

Introduction to molecular simulations

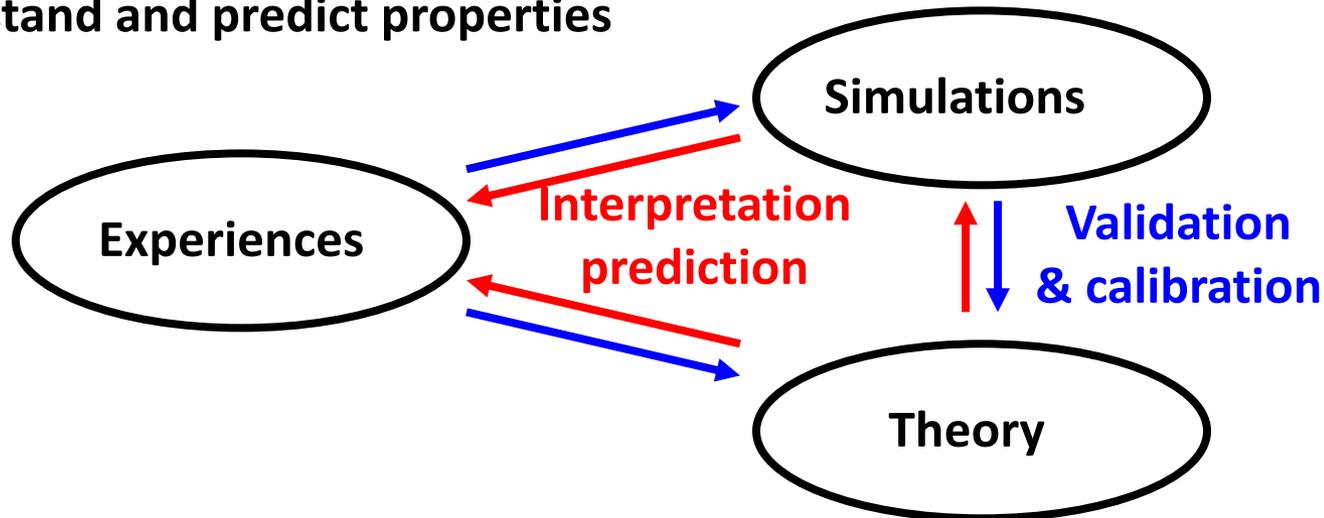
Introduction

Deduce **macroscopic structure, thermodynamic and dynamics** of a system from numerical simulations performed at the atomic scale

Simulations are numerical « experiences »

- 1) The system is prepared in a defined state
- 2) One lets it evolve
- 3) One measures observables

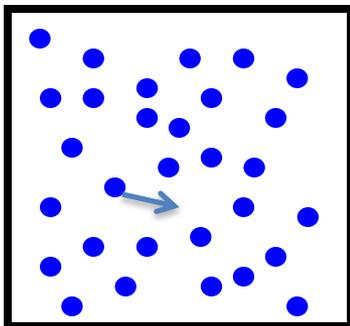
Understand and predict properties



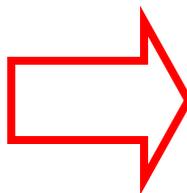
In the following, only **classical molecular simulations**: the atom is the smallest entity

Introduction

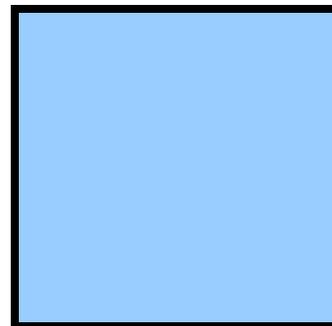
Microscopic scale



Statistical mechanics

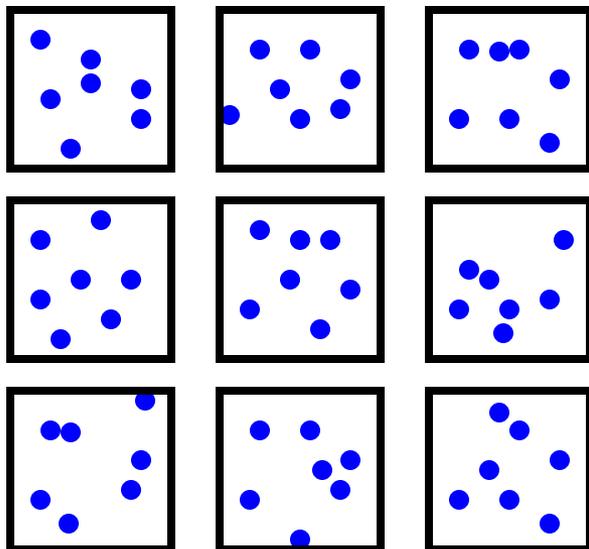


Macroscopic scale



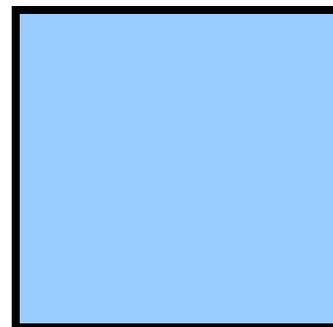
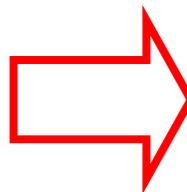
A particle i is characterized by its position r_i and its momentum $p_i = mv_i$

Pressure P , temperature T , internal energy U , entropy S , free energy F ...



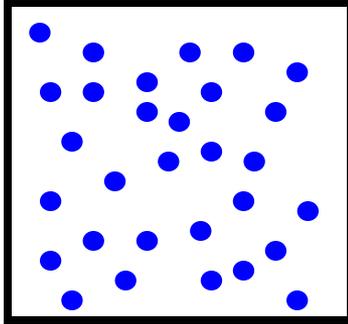
Average over the microstates

...



Introduction

Microscopic scale



A microstate is characterized by the positions \mathbf{r}_i and the momenta $\mathbf{p}_i = m\mathbf{v}_i$ of all its particles

Internal energy of the system (U or E or H):

$$H(\mathbf{r}_i^N, \mathbf{p}_i^N) = E_K + U_P = \sum_i \frac{\mathbf{p}_i^2}{2m} + U_P(\mathbf{r}_i^N)$$

(H is the hamiltonian)

Kinetic energy

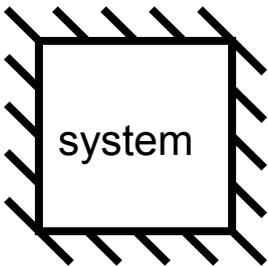
Potential energy (interactions between atoms)

$$\frac{1}{2} \sum_i \sum_{i \neq j} v_{ij}(\mathbf{r}_{ij}) \text{ if pair potential}$$

Introduction

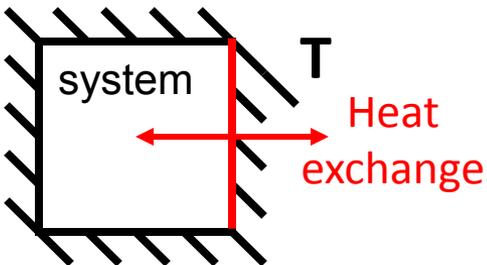
A macroscopic state is characterized by:

- **external constraints**, fixed by experimentalist
- **internal properties**, fluctuating around an average



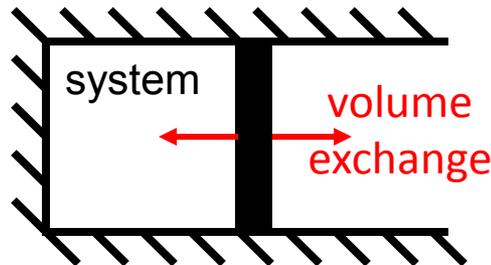
0) no external constraint, isolated system:
Microcanonical ensemble NVE

1) T fixed (by a thermostat)



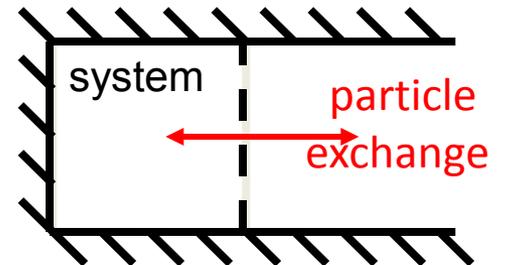
Energy E fluctuates

2) P fixed (by a barostat)



Volume V fluctuates

3) μ fixed by a reservoir



Number of particles
 N fluctuates

➔ The thermodynamic ensemble of the system depends on external constraints:
NVT, NPT, μ VT are the usual statistical ensembles.

Introduction

MICROCANONICAL ENSEMBLE : fixed N,V,E (isolated)

Fundamental postulate of statistical mechanics:

Given an isolated system in equilibrium, it is found with equal probability in each of its accessible microstates

$$\rightarrow P_i = \frac{1}{\Omega}$$



total number of accessible microstates corresponding to the same macrostate N,V,E

Thermodynamic potential: **Entropy**

$$S = k_B \ln \Omega$$

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

NB: the bigger the number of microstates, the higher the entropy

Introduction

MICROCANONICAL ENSEMBLE : fixed N,V,E (isolated)

Fundamental postulate of statistical mechanics:

Given an isolated system in equilibrium, it is found with equal probability in each of its accessible microstates



Microscopic quantity $P_i = \frac{1}{\Omega}$

total number of accessible microstates corresponding to the same macrostate N,V,E

Thermodynamic potential: Entropy

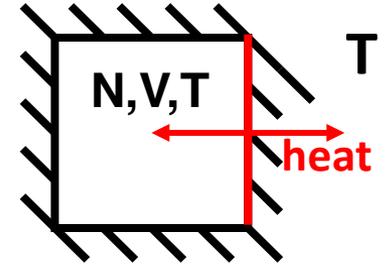
Macroscopic quantity $S = k_B \ln \Omega$

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

NB: the bigger the number of microstates, the higher the entropy

Introduction

CANONICAL ENSEMBLE : fixed N,V,T



The probability to find the system in a given microstate depends on its energy:

$$P_i = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} \quad \text{with} \quad \beta = 1/k_B T \quad \text{(Boltzmann distribution)}$$

Partition function: $Q(N, V, T) = \sum_i e^{-\beta E_i}$

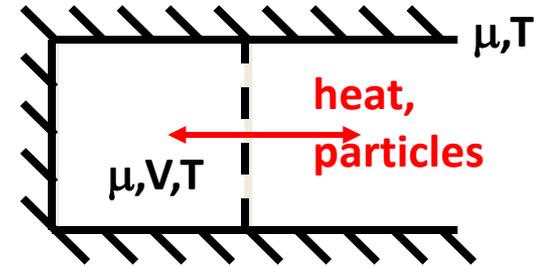
Thermodynamic potential: **free energy** ($F=U-TS$)

$$F = -k_B T \ln Q$$

$$dF = -SdT - PdV + \mu dN$$

Introduction

GRAND-CANONICAL ENSEMBLE : fixed μ, V, T



The probability to find the system in a given microstate depends on its energy and its number of particles:

$$P_i = \frac{e^{\beta\mu N_i - \beta E_i}}{\sum_i e^{\beta\mu N_i - \beta E_i}}$$

Partition function: $\Xi(\mu, V, T) = \sum_i e^{\beta\mu N_i - \beta E_i}$

Thermodynamic potential: **grand potential**

$$\Omega = -k_B T \ln \Xi$$

$$d\Omega = -SdT - PdV - Nd\mu$$

Introduction

Molecular simulations

- explore all the possible microstates of the system
- deduce macroscopic quantities by **averaging over the microstates**

$$\langle A \rangle = \frac{1}{M} \sum_{j=1}^M A_j$$

Macroscopic quantity

Value of A for microstate j

 **Molecular dynamics**

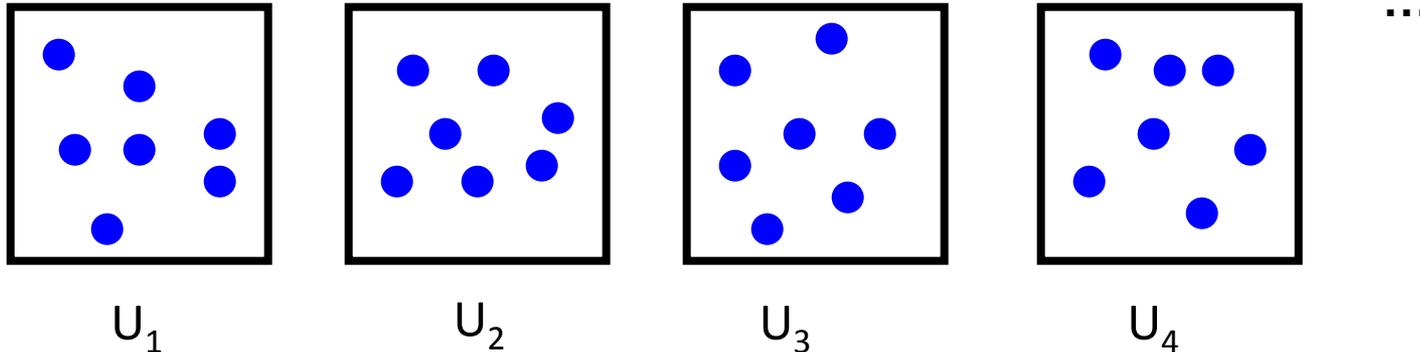
Monte Carlo

Introduction

Monte Carlo:

- Generate configurations (microstates) randomly
- Each configuration is generated a number of times proportionnal to its probability P_i

Example: in the canonical ensemble (N,V,T) : $P_i \propto \exp(-\beta U(\mathbf{r}^N))$

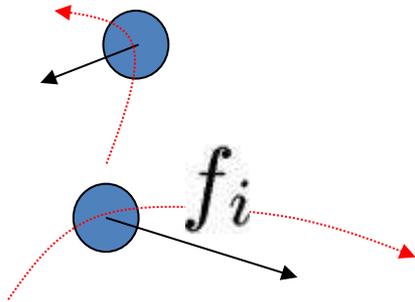


If $U_2 < U_1$, $P_2 > P_1$: state 2 will be generated more often than state 1

Measured macroscopic quantity = average on all the accessible microstates

Introduction

generate trajectories of the particles



Positions $\mathbf{r}(t)$ of all the particles



Forces $\mathbf{F}(t)$ on each particle



$$\frac{d^2\mathbf{r}}{dt^2} = \frac{1}{m}\mathbf{F}$$

Positions $\mathbf{r}(t+dt)$...

