

# Computational Techniques in Chemistry

## Session 3: Molecular simulation of a layered materials system

Valentina Erastova

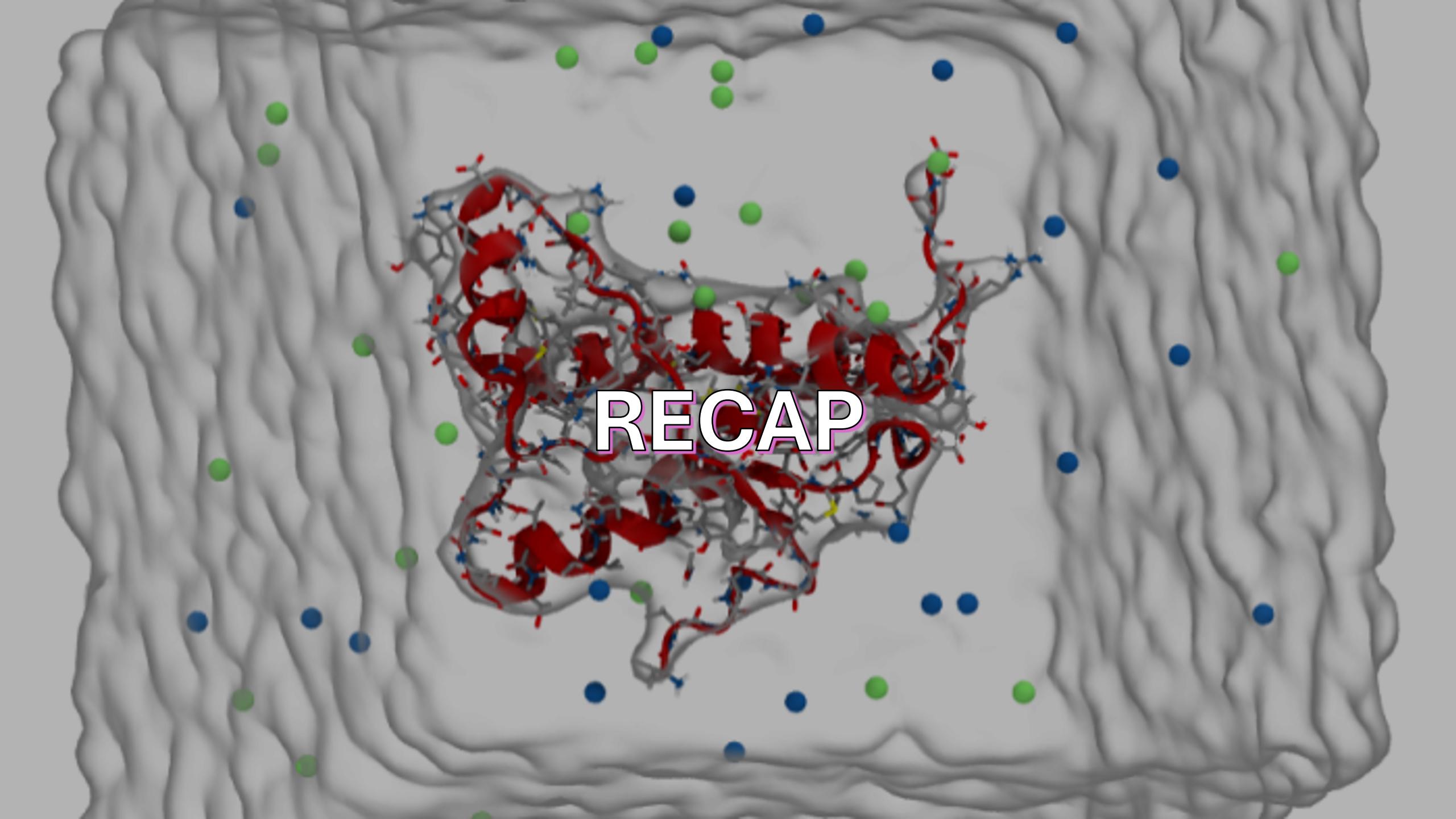
University of Edinburgh

January 2025

