Micromechanical modelling of clays: molecular simulations

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Introduction to molecular simulations

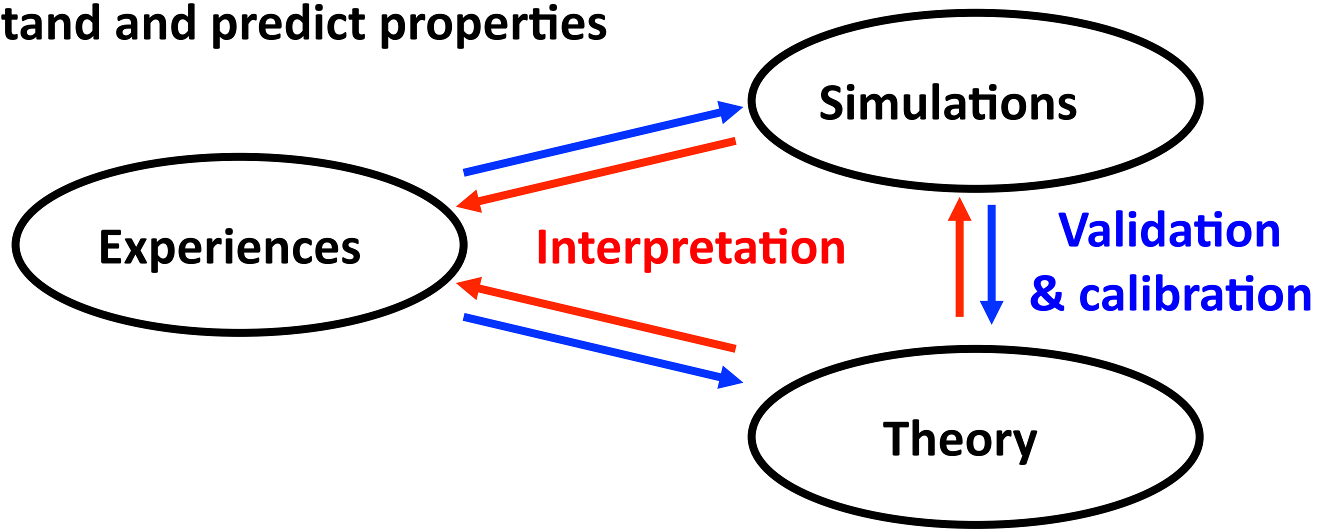
Introduction to molecular simulations

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

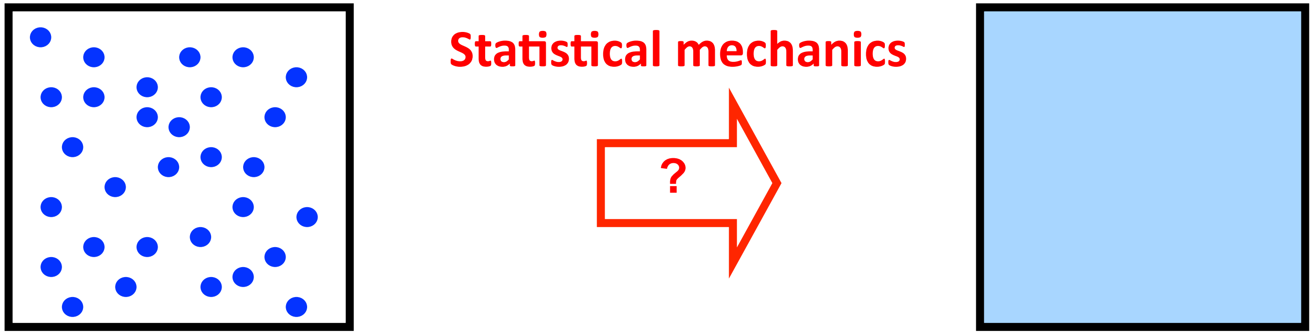
Understand and predict properties



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

Notions of statistical mechanics

Microscopic scale **Macroscopic scale**



Statistical mechanics

A particle *i* is characterized by its position $\mathbf{r}_i$ and its momentum $\mathbf{p}_i = m\mathbf{v}_i$

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

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

$$\boxed{H(\mathbf{r_i}^N, \mathbf{p_i}^N) = E_K + U_P = \sum_i \frac{\mathbf{p_i}^2}{2m} + U_P(\mathbf{r_i}^N)}$$

(*H* is the hamiltonian of the system, not enthalpy)

Kinetic energy

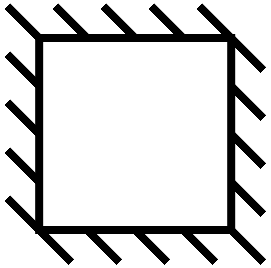
Potential energy (interactions between atoms)

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

Notions of statistical mechanics

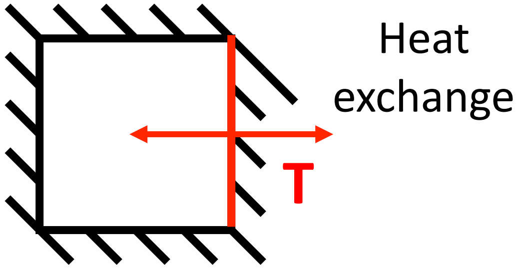
A macroscopic state is characterized by:

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



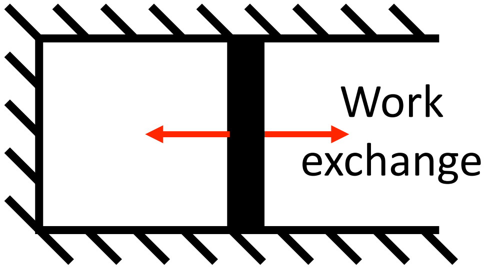
0) no external constraint, isolated system:
Microcanonical ensemble NVE

1) T fixed (by a thermostat)



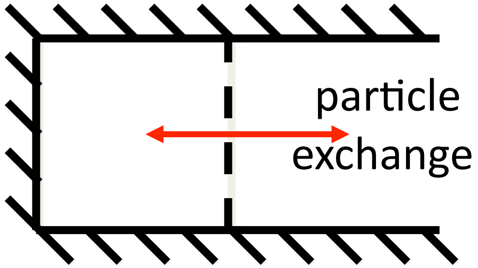
Energy E fluctuates

2) P fixed (by a barostat)



Volume V fluctuates

3) μ fixed by a reservoir



Number of particles N fluctuates

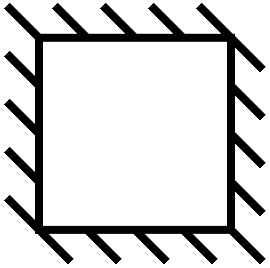
➡ The thermodynamic ensemble of the system depends on external constraints: **NVT, NPT, μVT** are the usual statistical ensembles.

Notions of statistical mechanics

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



$$\Rightarrow \quad P_i = \frac{1}{\Omega}$$

total number of accessible microstates (r^N,p^N) corresponding to the same macrostate N,V,E

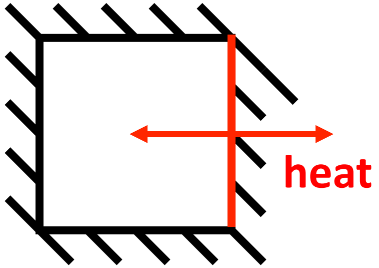
Thermodynamic potential: **Entropy**

$$S = k_B \ln \Omega$$

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}U + \frac{P}{T}\mathrm{d}V + \frac{\mu}{T}\mathrm{d}N$$

Notions of statistical mechanics

CANONICAL ENSEMBLE : fixed N,V,T



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

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

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

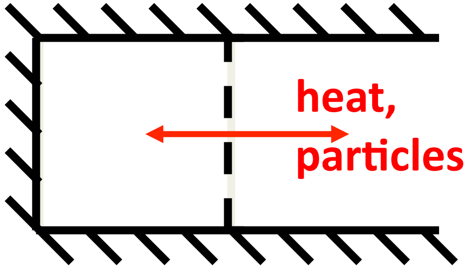
Thermodynamic potential: **free energy**

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

$$\mathrm{d}F = -S\mathrm{d}T - P\mathrm{d}V + \mu \mathrm{d}N$$

Notions of statistical mechanics

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**

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

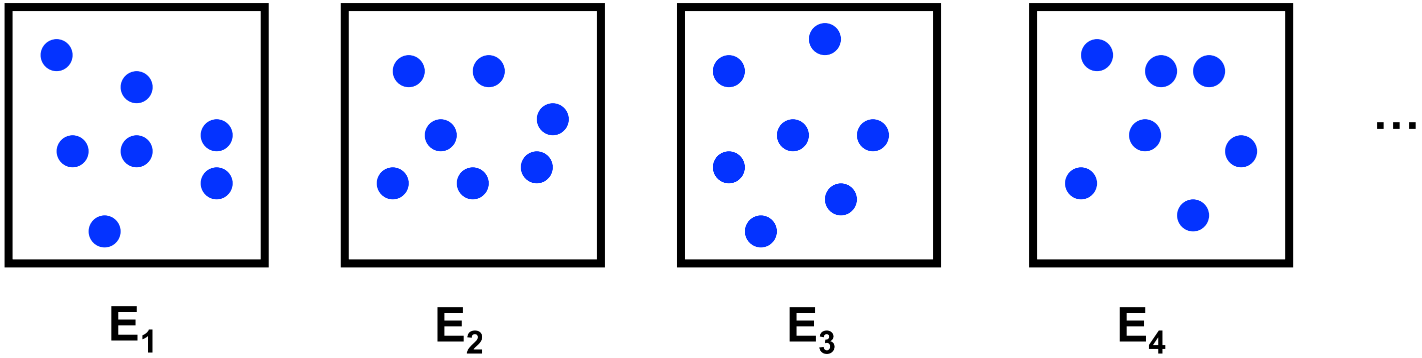
$$\mathrm{d}\Omega = -S\mathrm{d}T - P\mathrm{d}V - N\mathrm{d}\mu$$

Monte Carlo simulations

Monte Carlo: explore all the possible microstates of the system a number of times proportional to its probability

Exemple: in the canonical ensemble (N,V,T) :

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



Measured macroscopic quantity = **average on all the accessible microstates**

For a quantity A($\boldsymbol{r}^N$,$\boldsymbol{p}^N$):

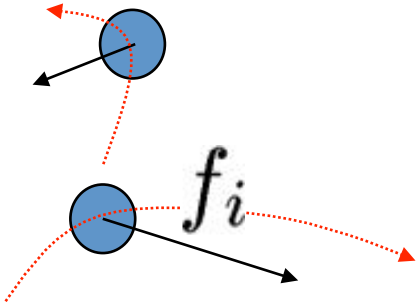
$$\boxed{\langle A \rangle = \sum_i P_i A_i}$$

When A($\boldsymbol{r}^N$) depends only on the particle positions (potential energy, density, …):

$$P_i \propto \exp(-\beta U(\mathbf{r}^N)) \quad \text{and} \quad < A > = \frac{\int \mathrm{d}\mathbf{r}^N \exp\left(-\beta U(\mathrm{r}^N)\right) A(\mathrm{r}^N)}{\int \mathrm{d}\mathbf{r}^N \exp\left(-\beta U(\mathrm{r}^N)\right)}$$

Molecular dynamics simulations

generate trajectories of the particles



Positions r(t) of all the particles

Forces F(t) on each particle

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

Positions 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

Molecular simulations: Force field

Monte Carlo: needs to calculate the **potential energy U_P** of the system

Molecular dynamics: needs to calculate the **forces** on the atoms $-\dfrac{\partial U_P(\mathbf{r_i}^N)}{\partial \mathbf{r_i}} = \mathbf{f}_{\rightarrow \mathbf{i}}$

U_P = sum of the interactions between all the atoms of the system

We need to define these interactions, i.e. a **force-field**

The classical force field can be fitted to reproduce experimental properties of the system (structure, thermodynamics) and/or from DFT calculations (taking electrons into account with quantum mechanics)

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

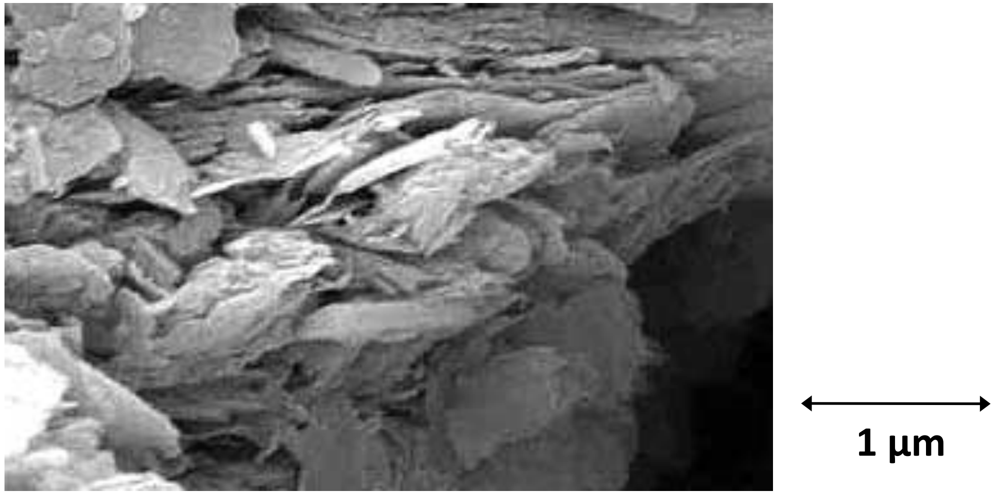
Molecular dynamics:

- transport properties

Clay minerals

Introduction on clay materials

Clays : rocks composed mainly of lamellar silicates . Abundant in sediments. Main constituent of soils.