Macroscopic quantity: **average on the trajectory**

ergodic hypothesis : over a long period of time, all the microstates have been encountered according to their probability, ie, average on time = statistical ensemble average

Introduction

Monte Carlo vs Molecular dynamics

Monte Carlo:

- More efficient to sample configurations and equilibrate systems
- allows simulations in grand canonical ensemble, impossible with molecular dynamics (where N must be fixed)
- Only thermodynamical and structural properties

Molecular dynamics:

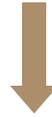
- transport properties

Introduction

Monte Carlo: needs to calculate the **potential energy** of the configuration

Molecular dynamics: needs to calculate the **forces** on the atoms

$$-\frac{\partial U_P(\mathbf{r}_i^N)}{\partial \mathbf{r}_i} = \mathbf{f}_{\rightarrow i}$$



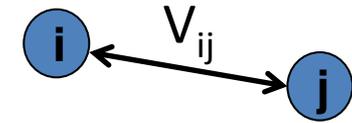
We need U_p = sum of the interactions between all the atoms of the system

We need to define these interactions, i.e. a **force-field**: ensemble of parameters and equations defining the interactions

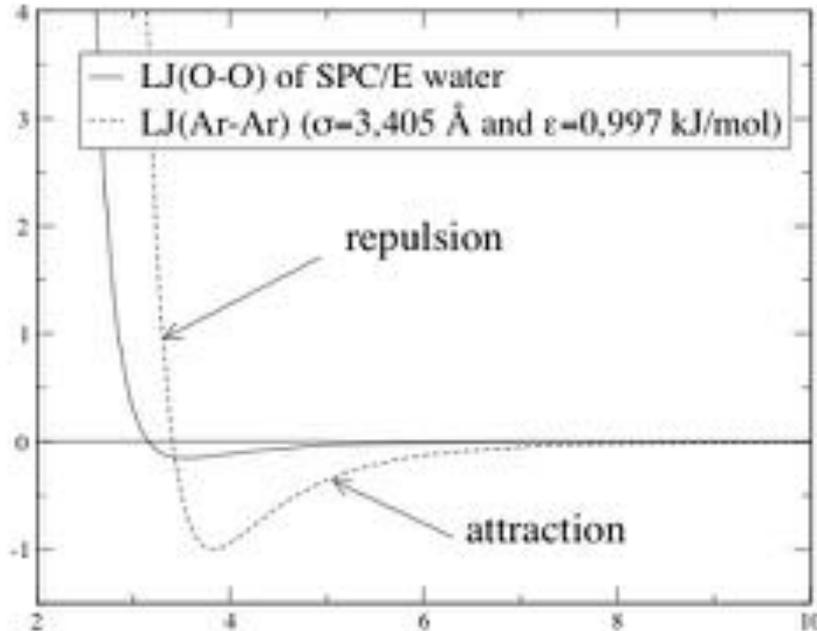
force-field

Force-field: examples of pair potentials

Short range potentials: **Van der Waals + repulsion**



- Lennard-Jones :



$$V_{ij}^{LJ} = 4\epsilon_{ij} \left[\overbrace{\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12}}^{\text{repulsion}} - \overbrace{\left(\frac{\sigma_{ij}}{r_{ij}}\right)^6}^{\text{dispersion}} \right]$$

- Buckingham $V_{ij} = A_{ij} \exp\left(-\frac{r_{ij}}{\sigma_{ij}}\right) - C_{ij} \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6$

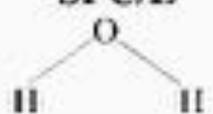
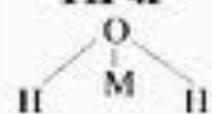
Long range potentials: **electrostatic**

$$V_{ij}^{el} = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}$$

(partial charges)

Force-field: the example of water

Rigid models

	 SPC/E	 TIP4P
$r(\text{O-H}), \text{\AA}$	1,0	0,9572
H-O-H, deg	109,47	104,62
$r(\text{O-M}), \text{\AA}$		0,15
$q(\text{O}), e$	-0,8476	
$q(\text{H}), e$	0,4238	0,52
$q(\text{M}), e$		-1,04
$\sigma_{\text{O}}, \text{\AA}$	3,165	3,154
$\epsilon_{\text{O}}, \text{kJ/mol}$	0,650	0,648

SPC, SPC/E, TIP5P,
TIP4P/2005, MCY,
etc...

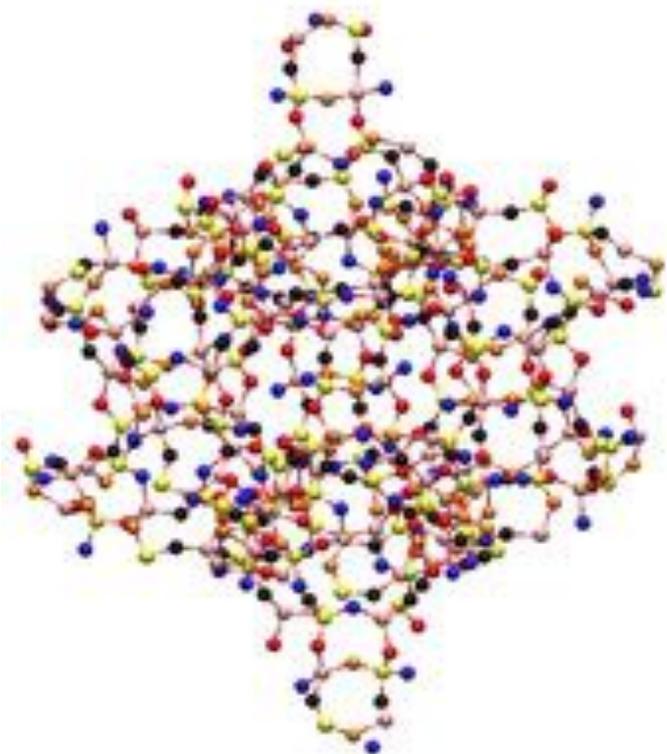
flexible models (with harmonic and/or anharmonic intramolecular potentials)

Polarizable models (with instantaneous dipoles or fluctuating charges which interact together)

Force-field: the example of zeolites

Demontis 1988, Nicholas 1991, and Hill 1995, Jaramillo 1999,
Gabrieli 2013, Bai 2013, Jeffroy 2014, Psofogiannakis 2015, Vujic 2016, Tesson 2016

Some are rigid, some are flexible, some are polarizable



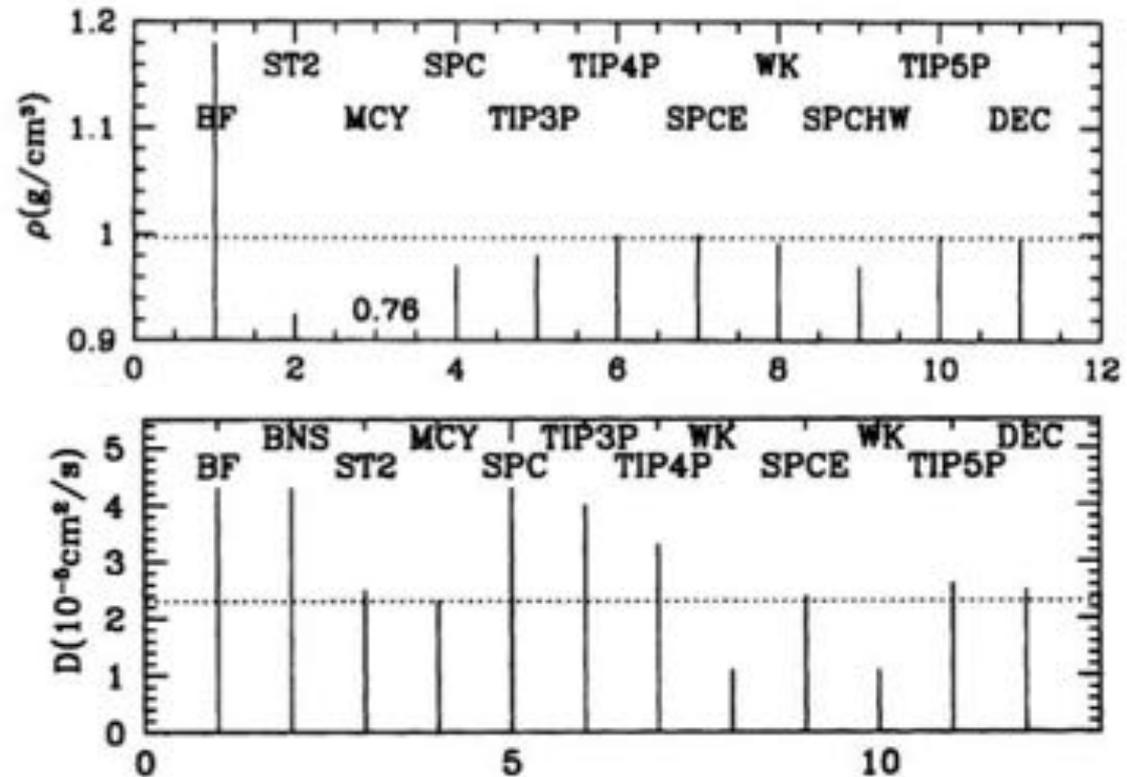
A force-field can be built in order to reproduce the results given by:

- **DFT calculations** (where electrons are taken into account)
- **experiments** (adsorption isotherms, crystallography, vibrations,...)

Force-field: accuracy

Water models

An accurate force-field for a given property can be bad for another one



The choice of the FF will depend on what we want to study

Force-field: choice criteria

The criteria for selecting a force-field include:

- accuracy
- transferability
- computational speed

Polarizable and flexible models are expected to be more realistic, but they cost more

The perfect force-field does not exist...

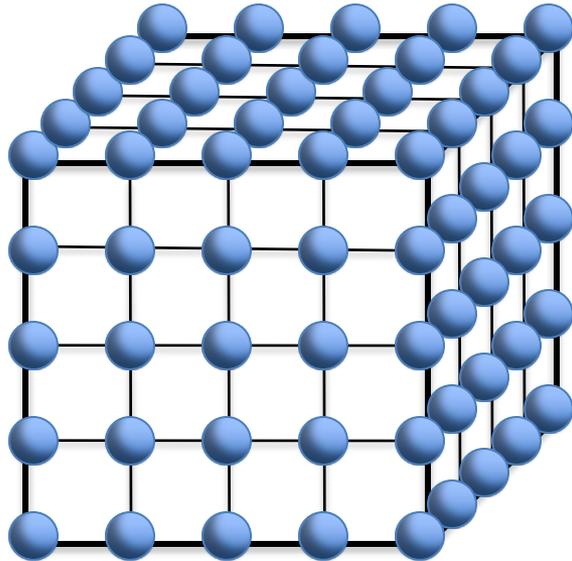
Simulation box

Simulation box: periodic boundary conditions

Example: 1 mL of water contains $0,3 \cdot 10^{23}$ molecules

→ impossible to simulate!

Powerful computer: some millions of atoms, but in general less



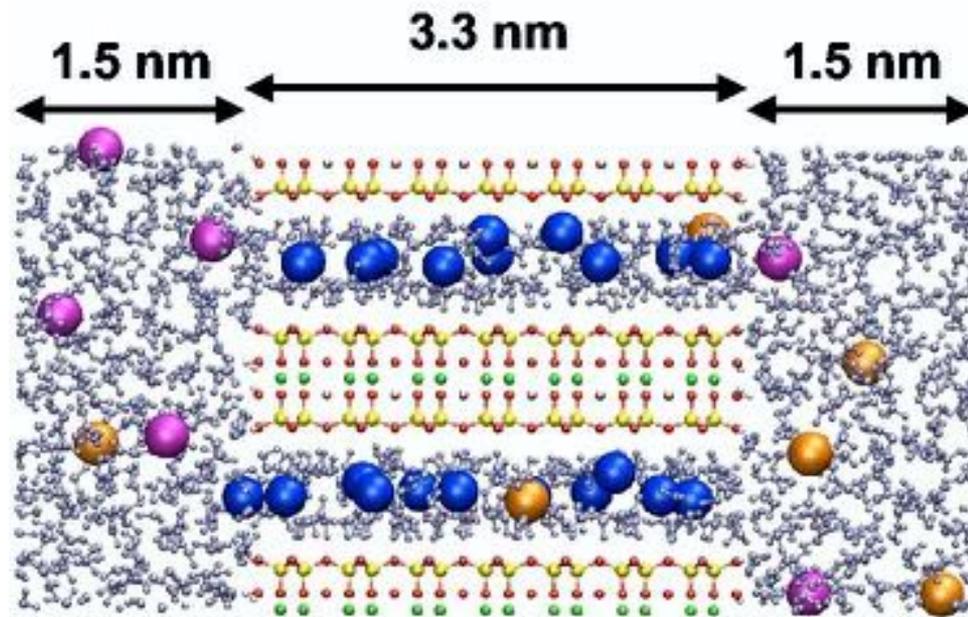
1000 atoms in a cube: 60% on the surfaces!

10^6 atoms in a cube: 6% ...

→ **Periodic boundary conditions**

Simulation box: periodic boundary conditions

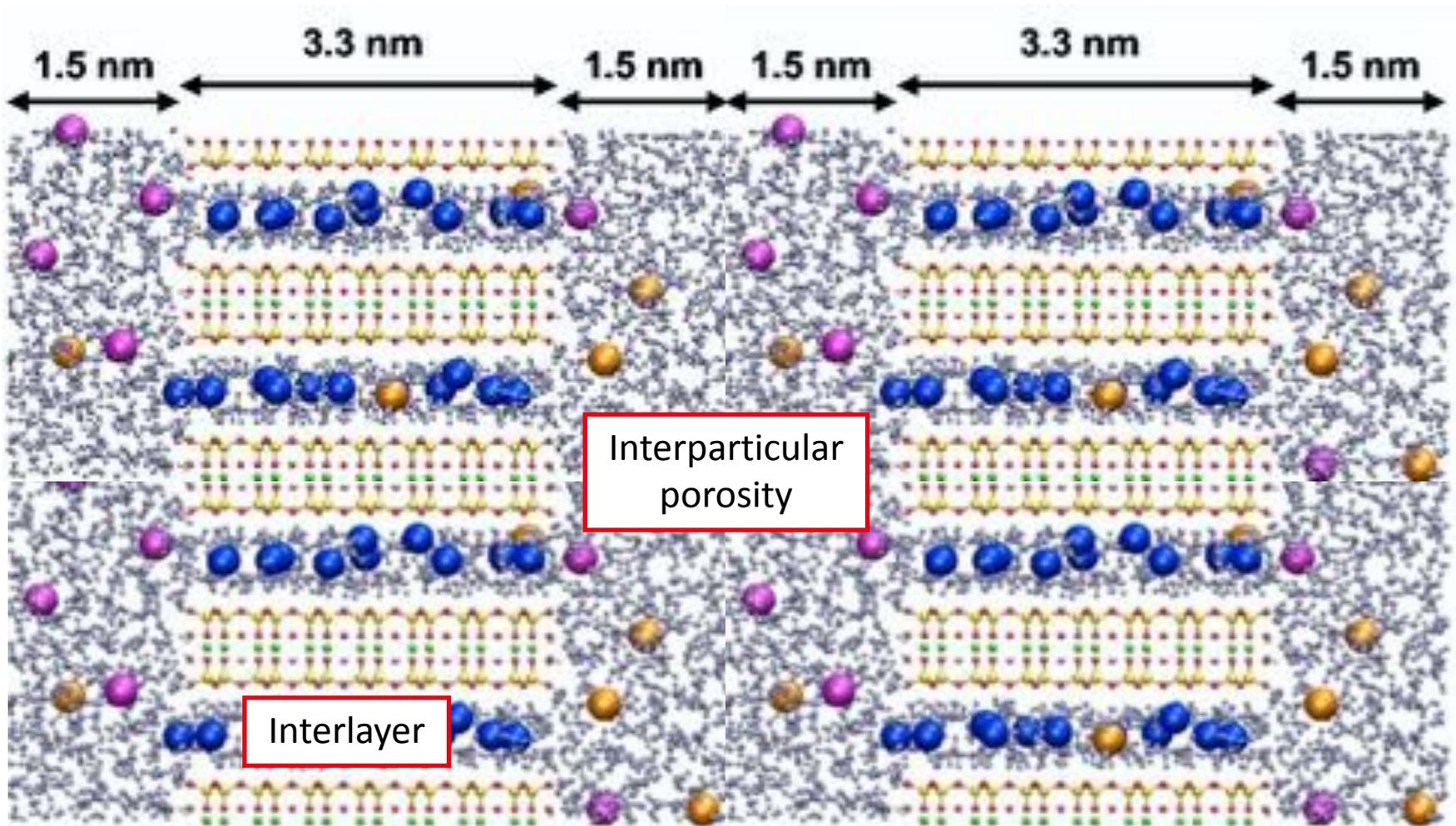
What does it mean?



