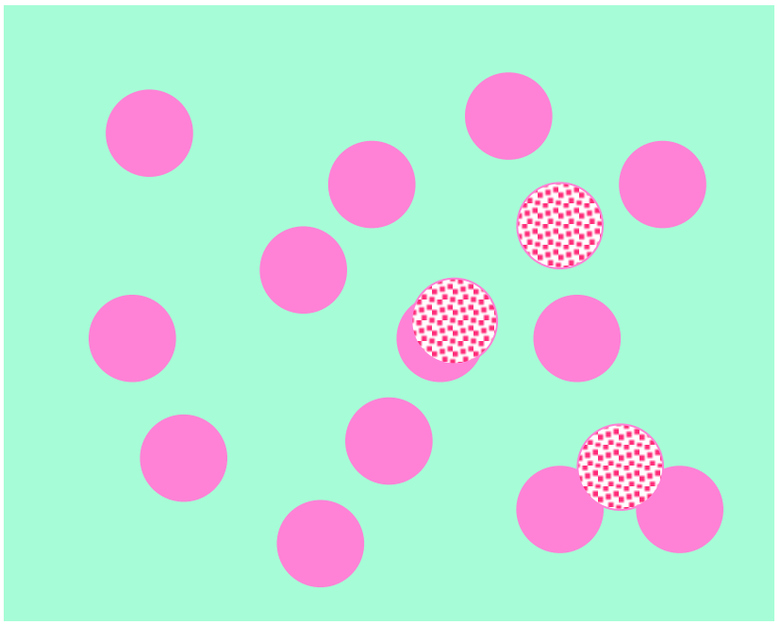
Algorithm 16 (Widom Test Particle Insertion)

```
      subroutine Widom                    excess chemical potential
                                          via the addition of test particles
      xtest=box*ranf()                    generate a random position
      call ener(xtest,entest)             determine energy
       wtest=wtest                        update Boltzmann factor in (7.2.5)
     +       +exp(-beta*entest)
       return
       end
```

Hard spheres

For the chemical potential we have

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



The hard sphere potential:

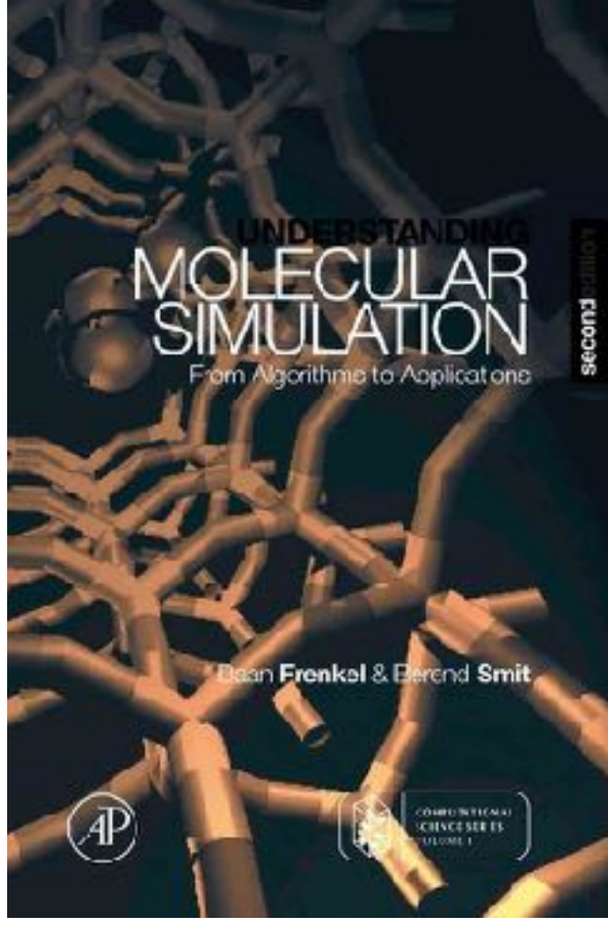
$$U(r) = \begin{cases} \infty & r \le \sigma \\ 0 & r > \sigma \end{cases}$$

If we insert a particle, we have

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

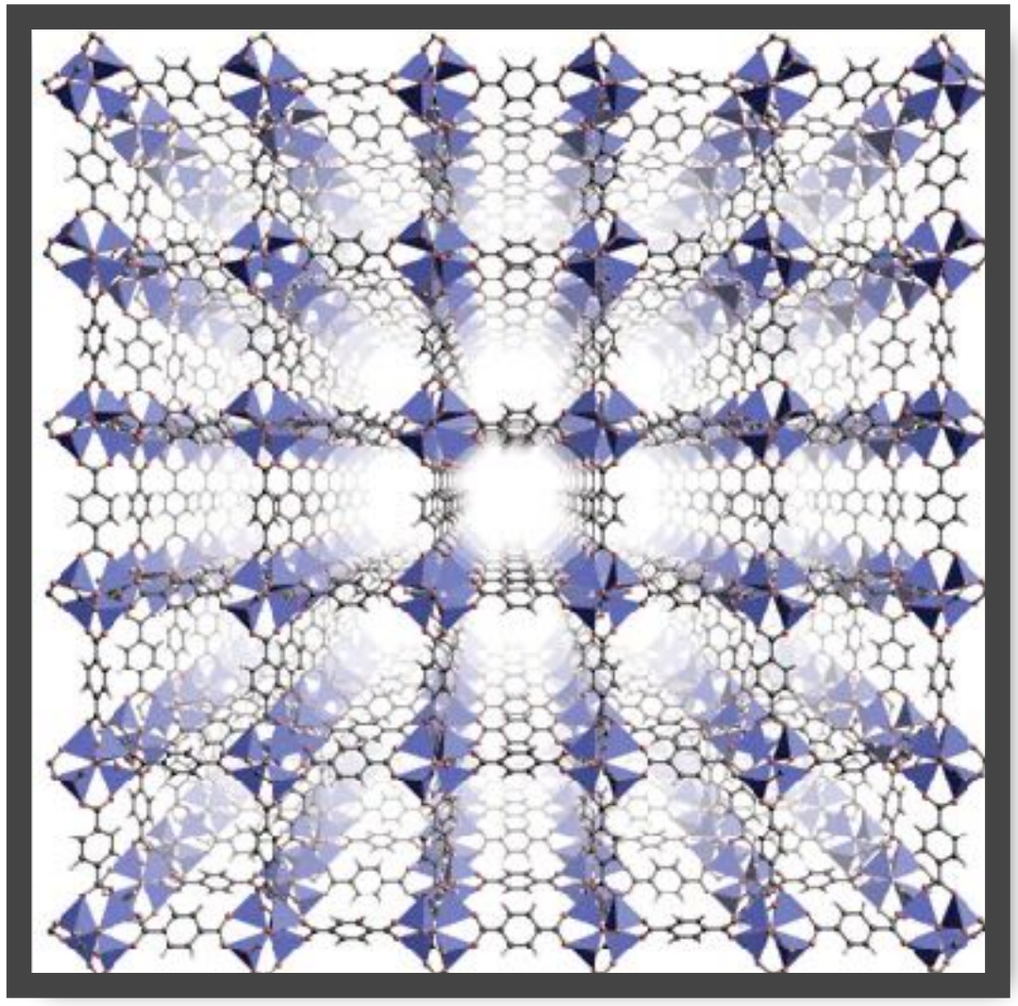
Probability to insert a test particle!

Simulation and Thermodynamics of Adsorption (part 2)