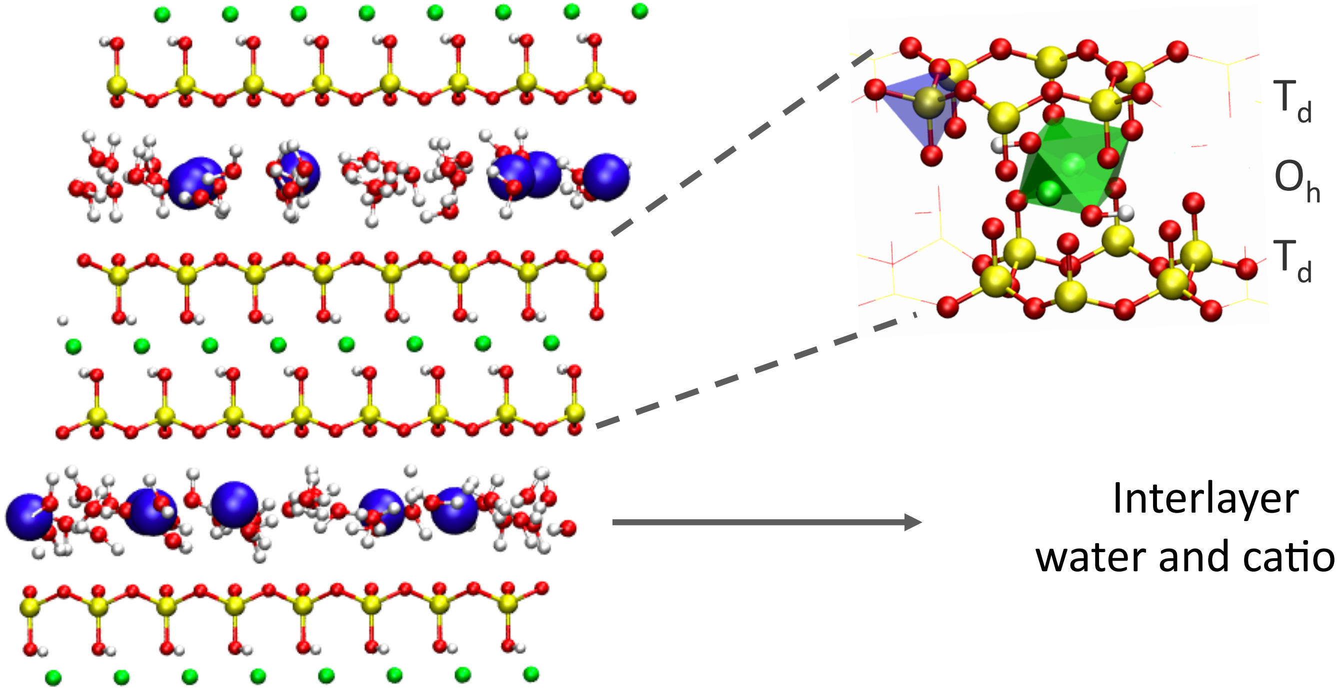
Properties: Large absorbing capacity, low permeability, sealing properties

Uses:
Ceramics (bricks, porcelain)
Cement industry
petroleum industry (muds for drilling oil wells)
Pharmaceutical industry and cosmetics
Waste storage (radioactive waste, CO_2), remediation

Introduction on clay materials: atomic structure

Ex: natural montmorillonite

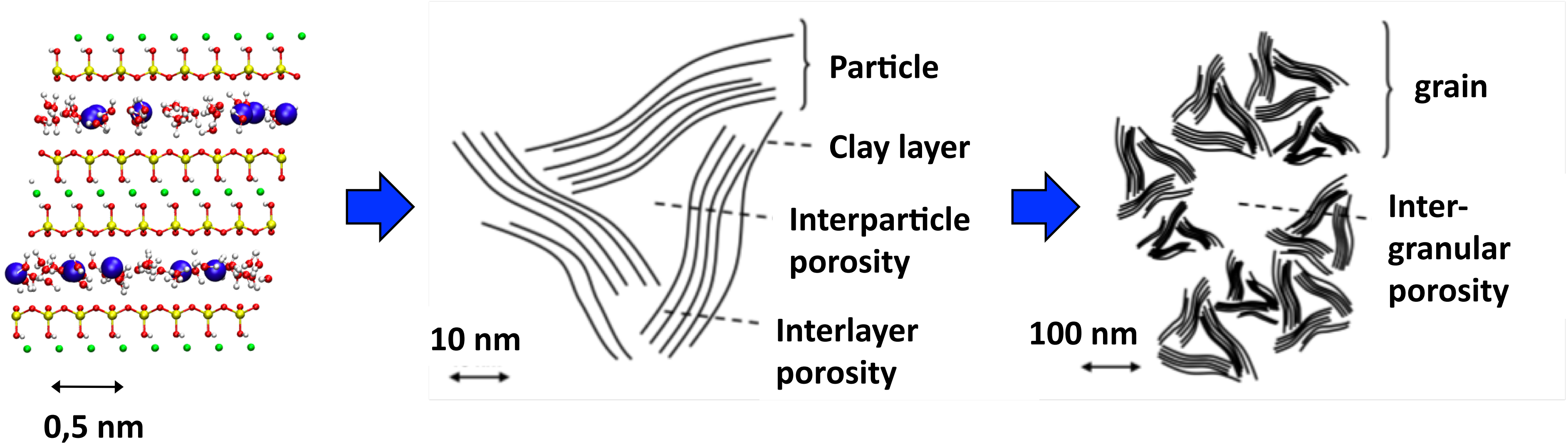
$(Si_{7.96}Al_{0.04})(Al_{3.10}Mg_{0.56}Fe_{0.16}^{II}\ Fe_{0.18}^{III})O_{20}(OH)_4Na_{0.36}Ca_{0.2}$



Interlayer
water and cations

Substitutions : negatively charged sheets, counterions (Na^+, Ca^+)

Introduction on clay materials: multi-porosity



Hydration : water content is crucial !

Introduction on clay materials: hydration

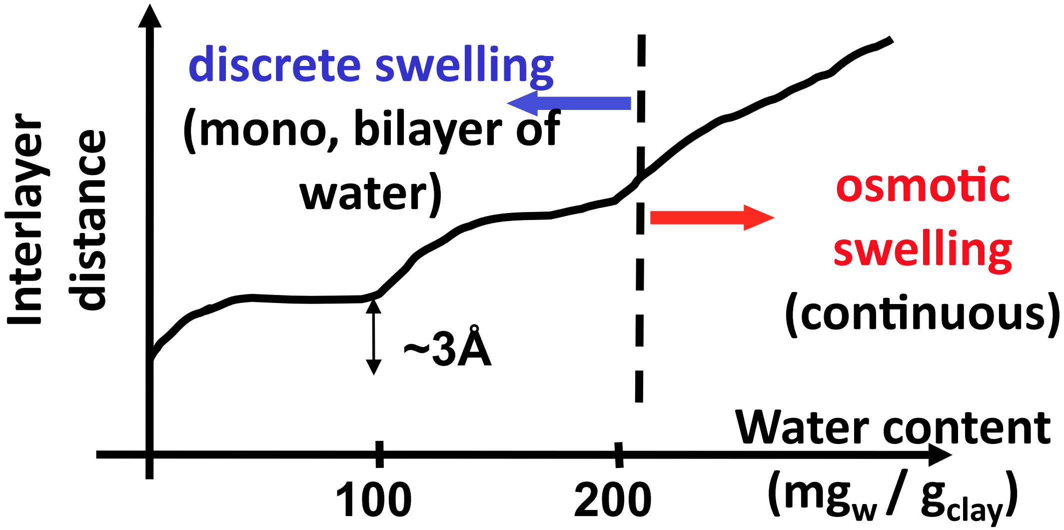
Increasing water content

dry to wet porous solid

paste

Gel to suspension

Evolution of the structure at the microscopic level:

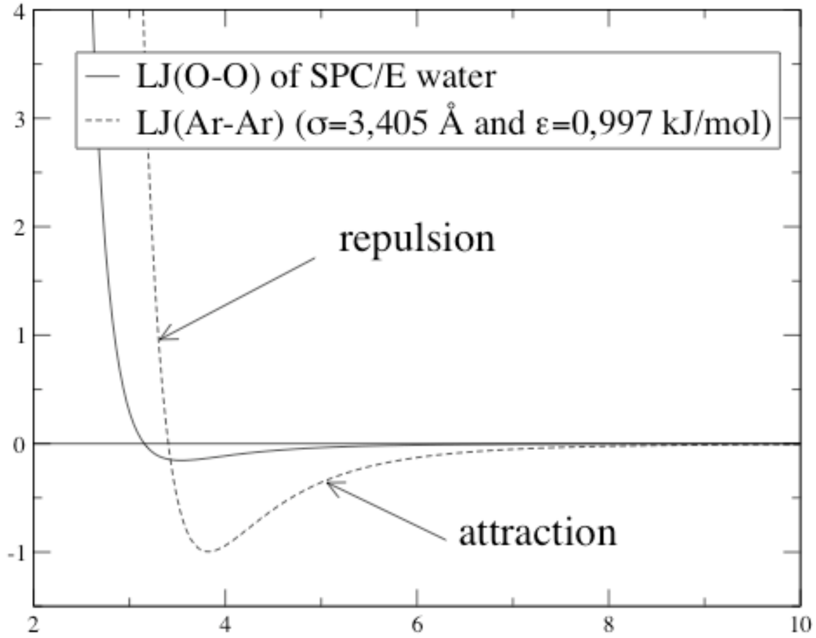


Molecular simulations
for the study of hydrated clay minerals

force-field

Short range potentials: Van der Waals + repulsion

Lennard-Jones :



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

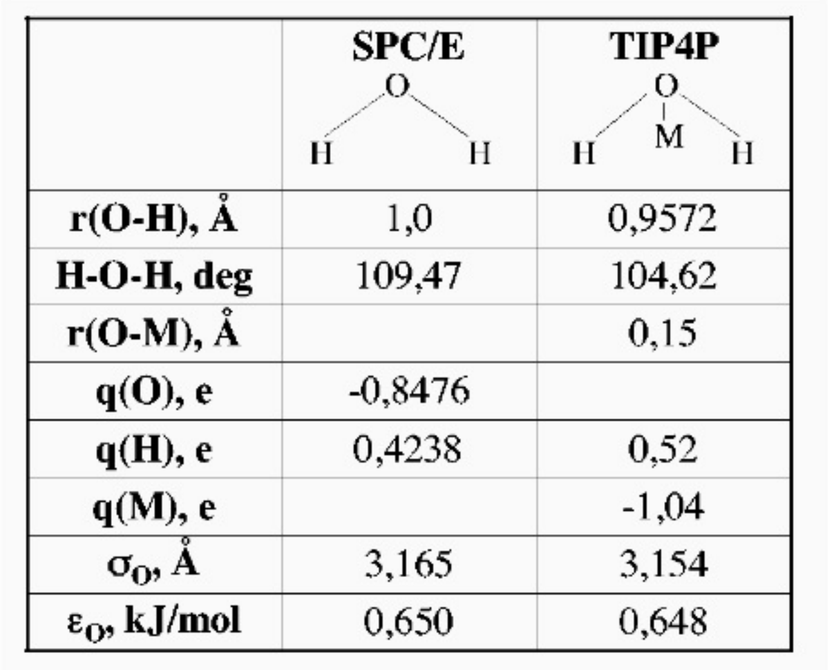
$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} \quad \text{and} \quad \sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$$

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)

Interaction potentials: water

Rigid models



	SPC/E	TIP4P
r(O-H), Å	1,0	0,9572
H-O-H, deg	109,47	104,62
r(O-M), Å		0,15
q(O), e	-0,8476	
q(H), e	0,4238	0,52
q(M), e		-1,04
σ_O, Å	3,165	3,154
ε_O, kJ/mol	0,650	0,648

SPC, TIP5P, TIP4P/2005, MCY, etc…

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

Polarizable models (with instantaneous dipoles or fluctuating charges)

interactions potentials: clay

Rigid clay layers (like a big rigid molecule)

$$V_{ij}(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} + 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

(Smith 98,
Skipper 95)

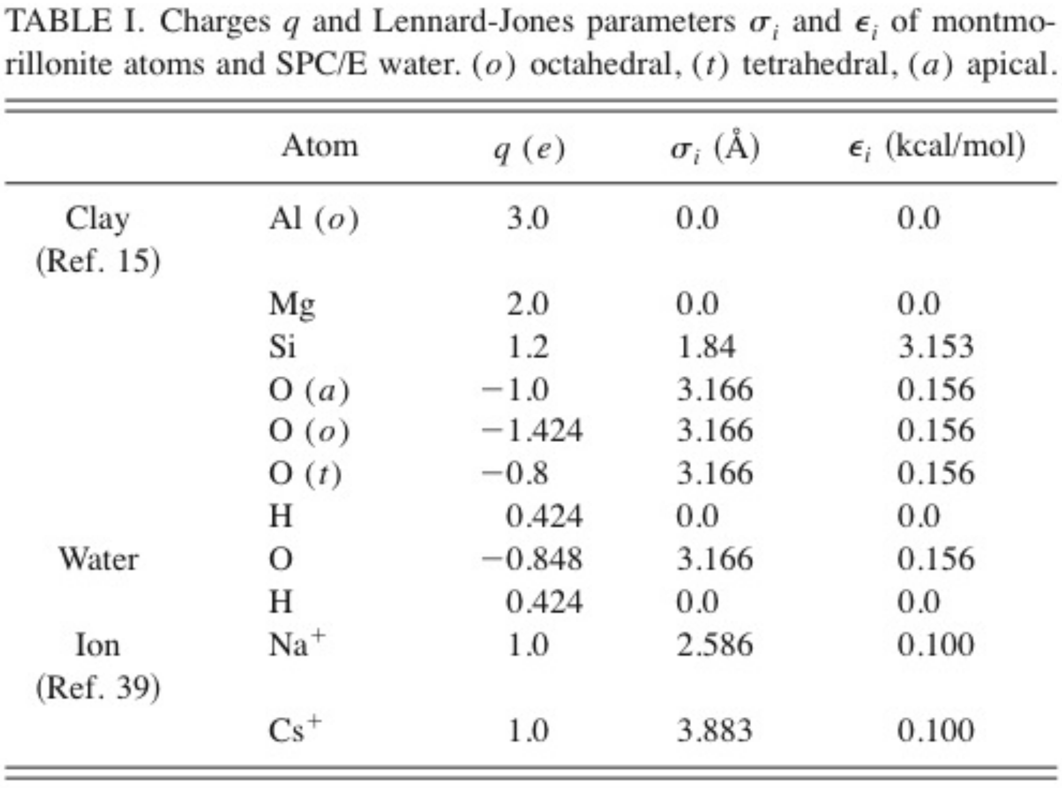
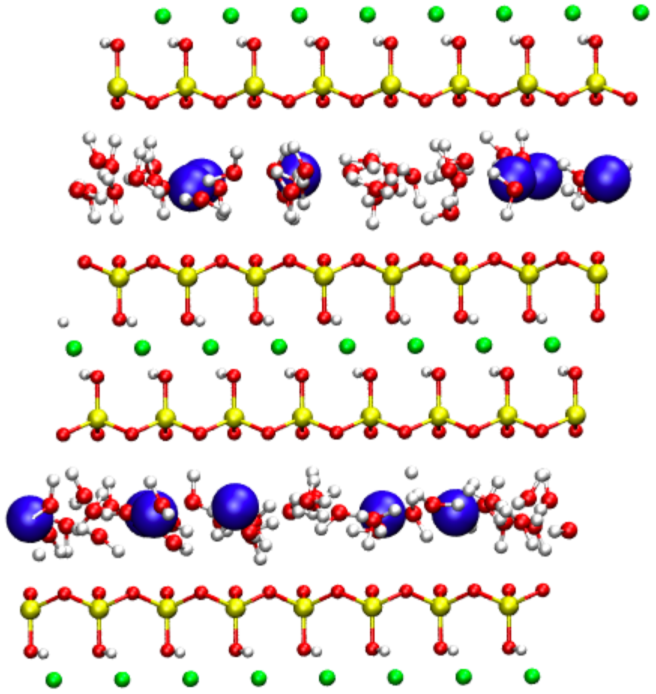


TABLE I. Charges q and Lennard-Jones parameters σ_i and ϵ_i of montmorillonite atoms and SPC/E water. (o) octahedral, (t) tetrahedral, (a) apical.

	Atom	q (e)	σ_i (Å)	ϵ_i (kcal/mol)
Clay (Ref. 15)	Al (o)	3.0	0.0	0.0
	Mg	2.0	0.0	0.0
	Si	1.2	1.84	3.153
	O (a)	−1.0	3.166	0.156
	O (o)	−1.424	3.166	0.156
	O (t)	−0.8	3.166	0.156
	H	0.424	0.0	0.0
Water	O	−0.848	3.166	0.156
	H	0.424	0.0	0.0
Ion (Ref. 39)	Na^+	1.0	2.586	0.100
	Cs^+	1.0	3.883	0.100



interactions potentials: clay

Flexible clay layers: clayFF (Cygan 2004)

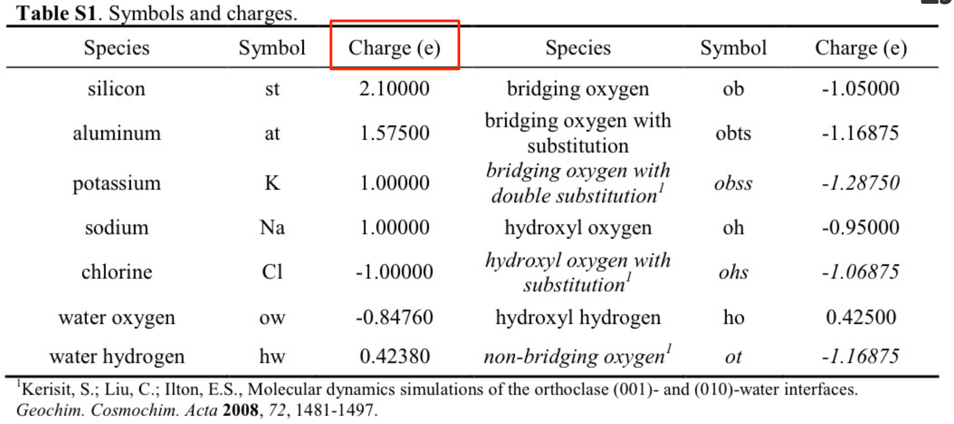


Table S1. Symbols and charges.