Simulation box of hydrated clay layers in contact with a water reservoir

Simulation box: periodic boundary conditions

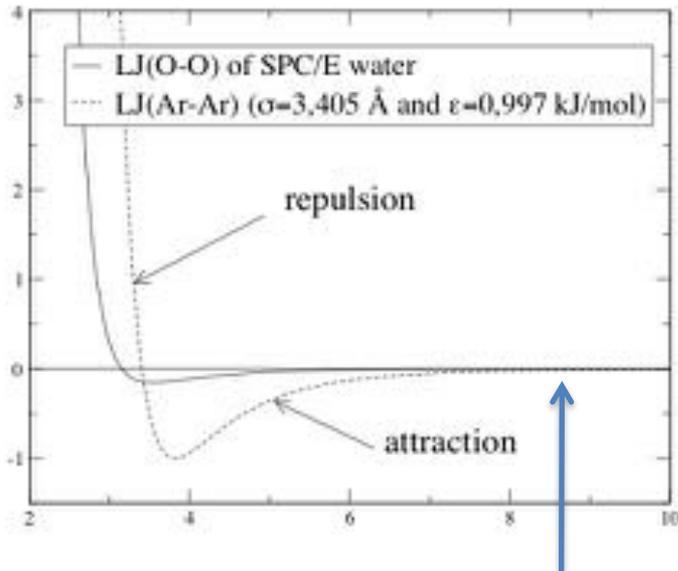
The simulated system is equivalent to...



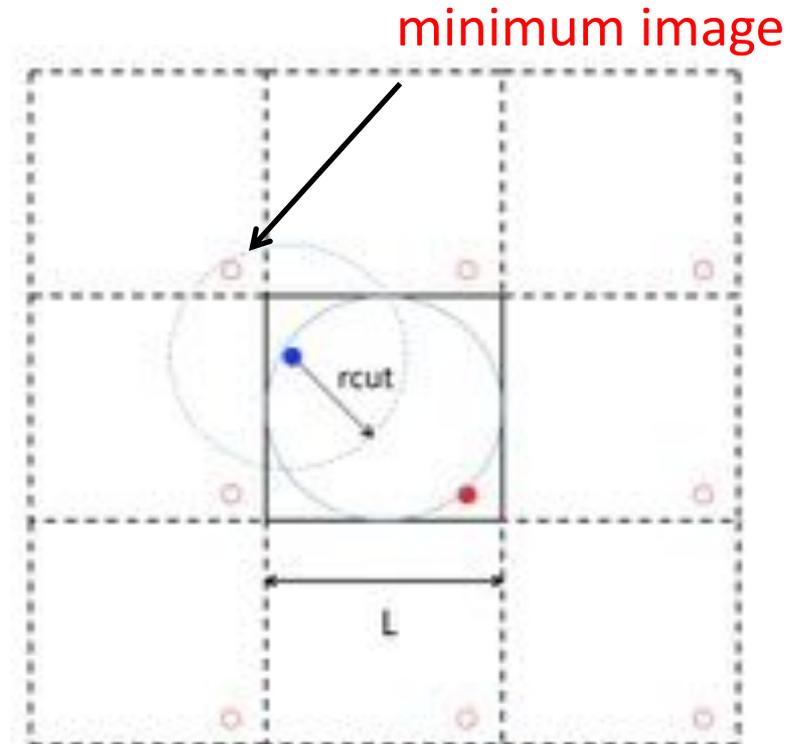
Simulation box: periodic boundary conditions

How then to calculate the interactions?

- **Short range interactions:** stop at r_{cut}



r_{cut} must be $>$ a few $\sigma(\text{LJ})$



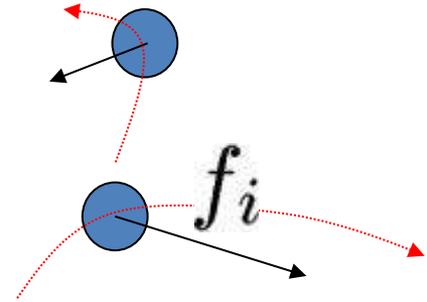
To take into account the minimum image only: L must be $>$ $2 r_{\text{cut}}$

- **Long range interactions (electrostatic):** Ewald summation (too long to explain)

Molecular Dynamics

MD: Equations of motion (NVE ensemble)

$$E = H(\mathbf{r}_i^N, \mathbf{p}_i^N) = E_K + U_P = \sum_i \frac{\mathbf{p}_i^2}{2m} + U_P(\mathbf{r}_i^N)$$



$$\left. \begin{aligned} \dot{\mathbf{r}}_i &= \frac{\partial H}{\partial \mathbf{p}_i} = \frac{\mathbf{p}_i}{m} \\ \dot{\mathbf{p}}_i &= -\frac{\partial H}{\partial \mathbf{r}_i} = -\frac{\partial U_P(\mathbf{r}_i^N)}{\partial \mathbf{r}_i} = \mathbf{f}_{\rightarrow i} \end{aligned} \right\} \Rightarrow m\ddot{\mathbf{r}}_i = \mathbf{f}_{\rightarrow i}$$

Conservation of total energy (NVE or isolated):



$$\frac{dH}{dt} = \sum_i \left(\frac{\partial H}{\partial \mathbf{r}_i} \frac{\partial \mathbf{r}_i}{\partial t} + \frac{\partial H}{\partial \mathbf{p}_i} \frac{\partial \mathbf{p}_i}{\partial t} \right) = 0 \Rightarrow E \text{ is constant}$$

MD: Verlet algorithm

How to generate a trajectory?

Choose a small timestep dt and use Taylor expansion:

$$\mathbf{r}_i(t + dt) = \mathbf{r}_i(t) + dt \frac{d\mathbf{r}_i}{dt}(t) + \frac{dt^2}{2!} \frac{d^2\mathbf{r}_i}{dt^2}(t) + \frac{dt^3}{3!} \frac{d^3\mathbf{r}_i}{dt^3}(t) + \mathcal{O}(dt^4)$$

$$\mathbf{r}_i(t + dt) = \mathbf{r}_i(t) + dt\mathbf{v}_i(t) + \frac{dt^2}{2m}\mathbf{f}_{\rightarrow i}(t) + \mathcal{O}(dt^3)$$

MD: Verlet algorithm

Velocity Verlet algorithm

Knowing $\mathbf{r}_i(t)$ and $\mathbf{v}_i(t)$, $\mathbf{r}_i(t+dt)$ can be calculated:

$$\mathbf{r}_i(t + dt) = \mathbf{r}_i(t) + dt\mathbf{v}_i(t) + \frac{dt^2}{2m}\mathbf{f}_{\rightarrow i}(t) + \mathcal{O}(dt^3)$$

Knowing $\mathbf{r}_i(t+dt)$, the forces $\mathbf{f}_i(t+dt)$ can be calculated, and then $\mathbf{v}_i(t+dt)$:

$$\mathbf{r}_i(t) = \mathbf{r}_i(t + dt) - dt\mathbf{v}_i(t + dt) + \frac{dt^2}{2m}\mathbf{f}_{\rightarrow i}(t + dt) + \mathcal{O}(dt^3)$$

$$\Rightarrow \mathbf{v}_i(t + dt) = \mathbf{v}_i(t) + \frac{dt}{2m}(\mathbf{f}_{\rightarrow i}(t) + \mathbf{f}_{\rightarrow i}(t + dt))$$

$\mathbf{r}_i(t+dt)$ and $\mathbf{v}_i(t+dt)$ are known



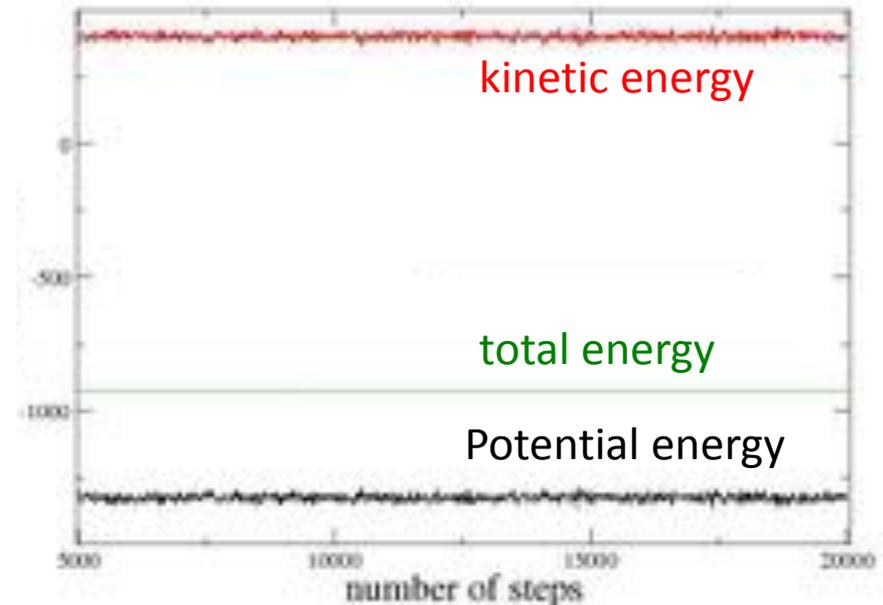
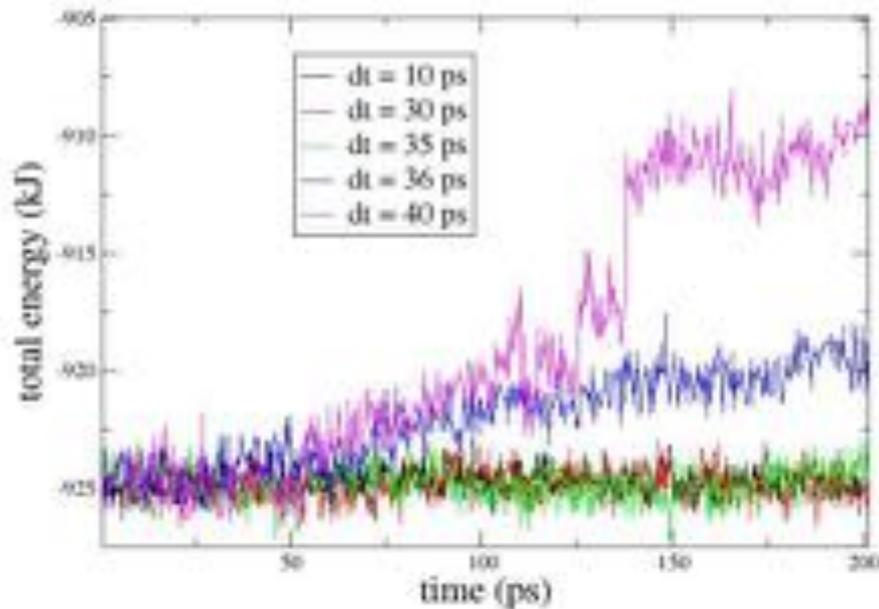
The positions and velocities are propagated

MD: Verlet algorithm

Check that $E=H(t)$ is constant. If not, dt is probably too high!

$$H(\mathbf{r}_i^N, \mathbf{p}_i^N) = E_K + U_P = \sum_i \frac{\mathbf{p}_i^2}{2m} + U_P(\mathbf{r}_i^N)$$

Ex: dense argon (T=119,8K)



MD: Controlling the temperature

At $t=0$, even if we start from a realistic configuration, the velocities of the atoms are unknown.

If we let the system evolve alone, the temperature (linked to the kinetic energy) will be bad...

Instantaneous temperature

$$E_K(t) = \sum_i \frac{m \mathbf{v}_i^2(t)}{2} = \frac{3Nk_B \mathcal{T}(t)}{2}$$

How to force the system to a given temperature?

MD: Controlling the temperature

Instantaneous temperature

$$E_K(t) = \sum_i \frac{m \mathbf{v}_i^2(t)}{2} = \frac{3Nk_B \mathcal{T}(t)}{2}$$

If the instantaneous temperature is different from the desired temperature T :

- Rescale $\mathbf{v}_i(t)$ during a certain number of steps :

$$\mathbf{v}'_i(t) = \sqrt{\frac{T}{\mathcal{T}(t)}} \mathbf{v}_i(t)$$

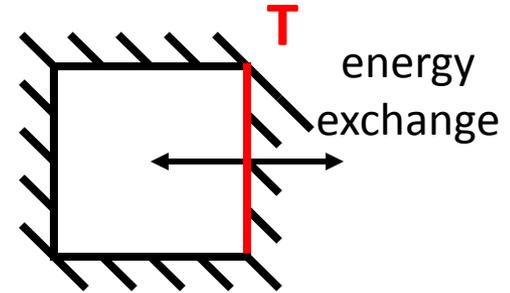
If $T > \mathcal{T}(t)$, the particles are accelerated
If $T < \mathcal{T}(t)$, the particles are slowed down

But can be used only in an **equilibration phase** (do not generate reliable trajectories)

MD: Controlling the temperature

- One can also use the **Nosé-Hoover algorithm**:

System coupled with a thermostat $\rightarrow (\xi, P_\xi)$



$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m}$$

$$\dot{\mathbf{p}}_i = \mathbf{f}_{\rightarrow i} - \frac{P_\xi}{Q} \mathbf{p}_i$$

$$\dot{\xi} = \frac{P_\xi}{Q}$$

$$\dot{P}_\xi = \sum_i \frac{\mathbf{p}_i^2}{m} - 3Nk_B T$$

$$E_K(t) = \sum_i \frac{m \mathbf{v}_i^2(t)}{2} = \frac{3Nk_B \mathcal{T}(t)}{2}$$

A return force is applied on the momenta depending on the difference between instantaneous E_K and $3Nk_B T/2$

MD: Controlling the temperature

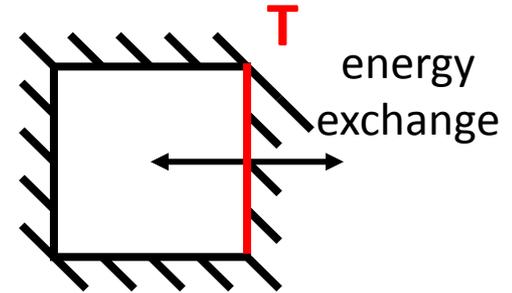
$$\begin{aligned}\dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m} \\ \dot{\mathbf{p}}_i &= \mathbf{f}_{\rightarrow i} - \frac{P_\xi}{Q} \mathbf{p}_i \\ \dot{\xi} &= \frac{P_\xi}{Q} \\ \dot{P}_\xi &= \sum_i \frac{\mathbf{p}_i^2}{m} - 3Nk_B T\end{aligned}$$



$$\frac{dH}{dt} = -2E_K \frac{P_\xi}{Q}$$

Energy dissipation:

- if $P_\xi > 0$, cooling
- if $P_\xi < 0$, heating



It can be shown that simulating a system in contact with a Nose-Hoover thermostat is equivalent to a system in the NVT ensemble.

