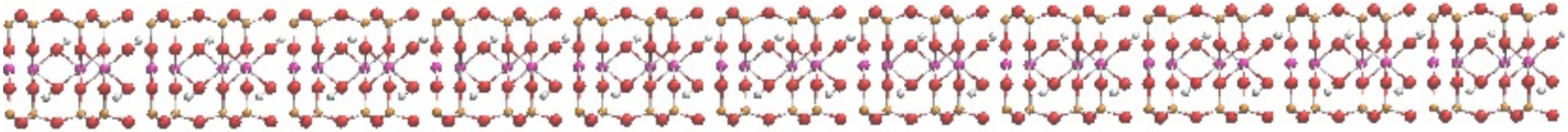

Getting familiar with molecular simulations

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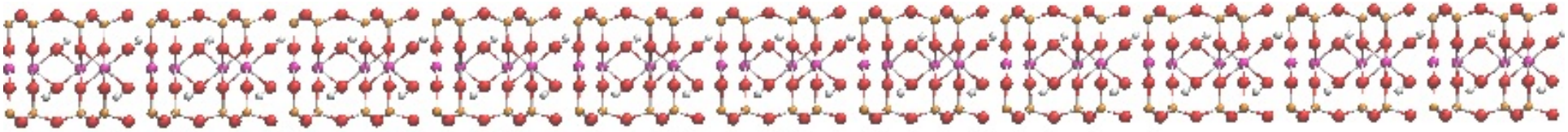


Contents

- Why model in molecular level

  Interest in montmorillonite

- Main methods of molecular modelling

  Molecular dynamics (MD) vs Monte Carlo (MC)

- Why MD

Why model in molecular level

Interest in the behaviour of montmorillonite; earlier work is not enough?

- modelling
  - many models are fitted parameters, thus guesses and lack closer understanding, e.g. surface complexation models
  - for highly compacted clay (low water content) the use of typical macroscopical models becomes questionable
- experiments
  - we see macroscopical changes but what happens in the microscopical level?
  - testing of new theories or systems which are difficult to produce in lab conditions, e.g. high temperature/pressure
  - better insight to K_d values

Main methods of molecular modelling

- Molecular dynamics (MD):
  specify atoms initial coordinates, forces, boundary conditions, ensemble and time step $\rightarrow$ MD solves the equation of motion giving time evolution of the system
  - ab initio method, numerically solve a mathematical problem
  - semiempirical approach, invent a model to mimic a phenomena $\Rightarrow$ reliable extrapolation of the model = ?
- Monte Carlo (MC)
- range of hybrid techniques of MD and MC (in e.g. swelling of bentonite)

MD vs MC: One needs to start with something

MD
time evolution
$\Downarrow$

- transport coefficients (diffusion in interlamellar space of montmorillonite)
- trajectories of counterions in montmorillonite

MC
equilibrates system

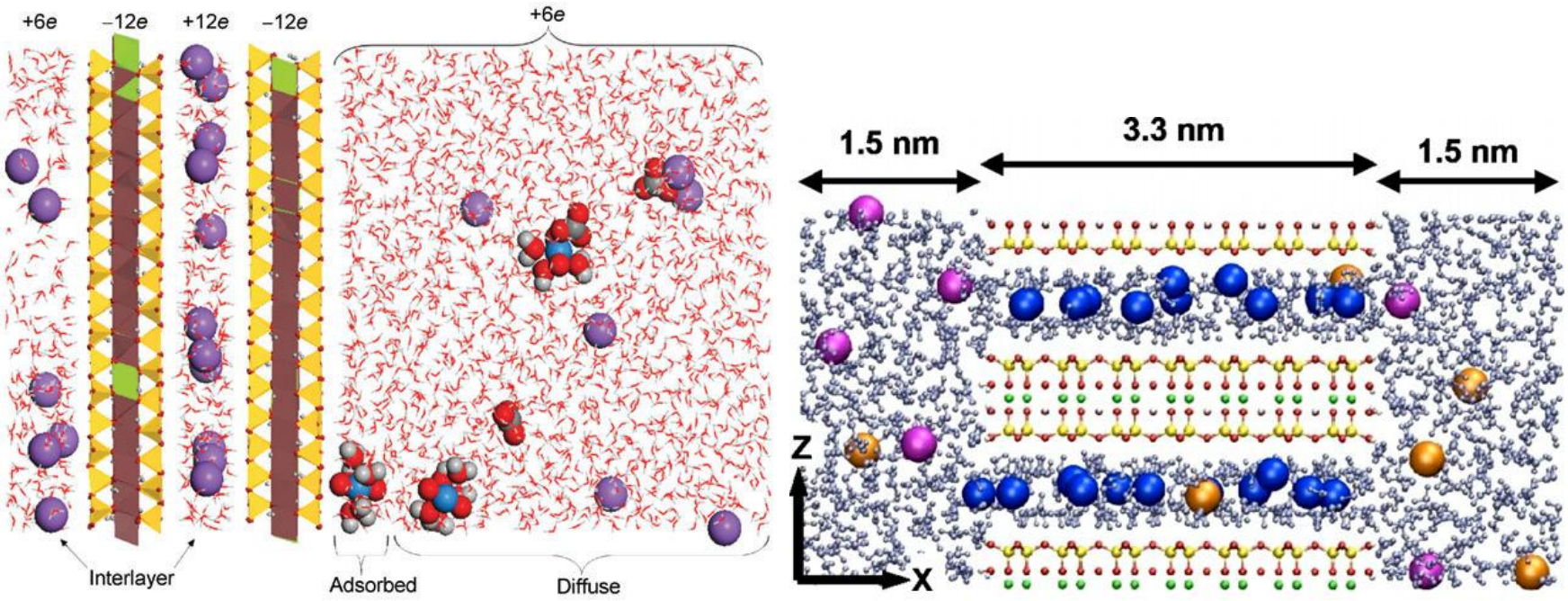
- wider choise of ensembles than in MD and more efficient
- thermodynamical and structural properties