Species	Symbol	Charge (e)	Species	Symbol	Charge (e)
silicon	st	2.10000	bridging oxygen	ob	-1.05000
aluminum	at	1.57500	bridging oxygen with substitution	obts	-1.16875
potassium	K	1.00000	*bridging oxygen with double substitution*[1]	*obss*	*-1.28750*
sodium	Na	1.00000	hydroxyl oxygen	oh	-0.95000
chlorine	Cl	-1.00000	*hydroxyl oxygen with substitution*[1]	*ohs*	*-1.06875*
water oxygen	ow	-0.84760	hydroxyl hydrogen	ho	0.42500
water hydrogen	hw	0.42380	*non-bridging oxygen*[1]	*ot*	*-1.16875*

[1] Kerisit, S.; Liu, C.; Ilton, E.S., Molecular dynamics simulations of the orthoclase (001)- and (010)-water interfaces. *Geochim. Cosmochim. Acta* **2008**, *72*, 1481-1497.

specific potential for hydroxyl groups

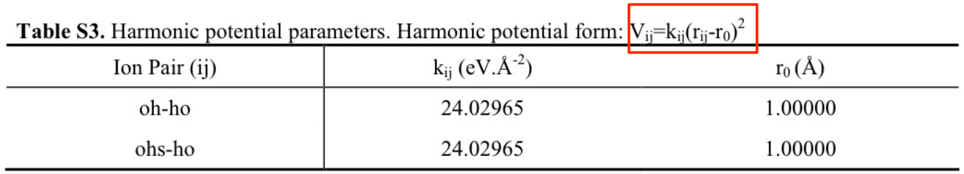


Table S3. Harmonic potential parameters. Harmonic potential form: $V_{ij}=k_{ij}(r_{ij}-r_0)^2$

Ion Pair (ij)	k_{ij} (eV.Å^{-2})	r_0 (Å)
oh-ho	24.02965	1.00000
ohs-ho	24.02965	1.00000

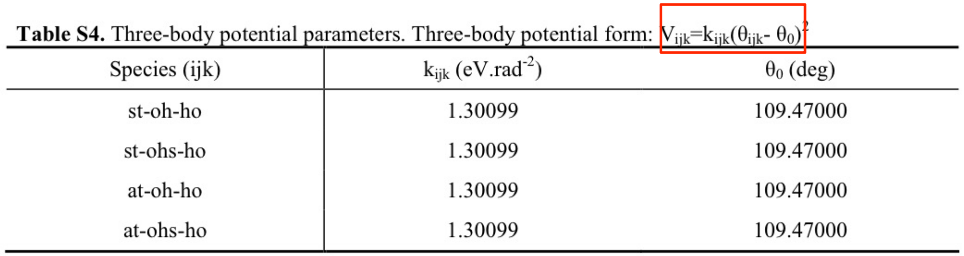


Table S4. Three-body potential parameters. Three-body potential form: $V_{ijk}=k_{ijk}(\theta_{ijk}-\theta_0)^2$

Species (ijk)	k_{ijk} (eV.rad^{-2})	θ_0 (deg)
st-oh-ho	1.30099	109.47000
st-ohs-ho	1.30099	109.47000
at-oh-ho	1.30099	109.47000
at-ohs-ho	1.30099	109.47000

Each atom is considered independently.
LJ and electrostatic interactions provide the cohesion of the clay layers

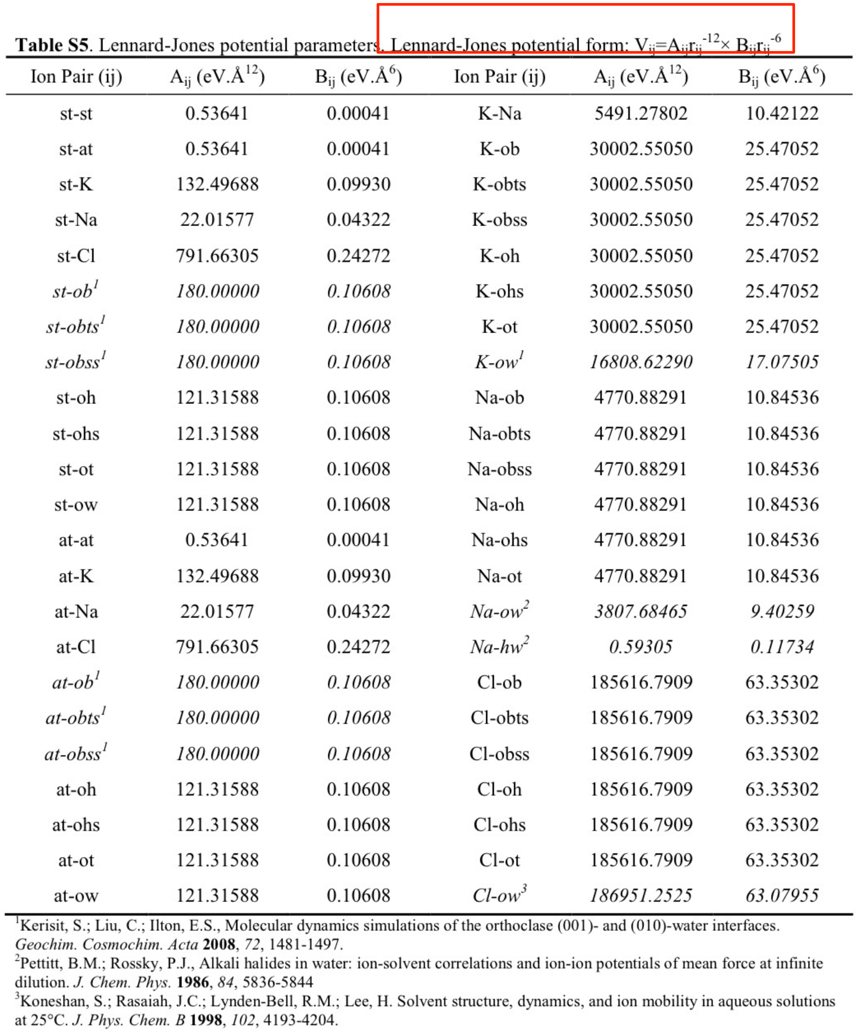


Table S5. Lennard-Jones potential parameters. Lennard-Jones potential form: $V_{ij}=A_{ij}r_{ij}^{-12}\times B_{ij}r_{ij}^{-6}$

Ion Pair (ij)	A_{ij} (eV.Å^{12})	B_{ij} (eV.Å^{6})	Ion Pair (ij)	A_{ij} (eV.Å^{12})	B_{ij} (eV.Å^{6})
st-st	0.53641	0.00041	K-Na	5491.27802	10.42122
st-at	0.53641	0.00041	K-ob	30002.55050	25.47052
st-K	132.49688	0.09930	K-obts	30002.55050	25.47052
st-Na	22.01577	0.04322	K-obss	30002.55050	25.47052
st-Cl	791.66305	0.24272	K-oh	30002.55050	25.47052
st-ob[1]	*180.00000*	*0.10608*	K-ohs	30002.55050	25.47052
st-obts[1]	*180.00000*	*0.10608*	K-ot	30002.55050	25.47052
st-obss[1]	*180.00000*	*0.10608*	*K-ow*[1]	*16808.62290*	*17.07505*
st-oh	121.31588	0.10608	Na-ob	4770.88291	10.84536
st-ohs	121.31588	0.10608	Na-obts	4770.88291	10.84536
st-ot	121.31588	0.10608	Na-obss	4770.88291	10.84536
st-ow	121.31588	0.10608	Na-oh	4770.88291	10.84536
at-at	0.53641	0.00041	Na-ohs	4770.88291	10.84536
at-K	132.49688	0.09930	Na-ot	4770.88291	10.84536
at-Na	22.01577	0.04322	*Na-ow*[2]	*3807.68465*	*9.40259*
at-Cl	791.66305	0.24272	*Na-hw*[2]	*0.59305*	*0.11734*
at-ob[1]	*180.00000*	*0.10608*	Cl-ob	185616.7909	63.35302
at-obts[1]	*180.00000*	*0.10608*	Cl-obts	185616.7909	63.35302
at-obss[1]	*180.00000*	*0.10608*	Cl-obss	185616.7909	63.35302
at-oh	121.31588	0.10608	Cl-oh	185616.7909	63.35302
at-ohs	121.31588	0.10608	Cl-ohs	185616.7909	63.35302
at-ot	121.31588	0.10608	Cl-ot	185616.7909	63.35302
at-ow	121.31588	0.10608	*Cl-ow*[3]	*186951.2525*	*63.07955*

[1] Kerisit, S.; Liu, C.; Ilton, E.S., Molecular dynamics simulations of the orthoclase (001)- and (010)-water interfaces. *Geochim. Cosmochim. Acta* **2008**, *72*, 1481-1497.

[2] Pettitt, B.M.; Rossky, P.J., Alkali halides in water: ion-solvent correlations and ion-ion potentials of mean force at infinite dilution. *J. Chem. Phys.* **1986**, *84*, 5836-5844

[3] Koneshan, S.; Rasaiah, J.C.; Lynden-Bell, R.M.; Lee, H. Solvent structure, dynamics, and ion mobility in aqueous solutions at 25°C. *J. Phys. Chem. B* **1998**, *102*, 4193-4204.

interactions potentials

The criteria for selecting a force-field include:

- accuracy
- transferability
- computational speed

An accurate force-field for the thermodynamics can be bad for the dynamics

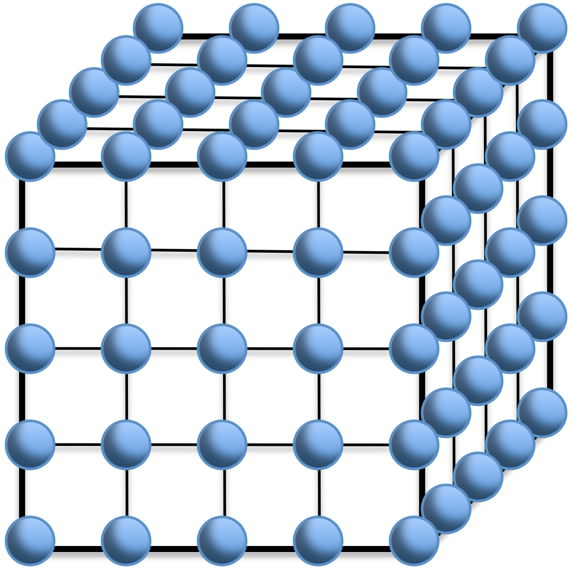
Polarizable and flexible models are expected to be more realistic, but they cost more

The perfect force-field does not exist…

Periodic boundary conditions

Example: 1 mL of water contains 0,3 .10^{23} molecules → impossible to simulate!

Powerful computer: some millions of atoms
In general less!



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

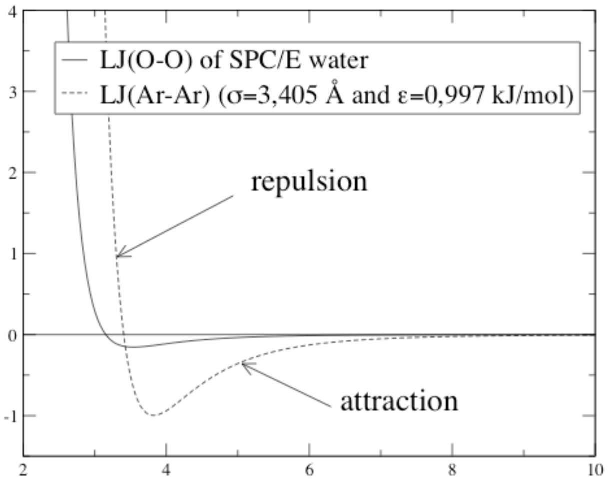
10^6 atoms in a cube: 6% ...

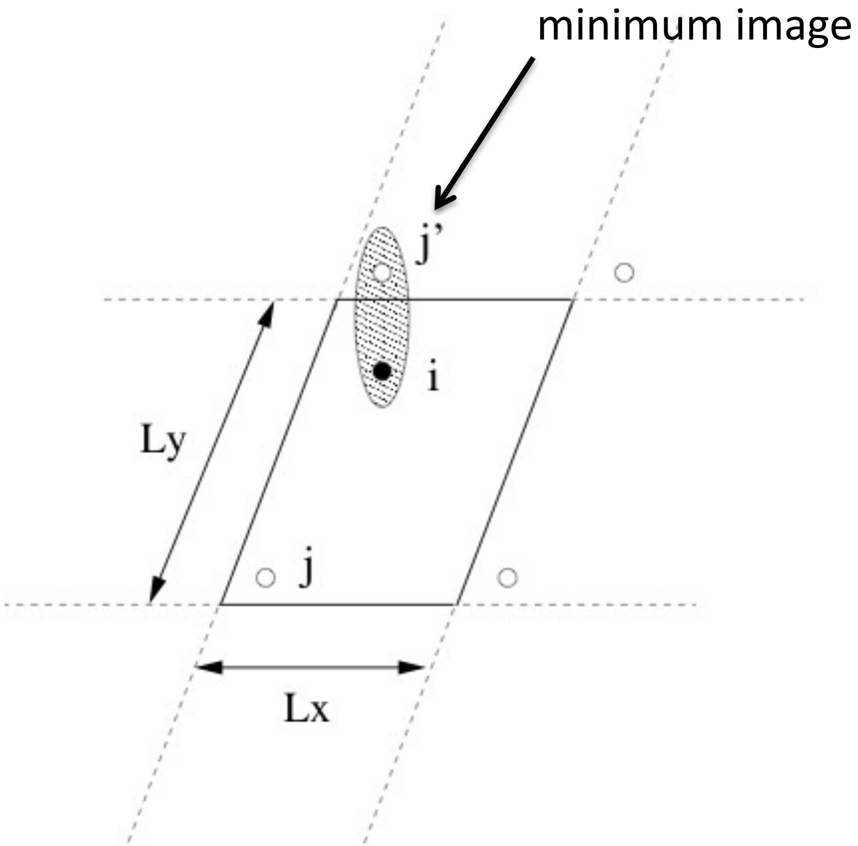
→ **Periodic boundary conditions**

Periodic boundary conditions

Short range interactions: until r_{cut}

r_{cut} must be > a few s(LJ)





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

Long range interactions (electrostatic): Ewald summation (reciprocal space)