 Nosé-Hoover thermostat is commonly used to **generate trajectories in the NVT ensemble**

Averaged properties

Averaged quantities

ergodic hypothesis : over a long period of time, all the microstates have been encountered according to their probability, ie, average on time = statistical ensemble average

Macroscopic quantity: average on the trajectory
(when the system is in equilibrium)

$$\langle A \rangle = \frac{1}{M} \sum_{j=1}^M A(\mathbf{r}^N)$$

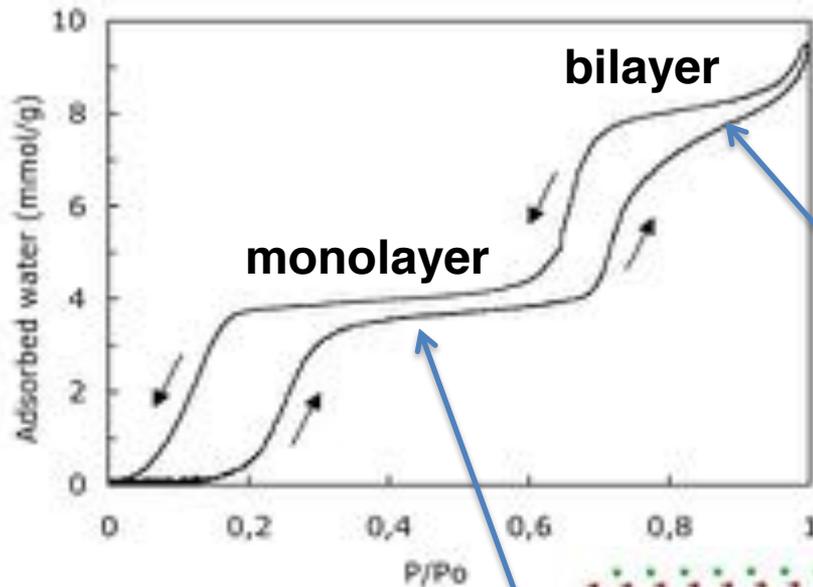
number of timesteps \nearrow M

\nwarrow A at time t_j

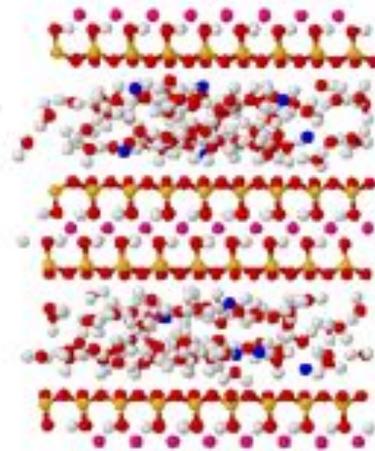
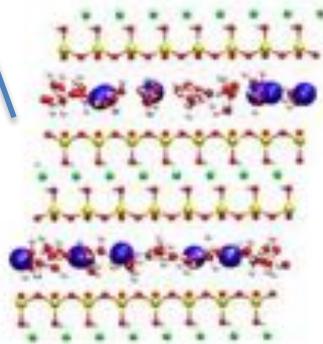
Structural properties

The **distribution functions** $\langle \rho(x) \rangle$, $\langle \rho(y) \rangle$, $\langle \rho(z) \rangle$
localize on average the atoms in the system

Example: study of clay hydration



Depending on the relative humidity, the clay will take one or two layers of water, or more...

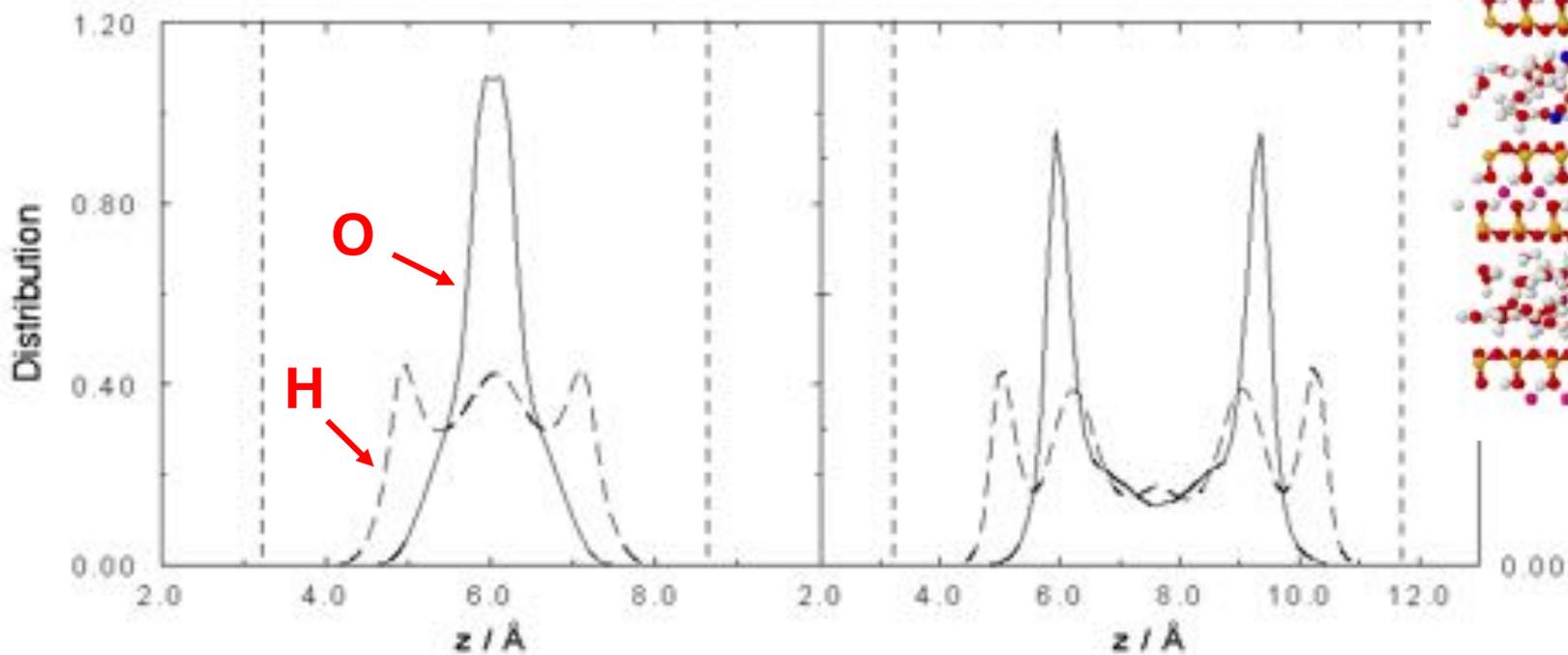


Structural properties

vertical distributions of water atoms

6 H₂O/Na⁺, Monolayer

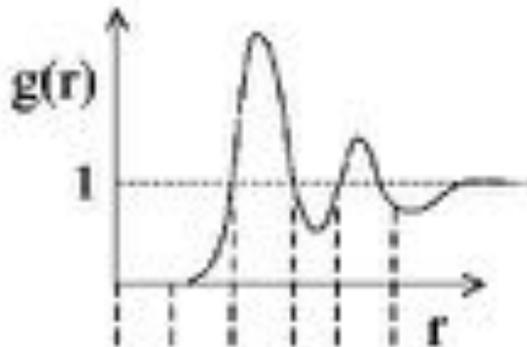
12 H₂O/Na⁺, Bilayer



reflects the probability of finding an atom at a given distance from the clay surface

Structural properties

radial distribution functions : $g(r)$



$dn_i(r)$ = number of particles in the annulus located between r and $r+dr$ from the particle i

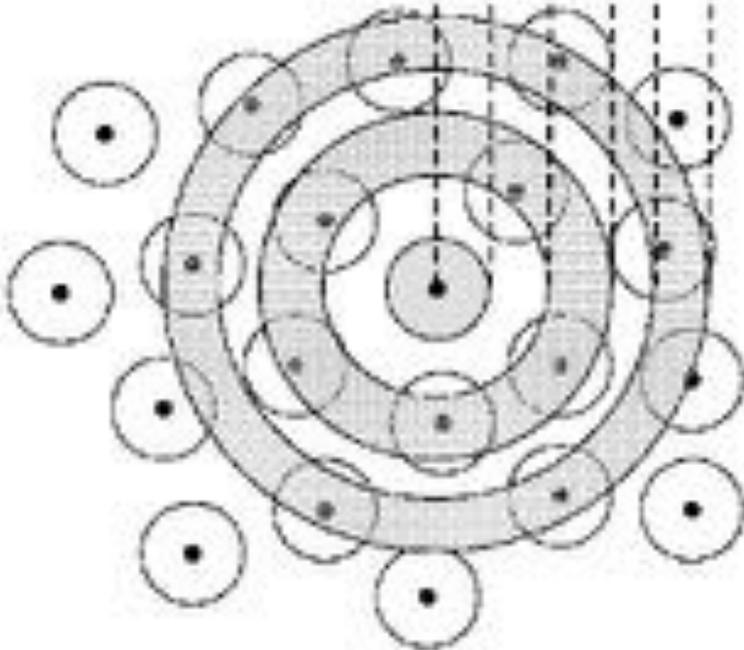
$$dn_i(r) = \rho g(r) dV$$

$dV = 4\pi r^2 dr$ is the volume of the annulus

$\rho = N/V$ is the concentration

Remark: in the case of a perfect gas (no interaction)

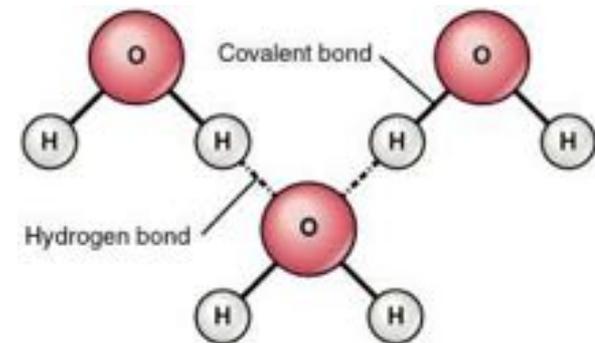
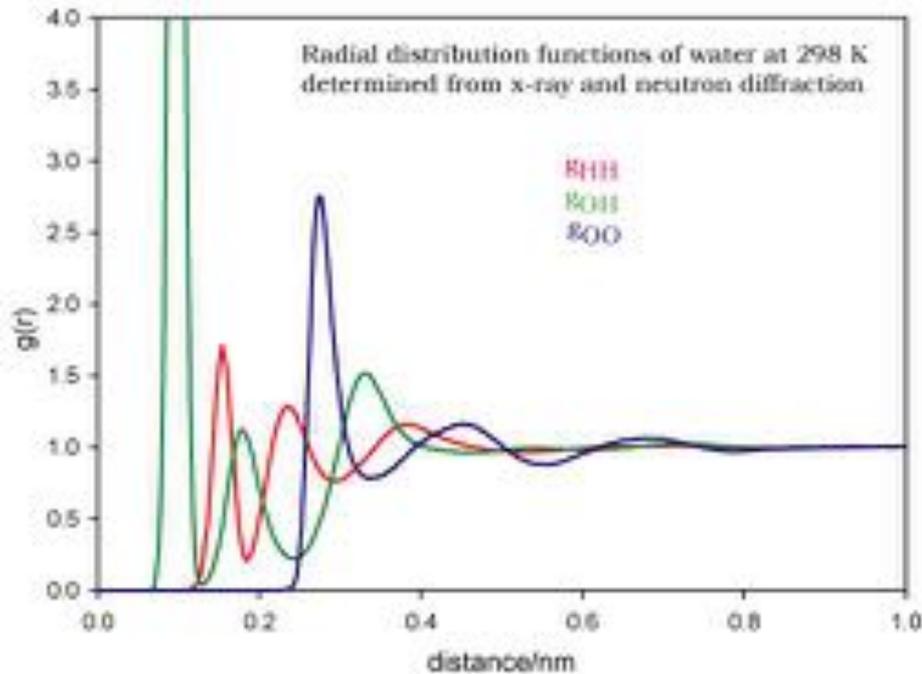
$$dn_i(r) = \frac{N}{V} dV \quad \rightarrow \quad g(r) = 1$$



Structural properties

radial distribution functions : $g(r)$

Bulk water



We see the structuring of the liquid phase, large oscillations for short distances, then slow decay to 1 (reflecting the average (bulk) density).

Thermodynamic properties

From partial derivatives:

$$dF = -PdV - SdT + \mu dN$$

$$P = - \left(\frac{\partial F}{\partial V} \right)_{T,N} \quad \text{and} \quad \mu = \left(\frac{\partial F}{\partial N} \right)_{V,T}$$

$$F = -k_B T \ln Q_{NVT} \quad \text{and} \quad Q_{NVT} = \frac{V^N}{\Lambda^{3N} N!} \int \exp(-\beta U(\mathbf{s}^N, V)) d\mathbf{s}^N$$

$$\rightarrow P = \frac{k_B T N}{V} + \frac{k_B T V^N}{Q_{NVT} \Lambda^{3N} N!} \int -\beta \left(\frac{\partial U(\mathbf{s}^N, V)}{\partial V} \right)_{T,N} \exp(-\beta U(\mathbf{s}^N, V)) d\mathbf{s}^N$$

$$\rightarrow P = \frac{k_B T N}{V} - \left\langle \left(\frac{\partial U(\mathbf{s}^N, V)}{\partial V} \right)_{T,N} \right\rangle$$

↑
perfect gas

Thermodynamic properties

$$P = \frac{k_B T N}{V} - \left\langle \left(\frac{\partial U(\mathbf{s}^N, V)}{\partial V} \right)_{T, N} \right\rangle$$

Yet

$$\frac{\partial U(\mathbf{r}^N)}{\partial V} = \sum_i \frac{\partial U(\mathbf{r}^N)}{\partial \mathbf{r}_i} \frac{\partial \mathbf{r}_i}{\partial V} = \frac{1}{3V} \sum_i \mathbf{f}_{\rightarrow i} \cdot \mathbf{r}_i$$

since $\frac{\partial \mathbf{r}_i}{\partial V} = \frac{1}{3V} \mathbf{r}_i$

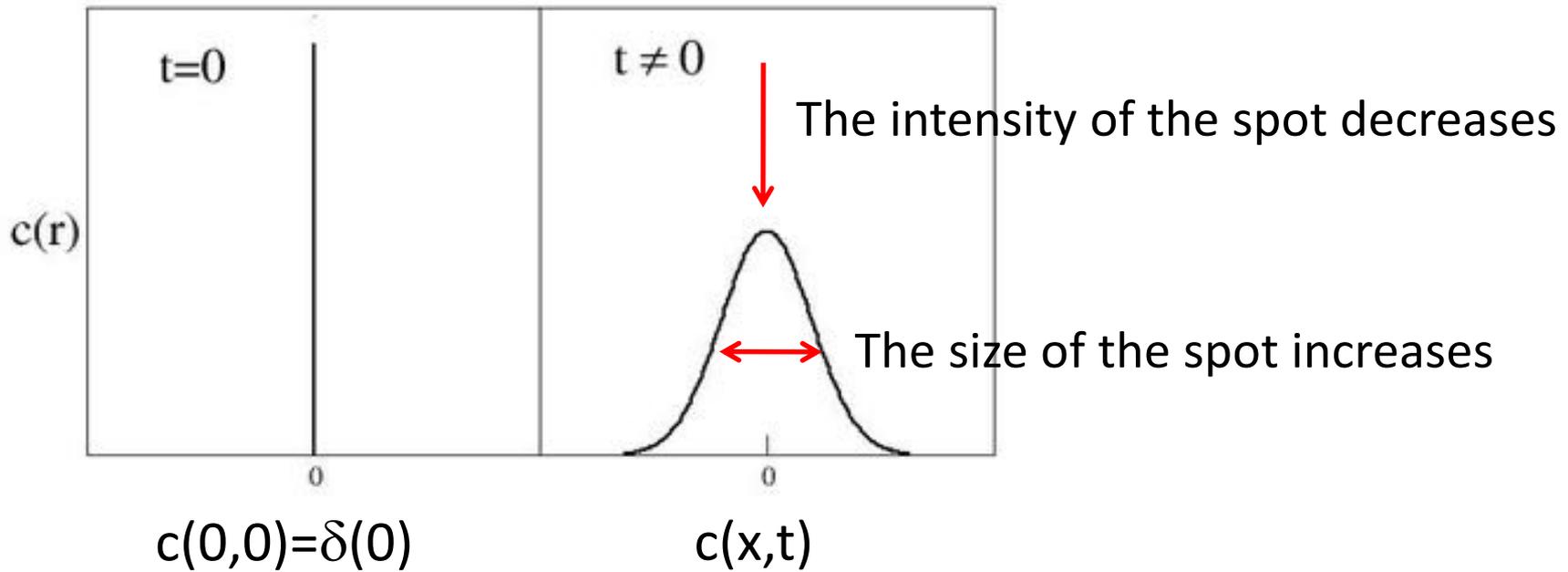
$$P = \frac{k_B T N}{V} + \left\langle \frac{1}{3V} \sum_i \mathbf{f}_{\rightarrow i} \cdot \mathbf{r}_i \right\rangle$$