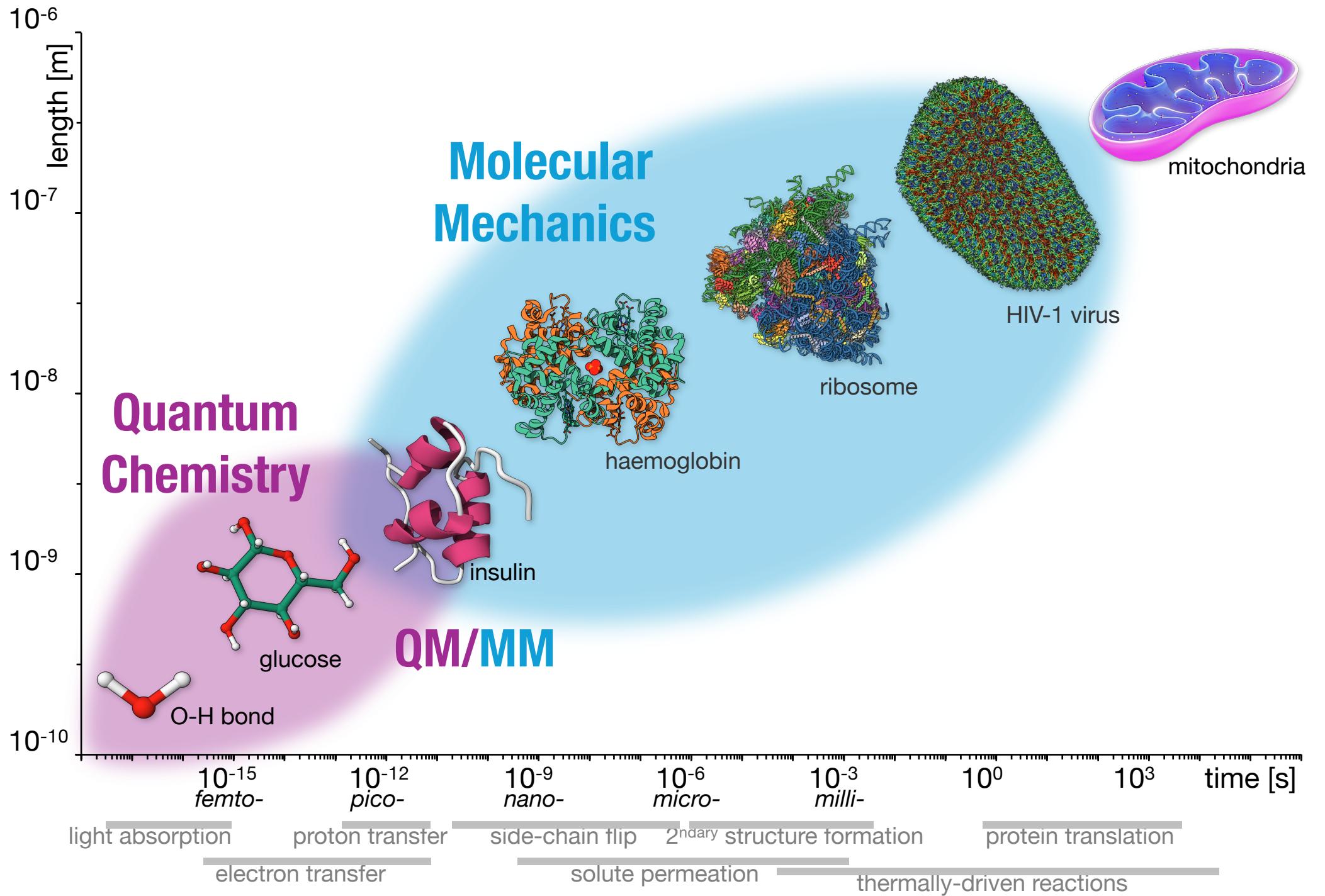
Big thanks to Matteo Degiacomi ([matteo.degiacomi@ed.ac.uk](mailto:matteo.degiacomi@ed.ac.uk)) and Hannah Pollak ([h.pollak@sms.ed.ac.uk](mailto:h.pollak@sms.ed.ac.uk)) for material development



