

Computational Techniques in Chemistry

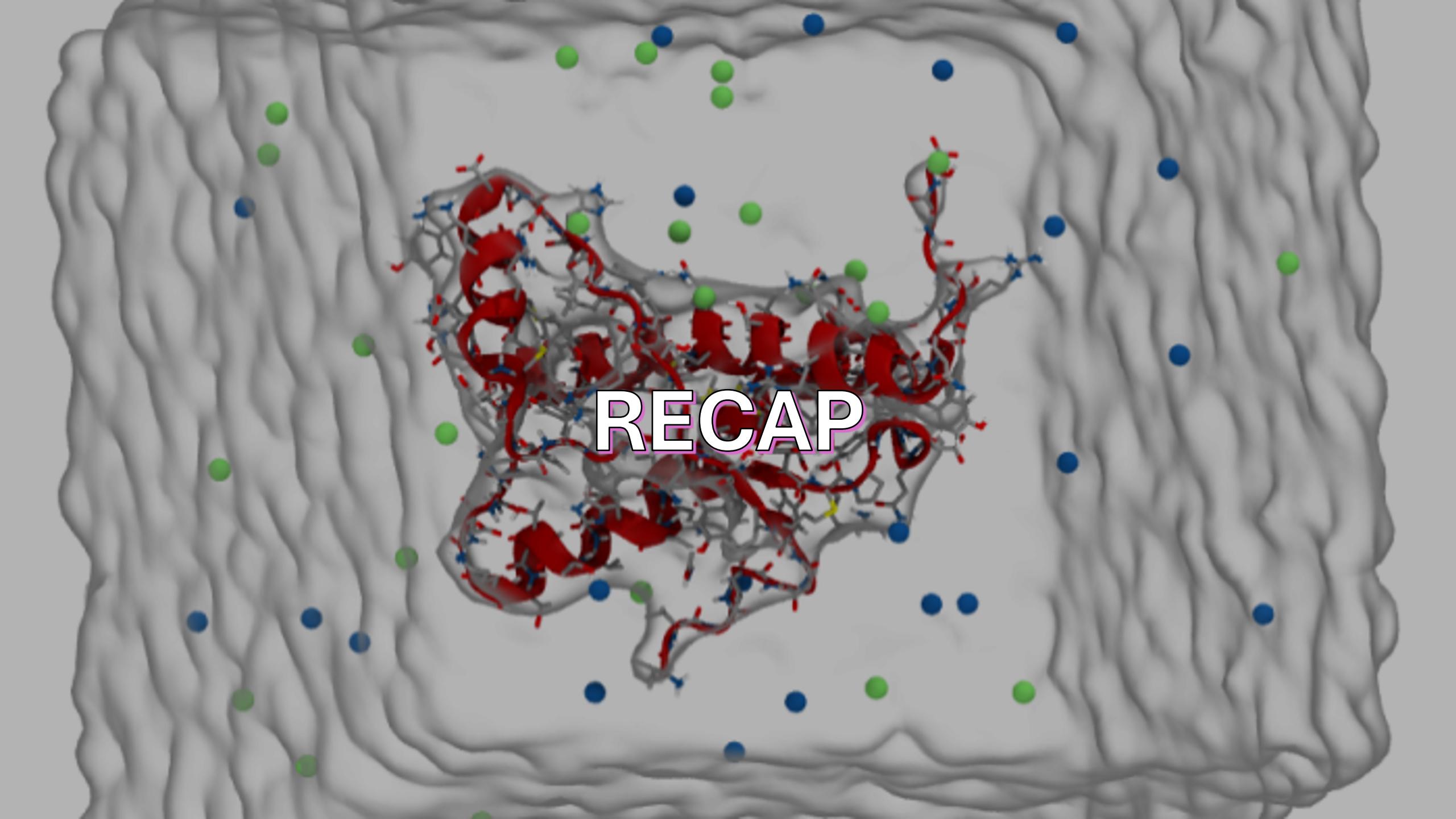
Session 3: Molecular simulation of a layered materials system

Valentina Erastova

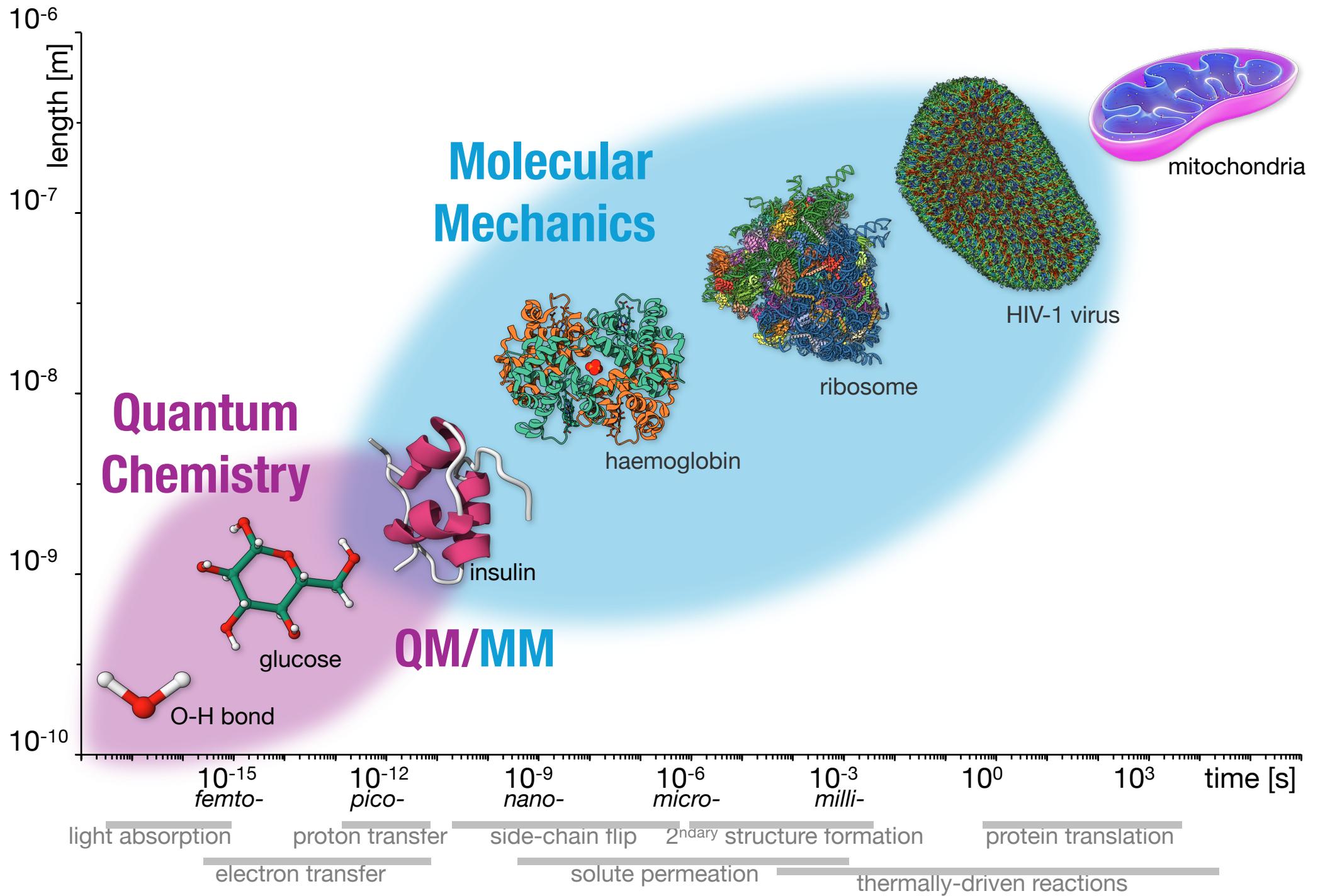
University of Edinburgh

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Hannah Pollak (h.pollak@sms.ed.ac.uk) for material development



RECAP



10^{-6}

[m]

Schrödinger equation

- Exact only for H and He
- Approximations:
 - *ab-initio*: directly derived
 - semi-empirical and empirical: fitted to experiments
- Properties that cannot be isolated: transition & excited states
- ~100 of atoms, ps motions

 10^{-9} 10^{-10}

femto-

pico-

nano-

micro-

milli-

10⁰10³

time [s]

light absorption

proton transfer

side-chain flip

2ndary structure formation

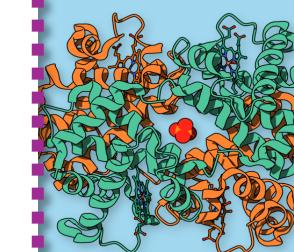
protein translation

electron transfer

solute permeation

thermally-driven reactions

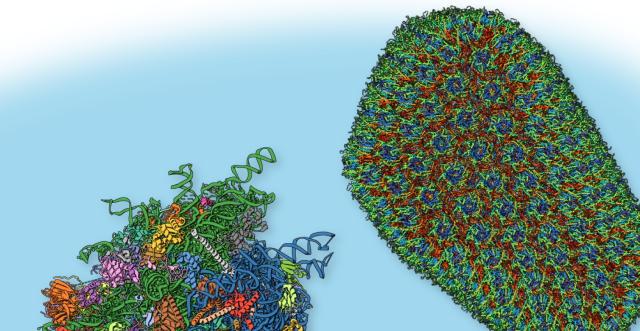
Molecular mechanics



haemoglobin



ribosome



HIV-1 virus



mitochondria

QM/MM



insulin

O-H bond

Newtonian Mechanics

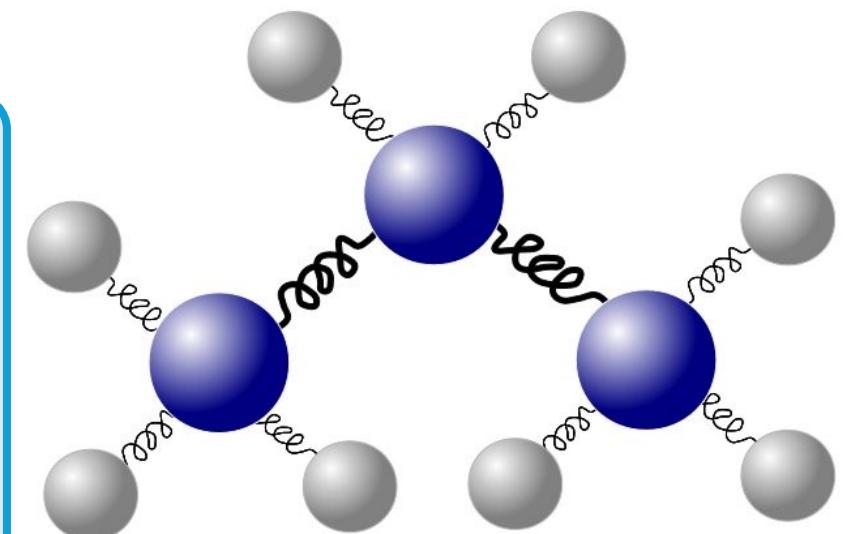
Each atom is a bead, connected by a spring
 ~100k of atoms, ns - μ s