Virial expression of the pressure

(easy to calculate since positions and forces are calculated at each timestep)

Dynamical quantities

Diffusion



Dynamical quantities

- Fick law:

flow \downarrow Concentration gradient \downarrow

$$\mathbf{j} = -D\nabla c$$

D is the **diffusion coefficient**

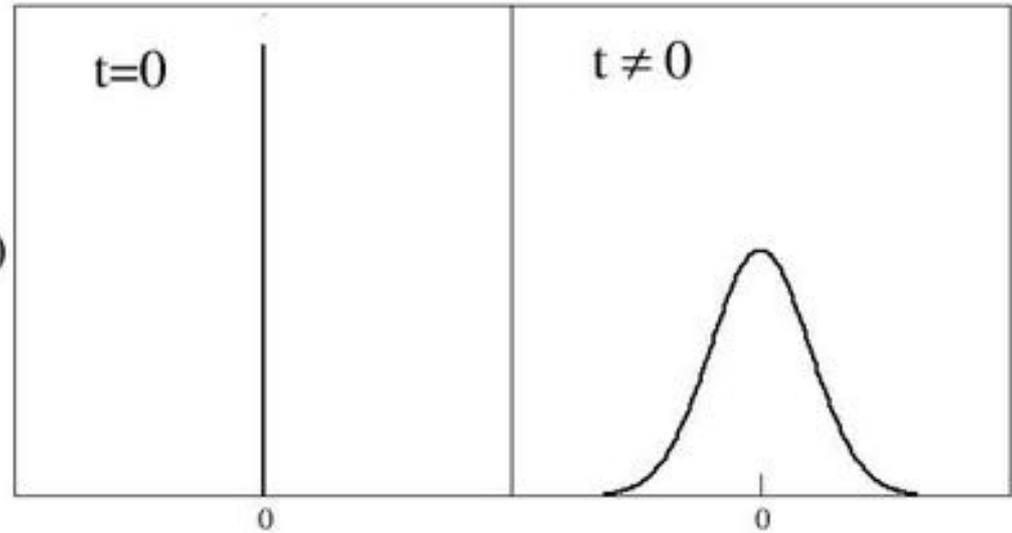
- Matter conservation:

$$\frac{\partial c}{\partial t} + \nabla \cdot \mathbf{j} = 0$$



$$\frac{\partial c}{\partial t} - D \frac{\partial^2 c}{\partial x^2} = 0$$

One dimension case



$$c(0,0)=\delta(0)$$

$$c(x,t)$$

$$\int c(x,t) dx = 1 \quad \forall t$$

$$c(x,t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

Dynamical quantities

How to calculate D in simulations?

Mean-squared displacement $\langle r^2(t) \rangle$ (MSD)

$$\langle X^2(t) \rangle = \int c(x, t) x^2 dx$$

$(c(x, t)$ is the probability to find the particle at x at time t)

$$\frac{d \langle X^2(t) \rangle}{dt} = D \int \frac{\partial^2 c(x, t)}{\partial x^2} x^2 dx \quad \rightarrow \quad \frac{d \langle X^2(t) \rangle}{dt} = 2D$$

One dimension case

$$\frac{d \langle r^2(t) \rangle}{dt} = 6D$$

three dimensions case

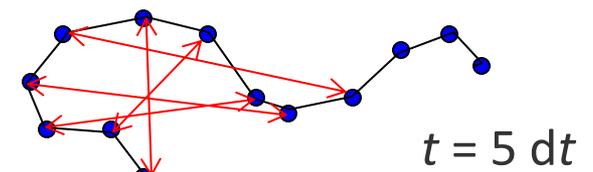
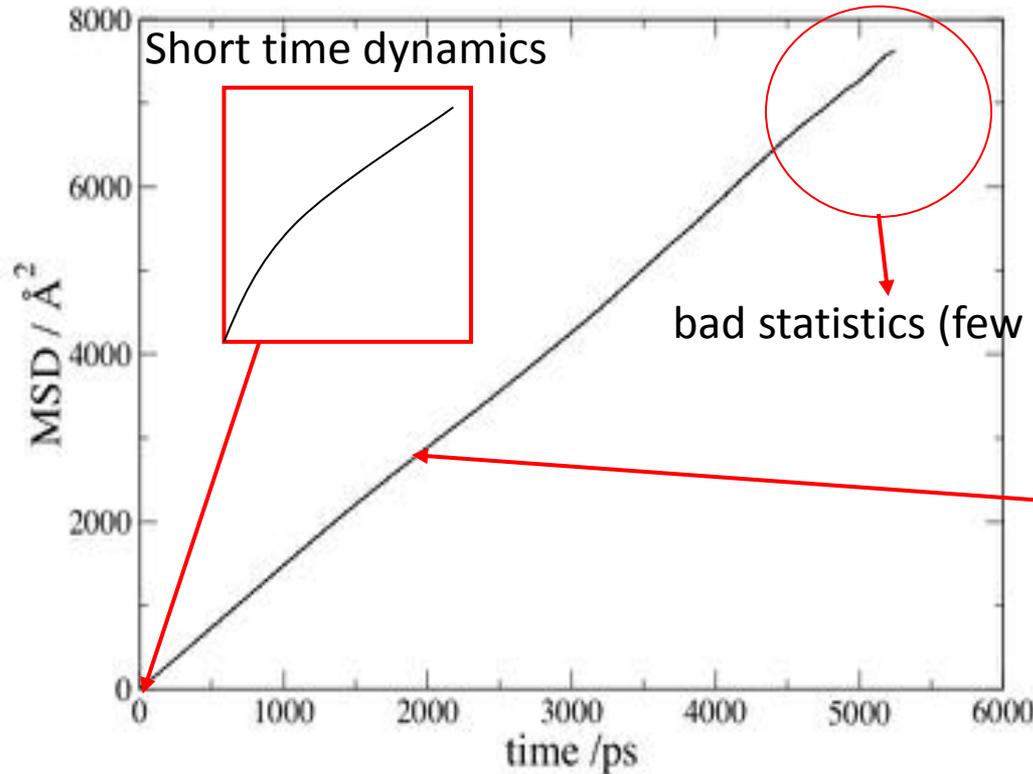
Dynamical quantities

Average over the particles:

$$\langle r^2(t) \rangle = \frac{1}{N} \sum_i \Delta r_i(t)^2$$

Average over time origins:

$$\begin{aligned} \langle r^2(t) \rangle &= \langle (\mathbf{r}(t) - \mathbf{r}(0))^2 \rangle = \frac{1}{N_\tau} \sum_\tau \langle (\mathbf{r}(t + \tau) - \mathbf{r}(t))^2 \rangle \\ &= \frac{1}{N_\tau N} \sum_\tau \sum_i (\mathbf{r}_i(t + \tau) - \mathbf{r}_i(t))^2 \end{aligned}$$

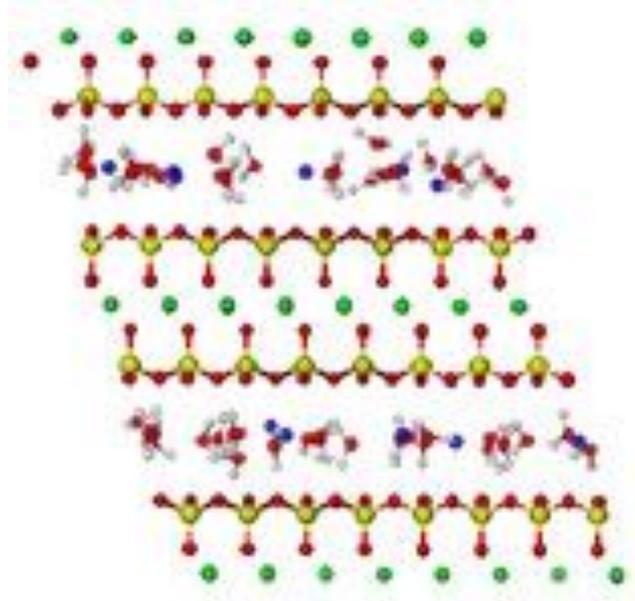


$$6D = \lim_{t \rightarrow \infty} \frac{d \langle r^2(t) \rangle}{dt}$$

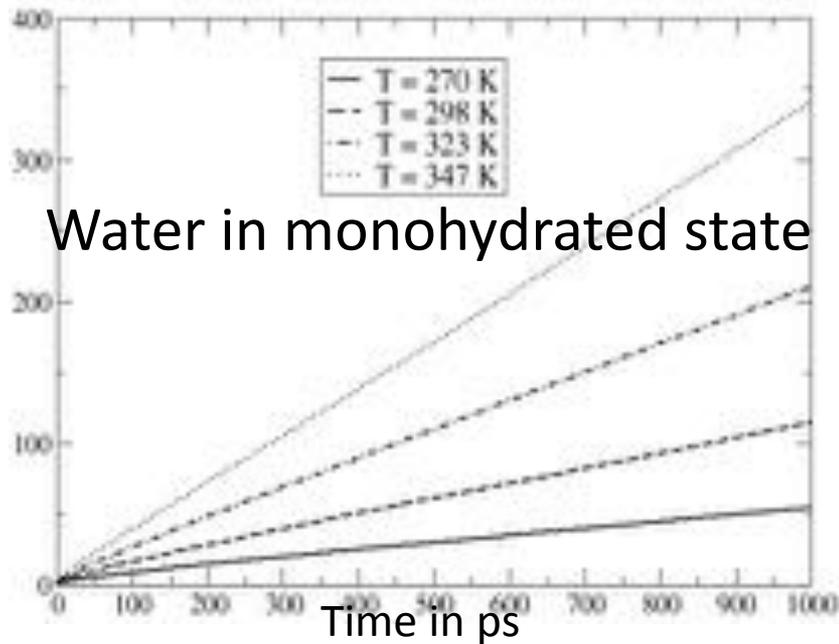
Dynamical quantities

Example on an **hectorite clay**:

The slope gives the diffusion coefficient parallel to the clay layers



$\langle x^2(t) + y^2(t) \rangle$ in \AA^2



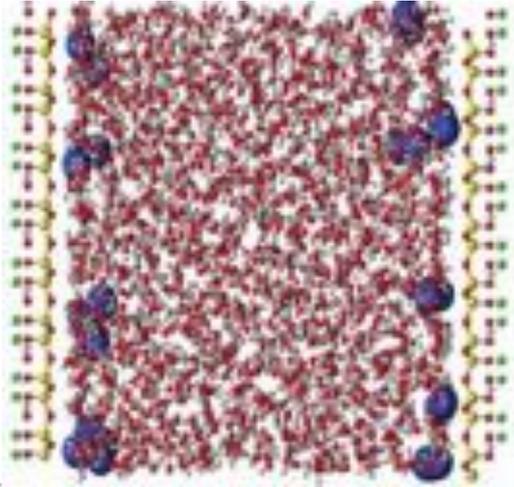
Water in monohydrated state

NB: the mean square displacement along z (direction perpendicular to the clay layers) tends towards a plateau (bonded motion): $D_z = 0$

The dynamics is slowed down in clays by a factor 3-4 for bihydrated clays and 6-8 for monohydrated clays (in agreement with QENS)

Dynamical quantities

Example: hydrodynamics in slit pores

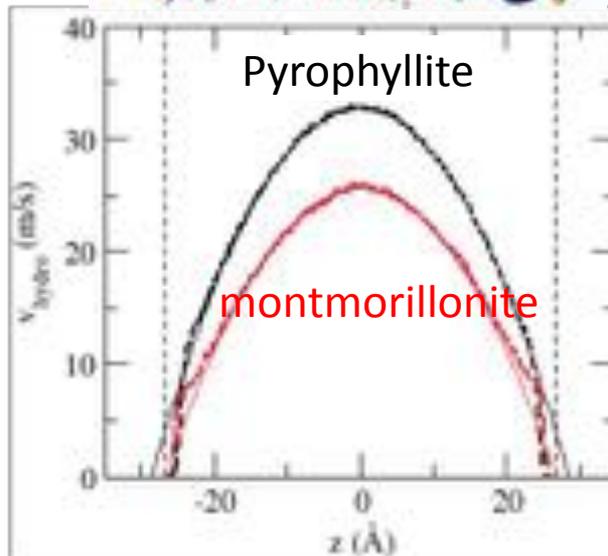


The fluid is submitted to a pressure gradient (non equilibrium molecular dynamic)

- The velocity profile is parabolic according to Stokes law (for pores of $L > 30 \text{ \AA}$):

$$-\eta \frac{d^2 v}{dz^2} = F_{vx}$$

- the fluid sticks or slips differently according to the type of surface



Velocity profile perpendicular to the surfaces

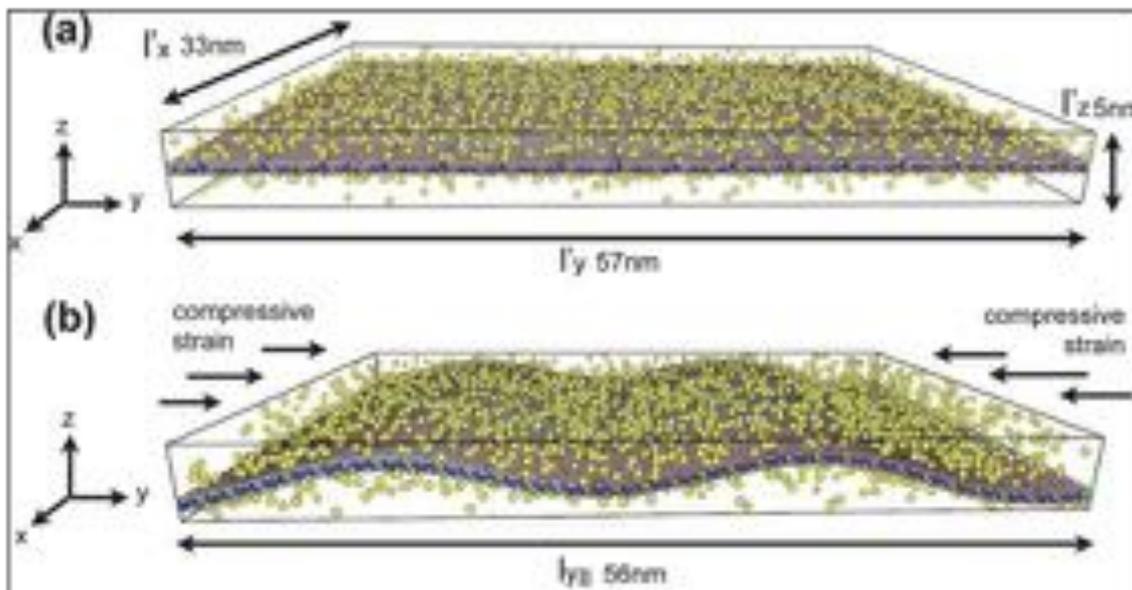
(Botan et al, *J. Phys. Chem. C*, 2011;
Botan et al, *J. Phys. Chem. C*, 2013)

mechanical quantities

Example 1: understand the role of clay in mechanical properties of clay-polymer nanocomposites

Mechanical response to a compressive strain on a clay:

Systems: one single flexible clay sheet surrounded by water or a stacking of clay sheets with a monolayer of water in between (very big systems)