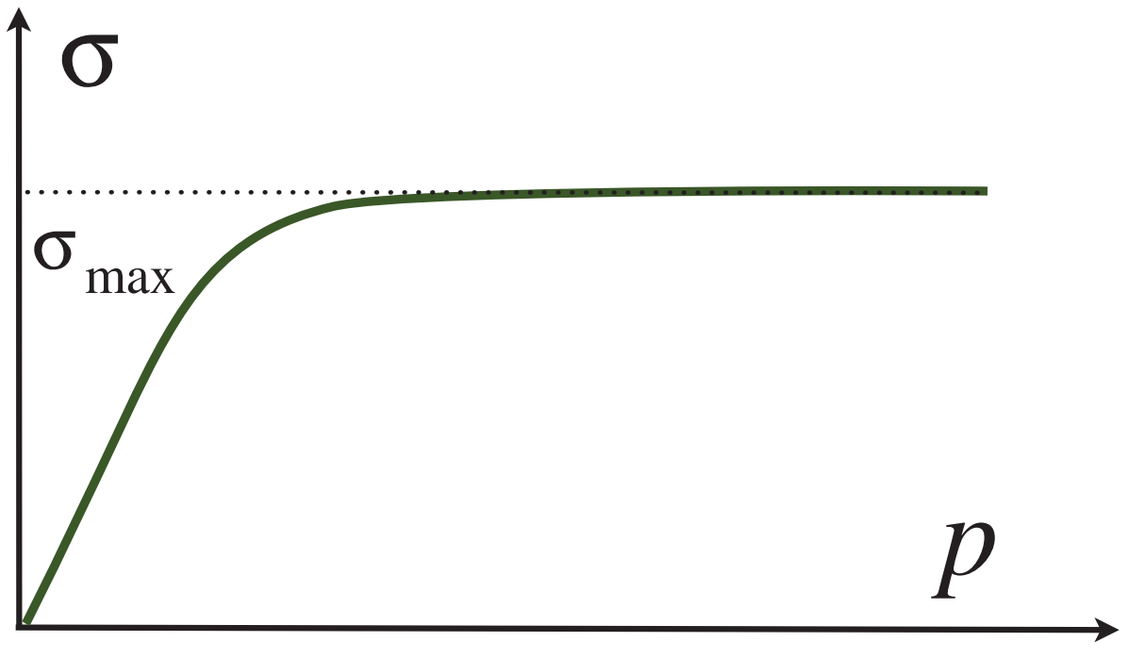


2.5.1 MOFs with open metal sites

Simulating a CO_2 isotherm of a MOF

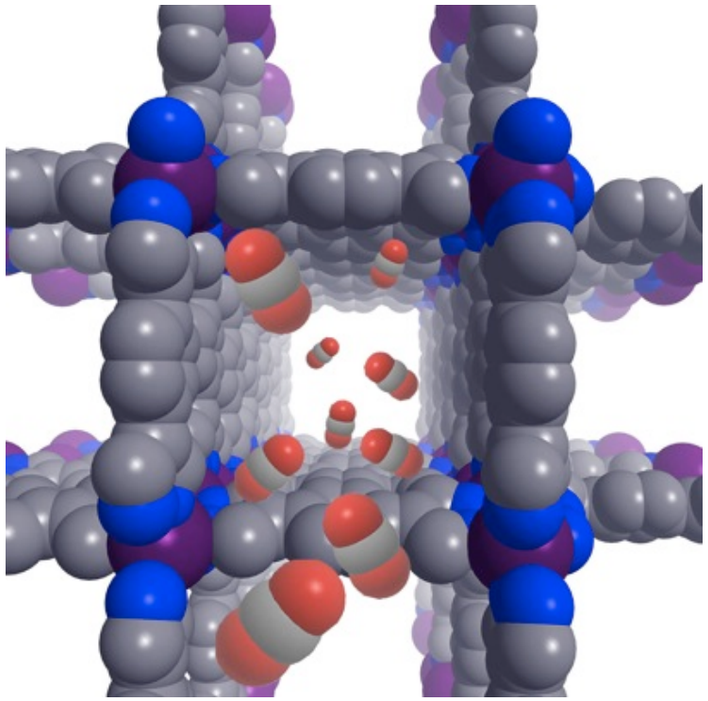


Metal Organic Framework

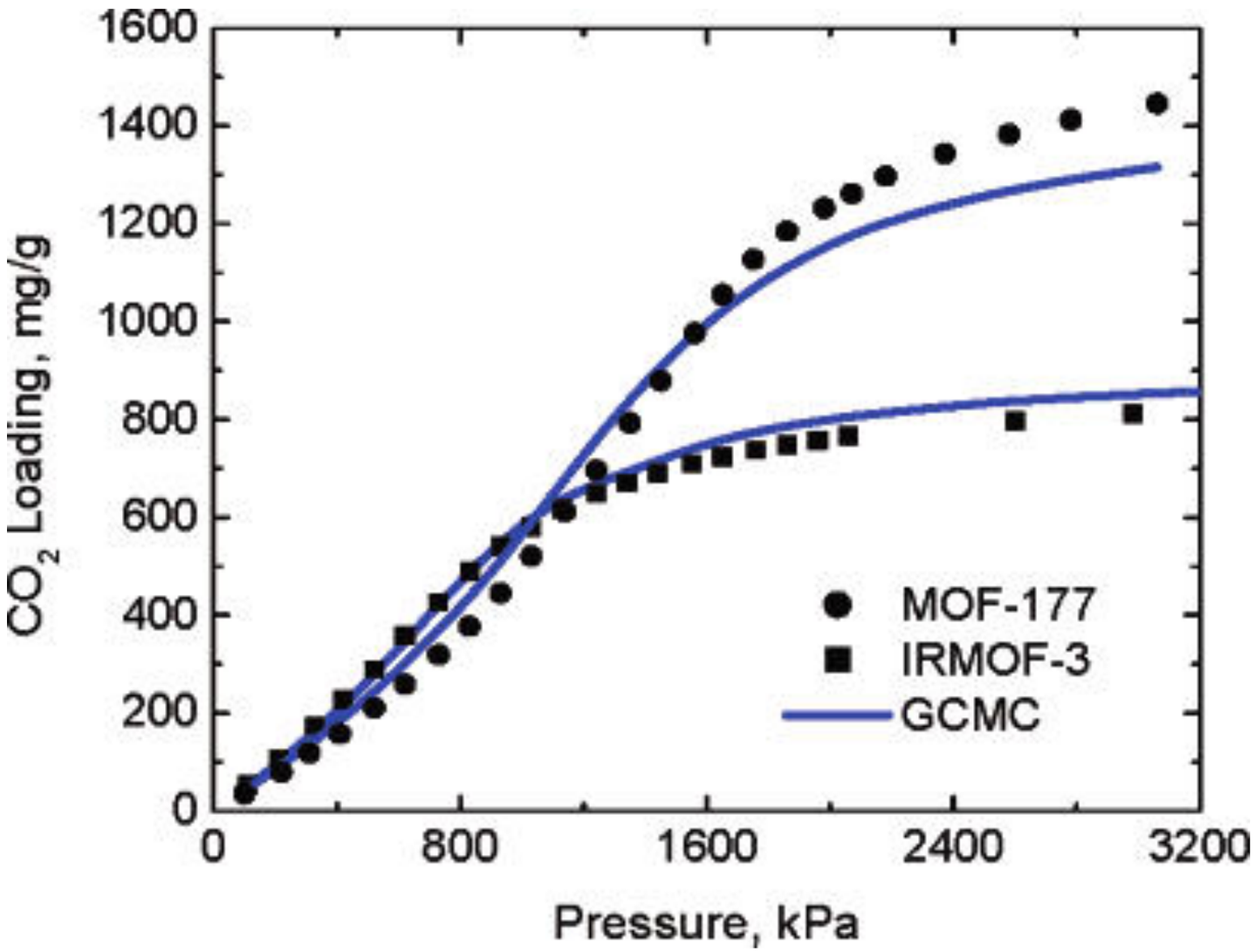


Prediction the adsorption isotherms

- MOF: crystal structure:
  - From the experimental X-ray structure
  - Clean the structure:
    - remove the solvent molecules
    - partial occupancy
    - put the H-atoms at the right position
  - Optimize the structure
  - Obtain the charges on the atoms of the MOF
- Assume the crystal is rigid
- Select a model for the guest-guest interactions (Trappe)
- Select a model for the guest-host interactions (universal force fields like UFF or Dreading)



If we are lucky



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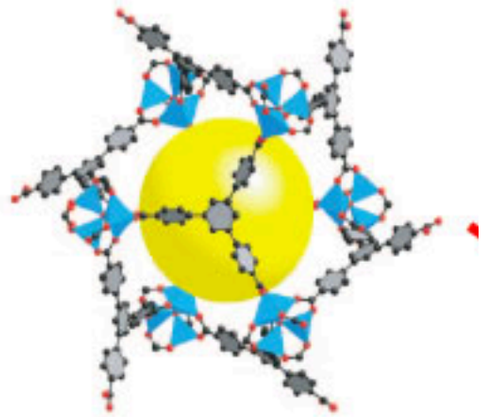
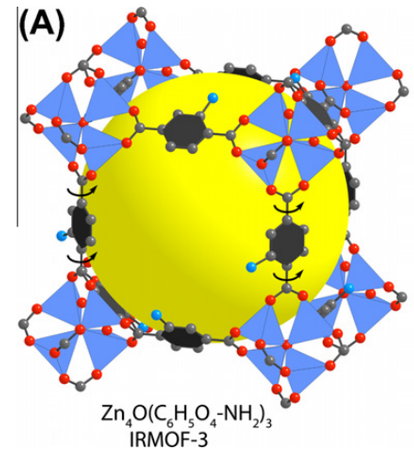