Force Field Methods

- A molecule is represented by a set of *balls* connected with *springs*

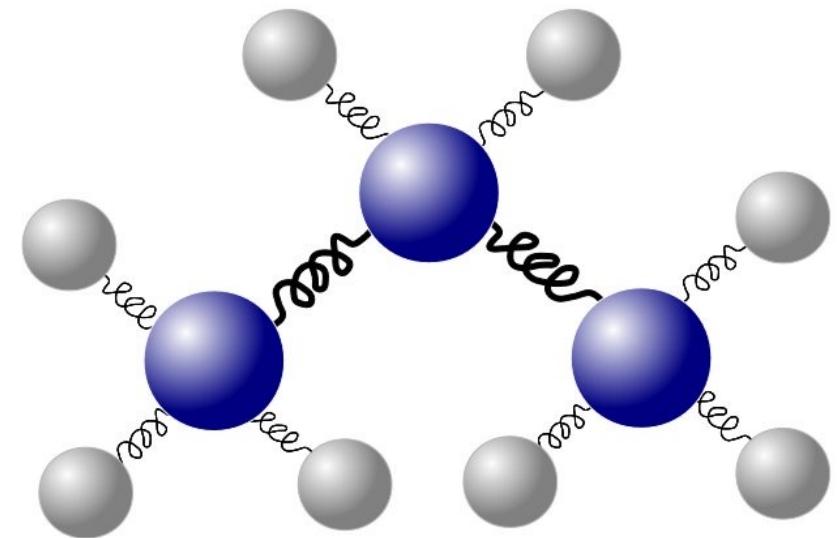
ASSUMPTIONS:

- Nuclei and electrons are combined in an atom, represented by a *ball*
- Balls have radius, constant charge and a given softness
- Covalent bonds are represented by *springs*
- Springs have an equilibrium length and can vary in stiffness



Force Field Methods

- A molecule is represented by a set of *balls* connected with *springs*
- System's energy depends on *classical* (Newtonian) interactions between balls and springs
- Interactions are described by pre-assigned parameters = *force fields*



Force Field Energy

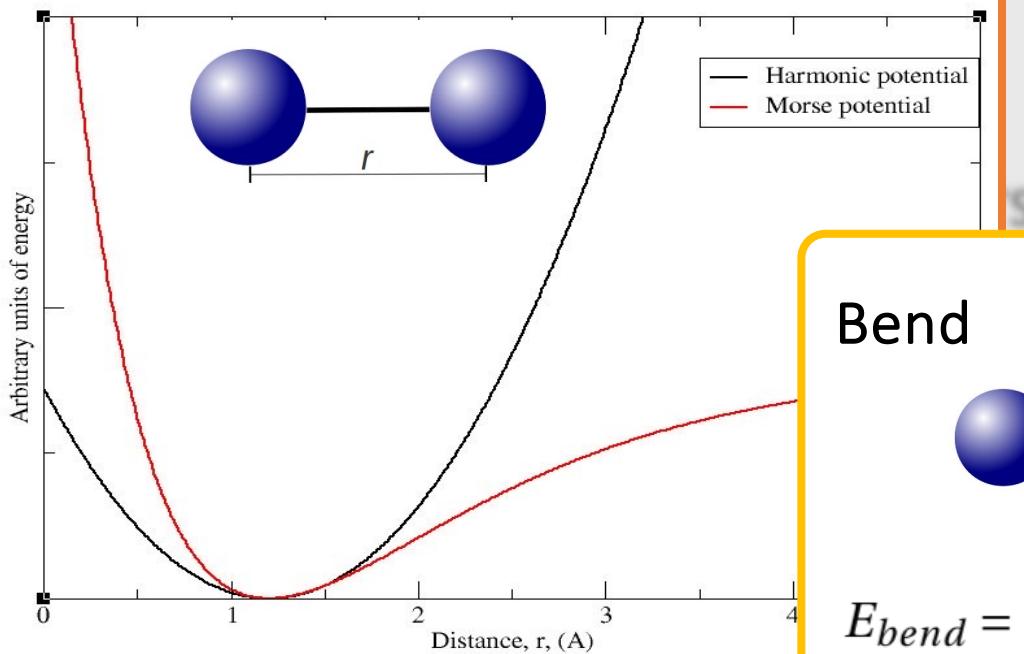
Force Field - set of parameters used in classical mechanical calculations

Potential Energy - the sum of all the interactions in it

$$E_{FF} = E_{str} + E_{bend} + E_{tors} + E_{VdW} + E_{el}$$

The equation $E_{FF} = E_{str} + E_{bend} + E_{tors} + E_{VdW} + E_{el}$ is displayed. Below the equation, a horizontal line with two brackets underneath it groups the terms. The first bracket groups E_{str} , E_{bend} , and E_{tors} under the label "bonded". The second bracket groups E_{VdW} and E_{el} under the label "non-bonded".

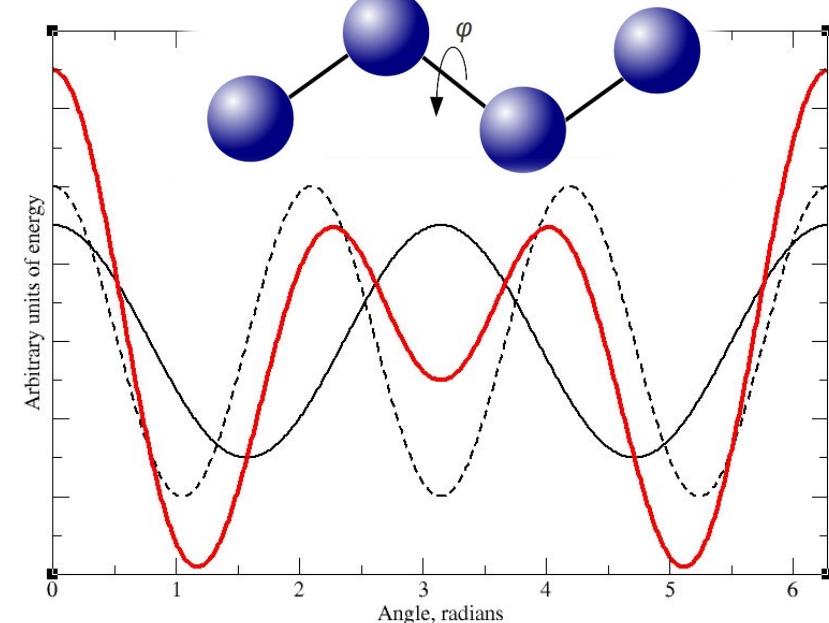
Bond Stretch $E_{str} = \frac{1}{2} k^{AB} (r^{AB} - r_0^{AB})^2$



Bend

$$E_{bend} = \frac{1}{2} k^{ABC} (\theta^{ABC} - \theta_0^{ABC})^2$$

Torsion $E_{tors} = \sum \frac{1}{2} V_n \cos n\phi$



$$E_{FF} = E_{str} + E_{bend} + E_{tors} + E_{VdW} + E_{el}$$

bonded

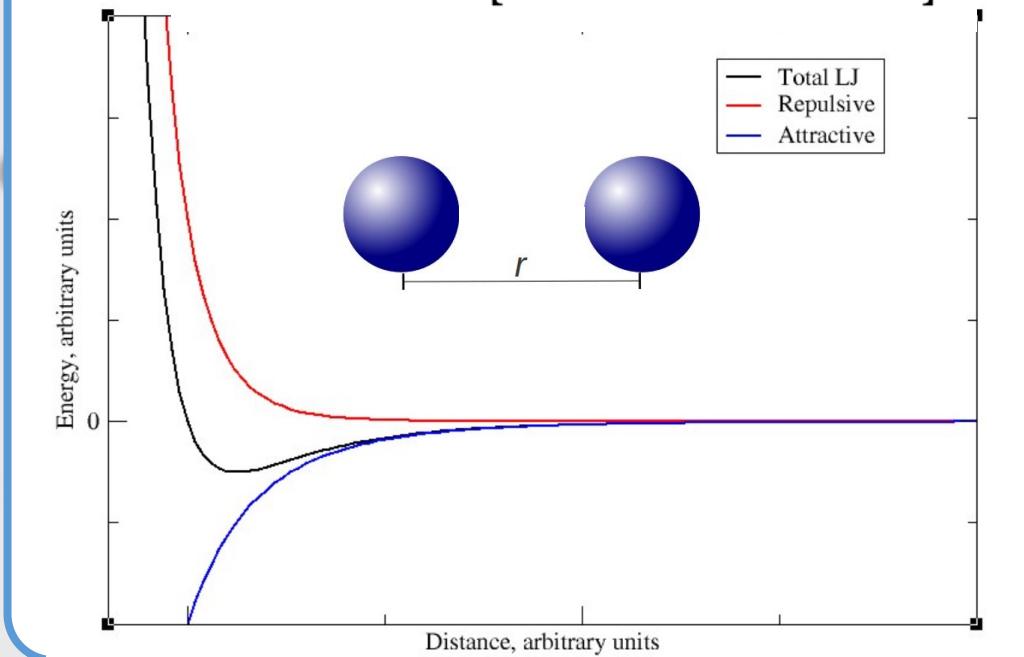
non-bonded

Force Field = set of

Potential Energy

Lennard-Jones

$$E_{VdW}^{LJ} = 4\epsilon^{AB} \left[\left(\frac{\sigma^{AB}}{r^{AB}} \right)^{12} - \left(\frac{\sigma^{AB}}{r^{AB}} \right)^6 \right]$$