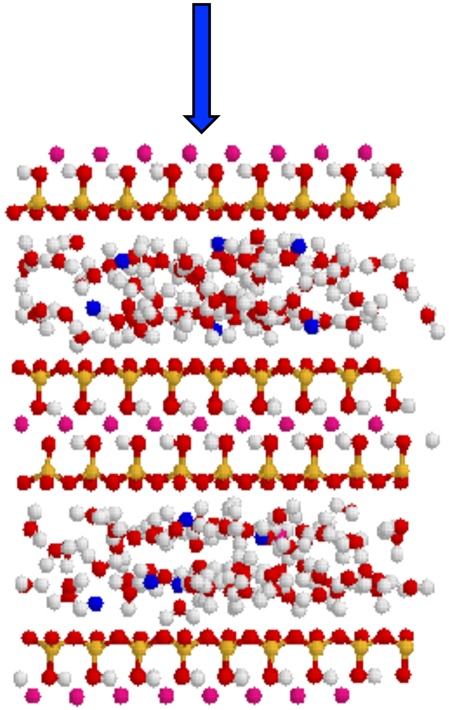
Examples of simulated systems

ps Longer times and distances ∞

Interlayer properties

Interparticle properties

Global properties



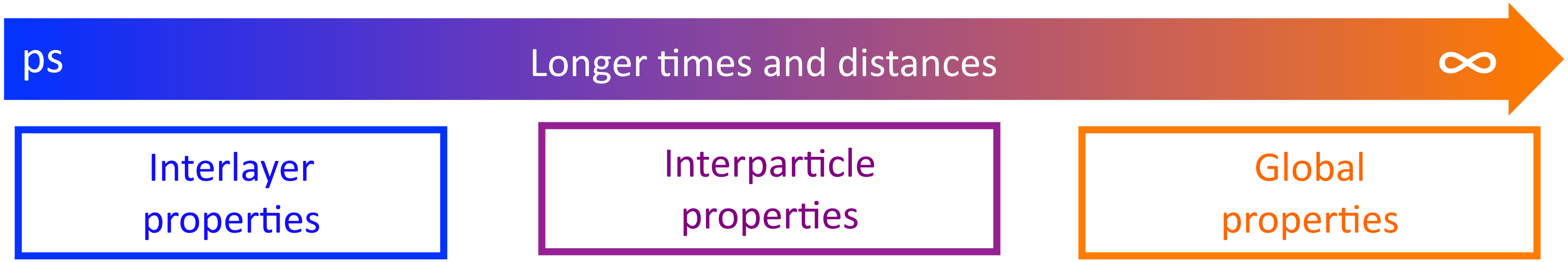
ideal clay $(Si_8)(Al_{3.25}Mg_{0.75})O_{20}(OH)_4Na_{0.75}$

Swelling behavior, mechanical properties

Thermodynamics of cation exchange

Structure and diffusion of mobile species

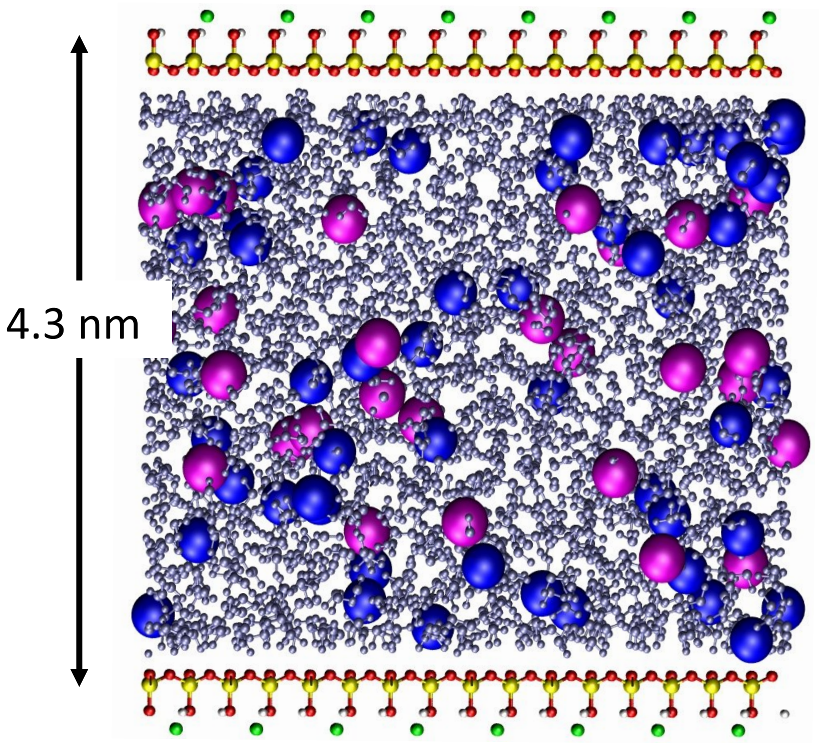
Examples of simulated systems



Interlayer properties

Interparticle properties

Global properties



Properties of the interface

Fluid flows, electrokinetic phenomena

Examples of simulated systems

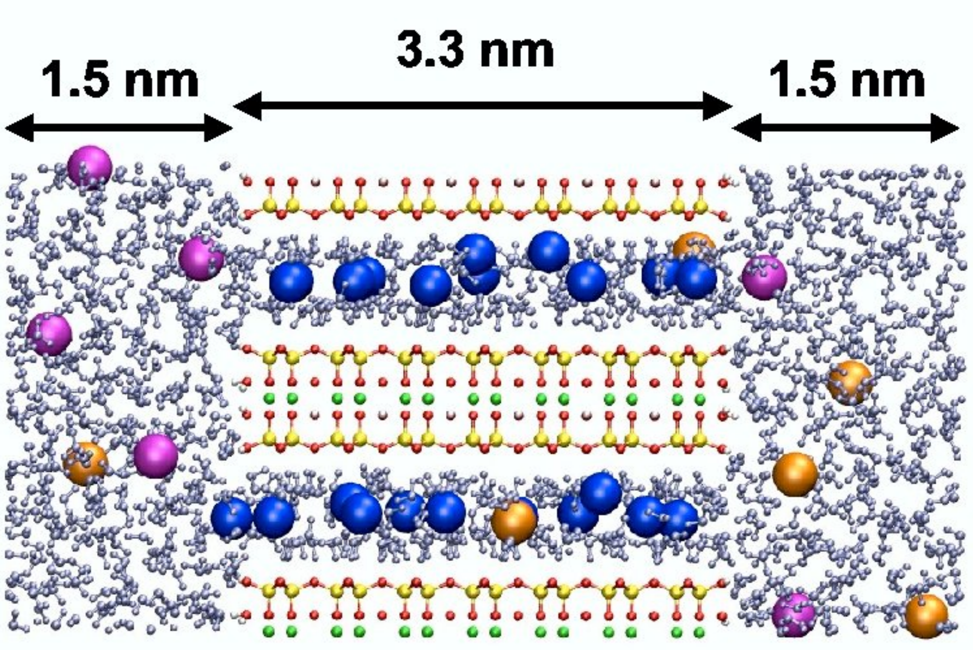
ps Longer times and distances ∞

Interlayer properties

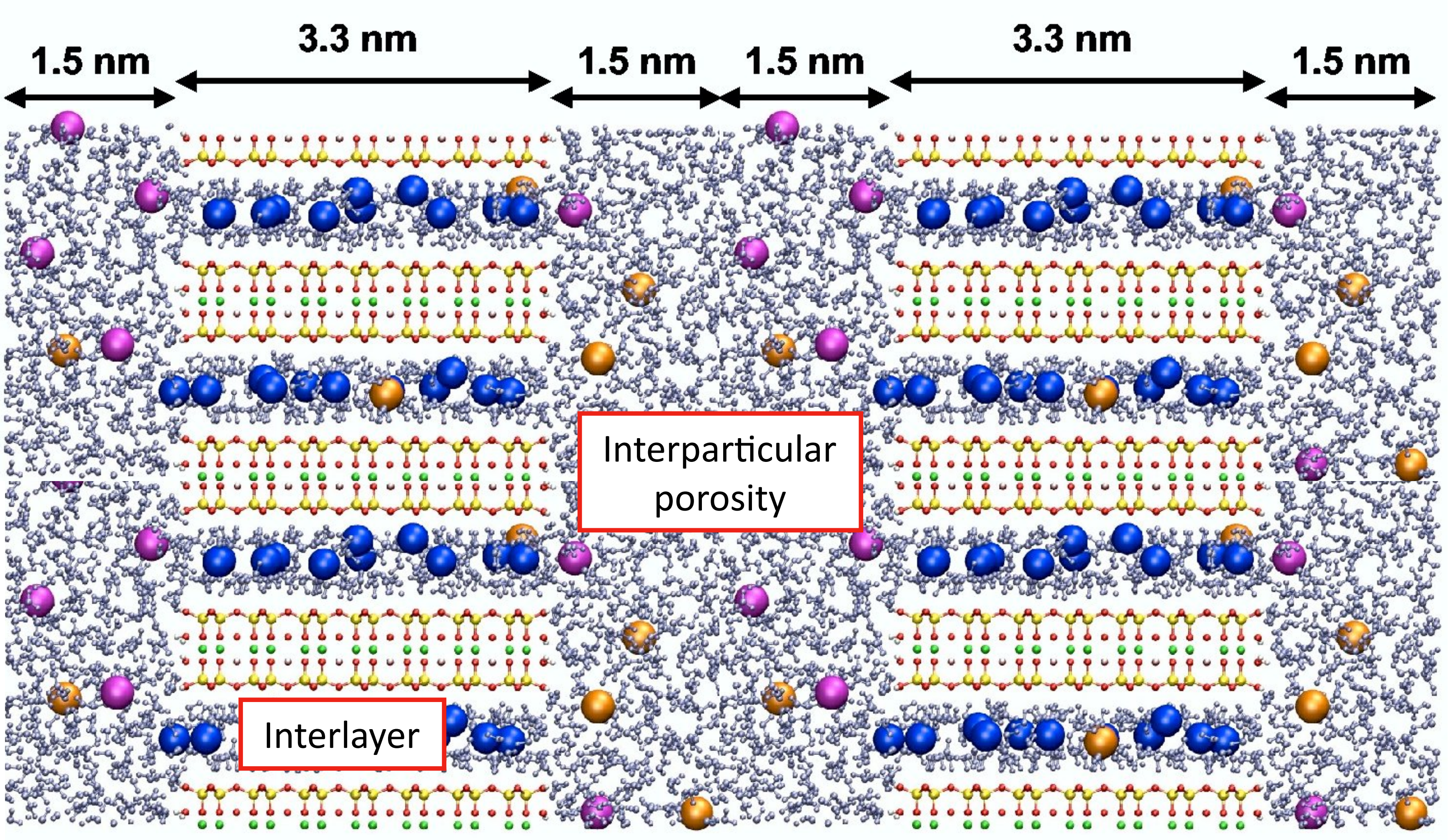
Interparticle properties

Global properties

Rate of exchange between the clay particle and the pore



periodic boundary conditions



Interparticular porosity

Interlayer

Monte Carlo simulations

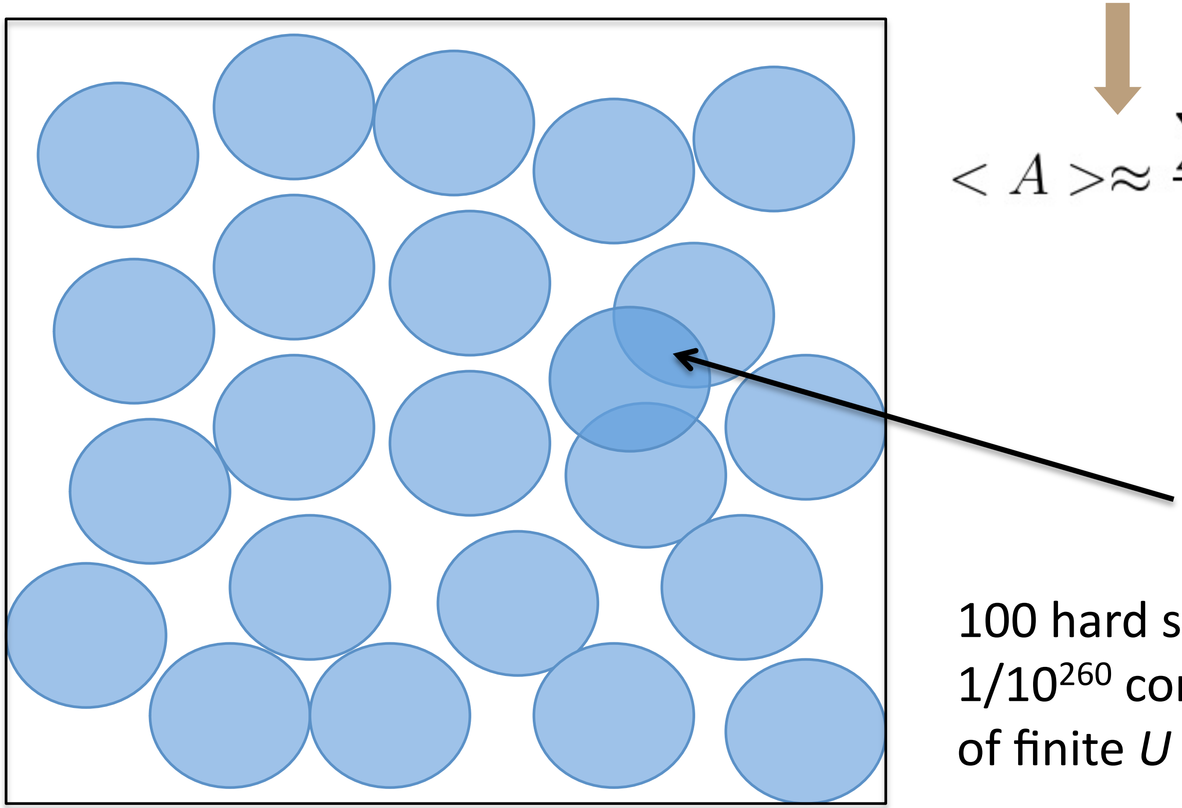
Application to clay minerals

Importance sampling: hard spheres

Example: canonical ensemble NVT

We want to calculate: $\langle A \rangle = \sum_i P_i A_i$ with $P_i \propto \exp(-\beta U(\mathbf{r}^N))$

What about generating a big number *M* of random configurations?



$$< A > \approx \frac{\sum_i^M \exp\left(-\beta U(\mathrm{r_i}^N)\right) A(\mathrm{r_i}^N)}{\sum_i^M \exp\left(-\beta U(\mathrm{r_i}^N)\right)}$$

But…..