THE UNIVERSITY of EDINBURGH  
School of Chemistry



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-

10<sup>0</sup>10<sup>3</sup>

time [s]

light absorption

proton transfer

side-chain flip

2<sup>nd</sup>ary structure formation

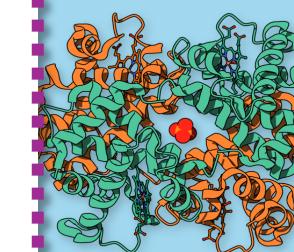
protein translation

electron transfer

solute permeation

thermally-driven reactions

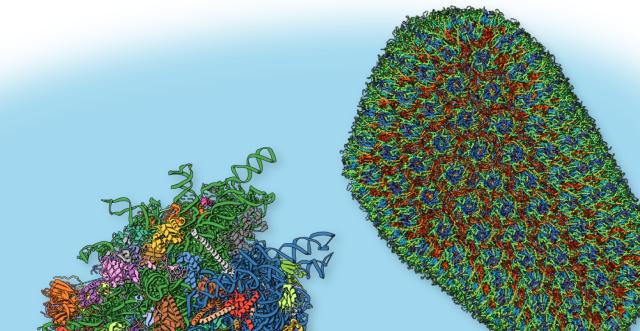
## Molecular mechanics



haemoglobin



ribosome

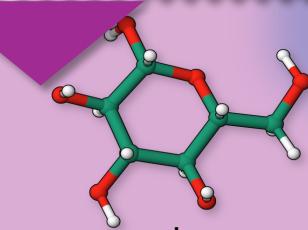


HIV-1 virus



mitochondria

## QM/MM



glucose



insulin

O-H bond

## Newtonian Mechanics

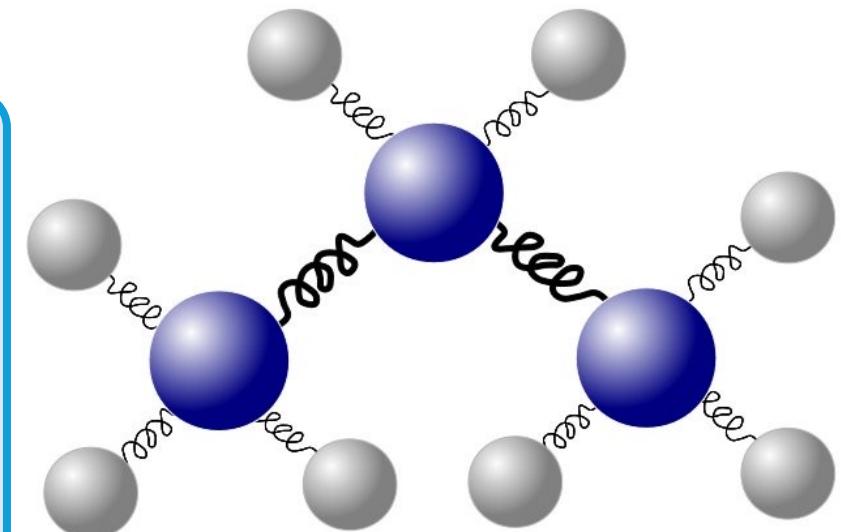
Each atom is a bead, connected by a spring  
 ~100k of atoms, ns -  $\mu$ s