Coulomb

$$E_{el} = \frac{1}{4\pi\epsilon_0} \frac{Q^A Q^B}{r^{AB}}$$

$$E_{FF} = E_{str} + E_{bend} + E_{tors} + E_{VdW} + E_{el}$$

bonded

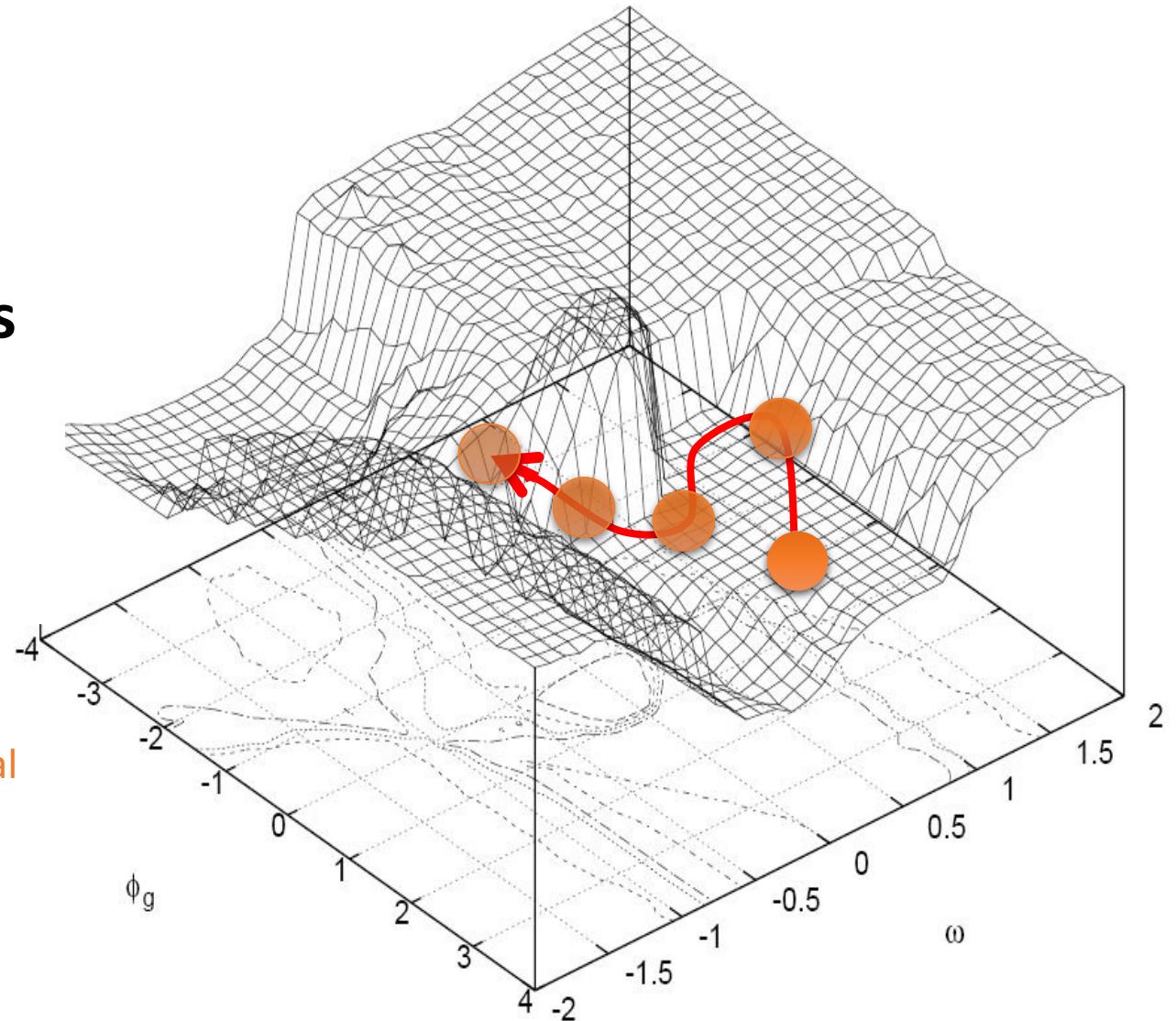
non-bonded

Potential Energy Landscape

- Atoms interact => generate forces
- **Sum** of all interactions generates an **energy landscape**
- Energy landscape determines **atoms motion**
- Classical equations of motion are solved step-by-step, by a *finite difference algorithm*
- **Newton's II law of motion** is:

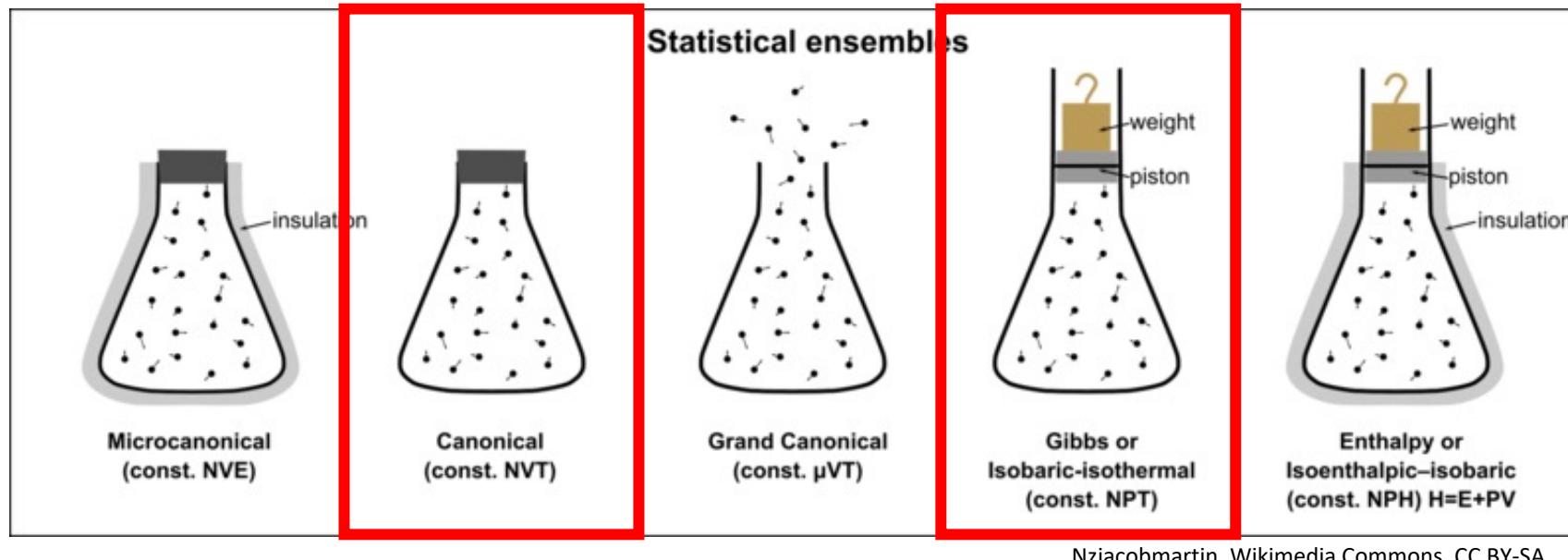
$$\frac{\text{acceleration}}{\text{mass}} = \mathbf{F}_i \quad \mathbf{F}_i = -\frac{\partial E}{\partial \mathbf{r}_i}$$

potential energy
position



How to control temperature and pressure?

Simulations can replicate a specific *thermodynamic ensemble*:



Nzjacobmartin, Wikimedia Commons, CC BY-SA

Addition of equations acting as:

thermostats (scaling atom velocities) – constant T

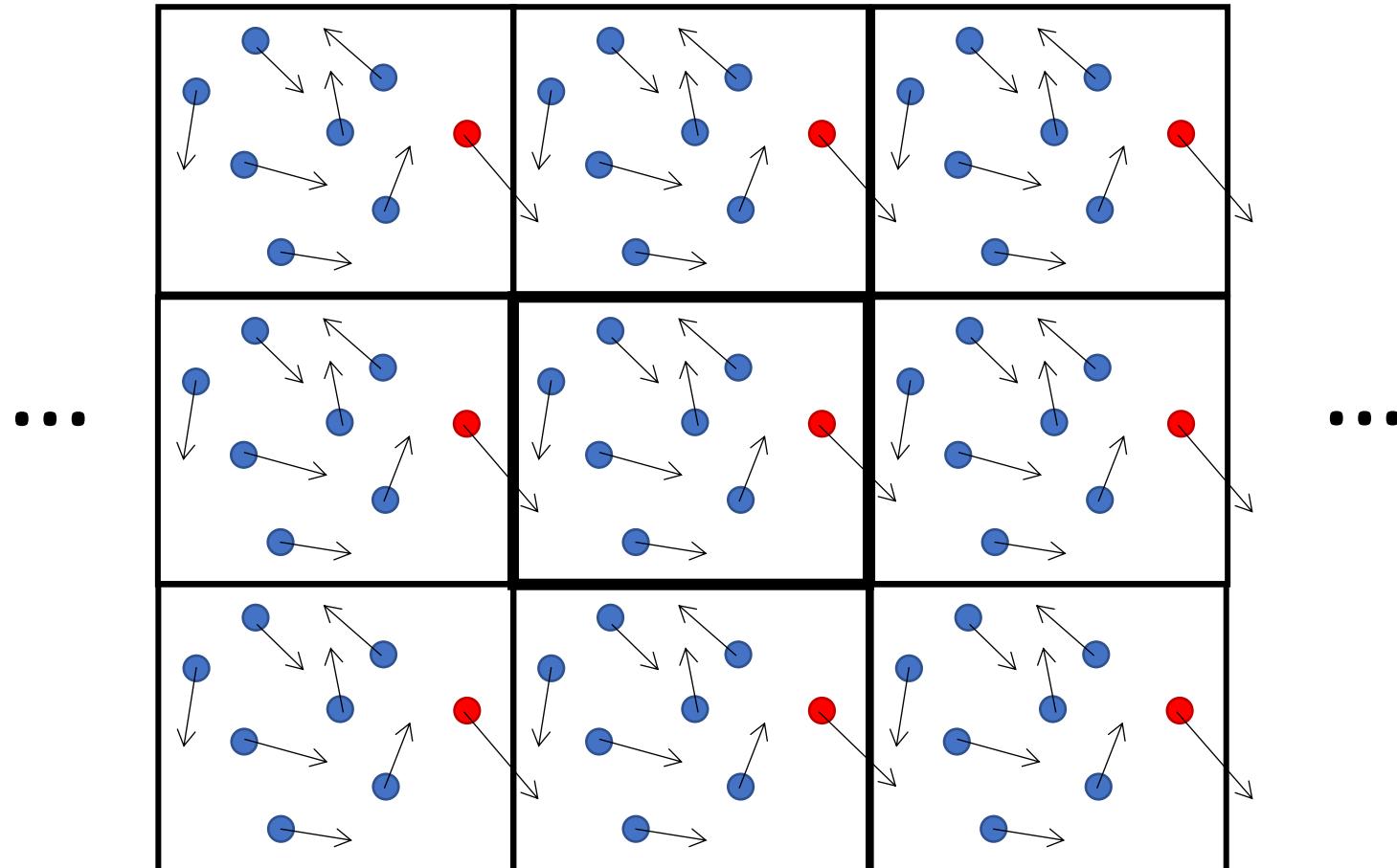
barostats (scaling positions) – constant P

e.g.: Berendsen, Nose-Hoover, Parrinello-Rahman, ...

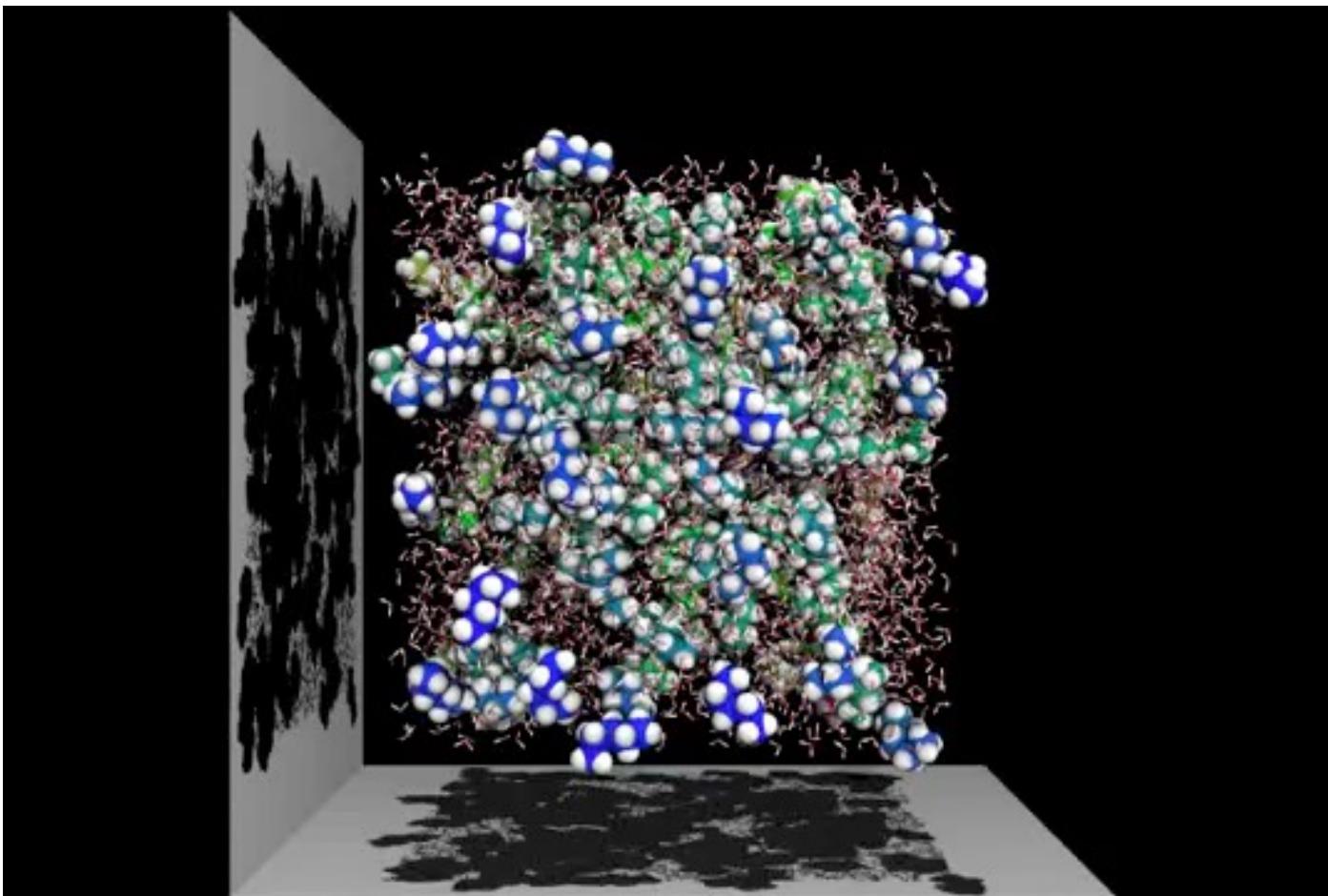
Is the simulation box finite?