Elastic constants are deduced from the calculation of the response stress

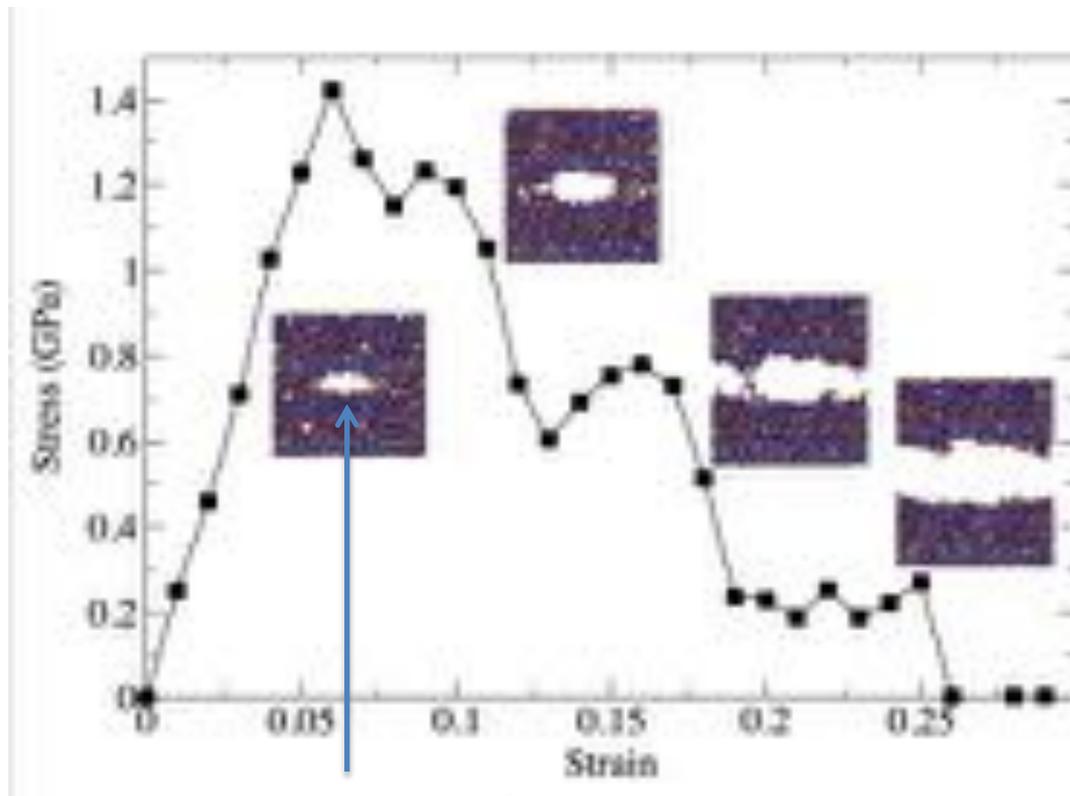
$$\sigma_{kl} = \frac{1}{V} \sum_{i=1}^N \left(\frac{m_i}{2} \mathbf{v}_i \mathbf{v}_i + \frac{1}{2} \sum_{j=1}^N \mathbf{F}_i \mathbf{r}_{ij} \right)_{kl}$$

(Suter et al., 2009)

mechanical quantities

Example 2: understand the fracturation of cements

Mechanical response to a vertical strain on CSH: propagation of a fracture



Preexisting fracture

The crack does not propagate instantly after a given critical strain (different from silica glass)

 Ductile behavior

(Bauchy et al., 2015)

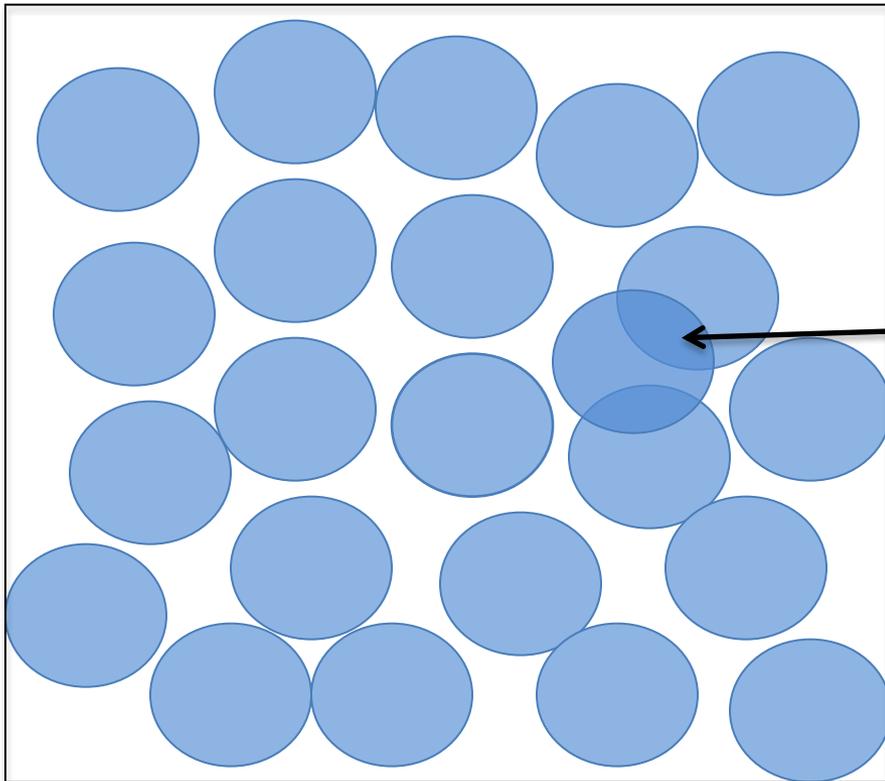
Monte Carlo method

Importance sampling

How to generate the microstates randomly (in the NVT ensemble)?

Example of hard spheres at freezing point (dense system):

A big number M of microstates are generated



$$P_i \propto \exp(-\beta U(\mathbf{r}^N))$$

$$\langle A \rangle \approx \frac{\sum_i^M \exp(-\beta U(\mathbf{r}_i^N)) A(\mathbf{r}_i^N)}{\sum_i^M \exp(-\beta U(\mathbf{r}_i^N))}$$

$$U = +\infty$$

100 hard spheres at freezing point: $1/10^{260}$ configurations of finite U !!!

Importance sampling

A clever way would be to sample the microstates according to the probability density:

$$P_i \propto \exp(-\beta U(\mathbf{r}^N))$$

The most probable states will be generated more often than the others...

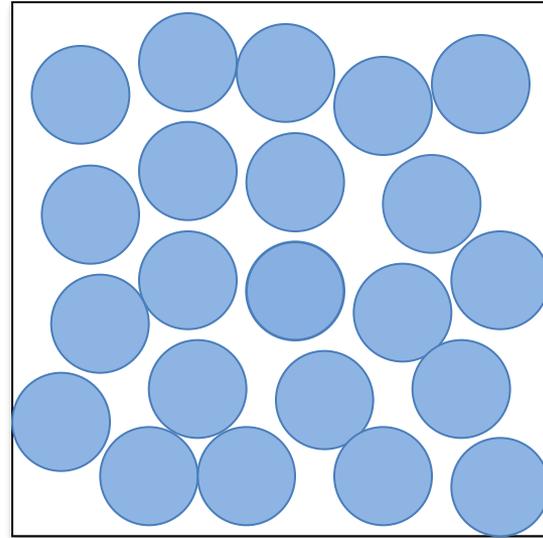


Metropolis method

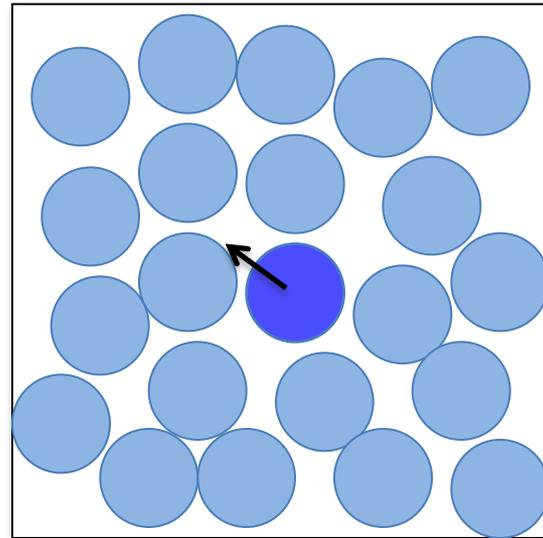
Metropolis method

The hard sphere case:

1) Start from a possible configuration (with no interpenetrated spheres)



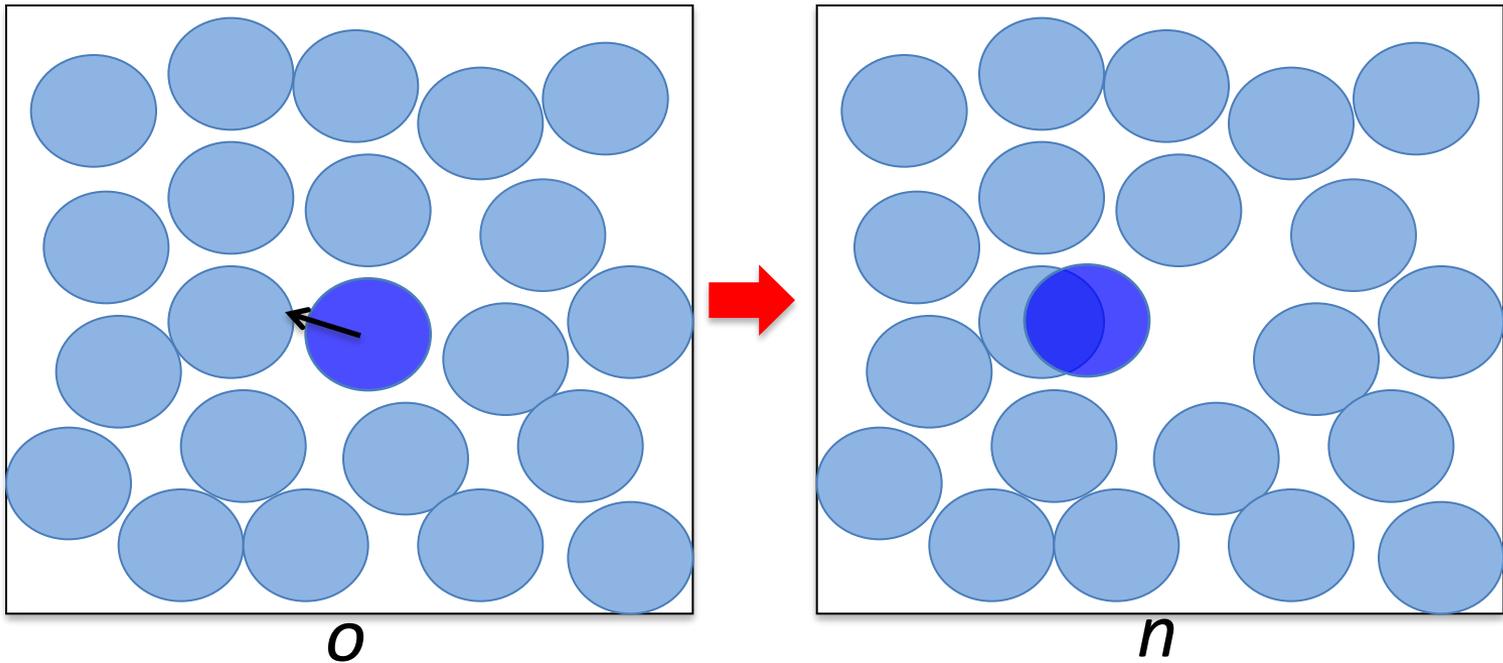
1) Generate a new state (n) from the old state (o) by moving a particle randomly



Metropolis method

The transition probability from the old state (o) to the new one (n) is

$$\Pi(o \rightarrow n) = \alpha(o \rightarrow n)acc(o \rightarrow n)$$



$\alpha(o \rightarrow n)$ Probability to generate n from o

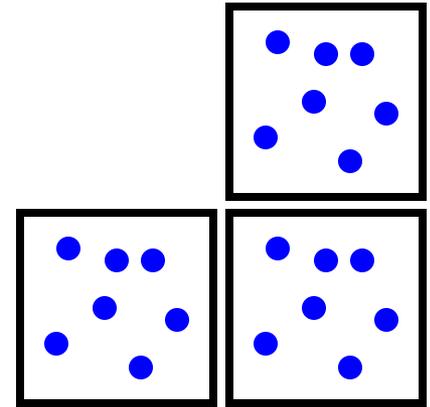
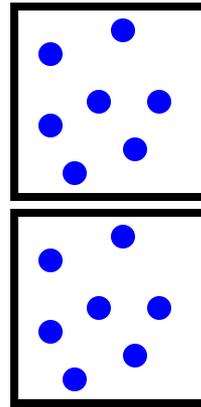
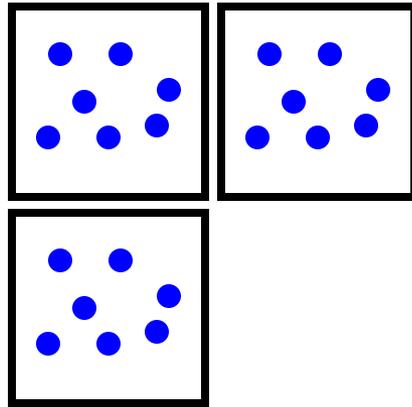
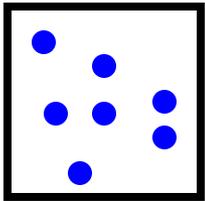
For a displacement $\alpha(o \rightarrow n) = \alpha(n \rightarrow o)$

$acc(o \rightarrow n)$ Probability to accept the displacement

Metropolis method

How to choose $acc(o \rightarrow n)$ to explore the microstates according to their probability?

Imagine a big number of identical systems at equilibrium: each microstate is seen a number of times proportionnal to $\exp(-\beta U_p)$

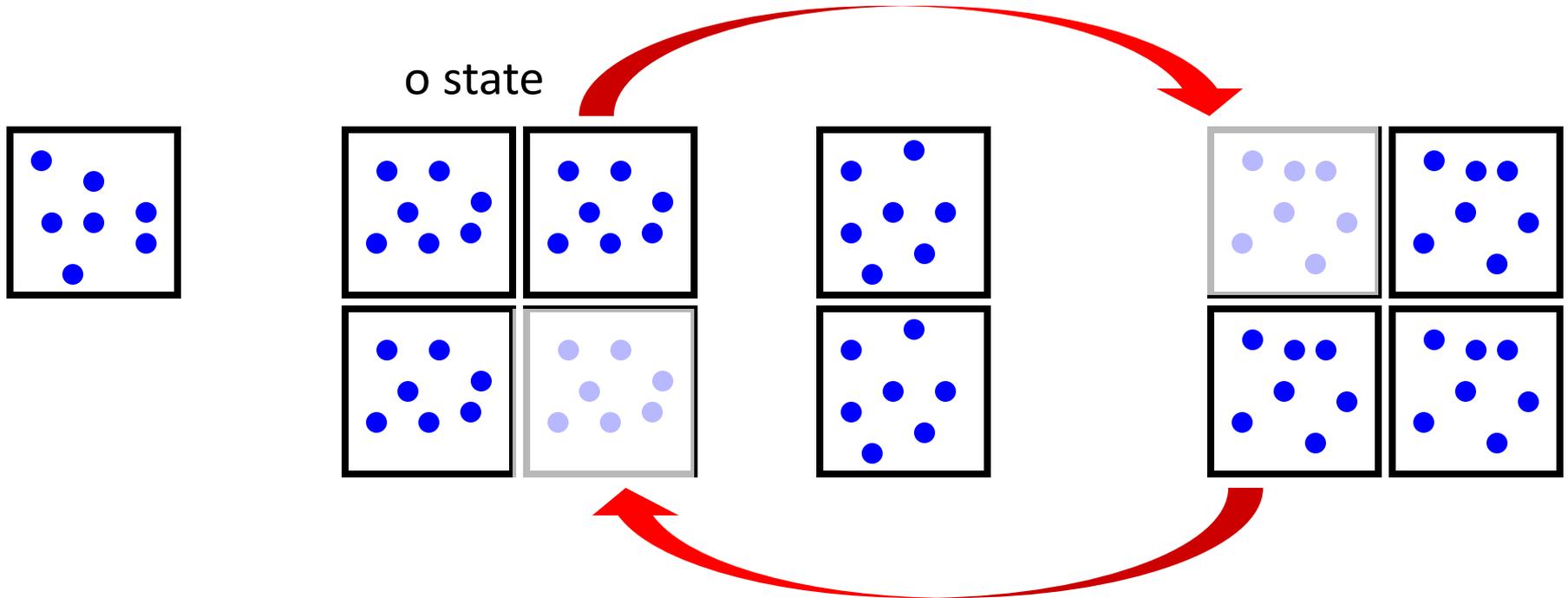


$$n_1 \propto \exp(-\beta U_{P1}) \quad n_2 \propto \exp(-\beta U_{P2}) \quad n_3 \propto \exp(-\beta U_{P3}) \quad n_4 \propto \exp(-\beta U_{P4})$$