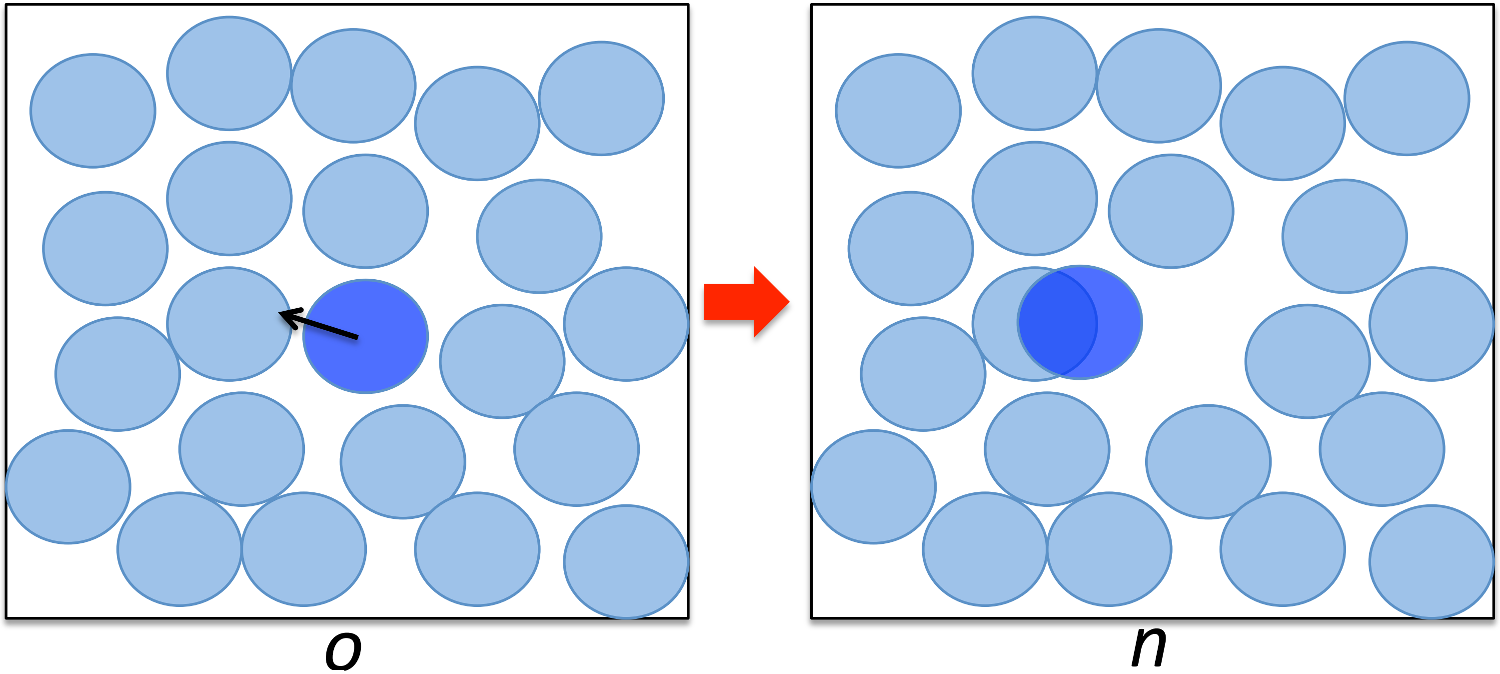
$U = +\infty$

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

Metropolis method

Metropolis method: allows to explore the phase space according to the probability of each microstate

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



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

In general $\alpha(o \rightarrow n)$ = $\alpha(n \rightarrow o)$

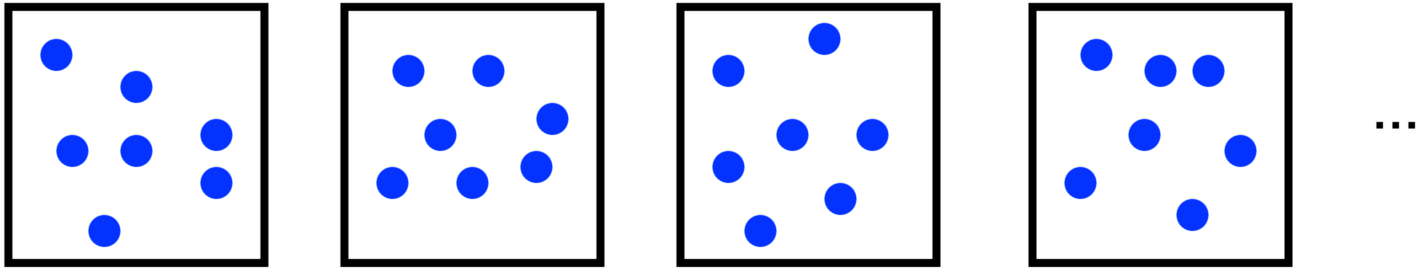
$acc(o \rightarrow n)$ Probability to accept *n*

Metropolis method

Imagine an ensemble formed by a big enough number *M* of parallel identical systems: each system is in an accessible microstate « i », such as the number of systems in microstate « i » n_i, is proportional to P_i

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

$$n_i = M\, P_i$$



Each parallel system can evolve. If equilibrium, n_i must be the same, then:

probability do leave *o* = probability to come back to *o*

$$n_o \sum_n \Pi(o \rightarrow n) = \sum_n n_n \Pi(n \rightarrow o)$$

Metropolis method

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

$$n_o \sum_n \Pi(o \rightarrow n) = \sum_n n_n \Pi(n \rightarrow o)$$

Stronger condition : **detailed balance**

$$n_o \Pi(o \rightarrow n) = n_n \Pi(n \rightarrow o)$$

$$\frac{\Pi(o \rightarrow n)}{\Pi(n \rightarrow o)} = \frac{\alpha(o \rightarrow n)acc(o \rightarrow n)}{\alpha(n \rightarrow o)acc(n \rightarrow o)} = \frac{n_n}{n_o}$$

with $n_i = M\, P_i$

$$P_i \propto \exp(-\beta U(\mathbf{r}^N)) \quad ➡ \quad \boxed{\frac{acc(o \rightarrow n)}{acc(n \rightarrow o)} = \exp[-\beta(U_n - U_o)]}$$

Metropolis algorithm

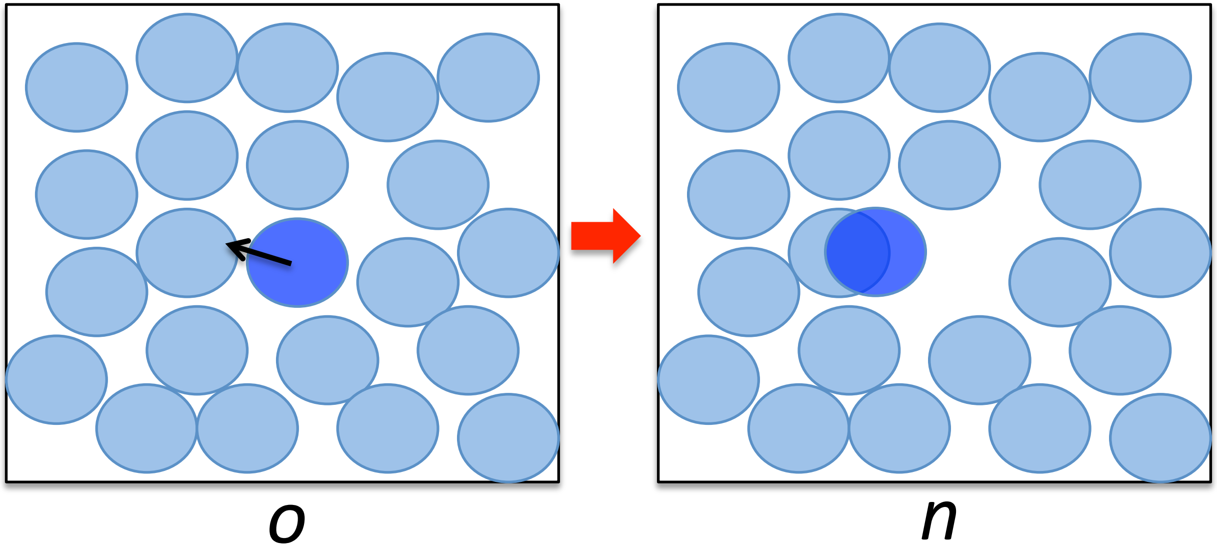
$$\frac{acc(o \rightarrow n)}{acc(n \rightarrow o)} = \exp[-\beta(U_n - U_o)]$$ is verified if

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

Metropolis criterion

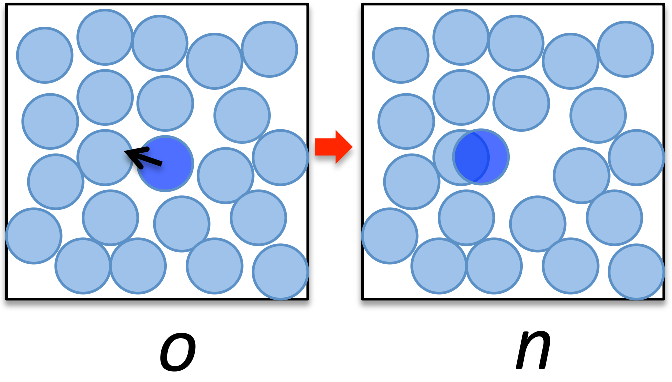
At step k, the system is in the configuration $\mathbf{r}(k)^N$ and the energy is $U(k) = U_o$. To move from step k to step $k+1$:

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



Metropolis algorithm

2. Calculate the energy $U(\mathbf{r}_n^N)$ of the new configuration.



$$U_n = +\infty$$

3. Apply the Metropolis criterion:

, etc...

$$U_n - U_o = +\infty$$

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

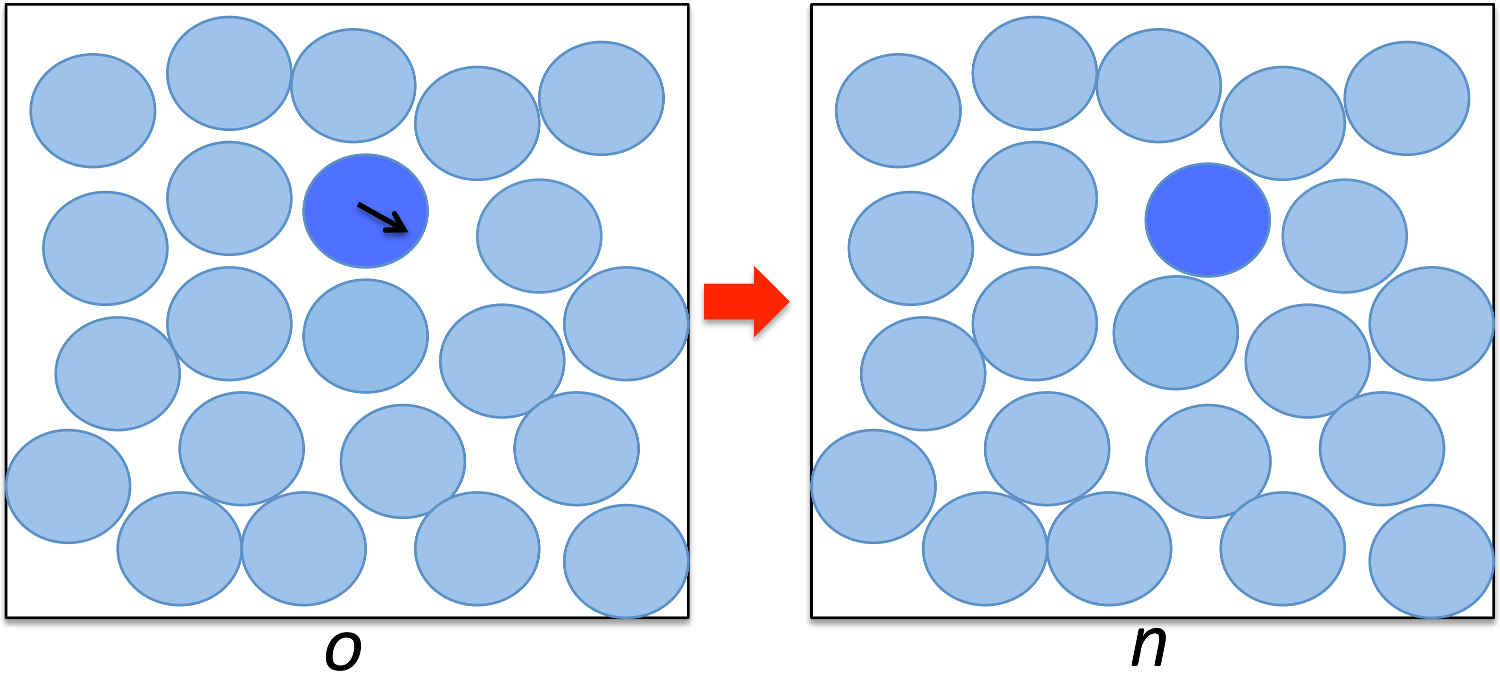
The configuration is rejected

➡ $$\boxed{\begin{array}{l} U_{k+1} = U_k = U_o \\ A = A + A_o \end{array}}$$

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 $U(\mathbf{r}_n^N)$ of the new configuration.

3. Apply the Metropolis criterion:

Suppose $U_n - U_o < 0$

Metropolis algorithm

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

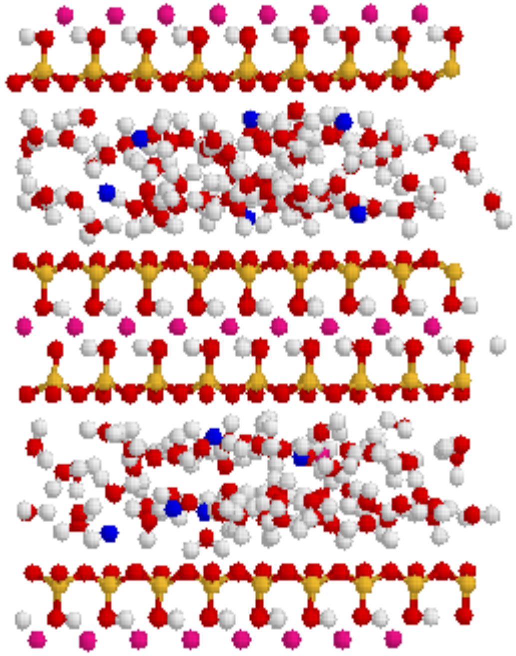
The configuration is accepted

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

Go back to step 1

At the end of the simulation, you can get the averages $< A >$ by dividing $\sum_k A(k)$ by the number of steps.

Clays in NVT ensemble



displacement of a particle chosen randomly:

- **water** molecule (translation + rotation)
- **cation**
- **clay** layers:

If rigid, only horizontally (V is fixed) and rotation forbidden (periodic boundary conditions)

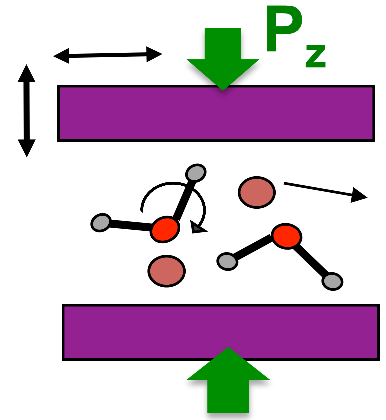
If flexible, each atom is moved independently inside the box

The displacements are chosen to give acceptable acceptance ratios (between 20 and 50 %)

Other ensembles

Various experimental conditions…

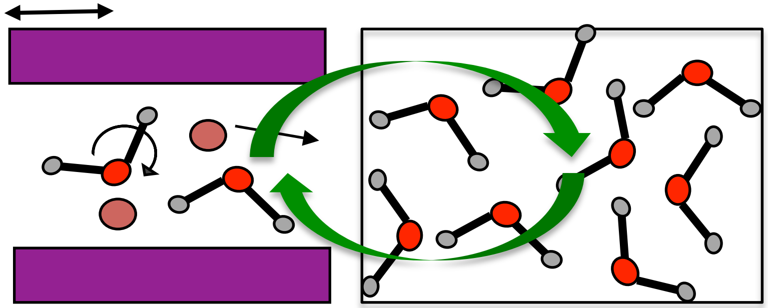
- external pressure P_z and T are fixed



➡ NP_zT ensemble
(V is allowed to vary)

- equilibrium with a reservoir: for example a clay in contact with an atmosphere at a fixed partial pressure P_w of water.

$$\mu_{water}(T,P_w) = \mu_{water}°(T)+RT\ln(P_w/P°)$$



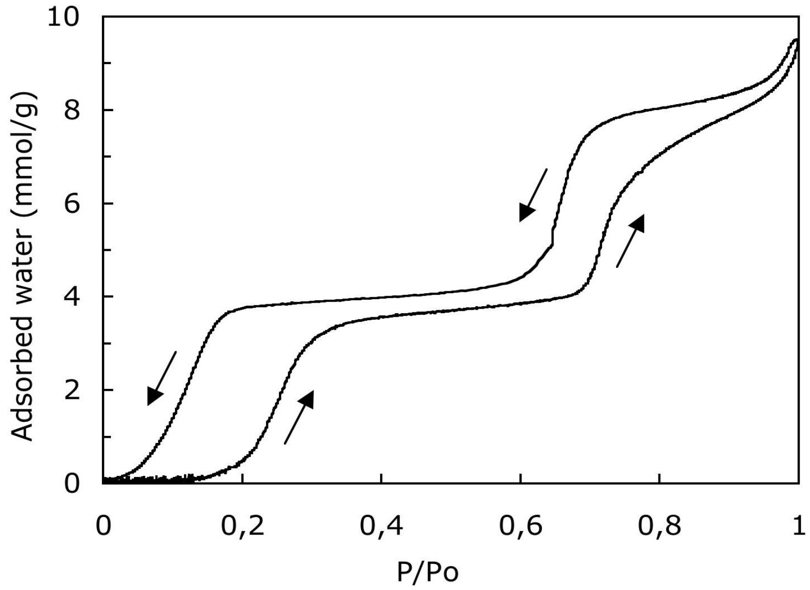
➡ μVT ensemble
(insertion and deletion of water molecules are allowed)