For **bulk properties** use *periodic boundary conditions* (PBC)

For **boundary effects** use wall, PBC in xy-direction, vacuum in NVT, ...



In each simulation timestep...



Set initial
conditions for x ,
 v and box size

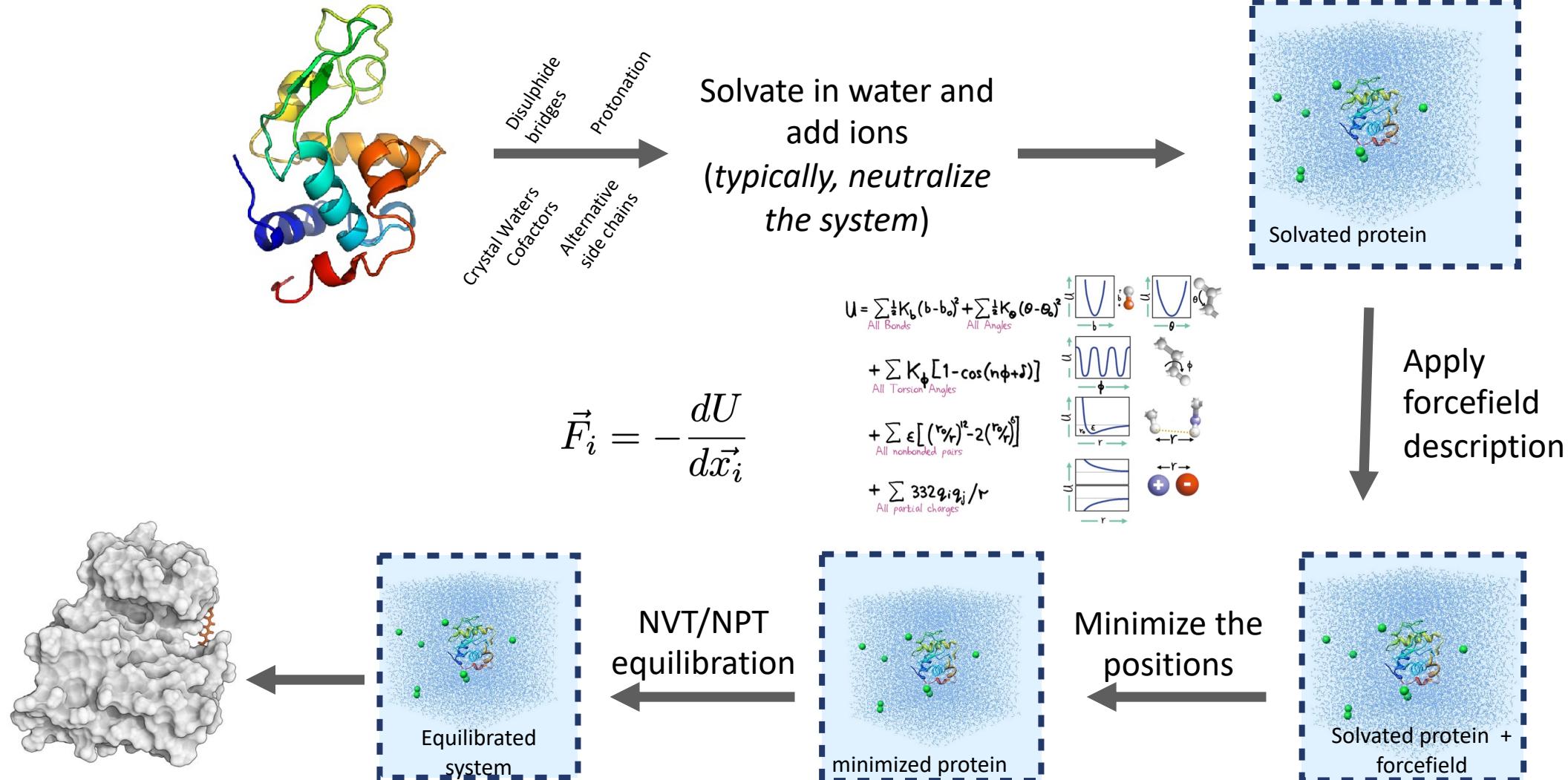
Compute forces

Compute new x'
and v' for all atoms

Scale x' and v'
with
thermo/barostat

Update x' and v'
(with pbc)

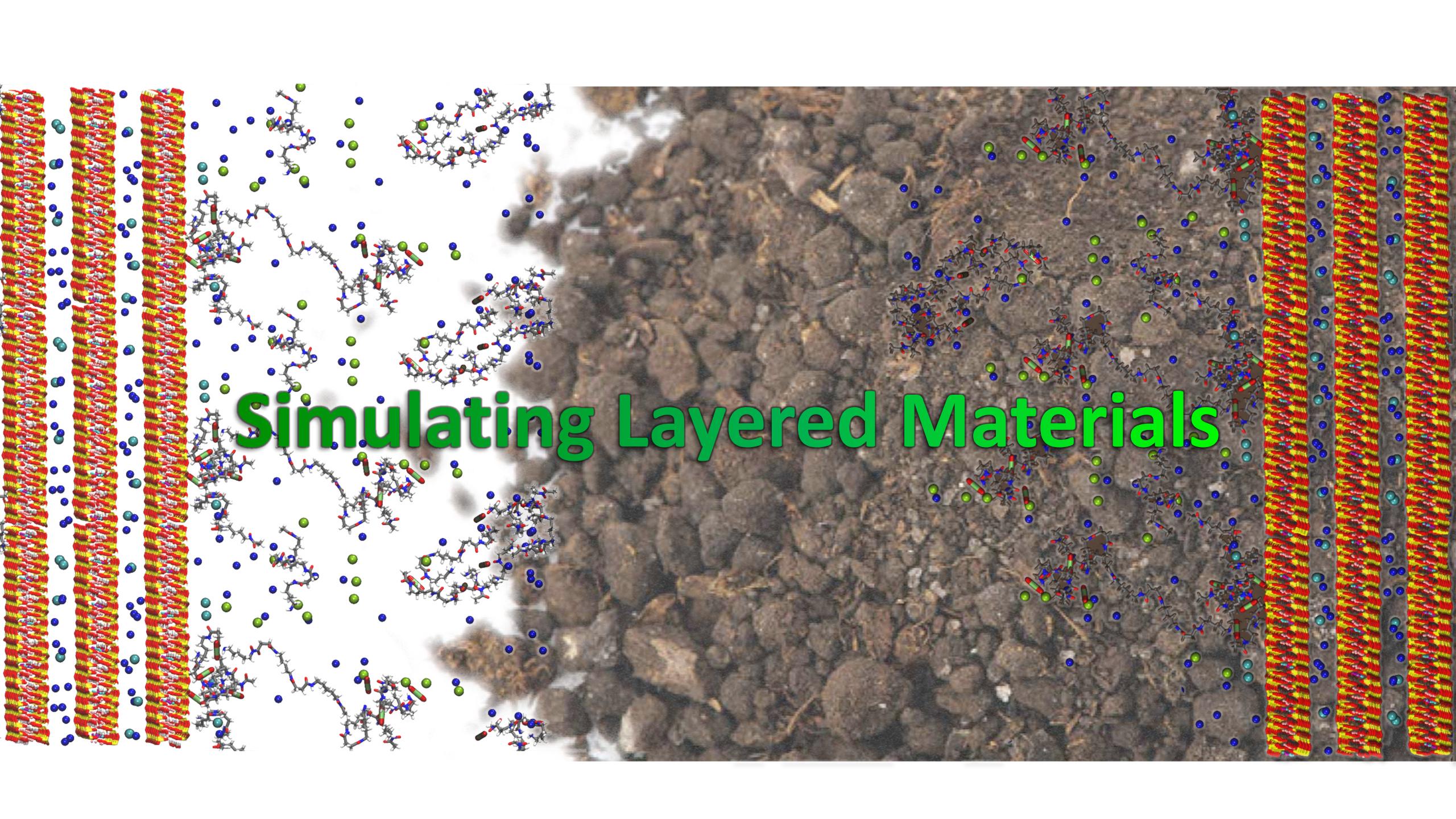
Molecular dynamics require multiple steps for the setup of simulations



Production simulation

http://www.bevanlab.biochem.vt.edu/Pages/Personal/justin/gmx-tutorials/lysozyme/01_pdb2gmx.html