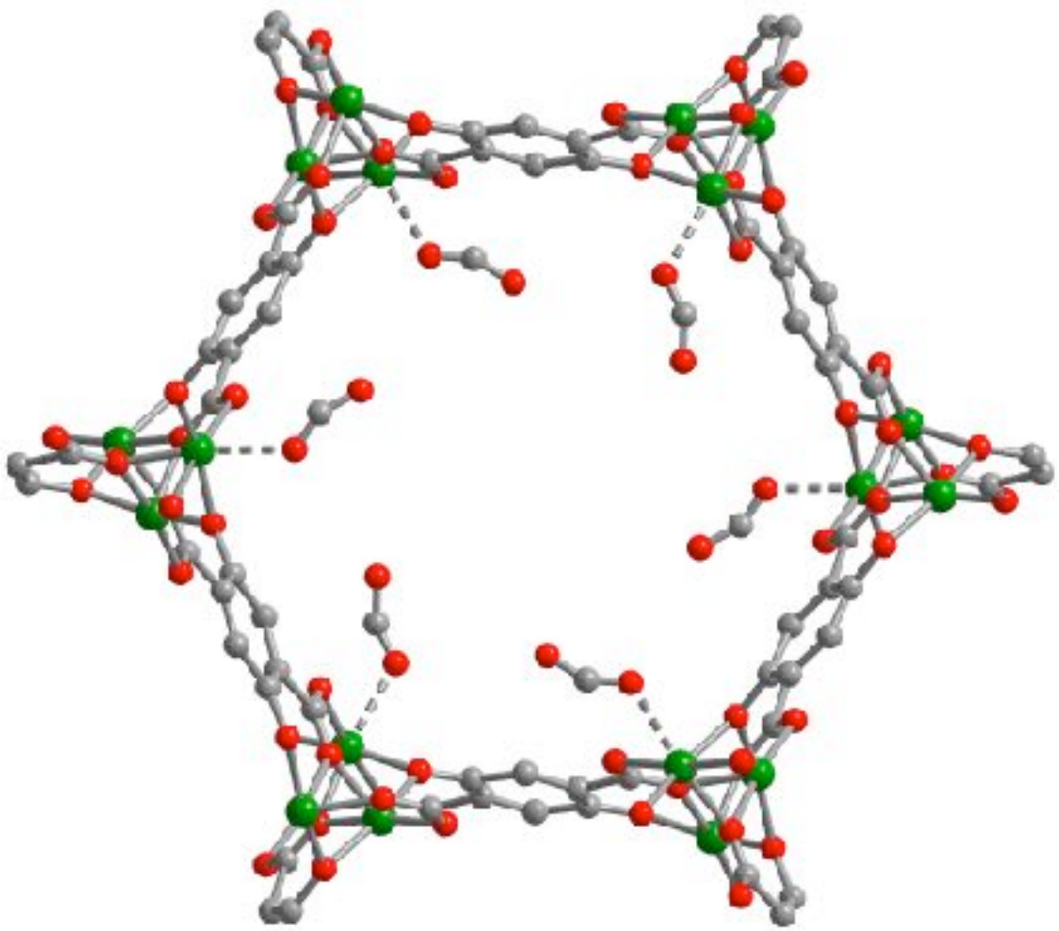
http://www.cchem.berkeley.edu/molsim/teaching/fall2011/CCS/Group7/structure.htm



doi:10.1016/j.molstruc.2011.07.037

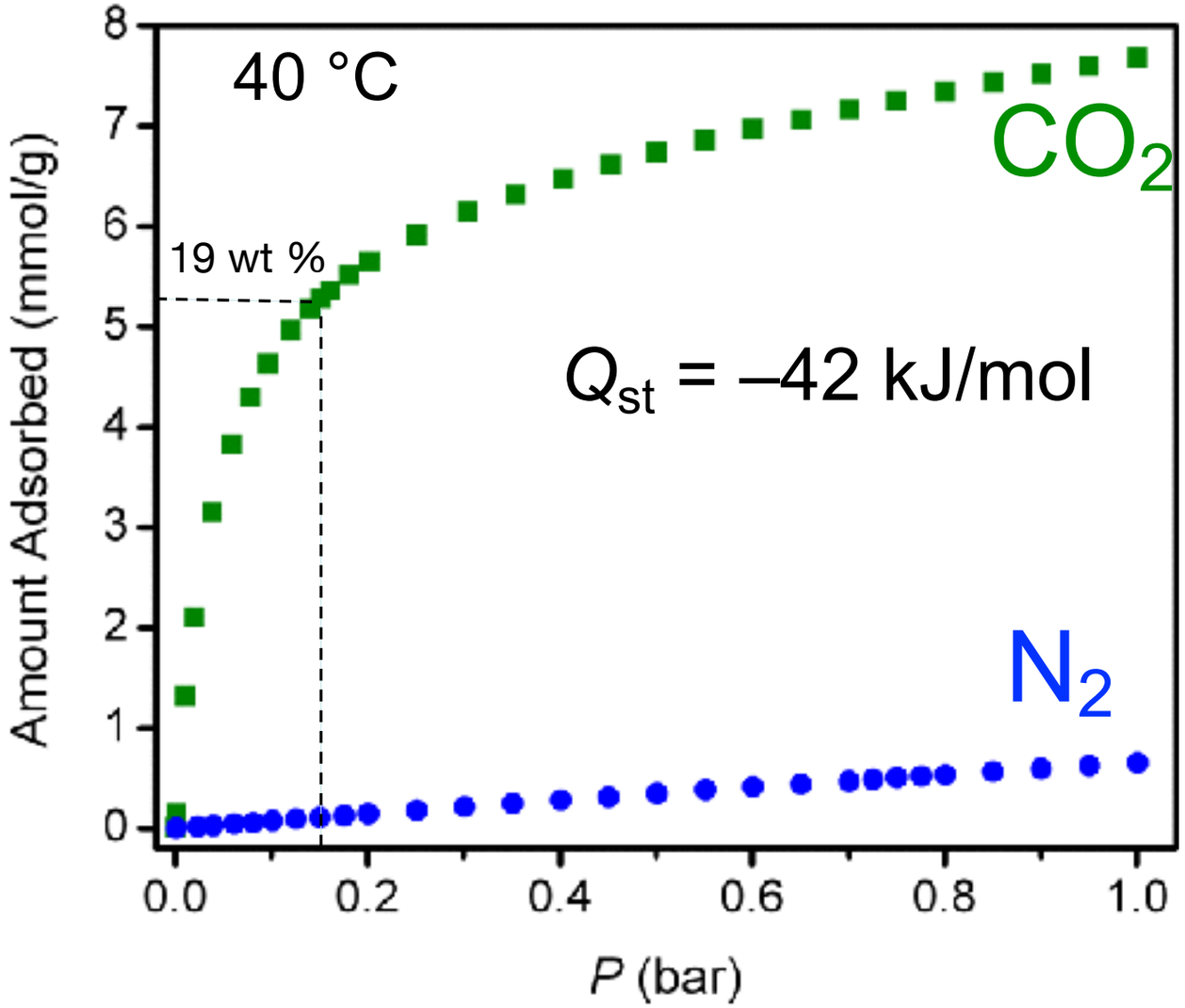
Walton, K. S.; Millward, A. R.; Dubbeldam, D.; Frost, H.; Low, J. J.; Yaghi, O. M.; Snurr, R. Q. *J. Am. Chem. Soc.* **2008**, *130*, 406.

High CO_2 Capacity for Mg-MOF-74



Mg2(dobdc) (Mg-MOF-74)

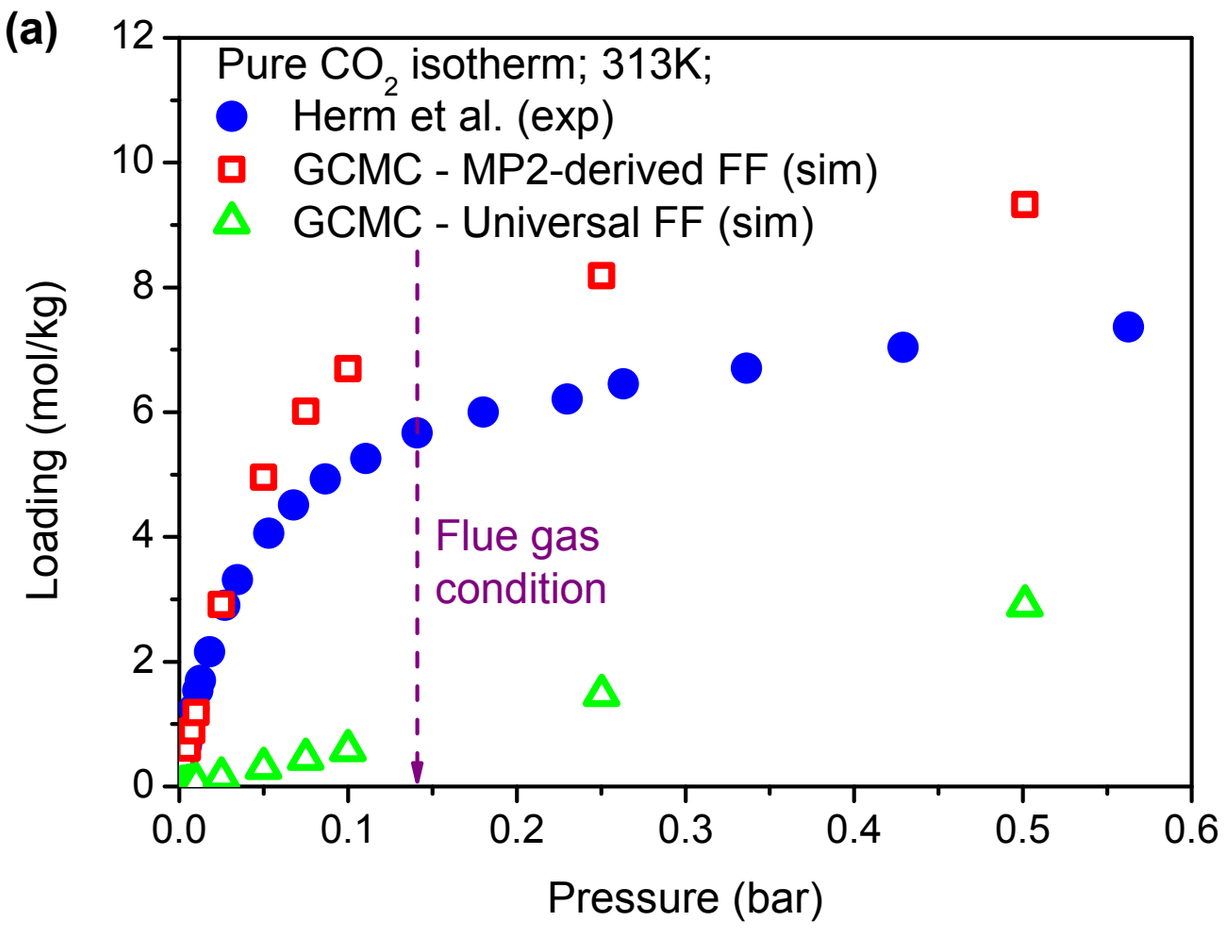
Open metal sites!