Limitations in MD

- # of atoms fixed
- # of atoms limited, more atoms $\longrightarrow$ longer computation time and more computing power needed
- limited simulation time, usually a few nanoseconds (step size around 1fs)
- no bond breaking included (requires reactive molecular dynamics)

Work around the world

- Swelling of montmorillonite [5]
- Behaviour of water in the interlamellar space of montmorillonite [3]
- Trajectories of counterions in interlamellar space (where the ions most likely are) [2]



Equilibrium snapshot of an adsortion simulation [1] and simulation box for interlayer/micropore exchange of water/ions [4]

Work so far..

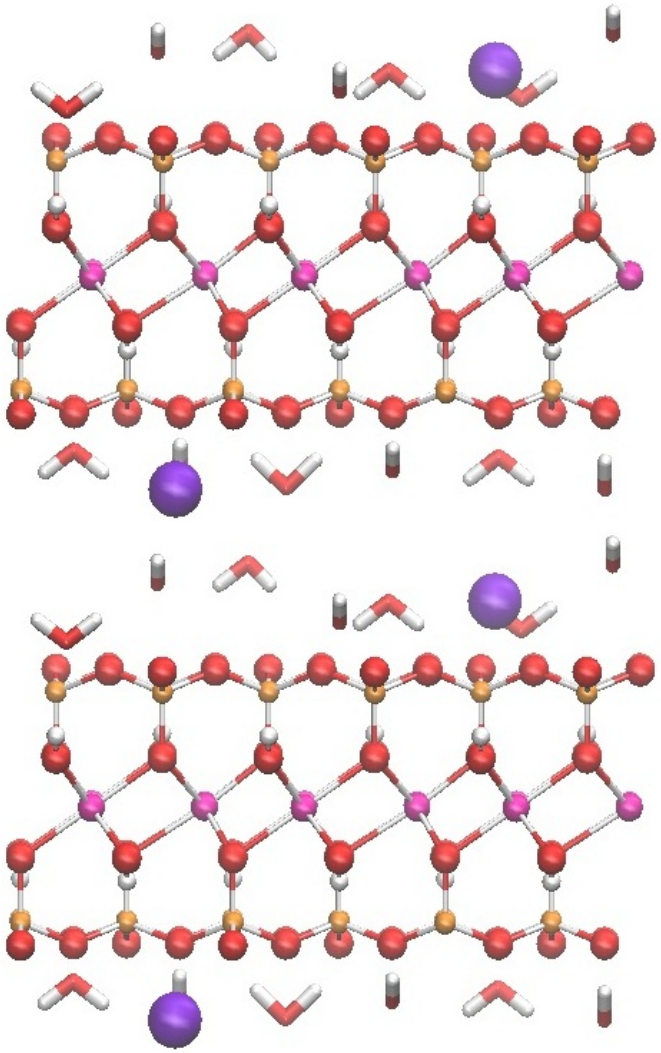


Figure 1: Snapshot of Na-montmorillonite structure (6 unit cells) containing aluminum atoms (pink), silicon (orange), oxygen (red) and hydrogen (white). The interlayer contains water molecules and sodium atoms (purple). Dimension 16,8Åx 28Å.

[1] J. A. Greathouse and R. T. Cygan. Molecular dynamics simulation of uranyl(vi) adsorption equilibria onto an external montmorillonite surface. *Physical Chemistry Chemical Physics*, (7):3580–3586, 2005.

[2] N. Malikova, V. Marry, J. F Dufrêche, C. Simon, P. Turq, and E. Giffaut. Temperature effect in a montmorillonite clay at low hydration–microscopic simulation. *Molecular Physics*, 102(18):1965–1977, 2004.

[3] V. Marry and P. Turq. Microscopic simulations of interlayer structure and dynamics in bihydrated heteroionic montmorillonites. *The Journal of Physical Chemistry B*, 107(8):1832 – 1839, 2003.

[4] Benjamin Rotenberg, Virginie Marry, Rodolphe Vuilleumier, Natalie Malikova, Christian Simon, and Pierre Turq. Water and ions in clays: Unraveling the interlayer/micropore exchange using molecular dynamics. *Geochimica et Cosmochimica Acta*, 71(21):5089–5101, 2007.

[5] Robert M. Shroll and David E. Smith. Molecular dynamics simulations in the grand canonical ensemble: Application to clay mineral swelling. *The Journal of chemical physics*, 111(19):9025, 1999.