# Force Field Methods

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

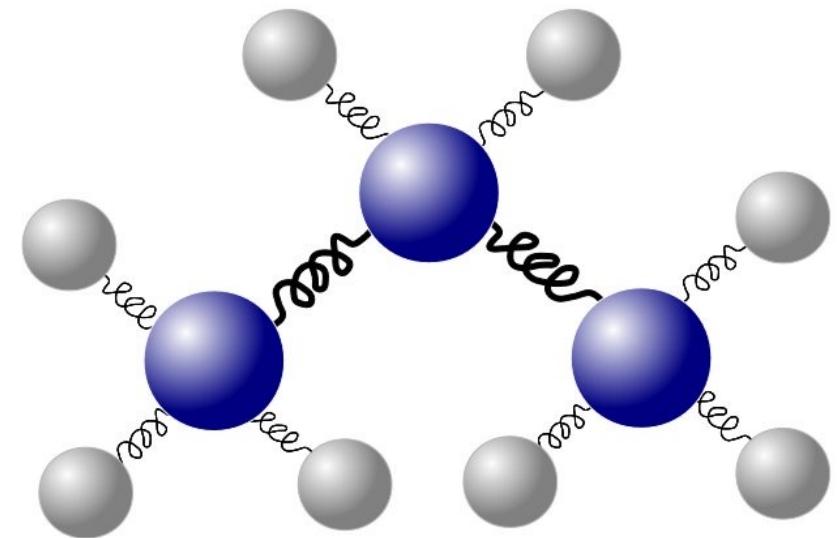
## ASSUMPTIONS:

- 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

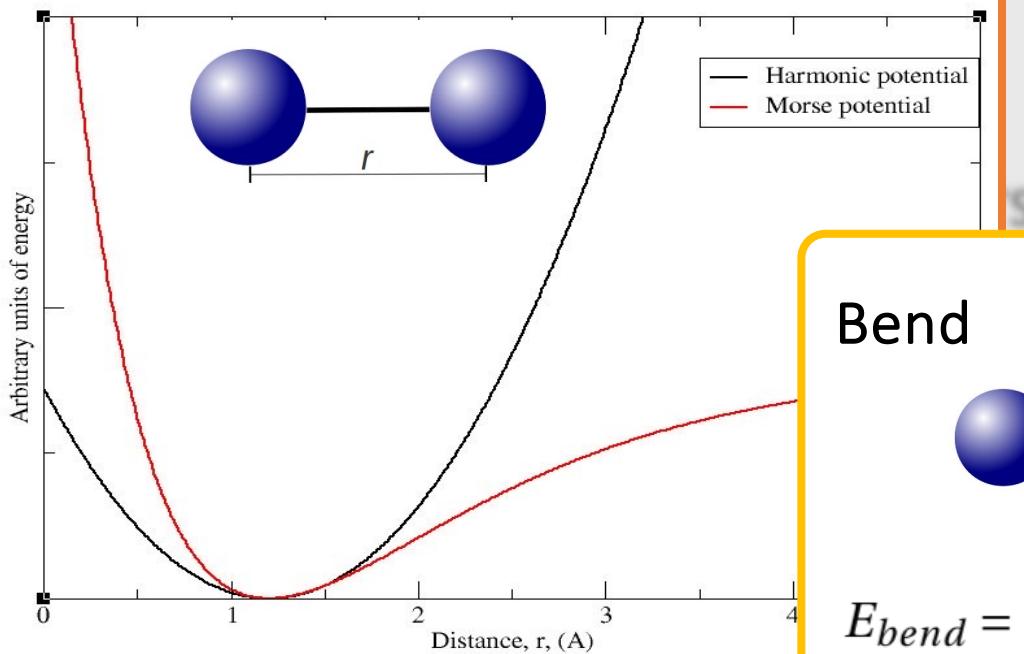
**Force Field** - set of parameters used in classical mechanical calculations

**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 a horizontal line. A bracket under the first four terms ( $E_{str}, E_{bend}, E_{tors}, E_{VdW}$ ) is labeled "bonded". Another bracket under the last term ( $E_{el}$ ) is labeled "non-bonded".