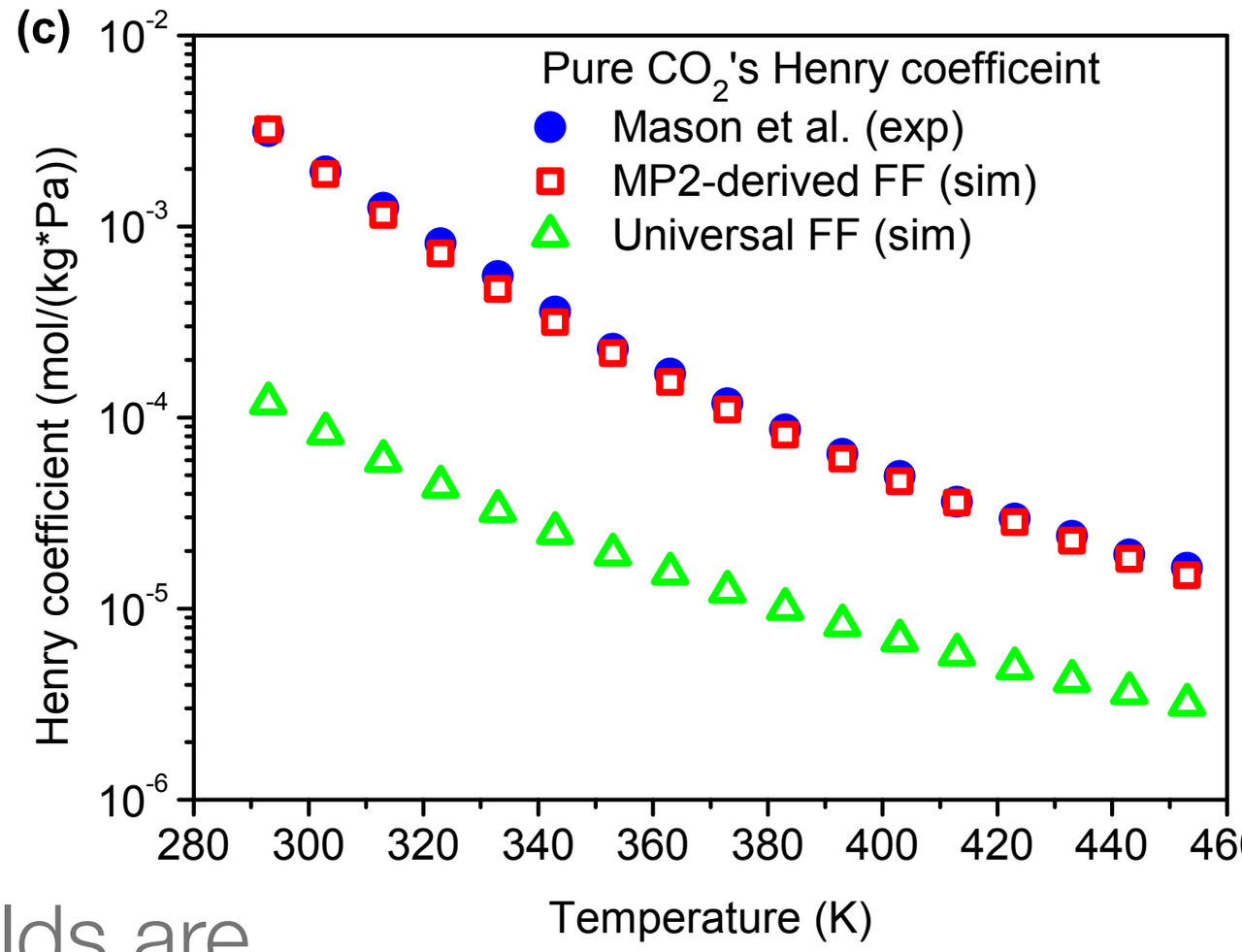


Queen, Brown, Britt, Zajdel, Hudson, Yaghi *J. Phys. Chem. C* 2011, *115*, 24915

Mason, Sumida, Herm, Krishna, Long *Energy Environ. Sci.* 2011, *4*, 3030

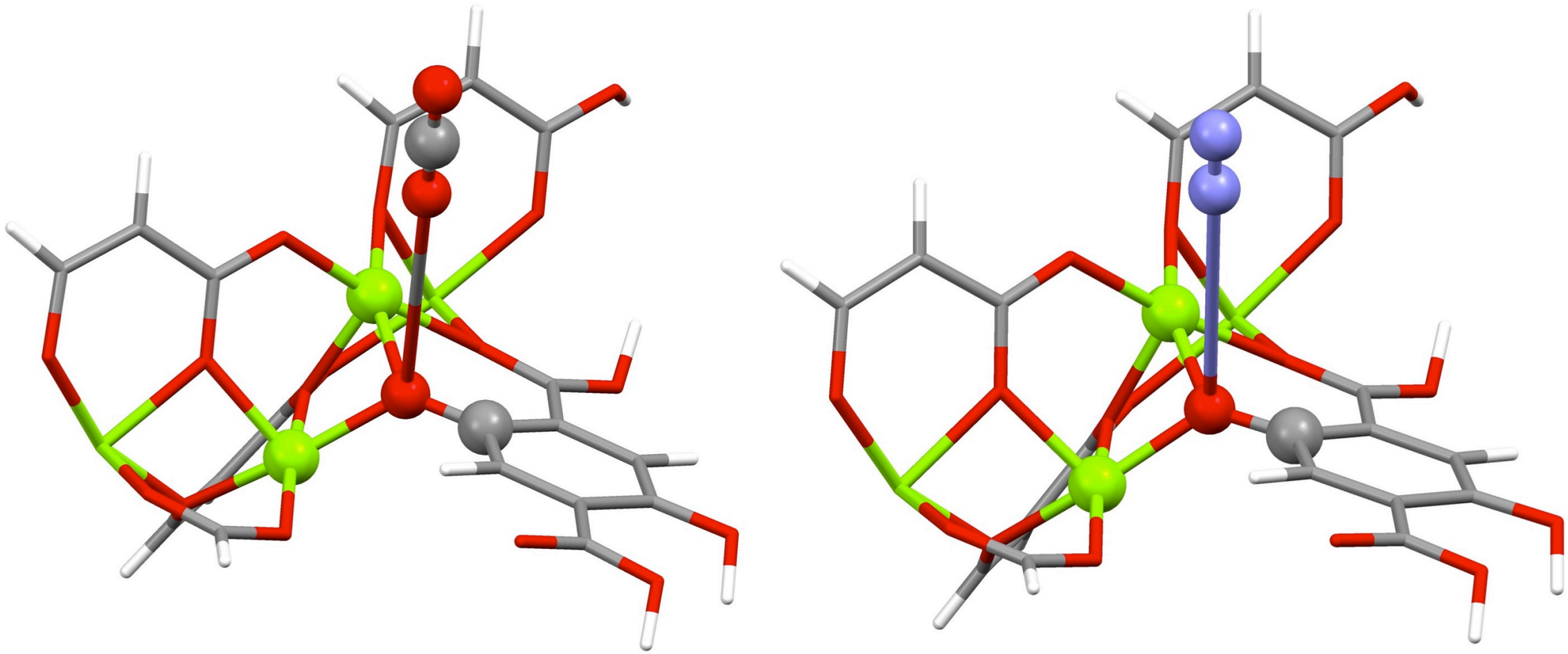
But we are not always that lucky





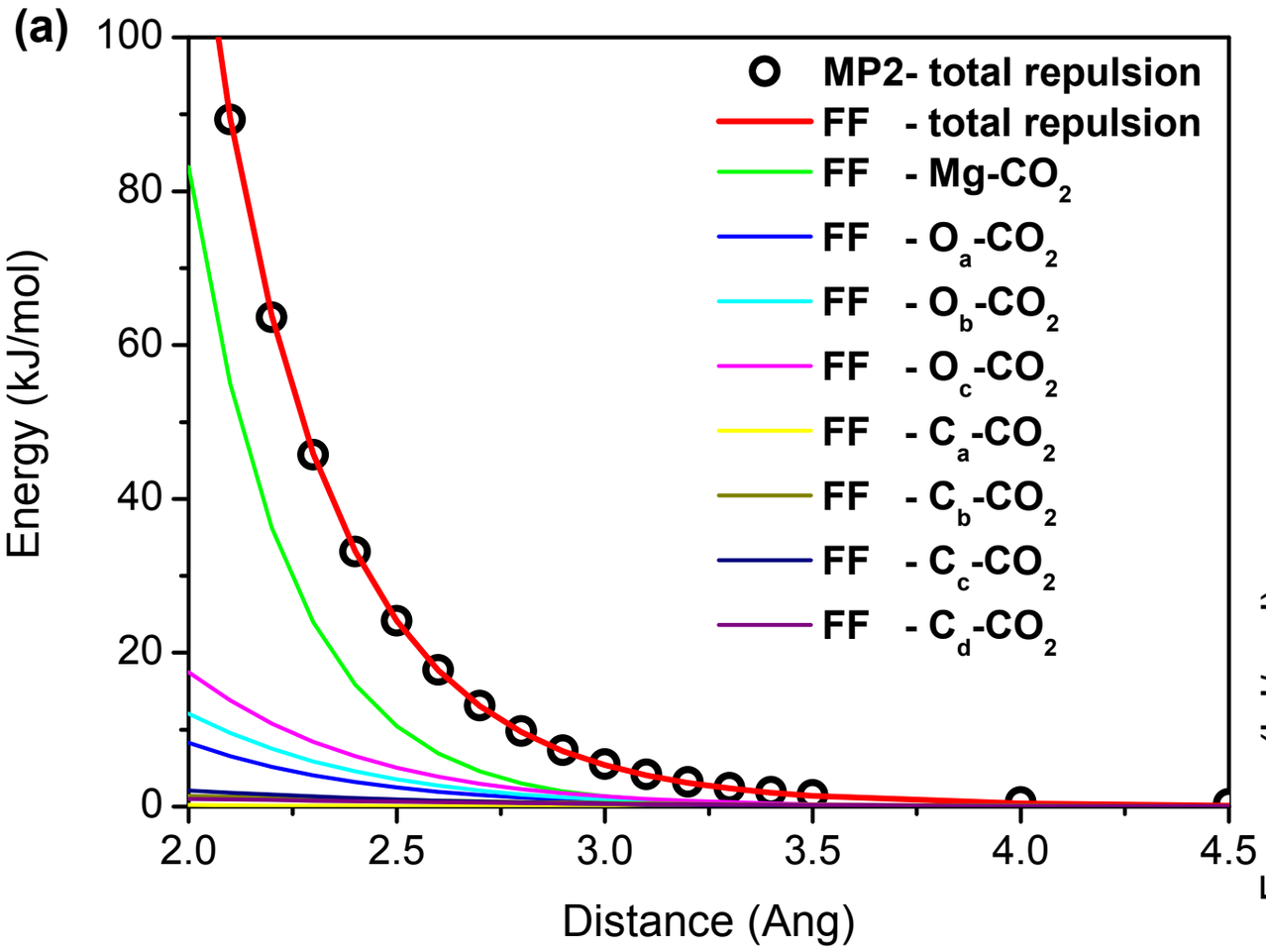