Application to the clay swelling

In general, the experimental conditions are:
External fixed T and P, clay in contact with a reservoir: fixed μ_{water}

Examples:

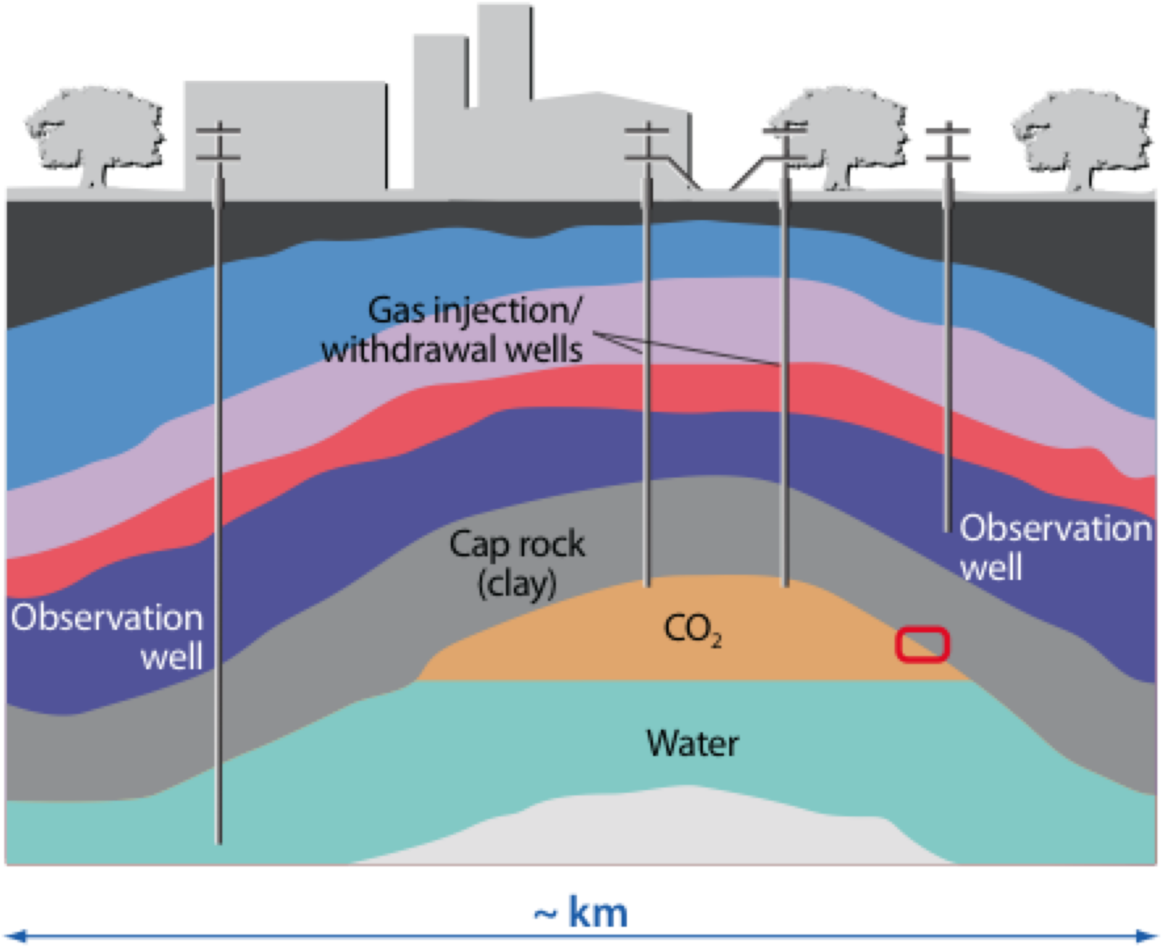
- a dry clay is left on a table. The atmosphere is at ambient T and P, and at a given humidity: the clay swells.



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

Application to the clay swelling

- Storage of supercritical CO_2 in salin aquifers

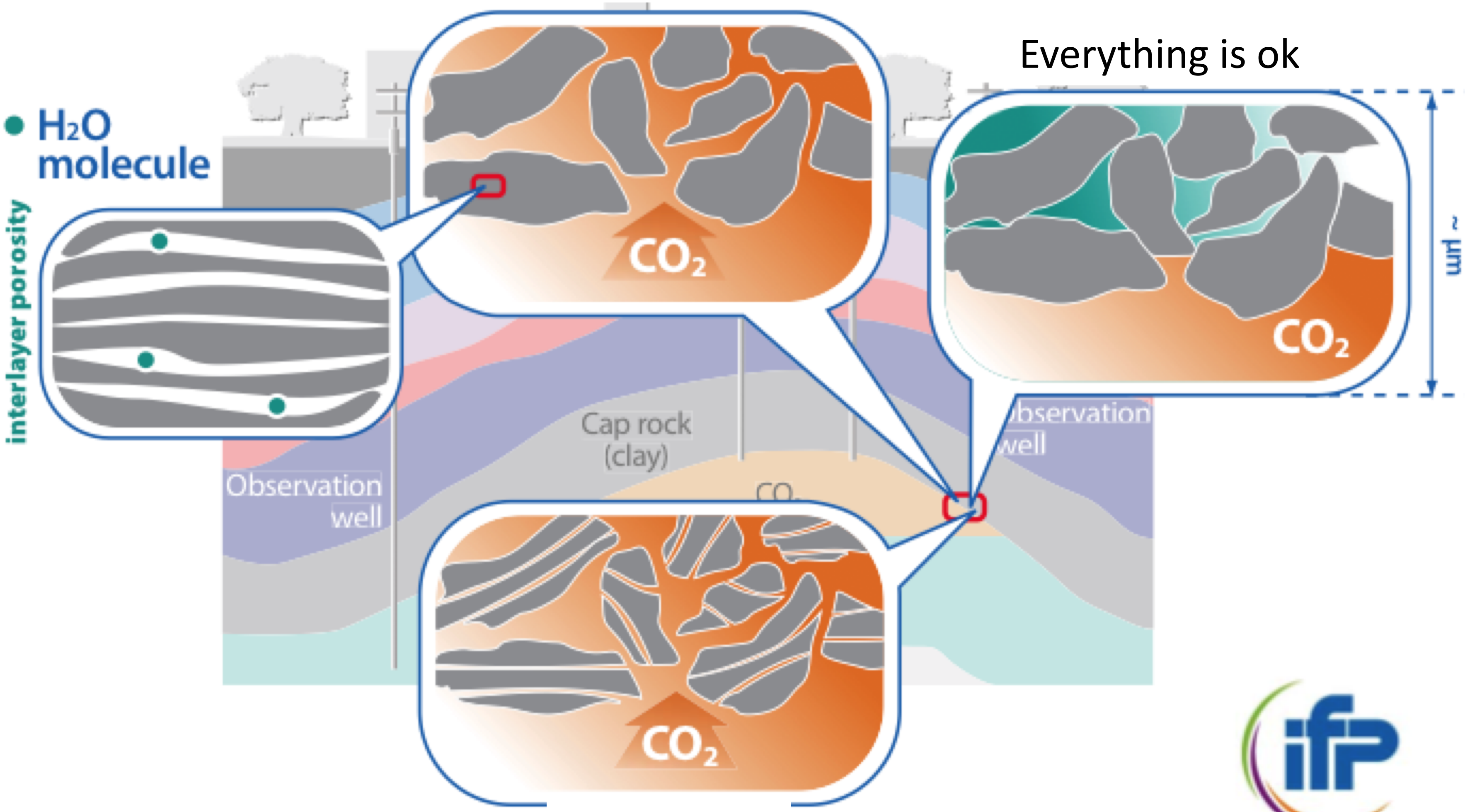


Application to the clay swelling

- Storage of CO_2 in salin aquifers

Various scenarios

The clay particles shrink (water goes out)

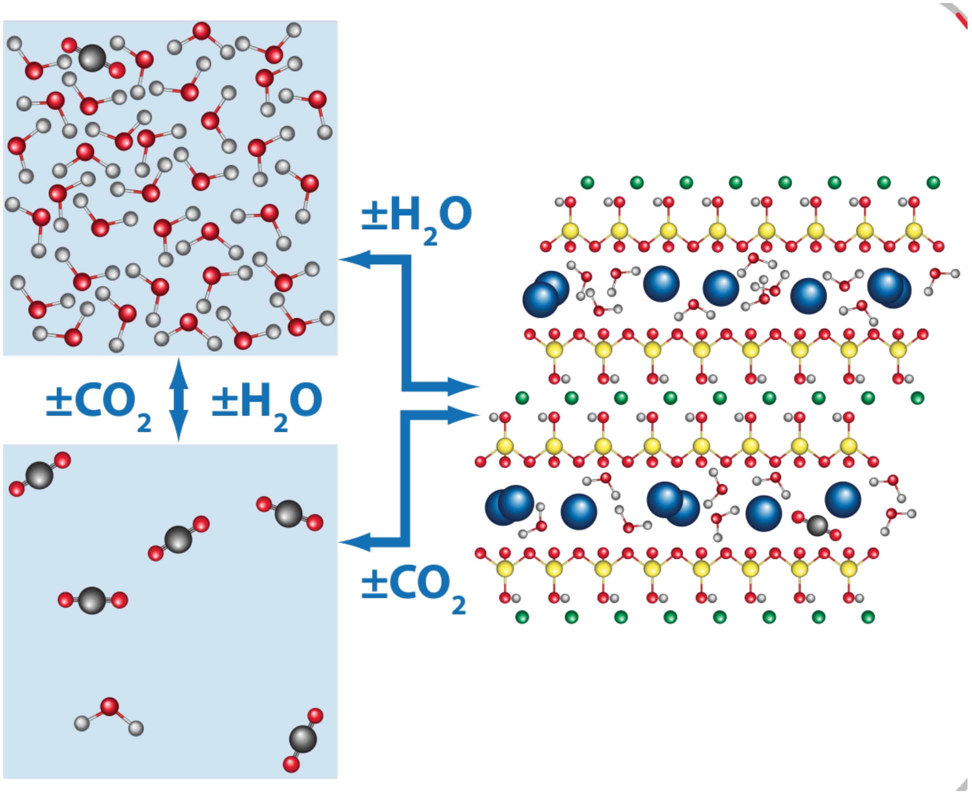


Everything is ok

fracturation

Application to the clay swelling

Here the experimental conditions are:
External fixed T and P, clay in contact with two reservoirs: one of water, one of CO2: fixed μ_{water} and μ_{CO2}



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

Application to the clay swelling

Determine the equilibrium states of the clay/water system:

They correspond to the minima of the thermodynamical function

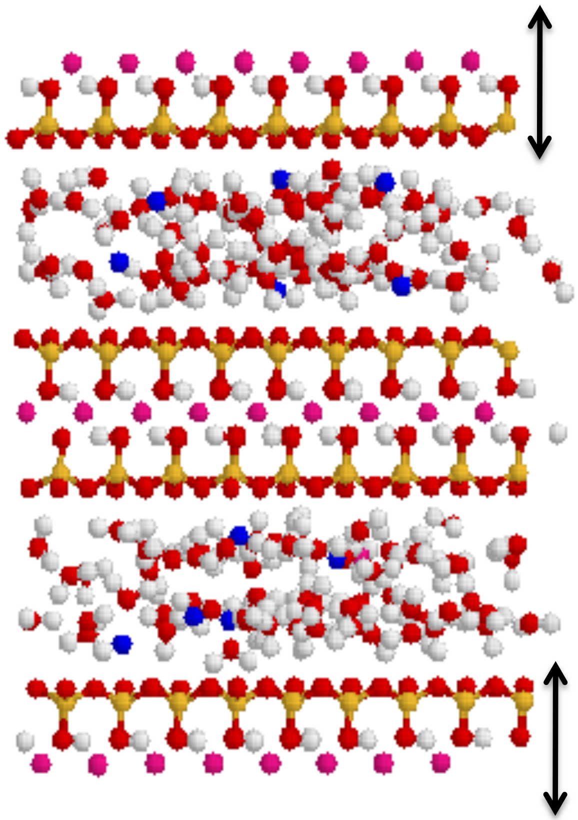
$$F = U - \mu_{ext}N + P_{ext}V - T_{ext}S$$

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:

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

Application to the clay swelling



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

At the end of each step :

- a symmetric phantom change of volume (rescaling positions of the molecules) ➡ dV
- calculation of dU

$\Big\}$ *n* times

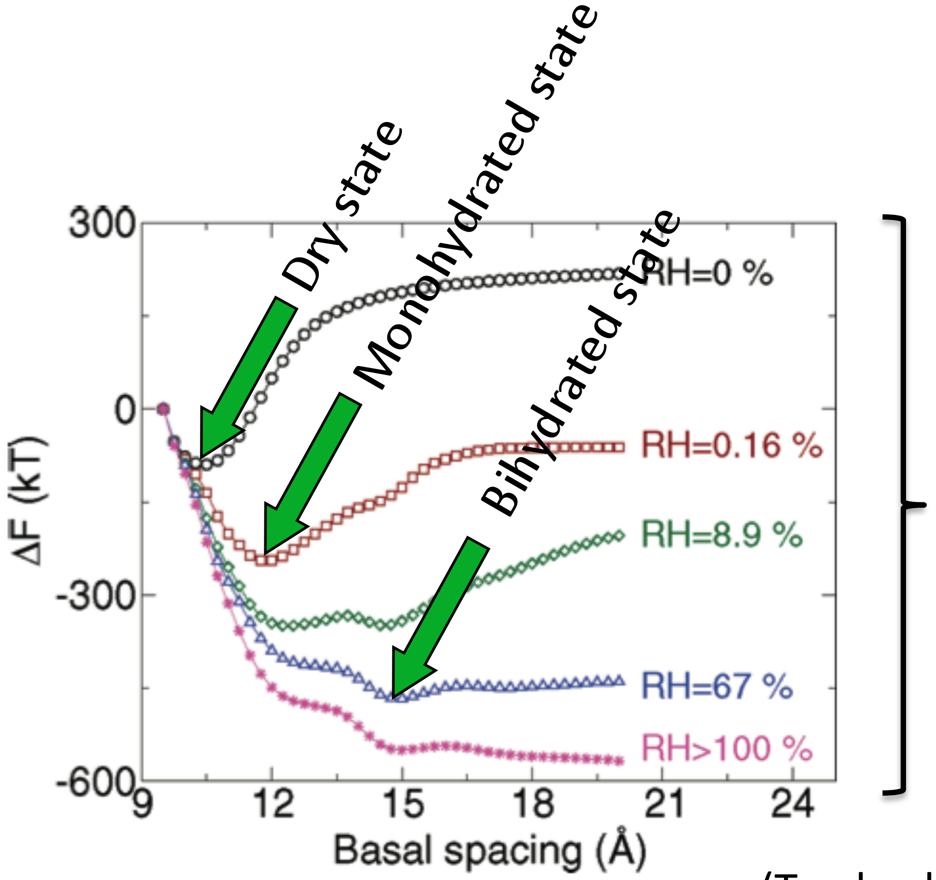
- average <dU/dV>=Σ(dU/dV)/*n* over every trial moves to calculate the pressure