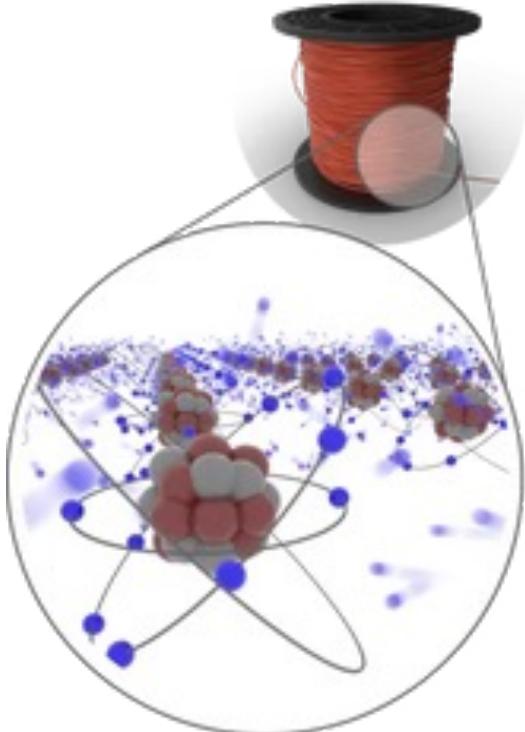
Levitt, *Nature Struct. Biol.*, 2001



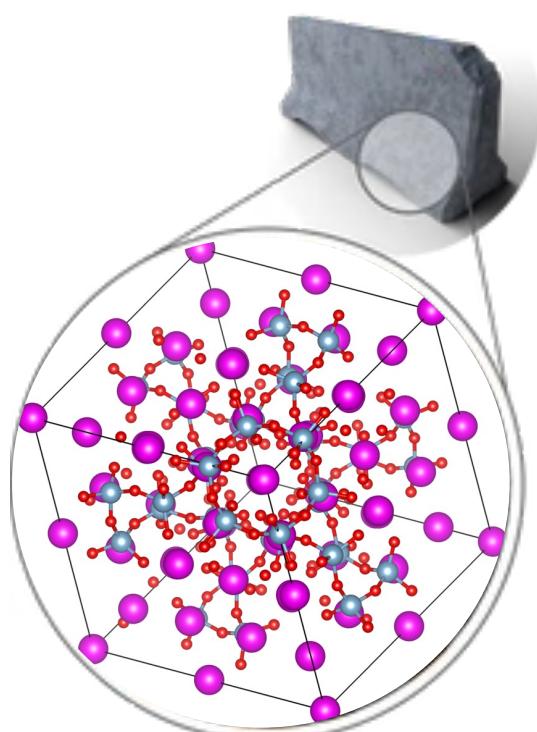
Simulating Layered Materials

Materials at the Nanoscale

Electric wire



Concrete wall



Rubber tire



Conducting electricity with free electrons of the metals

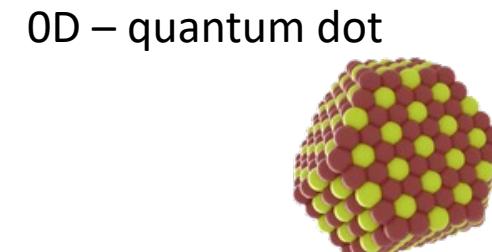
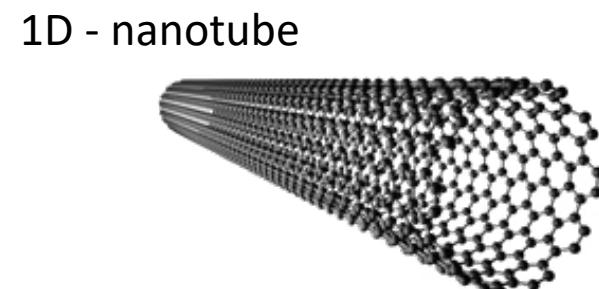
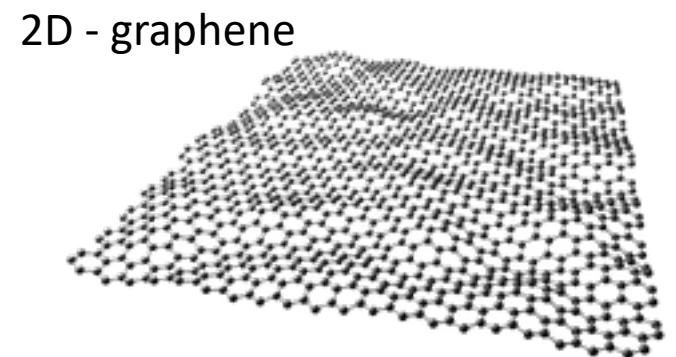
Cement holds together gravel and sand, creating an aggregate material

Polymer chains give rubber flexibility, while locked together in the rigid structure

Dimensionality of materials

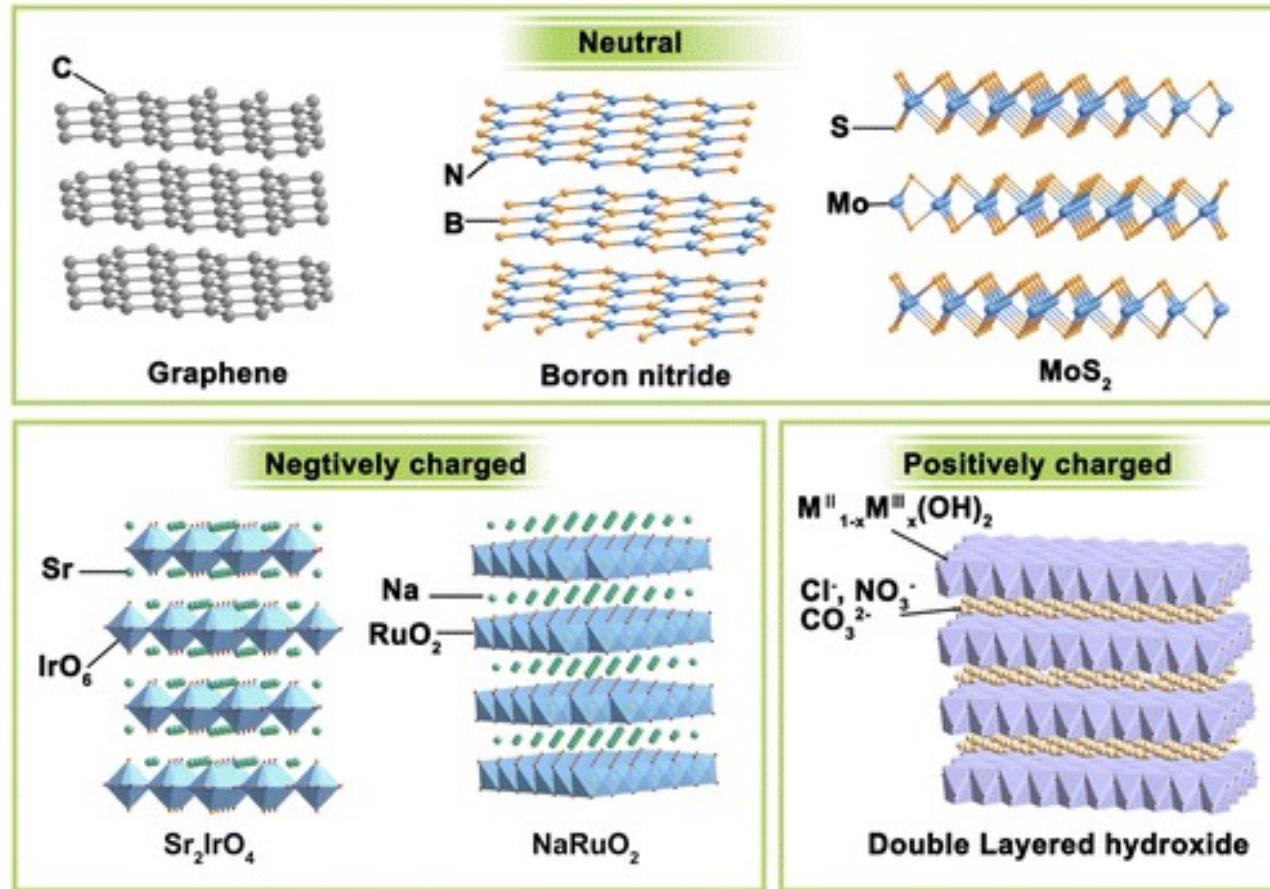
Nanoscopic dimension – where a scale is in nanometers in size, i.e., structure is at an atomic level.

Nanoscopic Dim. No.	Classification	Example
0	Bulk	Anything you can see by eye
1	2D (nanosheet)	Graphene
2	1D (nanotube or nanowire)	Carbon nanotube
3	0D (nanoparticle)	Quantum dot



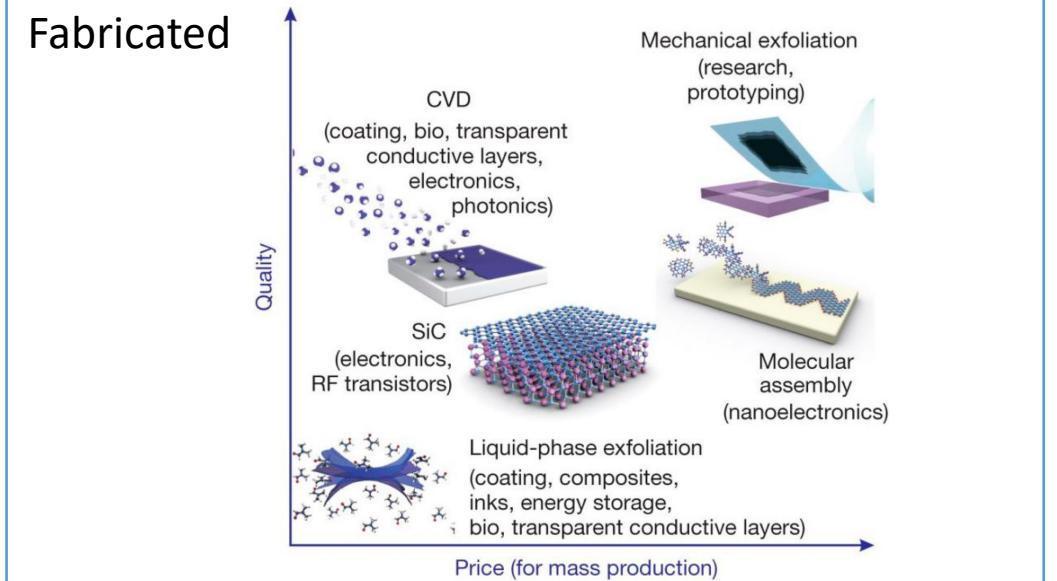
Why are layered materials of interest?

- *Mechanical properties: weak van der Waals interactions between planes + strong covalent bonds in the plane*
- *High surface areas per weight/volume: more active chemical sights for adsorption or reactions*
- *Confinement of electrons in a 2D plane: effecting its electronic and optical properties*