Open metal sites: the force fields are 2 orders of magnitude off!

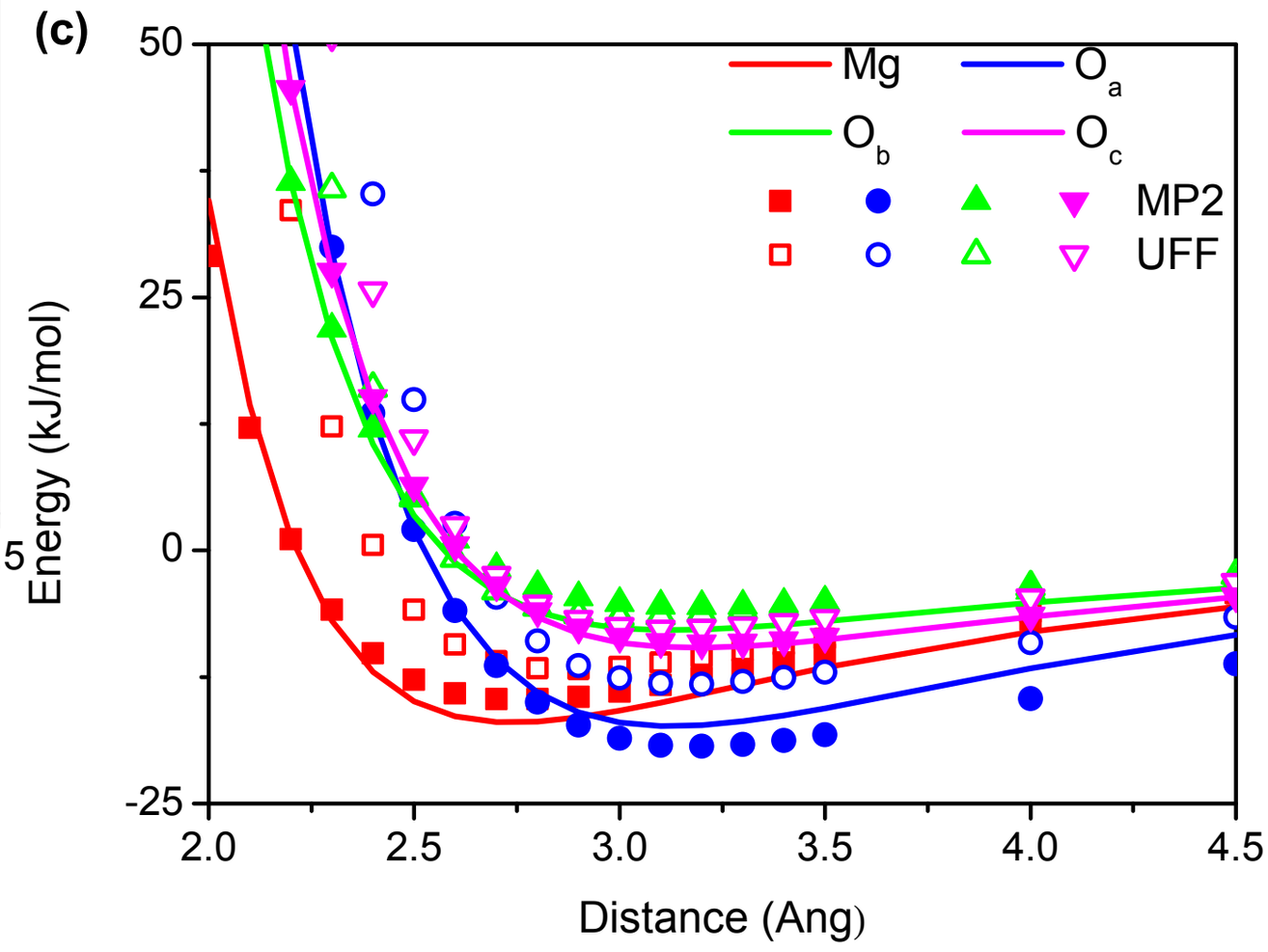
Force Fields: correction from quantum chemistry



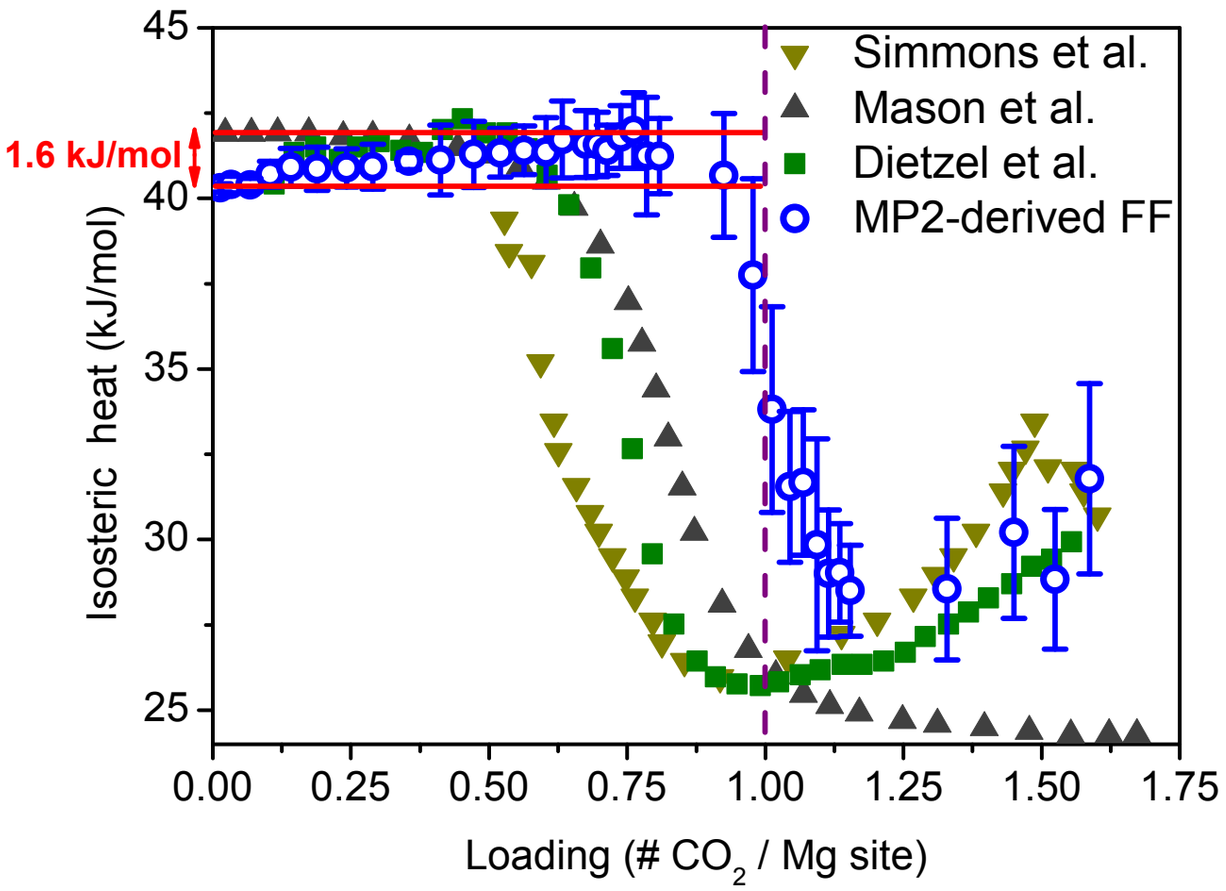
A. Dzubak, et al, Ab-initio Carbon Capture in Open-Site Metal Organic Frameworks Nat Chem (2012) http://dx.doi.org/0.1038/NCHEM.1432