Metropolis method

The distribution at equilibrium must be conserved

➔ If a system leaves the state o , another one should come back to o

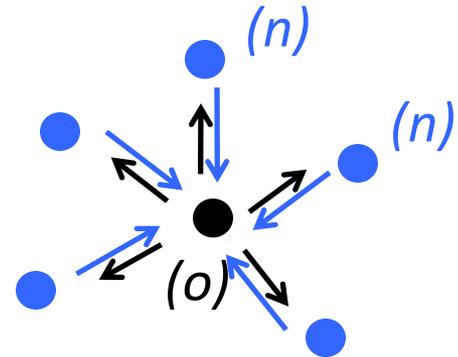


Metropolis method

At equilibrium, probability to leave o = probability to come back to o

$$P_o \sum_n \Pi(o \rightarrow n) = \sum_n P_n \Pi(n \rightarrow o)$$

↑
probability of the system to be found in o state



Stronger condition : **detailed balance** principle

$$P_o \Pi(o \rightarrow n) = P_n \Pi(n \rightarrow o)$$

$$\frac{\Pi(o \rightarrow n)}{\Pi(n \rightarrow o)} = \frac{\cancel{\alpha(o \rightarrow n)} acc(o \rightarrow n)}{\cancel{\alpha(n \rightarrow o)} acc(n \rightarrow o)} = \frac{P_n}{P_o}$$



$$\frac{acc(o \rightarrow n)}{acc(n \rightarrow o)} = \exp[-\beta(U_n - U_o)]$$

Metropolis algorithm

$$\frac{acc(o \rightarrow n)}{acc(n \rightarrow o)} = \exp[-\beta(U_n - U_o)] \text{ is verified if}$$

$$acc(o \rightarrow n) = \min(1, \exp[-\beta(U_n - U_o)])$$

Metropolis criterion

Proof:

$$\text{If } U_n \geq U_o, \quad \exp(-\beta(U_n - U_o)) \leq 1$$

$$\Rightarrow acc(o \rightarrow n) = \exp(-\beta(U_n - U_o))$$

$$\exp(-\beta(U_o - U_n)) \geq 1$$

$$\Rightarrow acc(n \rightarrow o) = 1$$

$$\rightarrow \frac{acc(o \rightarrow n)}{acc(n \rightarrow o)} = \exp(-\beta(U_n - U_o))$$

The same reasoning can be made in the case $U_n \leq U_o$

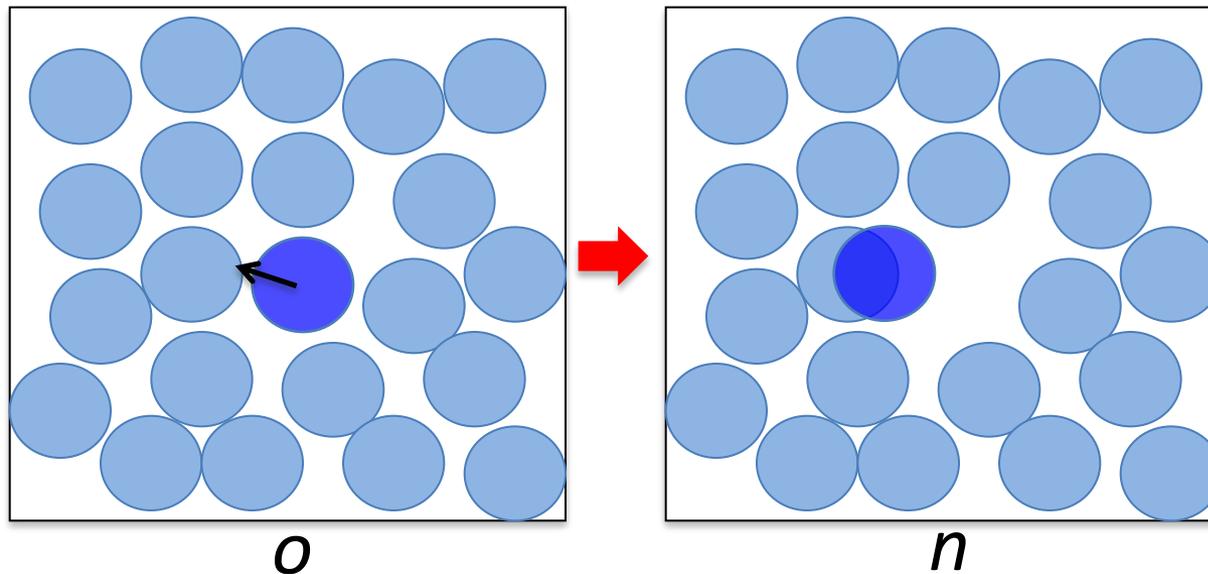
Metropolis algorithm

The hard sphere system:

At step k , the system is in the configuration $\mathbf{r}(k)^N$ and the energy is $U_o = U(k)$

To move from step k to step $k+1$:

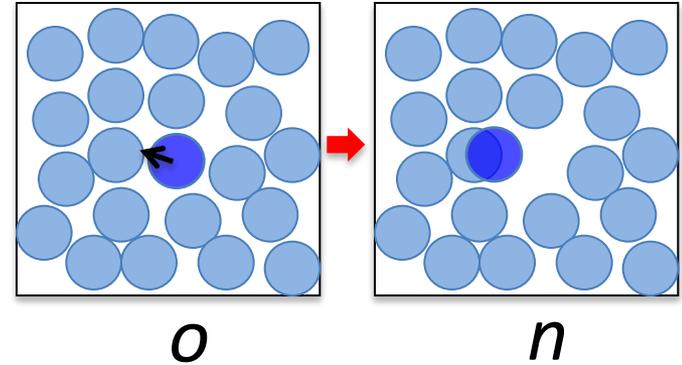
1) Choose a particle randomly and move it from Δ in a random direction.



Metropolis algorithm

2) Calculate the energy of the new configuration U_n

Here, $U_n = +\infty$



3) Apply the Metropolis criterion:

Here, $U_n - U_o = +\infty$

$$acc(o \rightarrow n) = \min(1, \exp[-\beta(U_n - U_o)]) \quad \rightarrow \quad acc = 0$$

The new configuration is rejected
The old configuration is kept

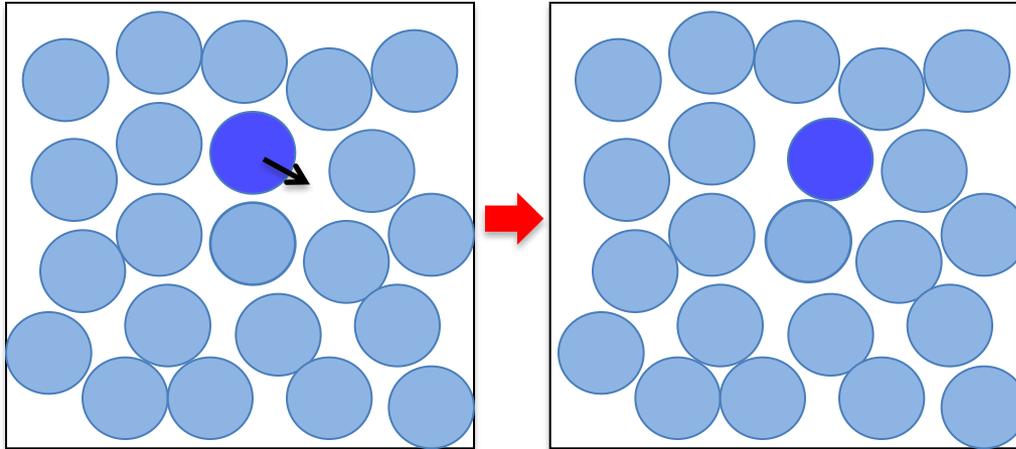


$$\begin{aligned} U_{k+1} &= U_k = U_o \\ A &= A + A_o \end{aligned}$$

Go back to step 1

Metropolis algorithm

1) Choose a particle randomly and move it from Δ in a random direction.



2) Calculate the energy of the new configuration U_n

3) Apply the Metropolis criterion: Let us suppose that $U_n - U_o < 0$

$$acc(o \rightarrow n) = \min(1, \exp[-\beta(U_n - U_o)]) \quad \rightarrow \quad acc = 1$$

$$\begin{aligned} U_{k+1} &= U_n \\ A &= A + A_n \end{aligned}$$

The new configuration is accepted

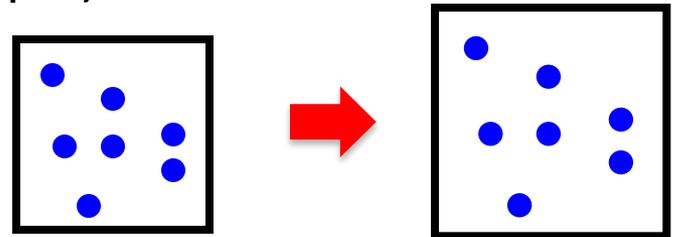
Go back to step 1

At the end of the simulation, $\langle A \rangle$ is obtained by dividing $A = \sum_k A(k)$ by the number of steps.

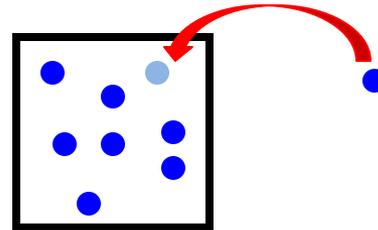
Metropolis algorithm

The algorithm has been illustrated with particle displacements, but any type of trials can be considered, as soon as detailed balance is respected:

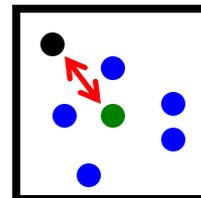
- Volume changes (in NPT ensemble for example)



- Insertion/deletion of particles



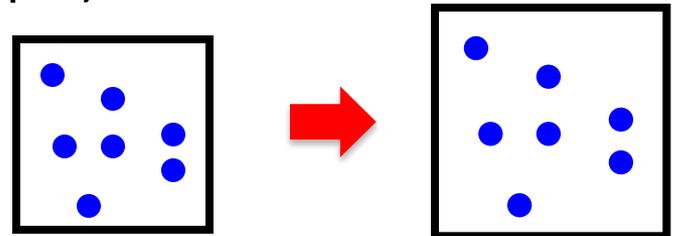
- exchange between particles



Metropolis algorithm

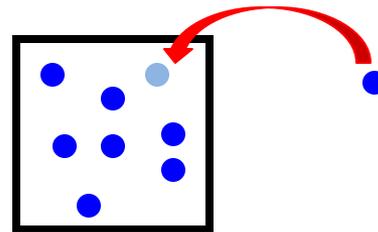
The algorithm has been illustrated with particle displacements, but any type of trials can be considered, as soon as detailed balance is respected:

- Volume changes (in NPT ensemble for example)

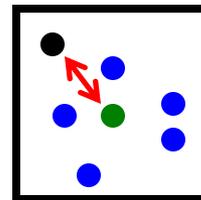


- Insertion/deletion of particles

Grand canonical ensemble



- exchange between particles



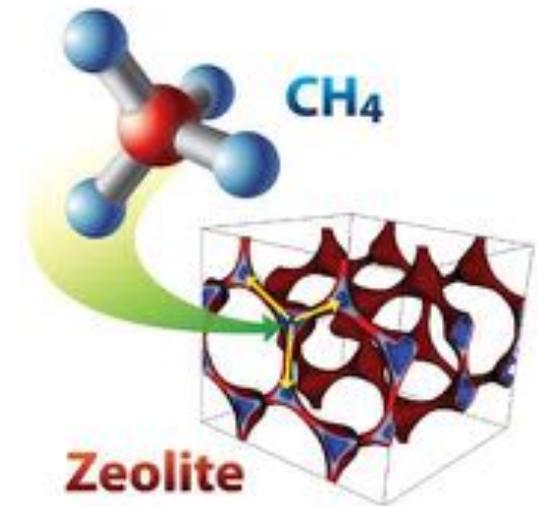
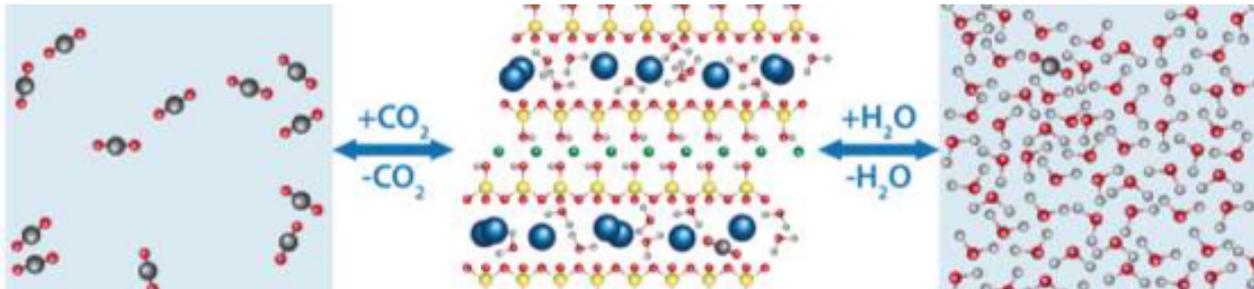
Monte Carlo in grand canonical ensemble

Simulations in grand-canonical ensemble

the system is in contact with a reservoir of particles (μ is fixed): N can vary (N is fixed in molecular dynamics simulations)

Examples: 1) adsorption in porous media

2) Influence of a supercritical reservoir of CO_2 on clay rock/water equilibrium



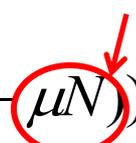
CH_4 trapping in zeolites

Monte Carlo in grand canonical ensemble

The probability to find the system around a given configuration (\mathbf{r}_i^N, N) is proportionnal to

$$P(N, r_i^N) \propto \exp(-\beta(U(r_i^N) - \mu N))$$

Chemical potential term



The algorithm is the same as before with the possibility of:

- a random particle displacement  equivalent to NVT
- a random insertion of a particle: the Metropolis criterion is