Application to the clay swelling

fixed μ_{ext} and T_{ext}

$F = U - \mu_{ext}N + P_{ext}V - T_{ext}S \rightarrow dF = -(P - P_{ext})\,dV$

Ambient T_{ext} and P_{ext}

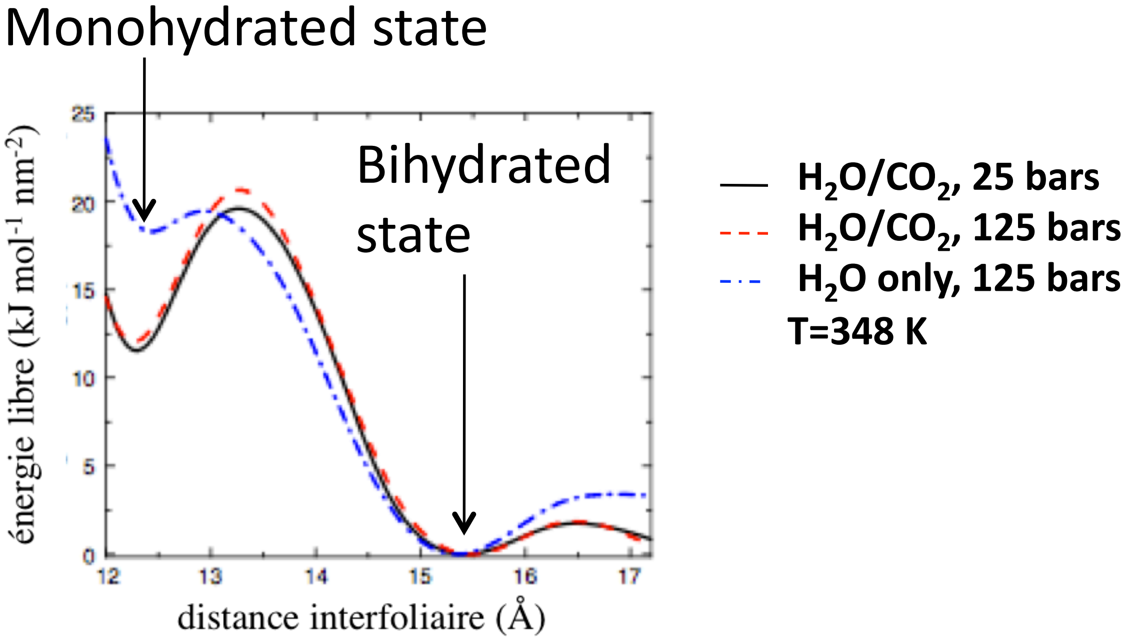


Various relative humidities (μ_{water})

(Tambach et al., 2004)

Application to the clay swelling

In the presence of supercritical CO_2, some CO_2 molecules enter interlayer spacings but no radical change of the equilibrium states of hydration is seen (no shrinkage):



Monohydrated state

Bihydrated state

— **H_2O/CO_2, 25 bars**
- - - **H_2O/CO_2, 125 bars**
-·- **H_2O only, 125 bars**
T=348 K

(Botan et al., 2010)

Molecular Dynamics

Application to clay minerals

Equations of motion (NVE ensemble)

$$H(\mathbf{r_i}^N, \mathbf{p_i}^N) = E_K + U_P = \sum_i \frac{\mathbf{p_i}^2}{2m} + U_P(\mathbf{r_i}^N)$$

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

Conservation of total energy (NVE):

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \sum_i \left(\frac{\partial H}{\partial \mathbf{r_i}} \frac{\partial \mathbf{r_i}}{\partial t} + \frac{\partial H}{\partial \mathbf{p_i}} \frac{\partial \mathbf{p_i}}{\partial t} \right) = 0$$

Velocity Verlet algorithm

How to generate a trajectory: choose a small timestep d*t* and…

Taylor expansion: $\mathbf{r_i}(t+\mathrm{d}t) = \mathbf{r_i}(t) + \mathrm{d}t\frac{\mathrm{d}\mathbf{r_i}}{\mathrm{d}t}(t) + \frac{\mathrm{d}t^2}{2!}\frac{\mathrm{d}^2\mathbf{r_i}}{\mathrm{d}t^2}(t) + \frac{\mathrm{d}t^3}{3!}\frac{\mathrm{d}^3\mathbf{r_i}}{\mathrm{d}t^3}(t) + \mathcal{O}(\mathrm{d}t^4)$

Knowing $r_i(t)$ and $v_i(t)$

$$\mathbf{r_i}(t+\mathrm{d}t) = \mathbf{r_i}(t) + \mathrm{d}t\mathbf{v_i}(t) + \frac{\mathrm{d}t^2}{2m}\mathbf{f}_{\rightarrow\mathbf{i}}(t) + \mathcal{O}(\mathrm{d}t^3)$$

Then $\mathbf{f}_{\rightarrow\mathbf{i}}(t+\mathrm{d}t)$ can be calculated

$$\mathbf{r_i}(t) = \mathbf{r_i}(t+\mathrm{d}t) - \mathrm{d}t\mathbf{v_i}(t+\mathrm{d}t) + \frac{\mathrm{d}t^2}{2m}\mathbf{f}_{\rightarrow\mathbf{i}}(t+\mathrm{d}t) + \mathcal{O}(\mathrm{d}t^3)$$

➡

$$\mathbf{v_i}(t+\mathrm{d}t) = \mathbf{v_i}(t) + \frac{\mathrm{d}t^2}{2m}(\mathbf{f}_{\rightarrow\mathbf{i}}(t) + \mathbf{f}_{\rightarrow\mathbf{i}}(t+\mathrm{d}t))$$

Velocity Verlet algorithm

Verlet algorithm

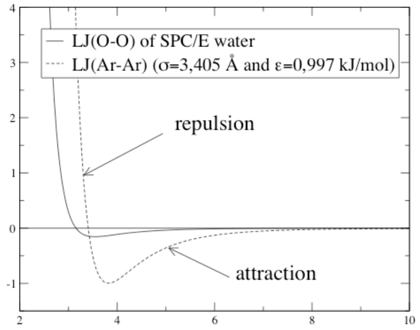
Check that *E=H(t)* is constant. If not, d*t* is probably too high!

$$H(\mathbf{r_i}^N, \mathbf{p_i}^N) = E_K + U_P = \sum_i \frac{\mathbf{p_i}^2}{2m} + U_P(\mathbf{r_i}^N)$$

Example: Lennard-Jones fluid

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

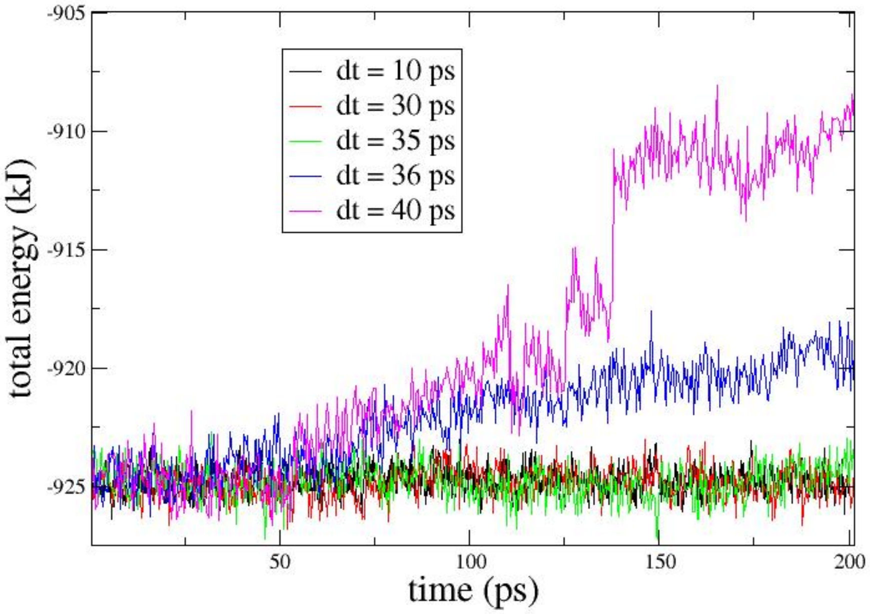
$$H(\mathbf{r_i}^N, \mathbf{p_i}^N) = E_K + U_P = \sum_i \frac{\mathbf{p_i}^2}{2m} + U_P(\mathbf{r_i}^N)$$

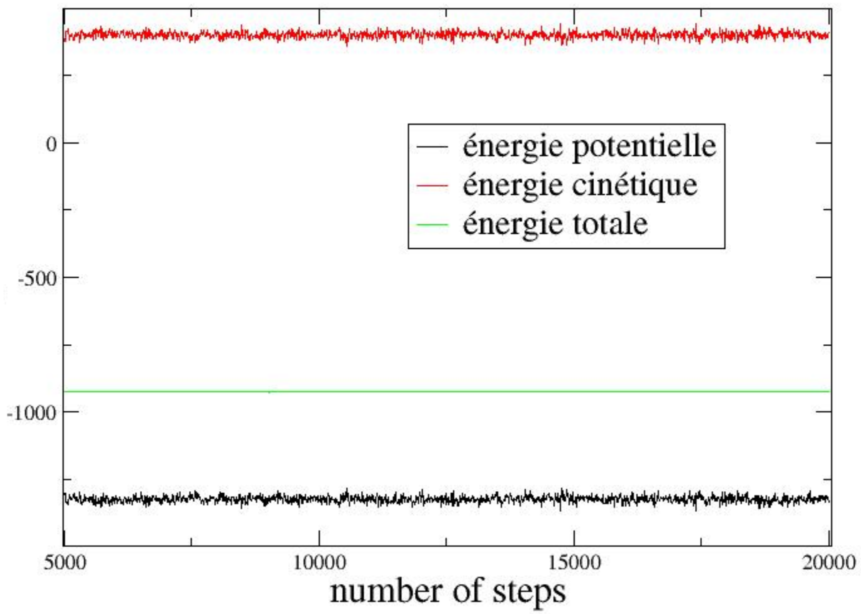


dense argon (T=119,8K)

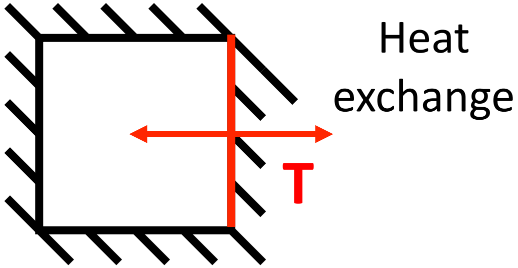
256 atoms

=13475 Å^3





Controlling the temperature: NVT simulations



One can also use the Nosé-Hoover algorithm:

System coupled with a thermostat ➡ (ξ, P_ξ)

$$\dot{\mathbf{r}}_\mathrm{i} = \frac{\mathbf{p}_\mathrm{i}}{m}$$

$$\dot{\mathbf{p}}_\mathrm{i} = \mathbf{f}_{\to \mathrm{i}} - \boxed{\frac{P_\xi}{Q}\mathbf{p}_\mathrm{i}}$$

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

$$\dot{P}_\xi = \sum_i \frac{{\mathbf{p}_\mathrm{i}}^2}{m} - 3Nk_BT$$

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

Controlling the temperature: NVT simulations

$$\frac{\mathrm{d}H}{\mathrm{d}t} = -2E_K \frac{P_\xi}{Q}$$ → Energy dissipation:

- if P_ξ < 0, cooling
- if P_ξ < 0, heating

$$H_{\text{Nosé}} = H(\mathbf{r}^N, \mathbf{p}^N) + \frac{P_\xi^2}{2Q} + 3Nk_BT\xi = C$$

is the new constant of the motion

the new partition function $\Omega_T(N, V, C)$ generated with this new hamiltonian is proportional to $Q(N, V, T)$

→ Equivalent to NVT ensemble

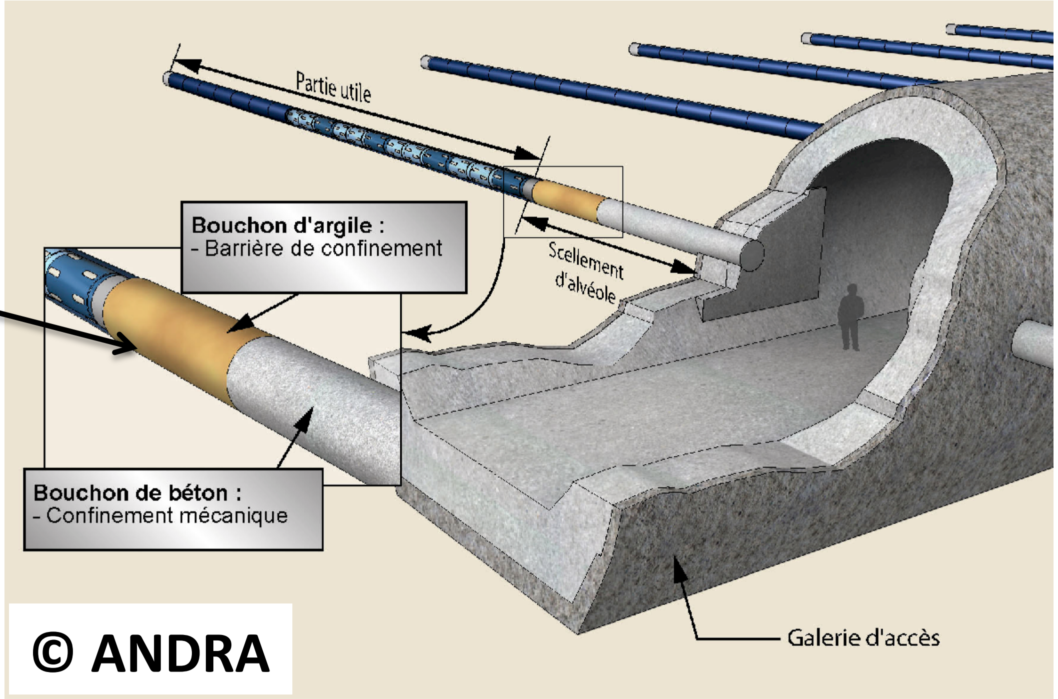
Application to the diffusion in clays

- Geological storage of radioactive waste:

Engineered barrier : compacted bentonite plugs

Natural barriers : Callovo-Oxfordian argilites (clay)

Because of the vicinity of the radioactive waste, T can be high (until 360 K)



© ANDRA

The water is the vector of the motion of radioactive elements through the barrier. As the clay is compacted, the motion is mainly diffusive....

Application to the diffusion in clays

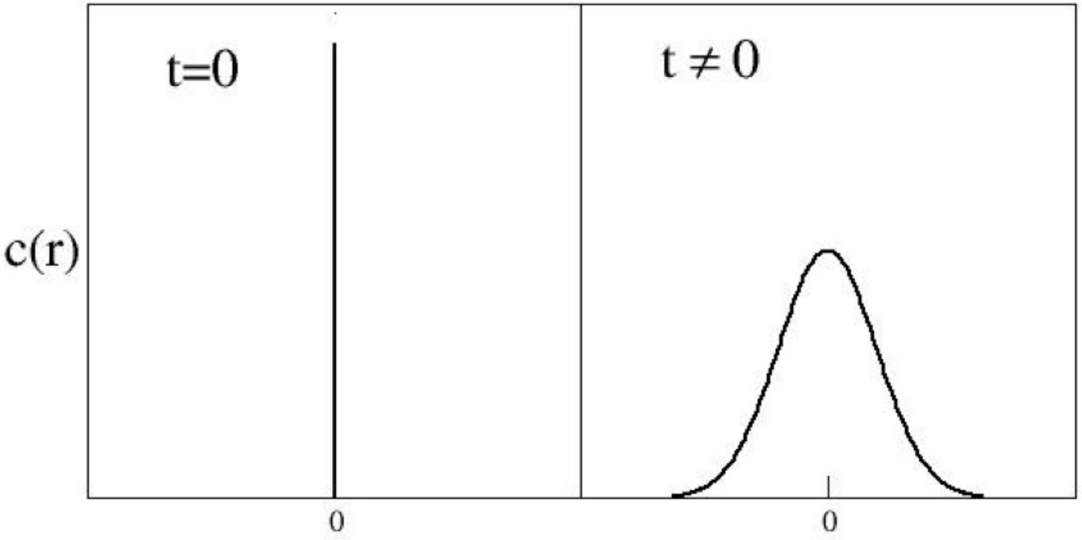
Fick law:

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

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

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

Diffusion of a tracer particle



c(0,0)=δ(0)

c(x,t)

$$\int c(x,t)\mathrm{d}x = 1 \quad \forall\, t$$

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

Application to the diffusion in clays

How to calculate D in simulations?