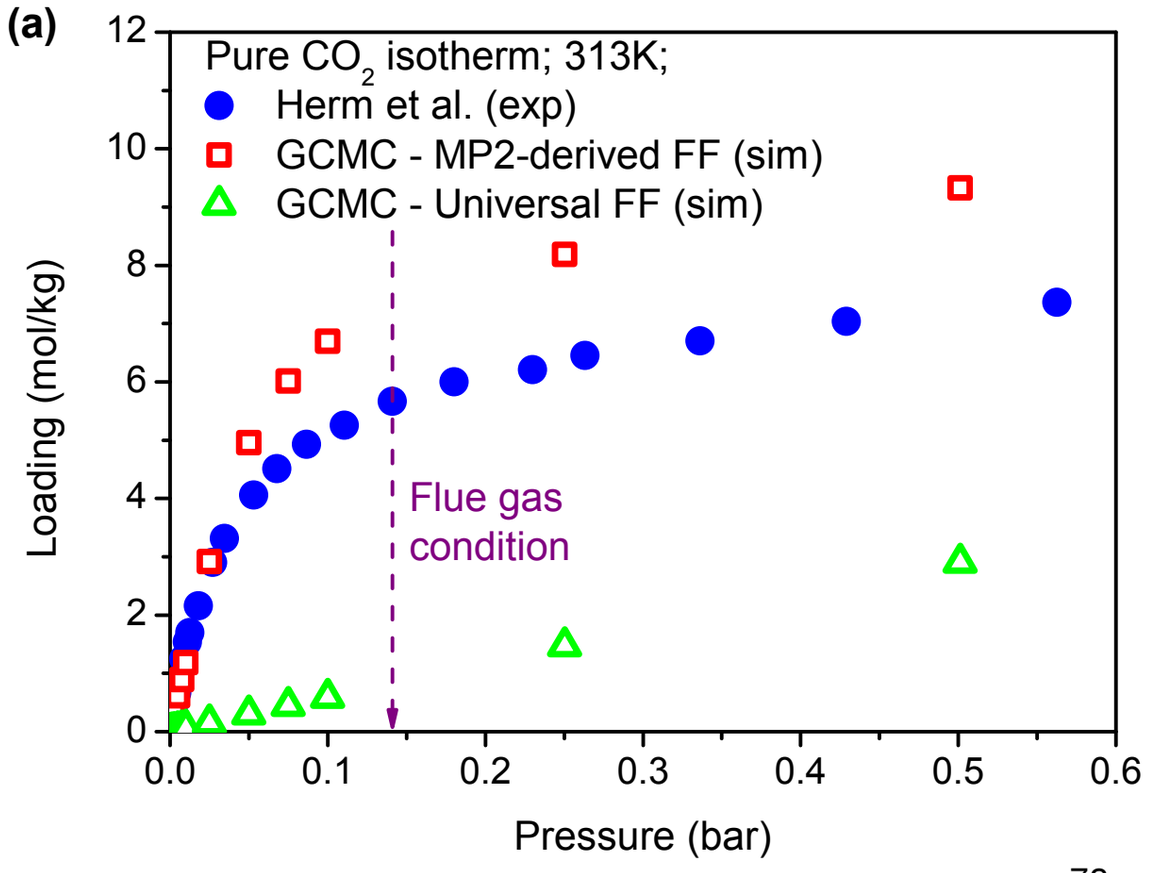
Force Fields



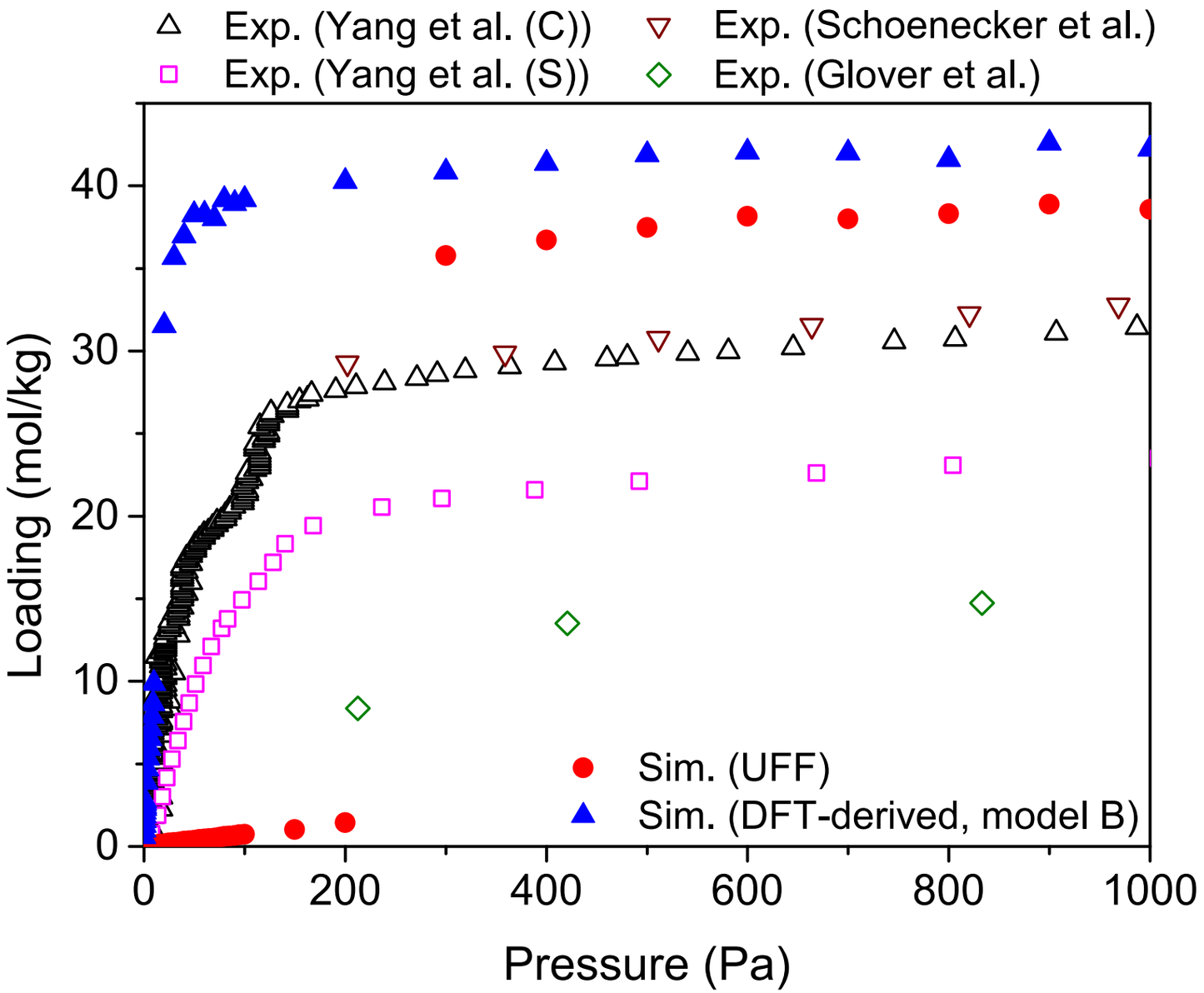


Predictions?