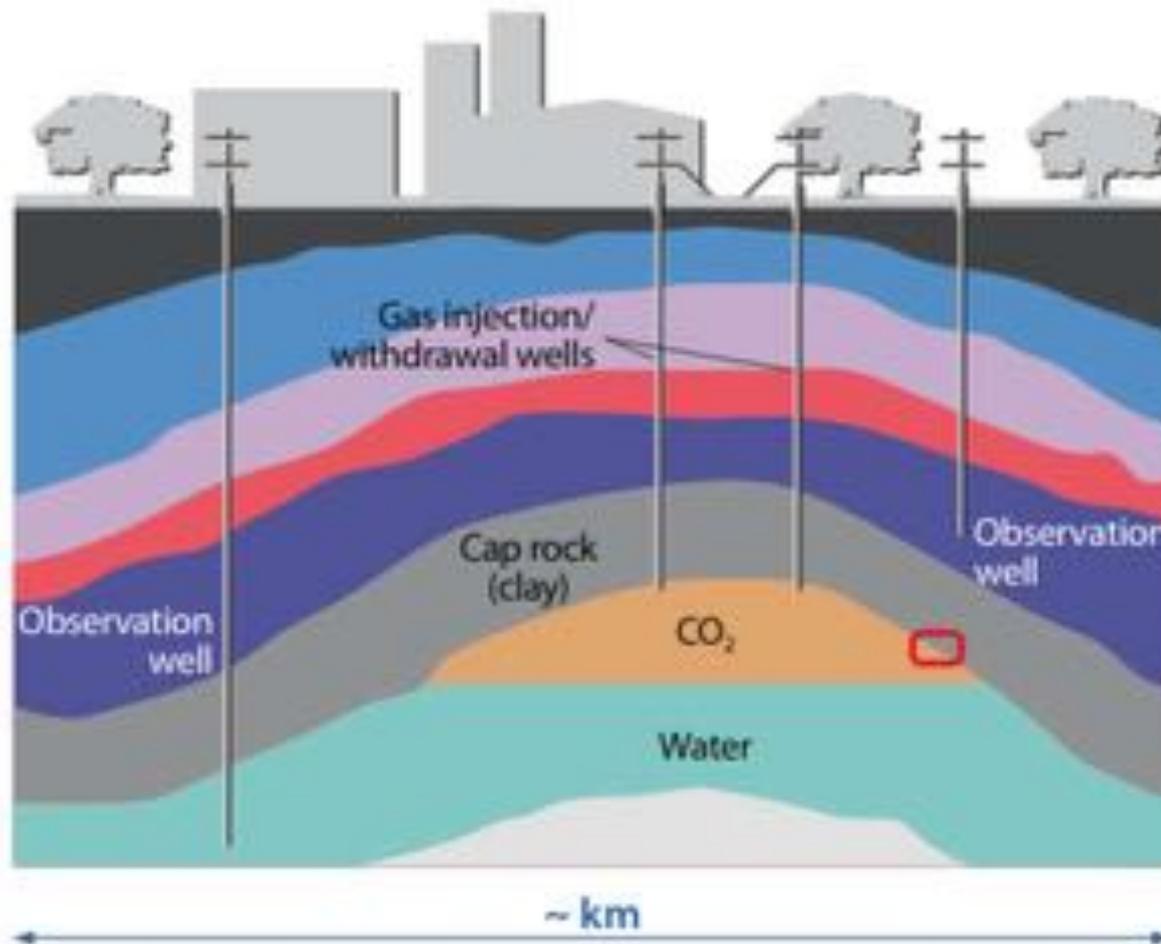
$$acc(N \rightarrow N+1) = \min\left(1, \frac{V}{\Lambda^3(N+1)} \exp[-\beta(U(N+1) - U(N) - \mu)]\right)$$

- a removal of a random particle: the Metropolis criterion is

$$acc(N \rightarrow N-1) = \min\left(1, \frac{\Lambda^3 N}{V} \exp[-\beta(U(N-1) - U(N) + \mu)]\right)$$

Monte Carlo in grand canonical ensemble: application

Application: Influence of a supercritical reservoir of CO_2 on clay rock/water equilibrium



CO_2 storage in saline aquifers

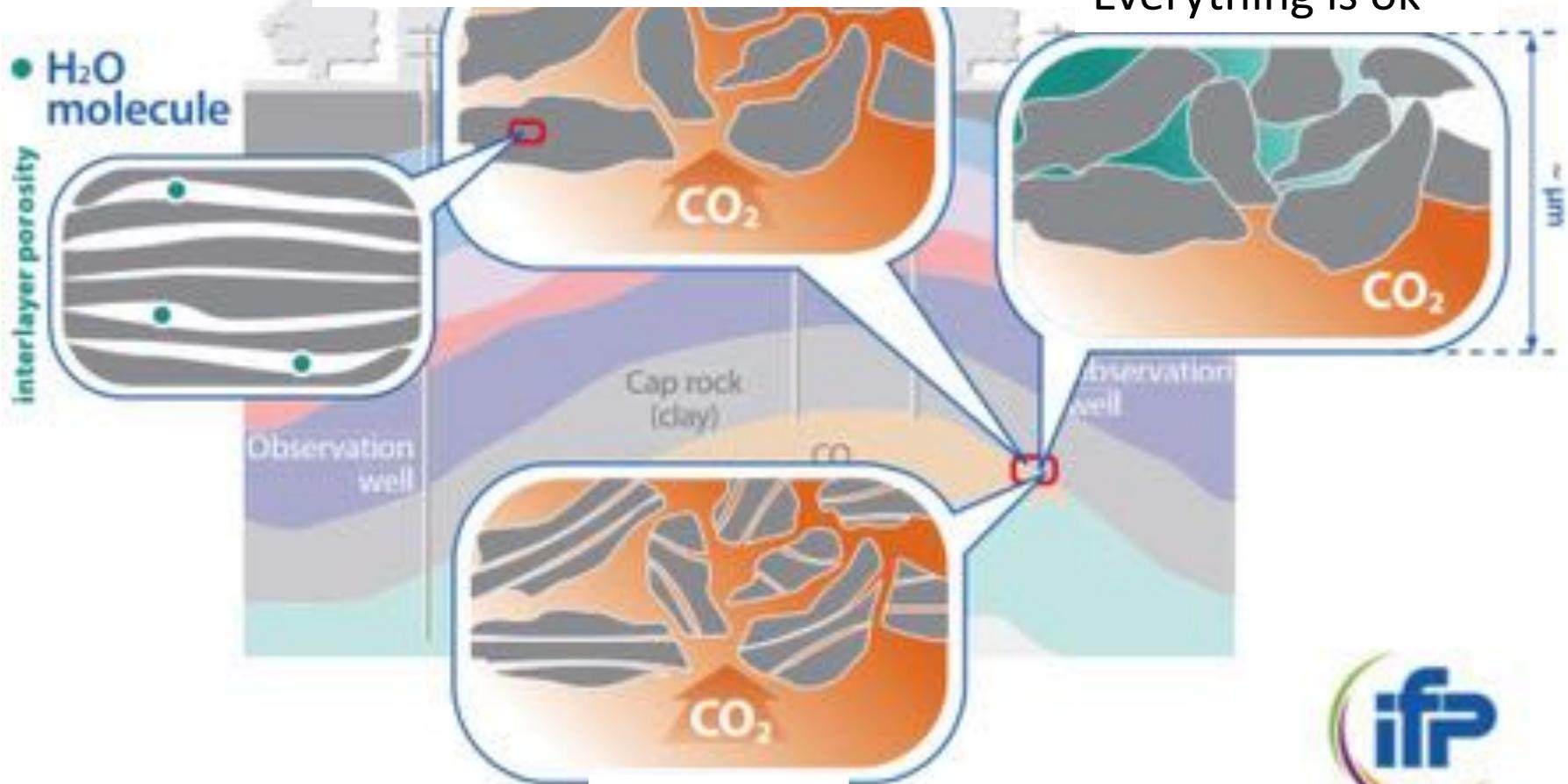
Monte Carlo in grand canonical ensemble: application

Storage of CO₂ in saline aquifers

Various scenarios

The clay particles shrink (water goes out)

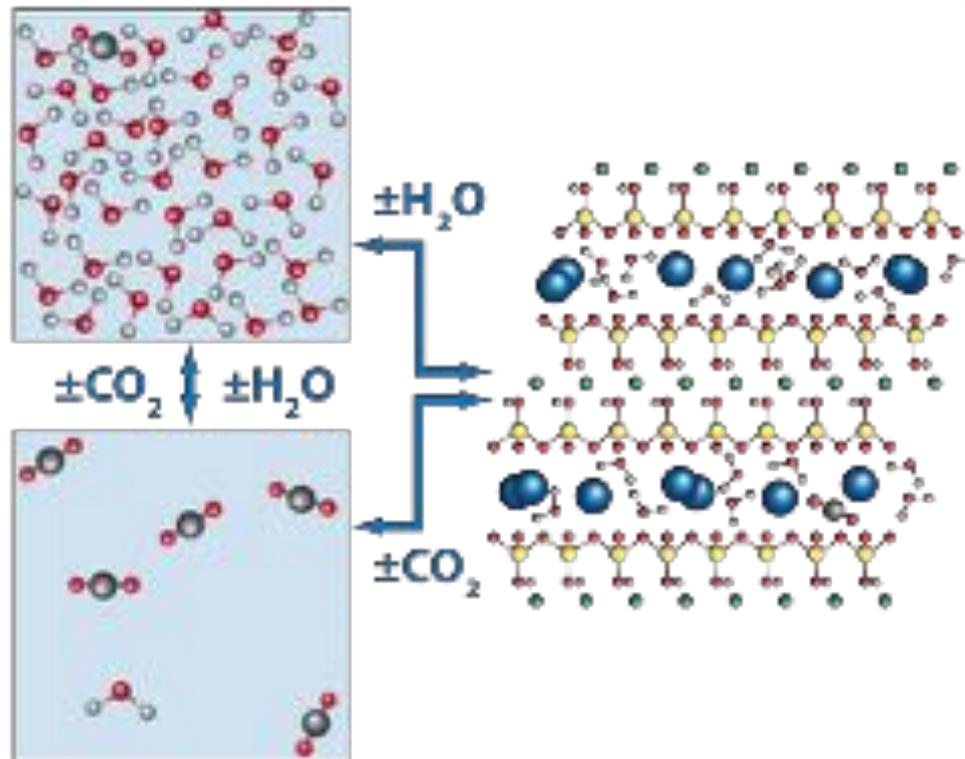
Everything is ok



Monte Carlo in grand canonical ensemble: application

Here the experimental conditions are:

External fixed T and P , clay in contact with two reservoirs: one of water, one of CO_2 : fixed μ_{water} and μ_{CO_2}



Monte Carlo simulations can **predict** the behavior of hydrated clay particles when in contact with supercritical CO_2 ...

Monte Carlo in grand canonical ensemble: application

Determine the equilibrium states of the clay/water system:

They correspond to **the minima of the thermodynamical function**

$$F = U - \mu_{\text{ext}} N + P_{\text{ext}} V - T_{\text{ext}} S$$

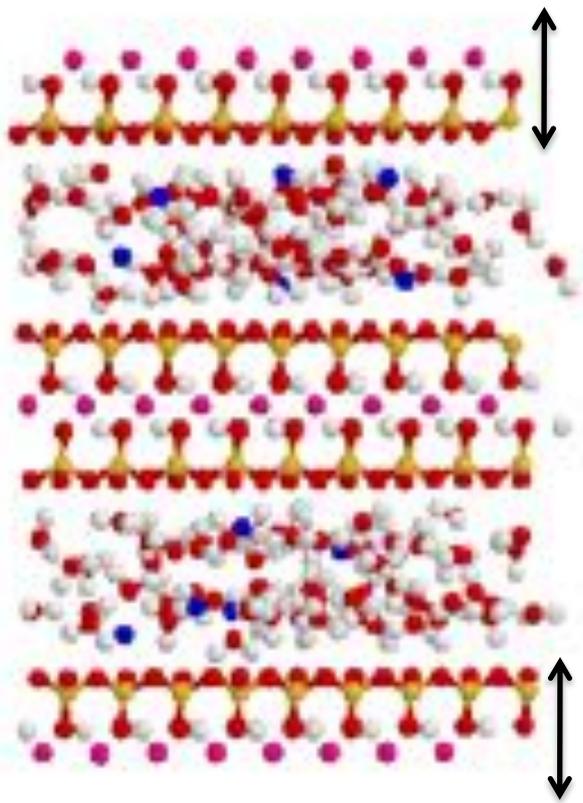
$$F = U - \mu_{\text{ext}} N + P_{\text{ext}} V - T_{\text{ext}} S \quad \xrightarrow{\text{fixed } \mu_{\text{ext}} \text{ and } T_{\text{ext}}} \quad dF = - (P - P_{\text{ext}}) dV$$

Simulations at same T_{ext} and μ_{ext} , for various V , are performed.
(grand canonical ensemble)

For each simulation, the pressure is calculated thanks to:

$$P = \frac{k_B T N}{V} - \left\langle \left(\frac{\partial U(\mathbf{s}^N, V)}{\partial V} \right)_{T, N} \right\rangle$$

Monte Carlo in grand canonical ensemble: application



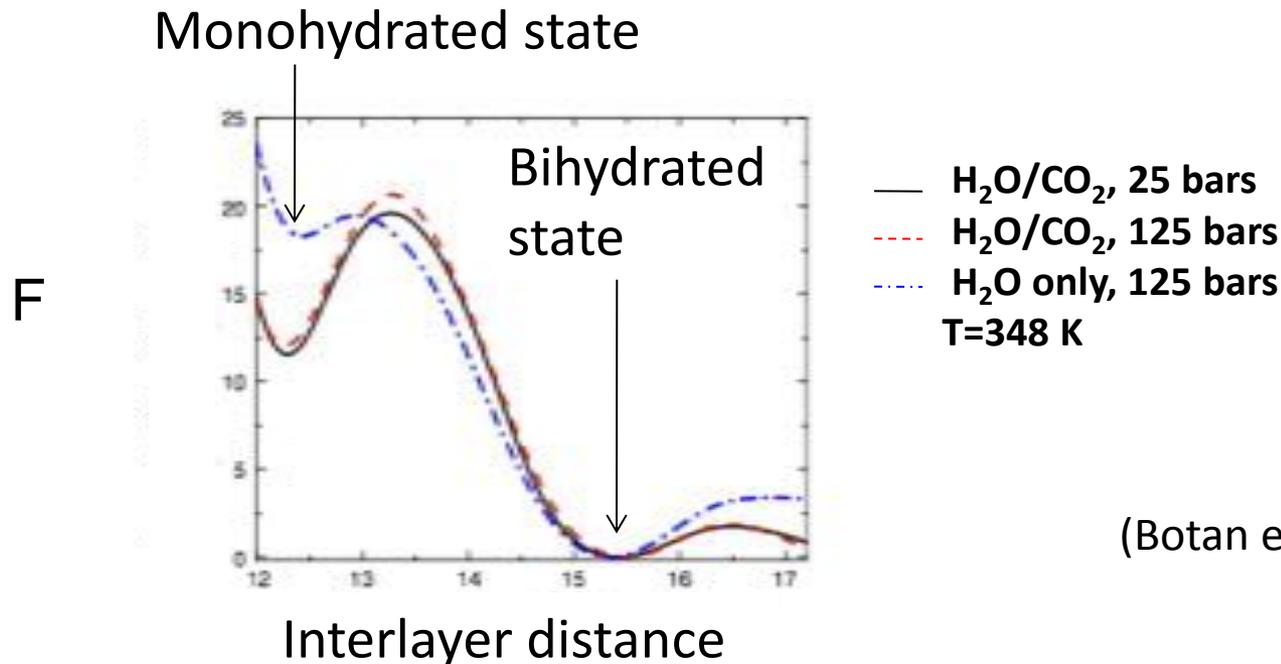
$$P = \frac{k_B T N}{V} - \left\langle \left(\frac{\partial U(\mathbf{s}^N, V)}{\partial V} \right)_{T, N} \right\rangle$$

At the end of each step :

- a symmetric phantom change of volume (rescaling positions of the molecules) $\rightarrow dV$
 - calculation of dU
- } n times
- average $\langle dU/dV \rangle = \Sigma(dU/dV)/n$ over every trial moves to calculate the pressure

Monte Carlo in grand canonical ensemble: application

$$dF = -(P - P_{\text{ext}}) dV$$



(Botan et al., 2010)

In the presence of supercritical CO₂, some CO₂ molecules enter interlayer spacings but no radical change of the equilibrium states of hydration is seen (no shrinkage):

Thank you for your attention