<https://doi.org/10.1039/D3GC01822A>

Fabricated



<https://doi.org/10.3390/nano8110942>

Natural

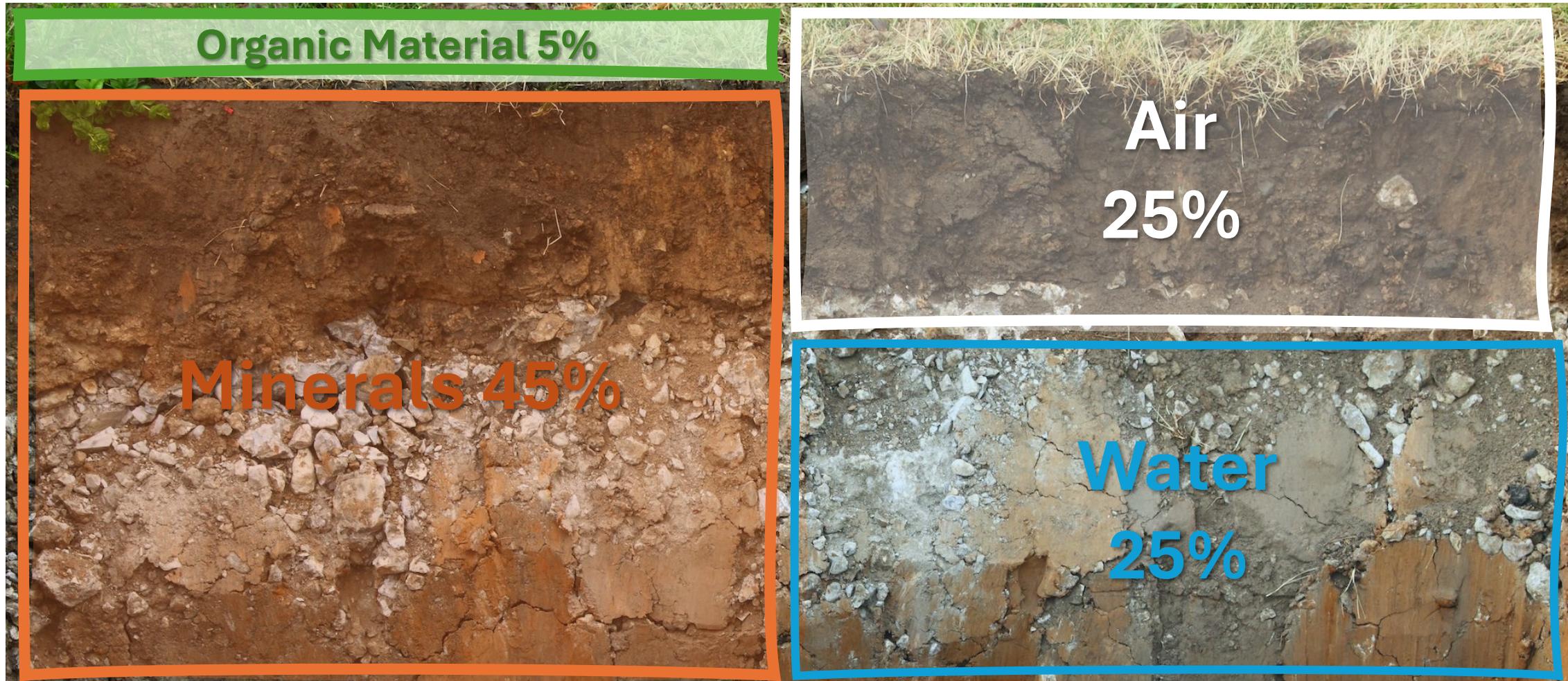


Layered double hydroxide

The Soil



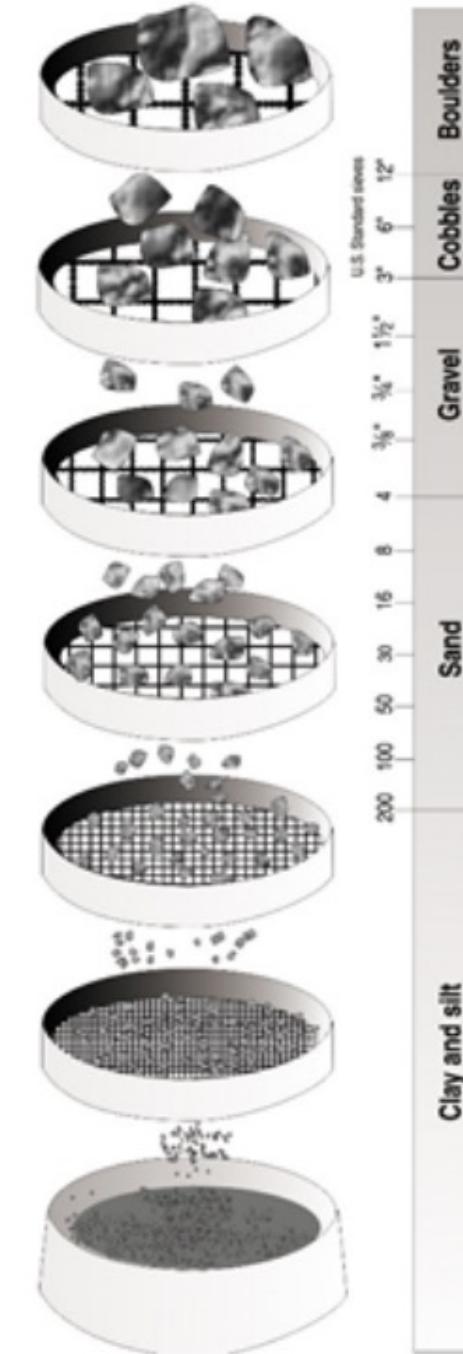
The Soil



Minerals in the Soil



Minerals in the Soil

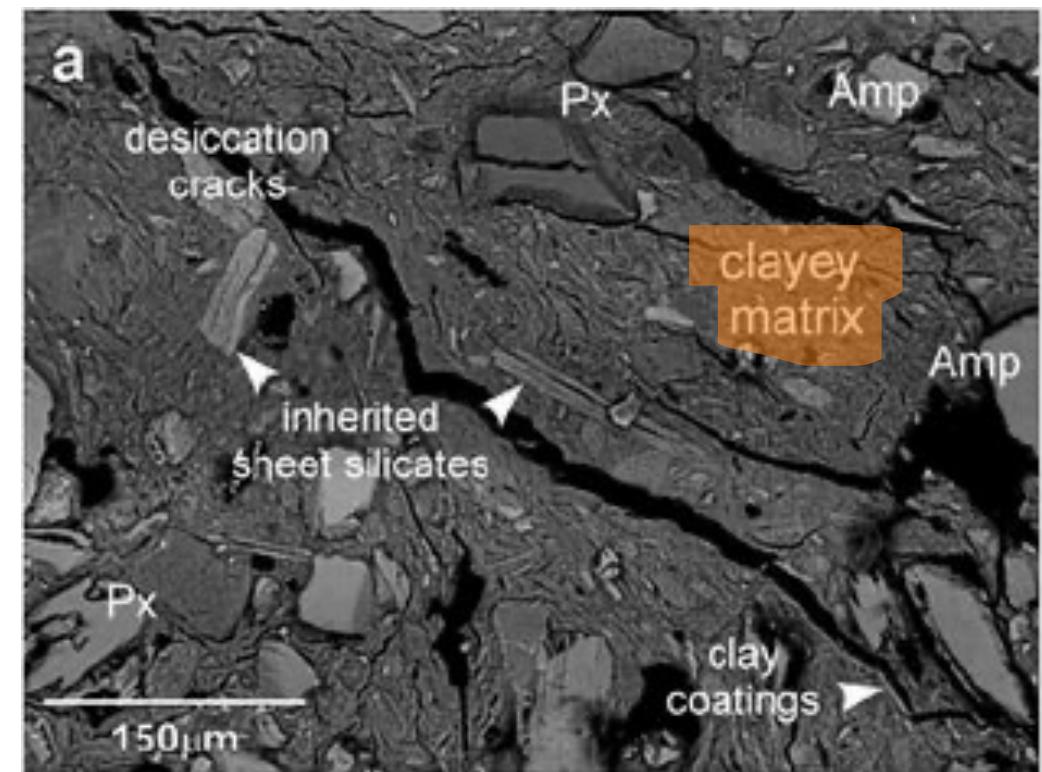


**Sand
40%**

**Silt
40%**

**Clay
10%**

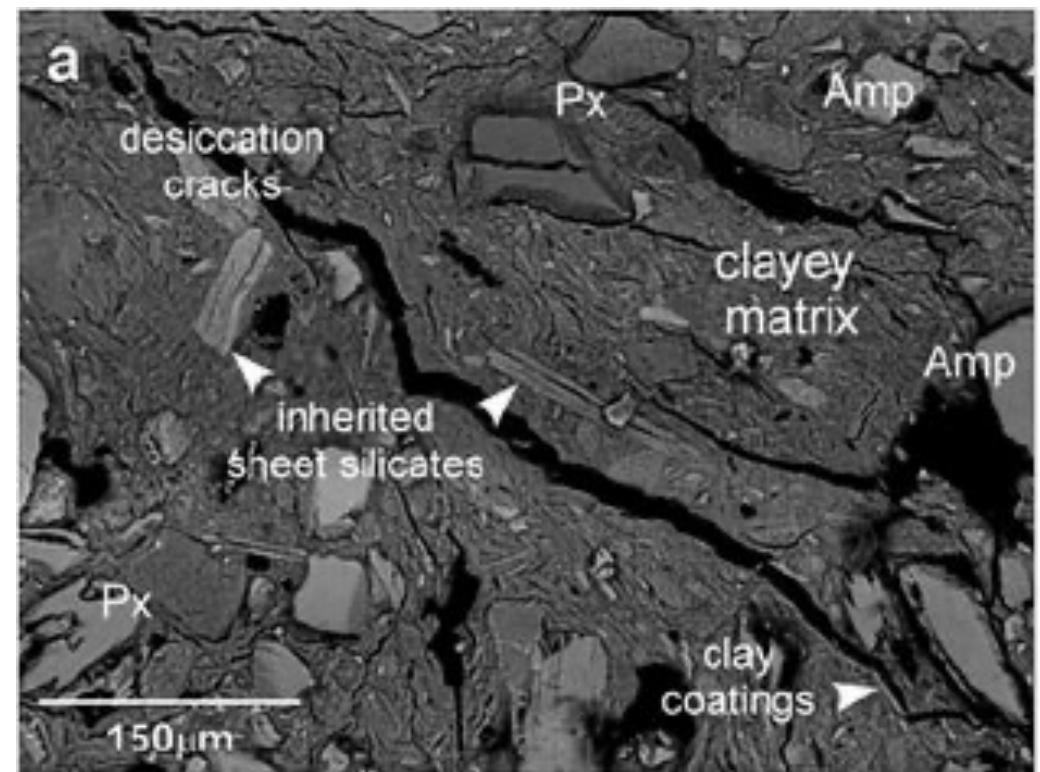
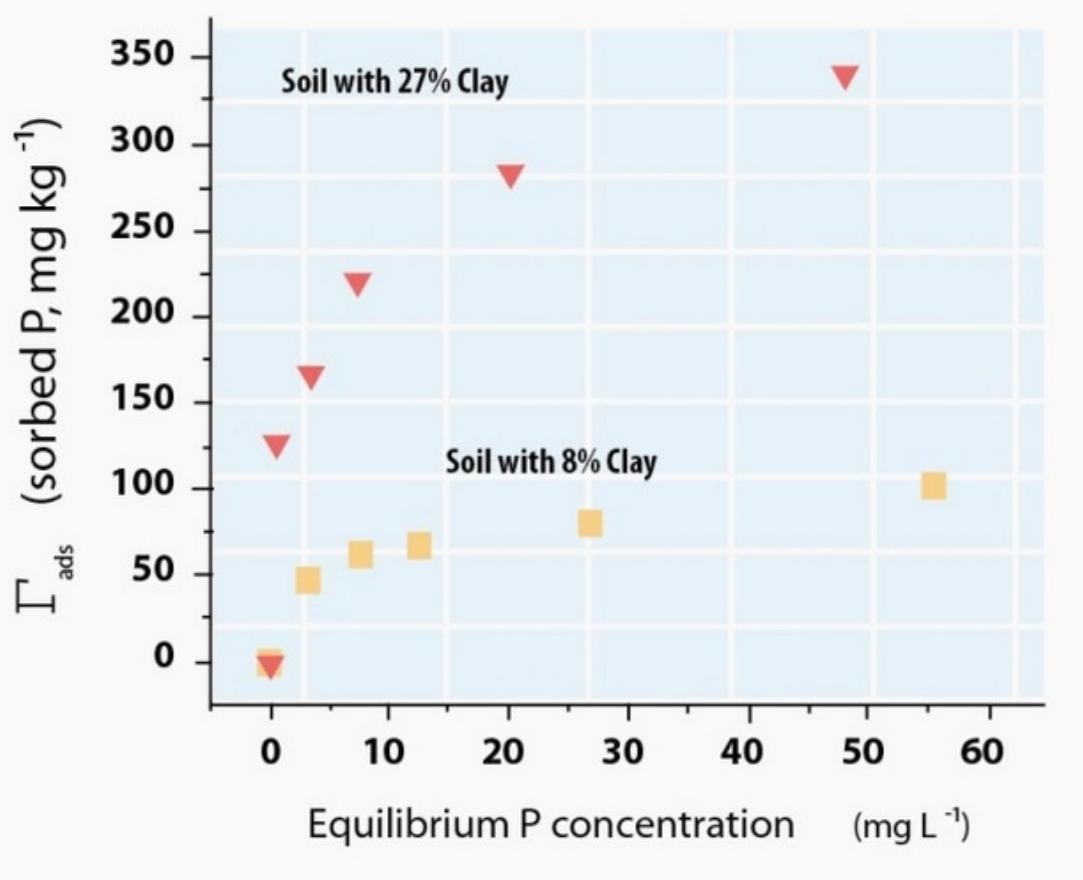
Minerals in the Soil



SEM of a Soil Sample
from [DOI: 10.1127/0935-1221/2011/0023-2084](https://doi.org/10.1127/0935-1221/2011/0023-2084)

Why Clay?