Mean-squared displacement < **r**^{2}(t) > (MSD)

$$< X^2(t) >= \int c(x,t)x^2 \mathrm{d}x$$

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

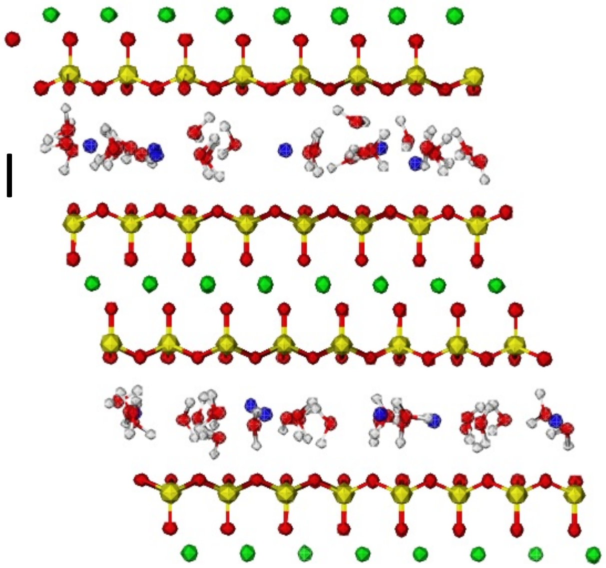
using $$\frac{\partial c}{\partial t} - D\frac{\partial^2 c}{\partial x^2} = 0$$

$$\frac{\mathrm{d} < X^2(t) >}{\mathrm{d}t} = D \int \frac{\partial^2 c(x,t)}{\partial x^2} x^2 \mathrm{d}x \Rightarrow \frac{\mathrm{d} < X^2(t) >}{\mathrm{d}t} = 2D$$

$$\boxed{\frac{\mathrm{d} < r^2(t) >}{\mathrm{d}t} = 6D}$$

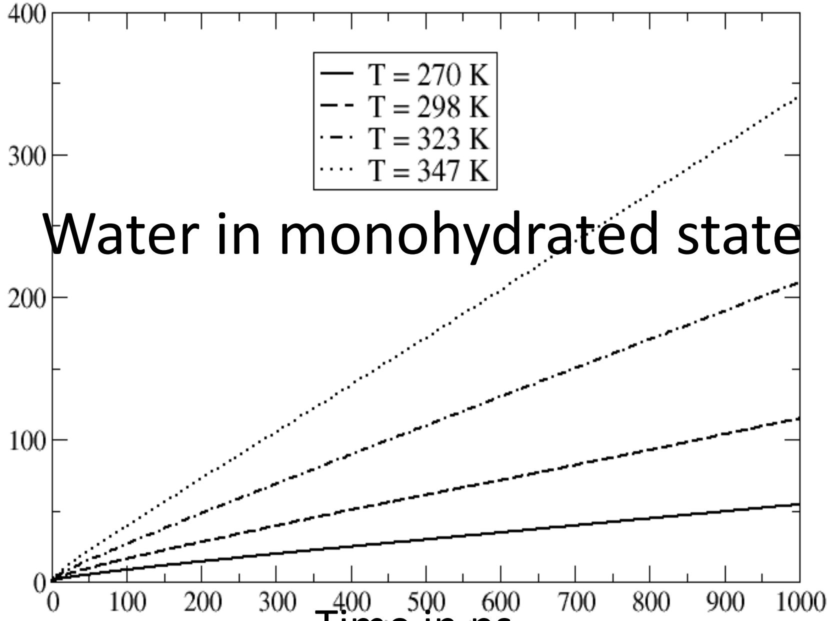
Application to the diffusion in clays

Example on an **hectorite clay**:



The slope gives de diffusion coefficient parallel to the clay layers

$<x^2(t)+y^2(t)>$ in Å^2



Water in monohydrated state

Time in ps

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)

Non equilibrium molecular dynamics

Application to clay minerals

Non equilibrium molecular dynamics

Apply a **perturbation** on the equilibrated system

↓

Measure the response to the perturbation

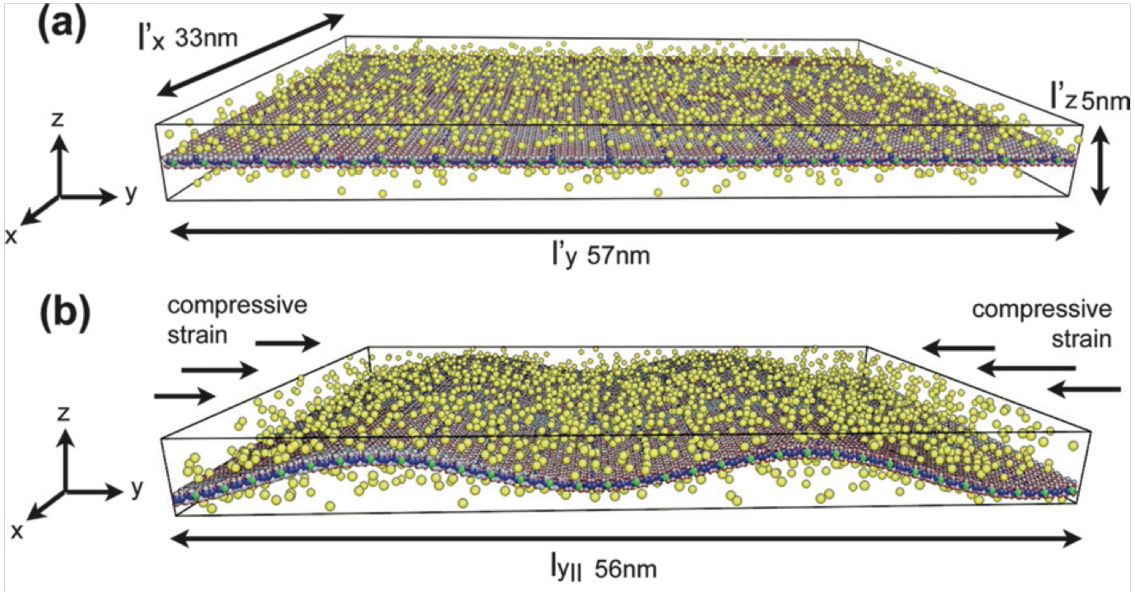
Two examples of applications on clays….

Application to mechanical properties of clays

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

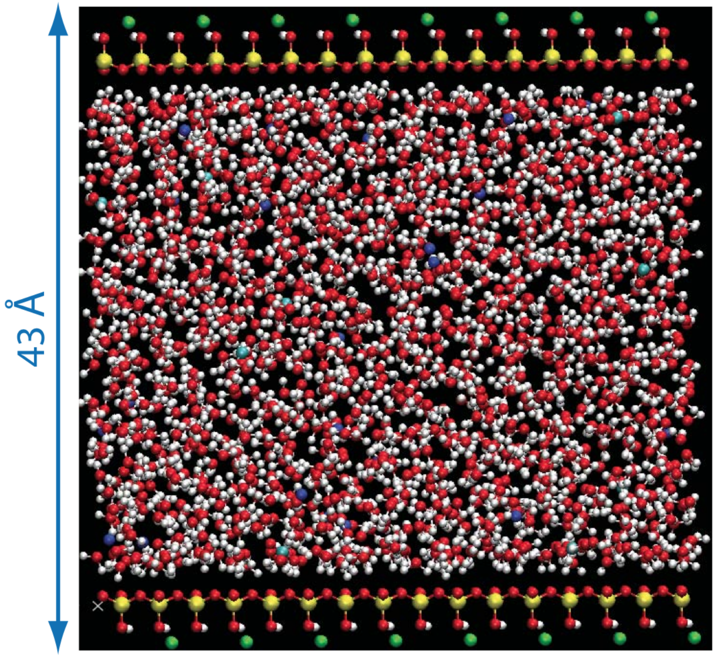
$$\sigma_{kl} = \frac{1}{V}\sum_{i=1}^{N}\left(\frac{m_i}{2}\mathbf{v}_i\mathbf{v}_i + \frac{1}{2}\sum_{j=1}^{N}\mathbf{F}_i\mathbf{r}_{ij}\right)_{kl}$$

(Suter et al., 2009)

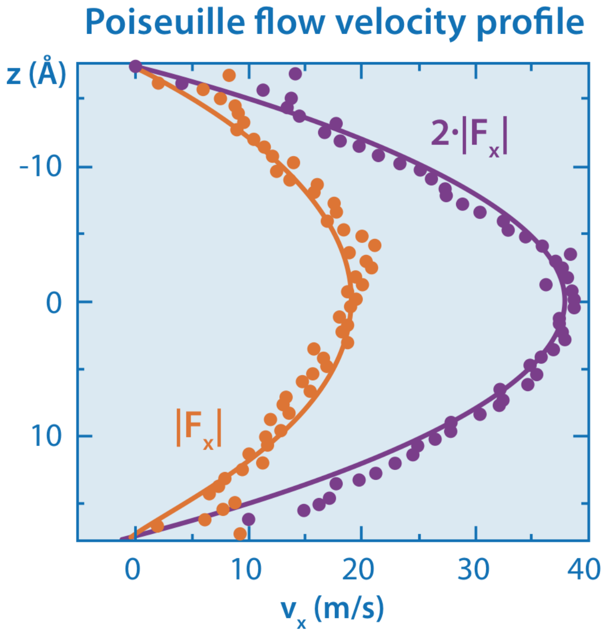
Application to fluid flows determination in clays

Describe properly fluid flows in clay minerals: calibrate continuous solvent description on molecular dynamics

Fluid velocity induced by a constant force parallel to the clay layers:



F_x=const

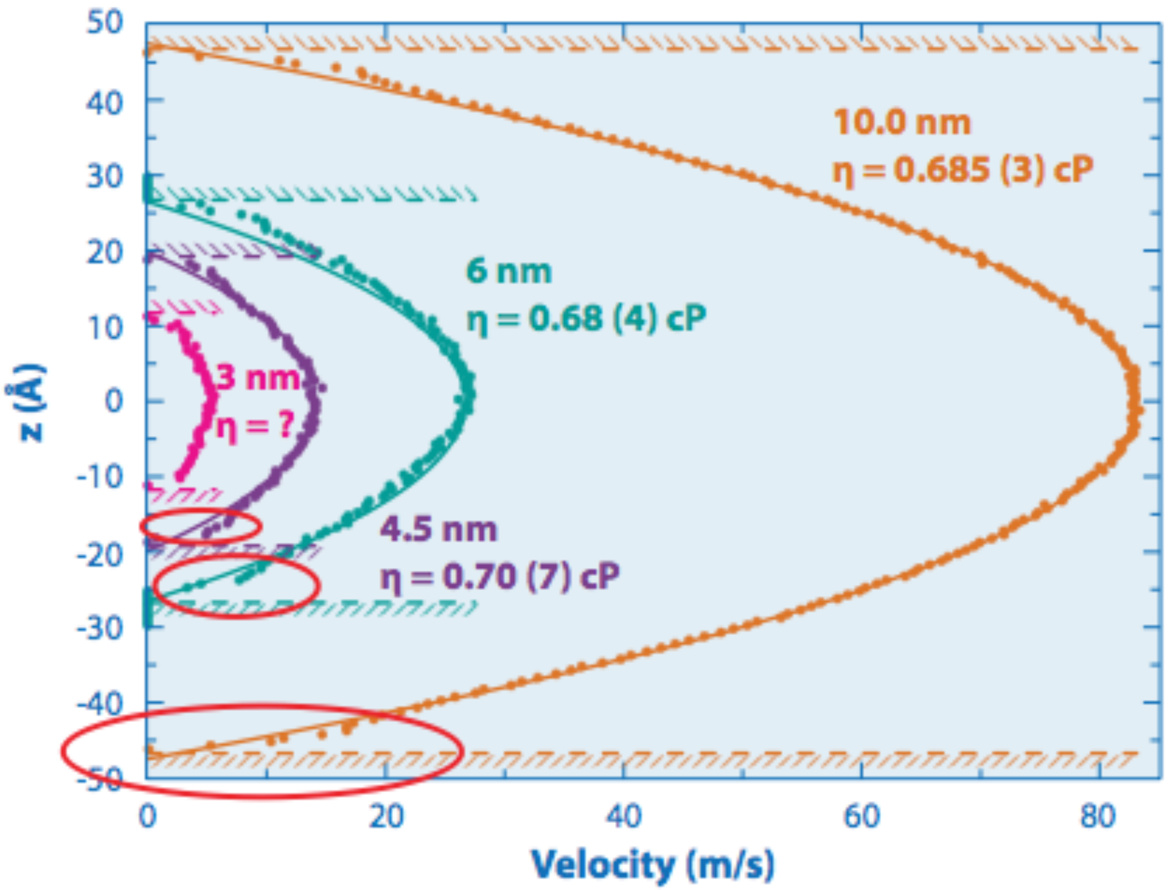

Poiseuille flow velocity profile

Stokes: $-\eta\Delta^2\mathbf{v} = \mathbf{F}_\mathbf{v}$ and $\mathbf{v} = v(z)\mathbf{u}_\mathbf{x}$ → $-\eta\frac{\mathrm{d}^2 v}{\mathrm{d}z^2} = F_{vx}$

Can Stokes equation describe correctly fluid velocity profiles?

Non equilibrium molecular dynamics

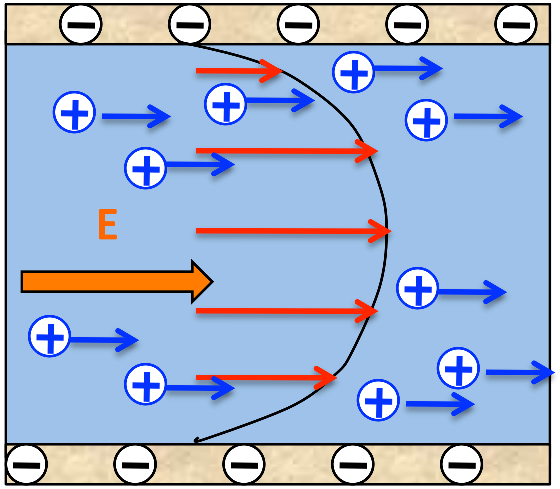
Yes, but a slipping condition must be taken into account at the surface to retrieve a quantitative agreement between MD and theory

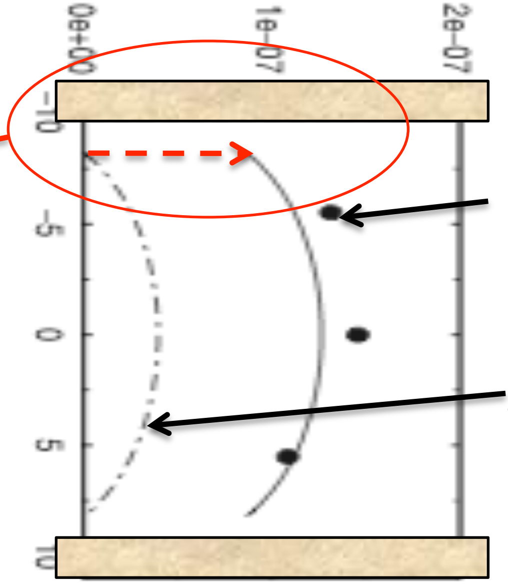


Non equilibrium molecular dynamics

The same trend was found with electroosmosis

perturbation: Electrostatic field





(v/E in $m^2s^{-1}V^{-1}$)

Slipping condition

Molecular dynamics

Analytical theory without slip

(Dufrêche et al., 2005)