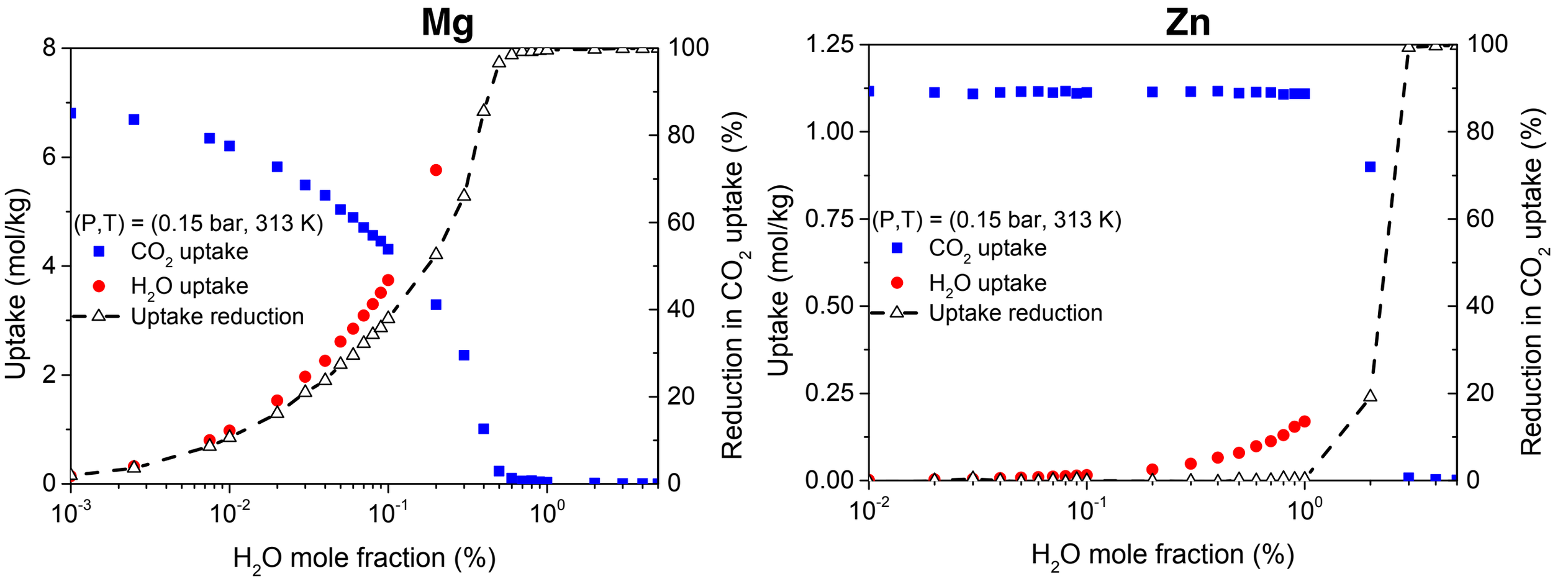


Water isotherms?



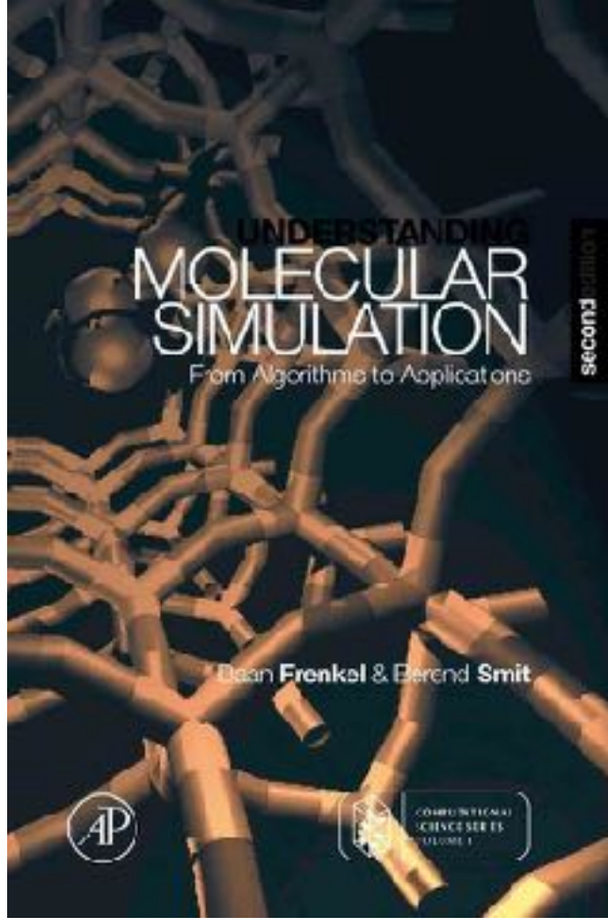
L.-C. Lin *et al. J. Chem. Theory Comput.* **2014**.

Water-CO_2 mixtures



L.-C. Lin *et al. J. Chem. Theory Comput.* **2014**.

Simulation and Thermodynamics of Adsorption (part 2)



2.5.2 Xe/Kr separations

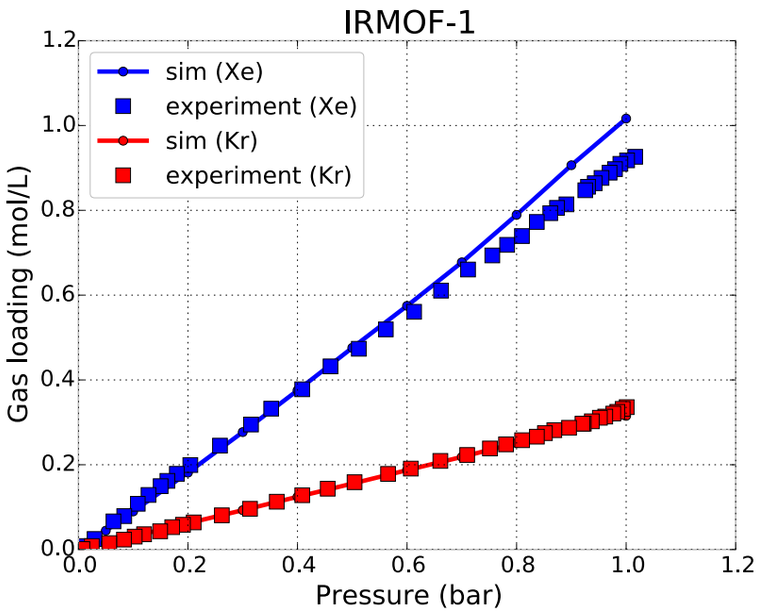
Separations of Xe/Kr

- Nuclear energy reprocessing: Xe - Kr isotopes are produced (i.e., ^{85}Kr with $t_{1/2}$ = 10.8 y)
- Xe used in several applications : cryogenic distillation of air:
  - pure Xe $5000 kg

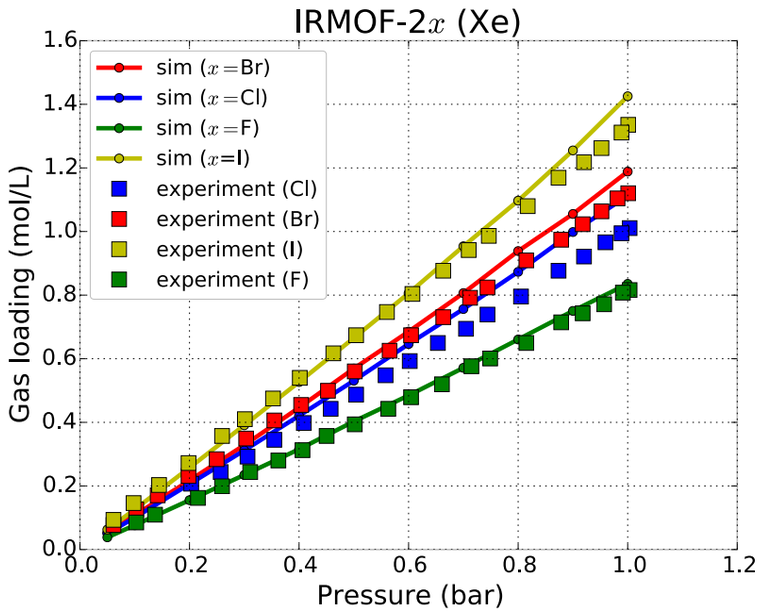
D. Banerjee, C. M. Simon, A. M. Plonka, R. K. Motkuri, J. Liu, X. Chen, B. Smit, J. B. Parise, M. Haranczyk, and P. K. Thallapally, *Metal-organic framework with optimally selective xenon adsorption and separation* Nat. Comm. **7** (11831) (2016) http://dx.doi.org/10.1038/ncomms11831

C. M. Simon, R. Mercado, S. K. Schnell, B. Smit, and M. Haranczyk, *What Are the Best Materials To Separate a Xenon/Krypton Mixture?* Chem. Mat. **27** (12), 4459 (2015) http://dx.doi.org/10.1021/acs.chemmater.5b01475