Phosphorus sorption by different soils



SEM of a Soil Sample
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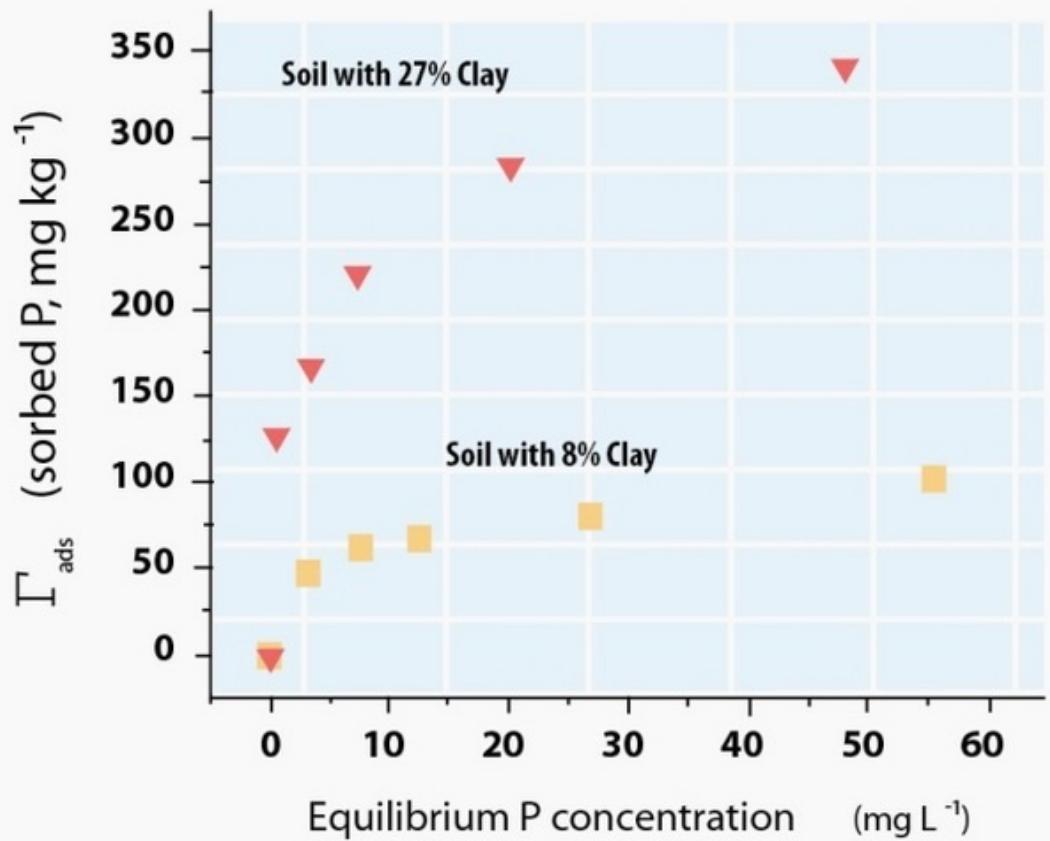
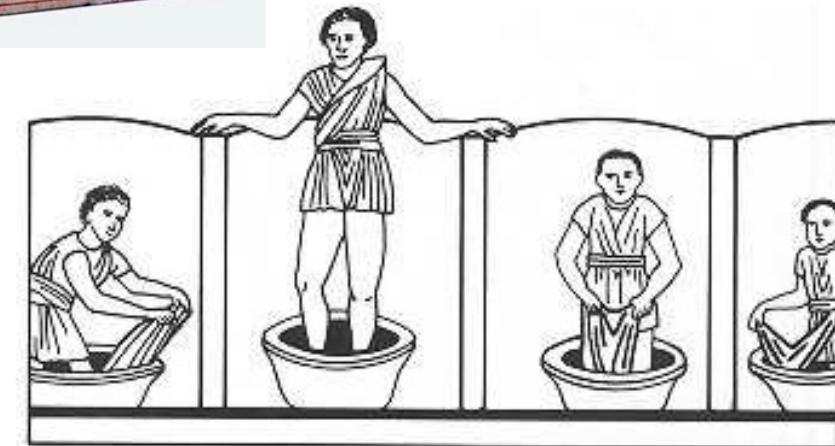


Figure from A Thompson & KW Goyne (2012) *Nature Education Knowledge*



Fuller's Earth or Bleaching Earth
pre-3000 BC
Mesopotamia, Egypt & Greece



A fuller treading the cloth, others rinsing

Smectite – group of swelling clays
Greek *smectis* (fuller's earth) and *smechein* (wipe off, clean)

Read more: K Beneke & G Lagaly (2002). From Fuller's earth to bleaching earth: a historical note. *ECGA Newsletter*, 5

What is Smectite?

Clays have a variety of sorption behaviors for many components, all driven by their atomic-level structures

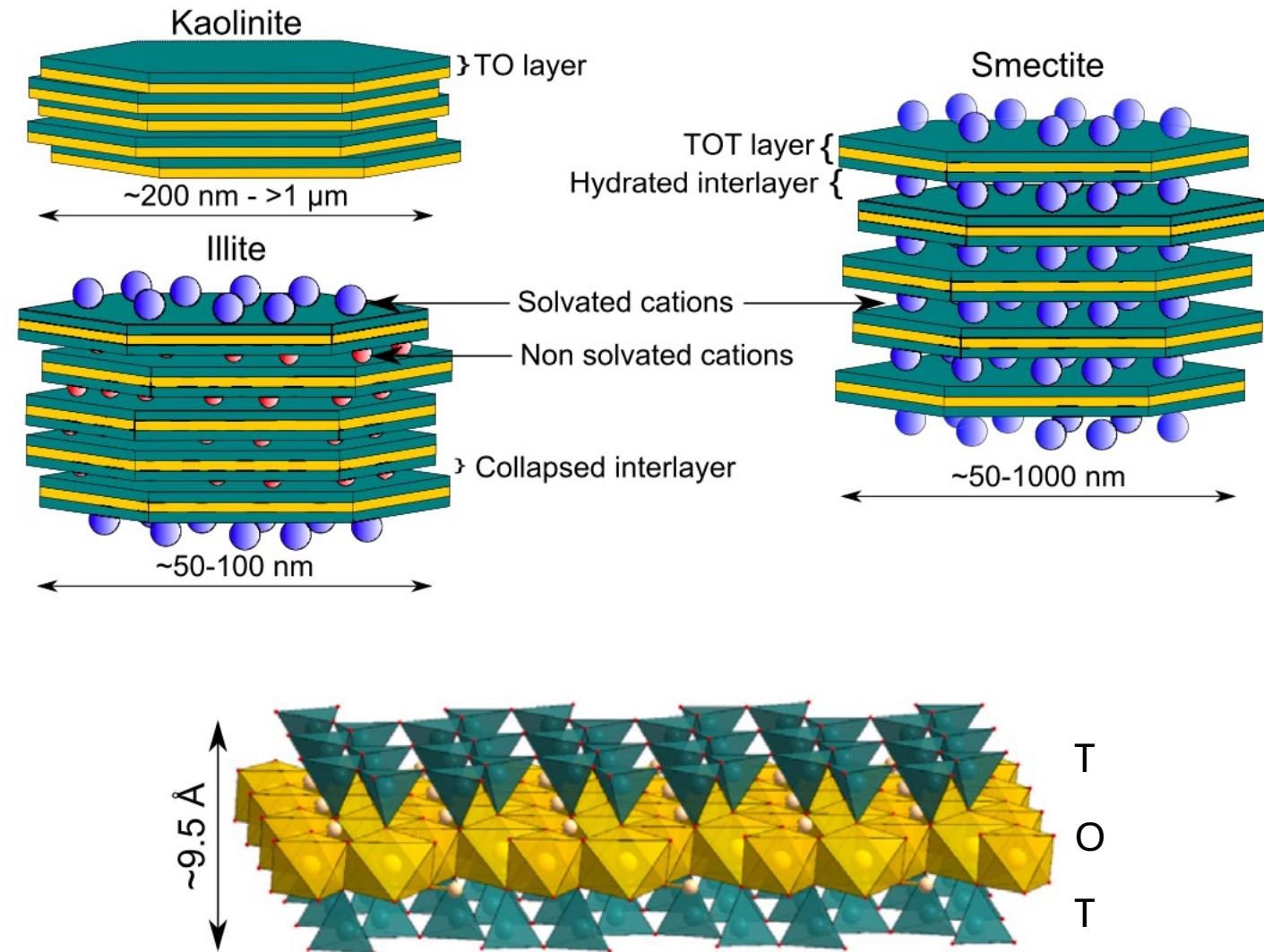
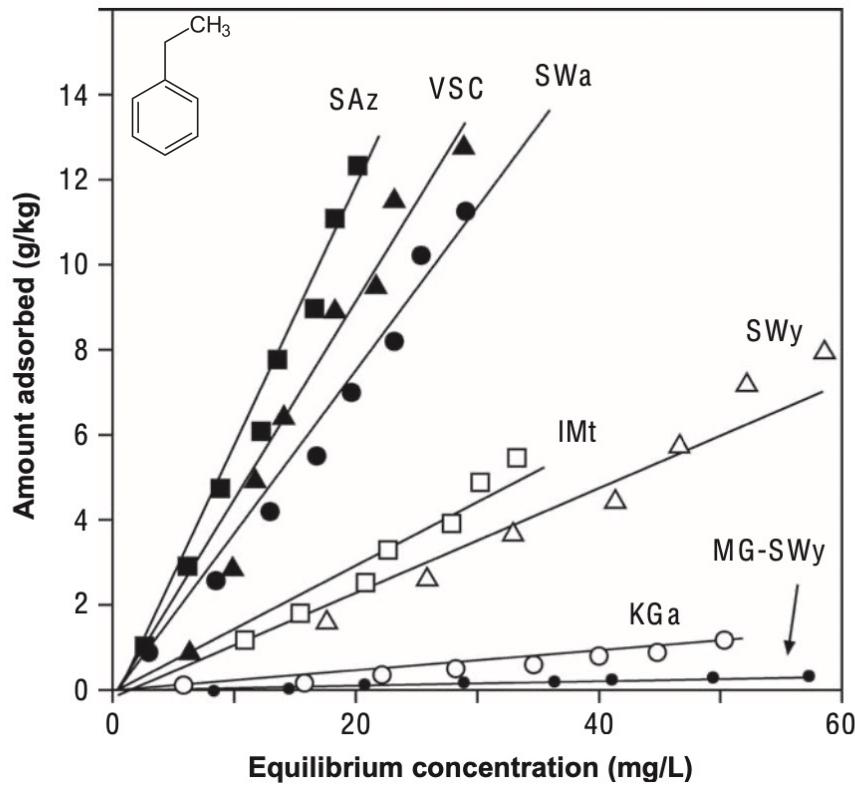
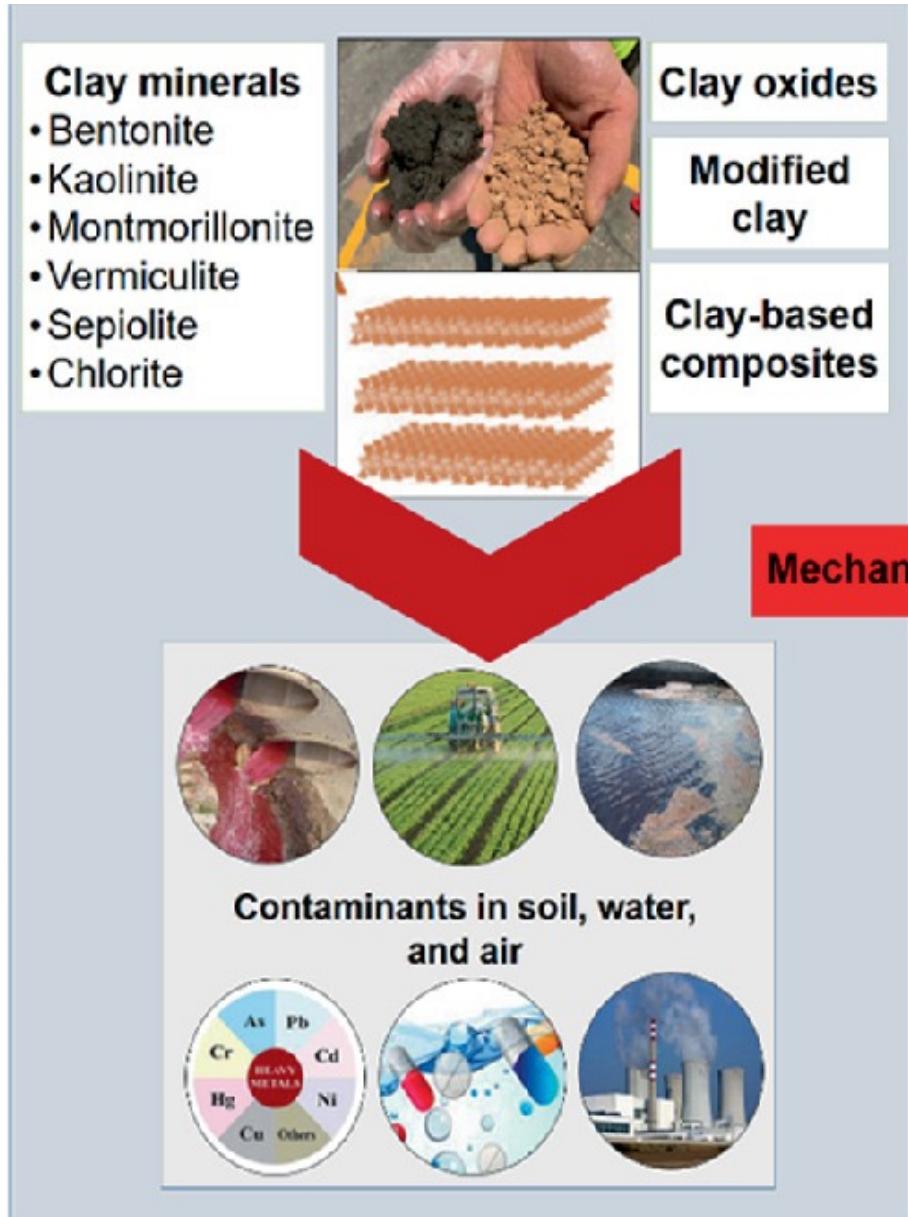