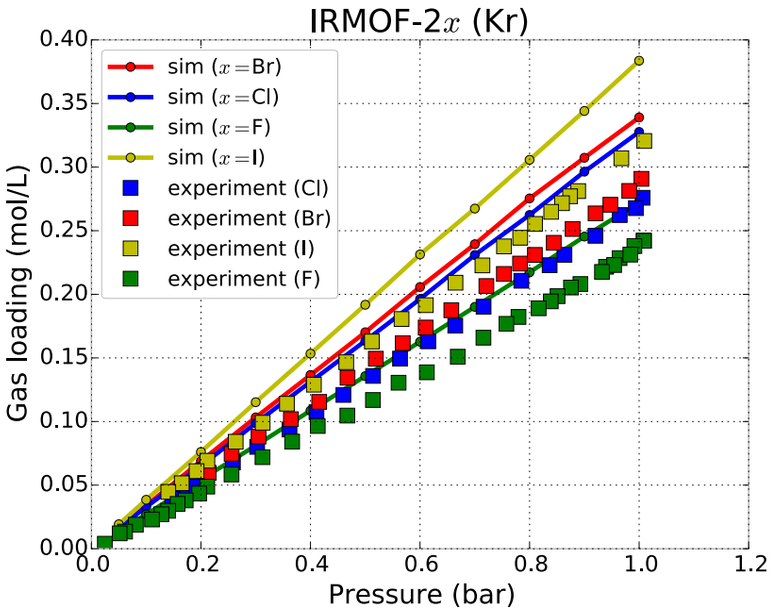
Comparison with experimental data



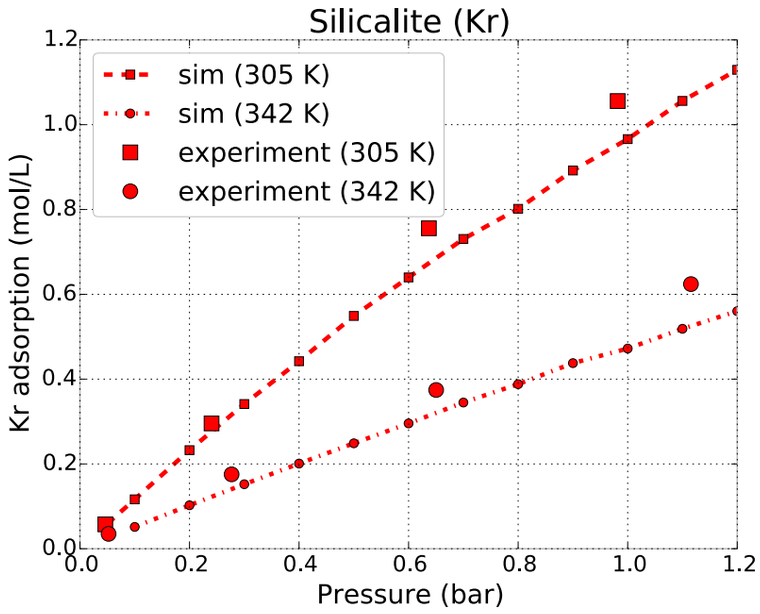
(a)



(b)



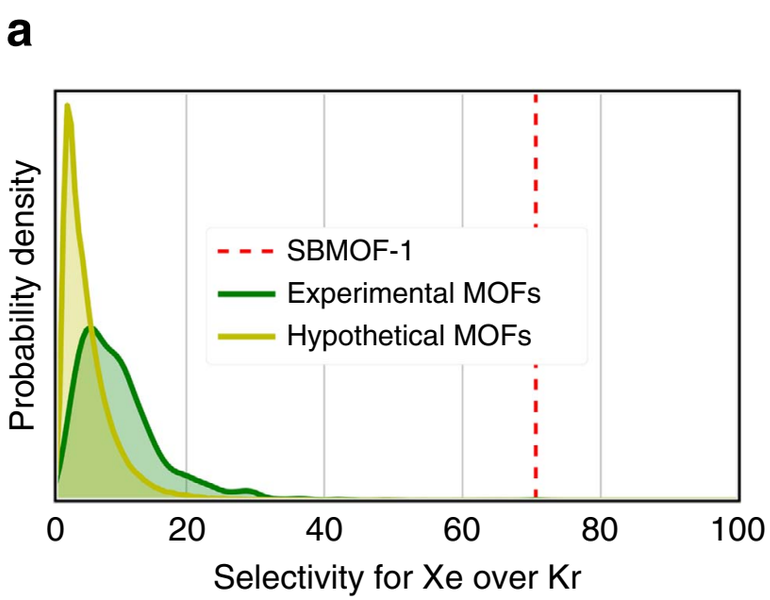
(c)

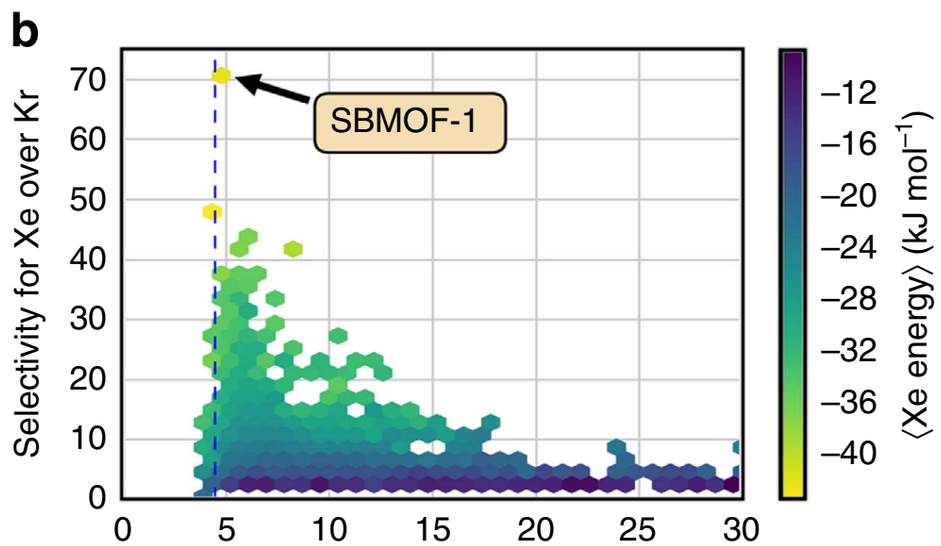


(d)

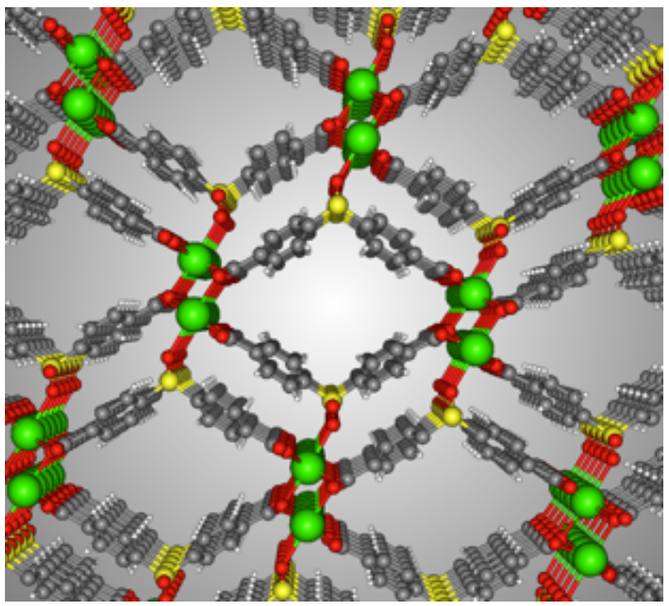
C. M. Simon, et al *What Are the Best Materials To Separate a Xenon/Krypton Mixture?* Chem. Mat. **27** (12), 4459 (2015) http://dx.doi.org/10.1021/acs.chemmater.5b01475

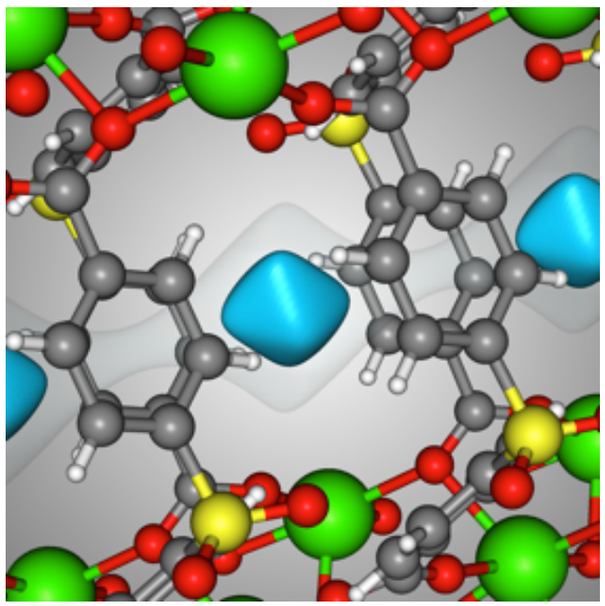
Screening



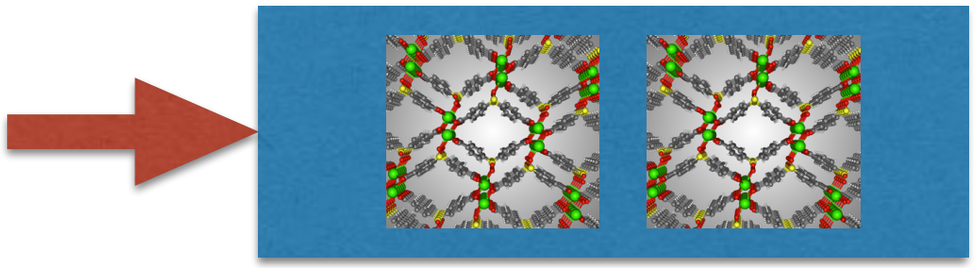


Top performing: SBMOF-1





Experiments: SBMOF-1



Model Mixture:

O_2, N_2, CO_2, Kr, Xe

(400 ppm Xe, 40 ppm Kr,
78.1% N_2, 20.9% O_2,
0.03% CO_2, and 0.9% Ar)

D. Banerjee, et al, *Metal-organic framework with optimally selective xenon adsorption and separation* Nat. Comm. **7** (11831) (2016) http://dx.doi.org/10.1038/ncomms11831