Figure from Jaynes & Boyd (1991). Soil Sci. Soc. Am. J. 55

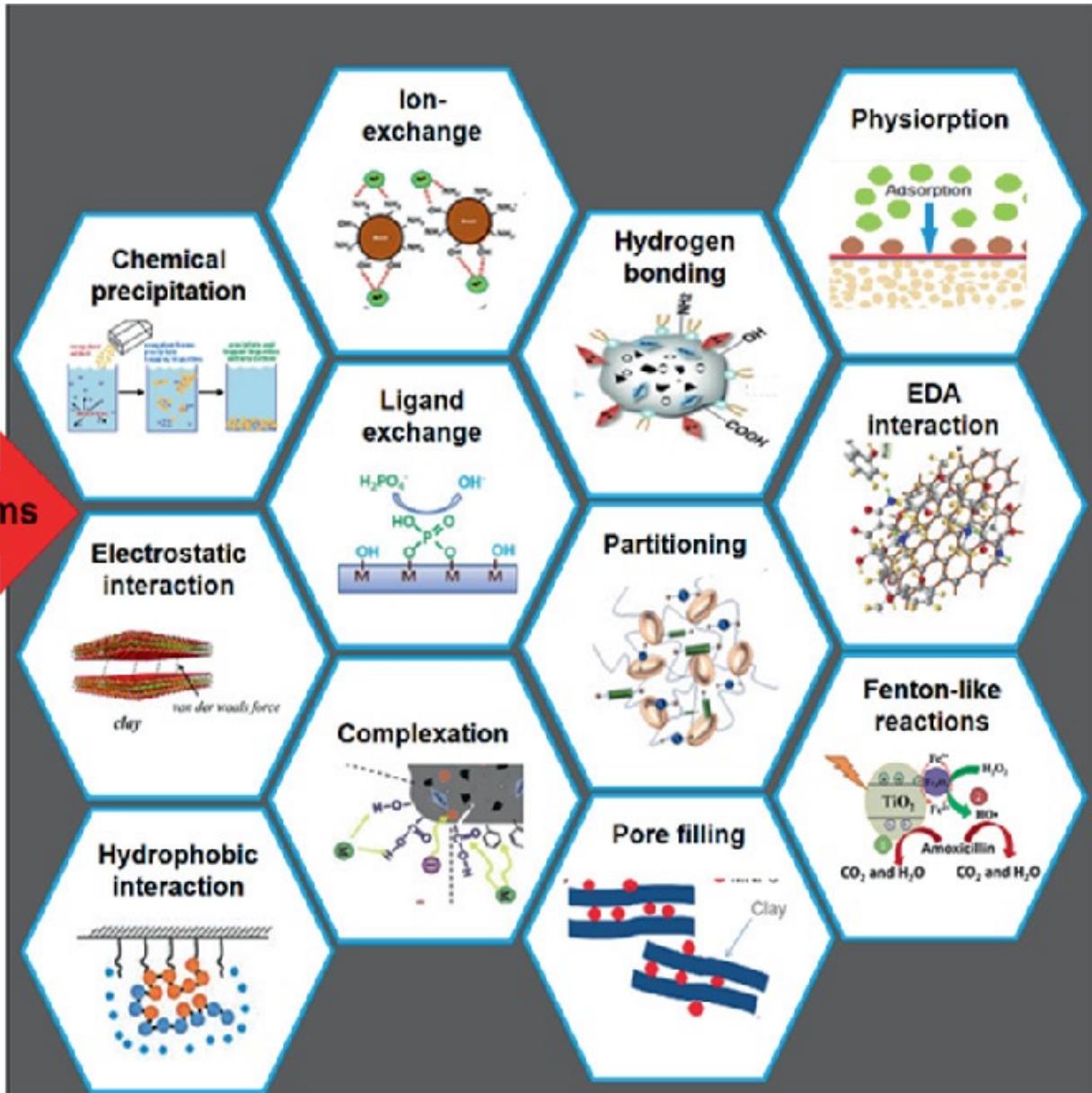
Figure from Developments in Clay Science, Vol. 6C. DOI: 10.1016/B978-0-08-100027-4.00001-2

Clay minerals for pollution management:

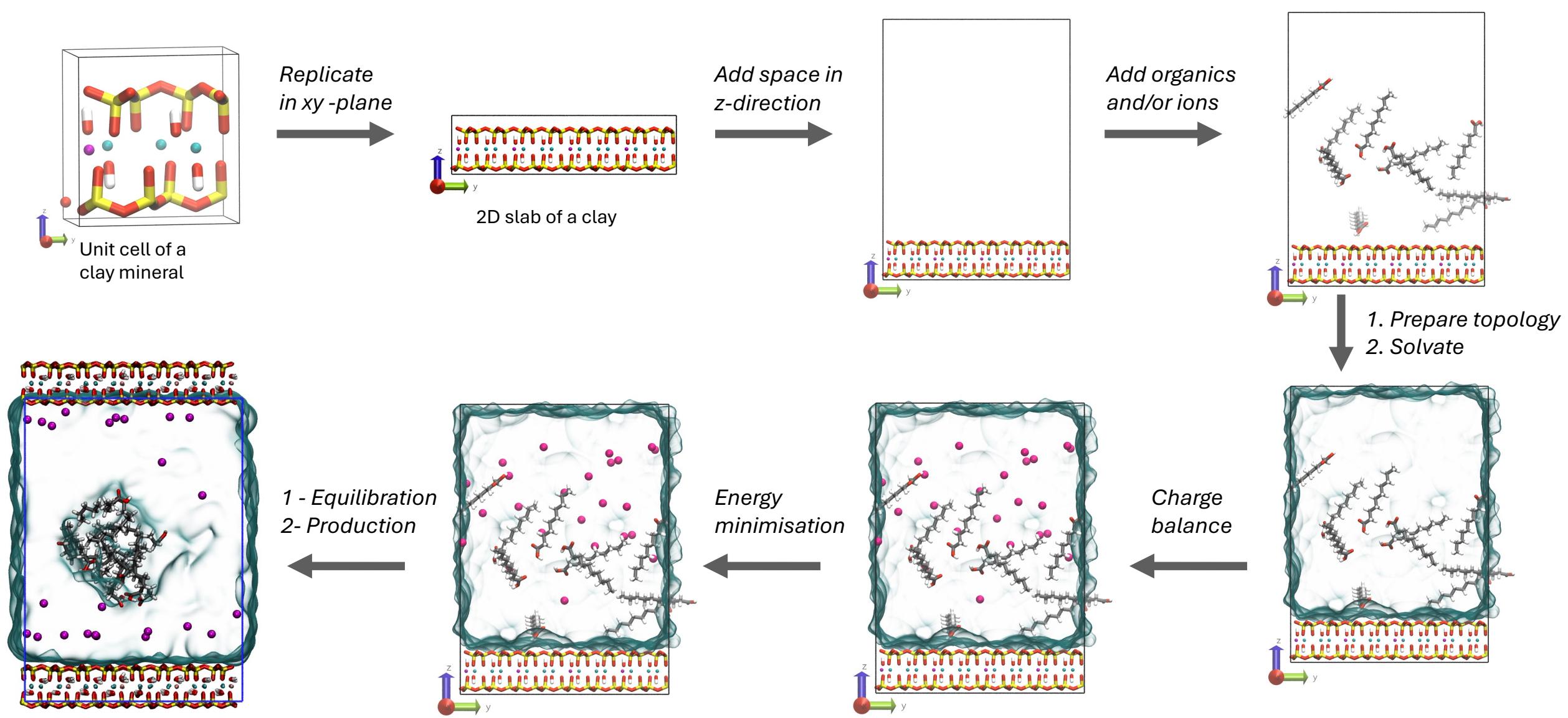
Advanced modifications, composites, nanobased material
Low cost
Abundant
Easy to dispose
Recyclable



Mechanisms



How do I start modeling clay mineral system?



$$\delta_t^2 = \delta_d^2 +$$

δ_{sol} - dispersive
 δ_p - polar
 δ_n - hydrogen

Solvent performance

$$R_a^2 = 4(\delta_d^{\text{sol}} -$$



Questions?