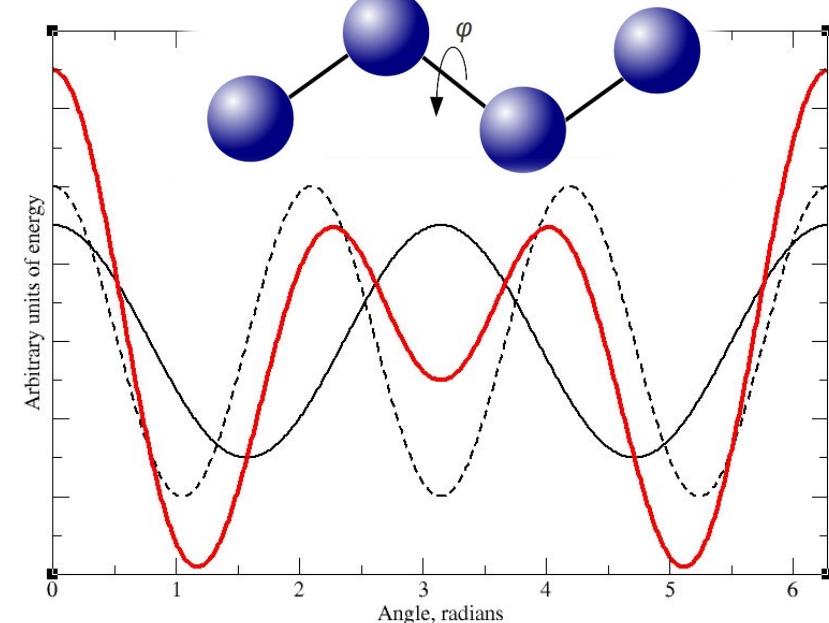
**Bond Stretch**  $E_{str} = \frac{1}{2} k^{AB} (r^{AB} - r_0^{AB})^2$



**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

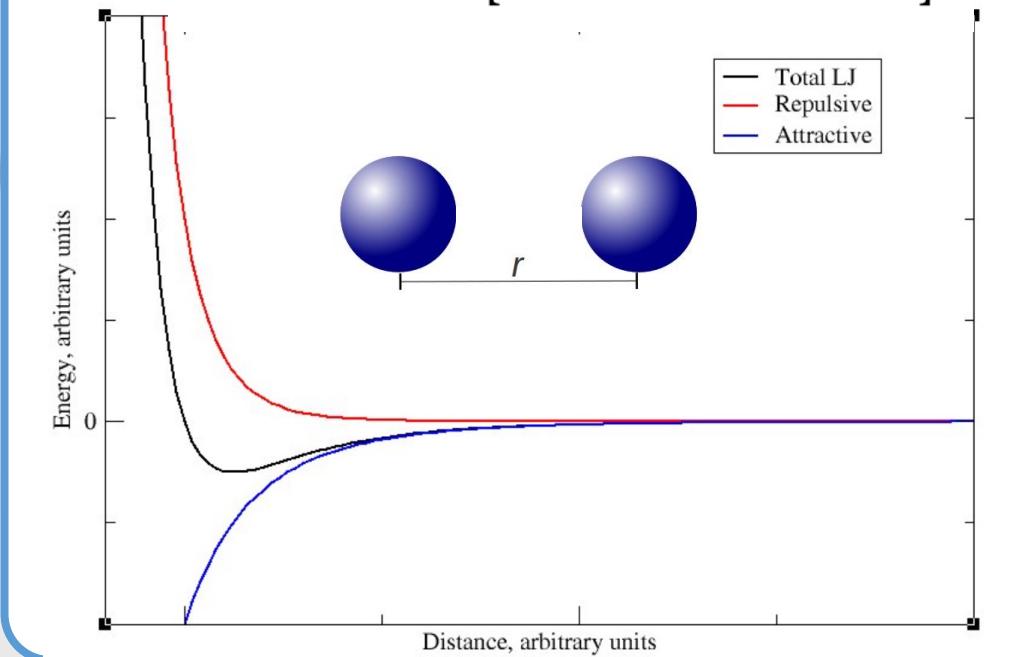
non-bonded

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

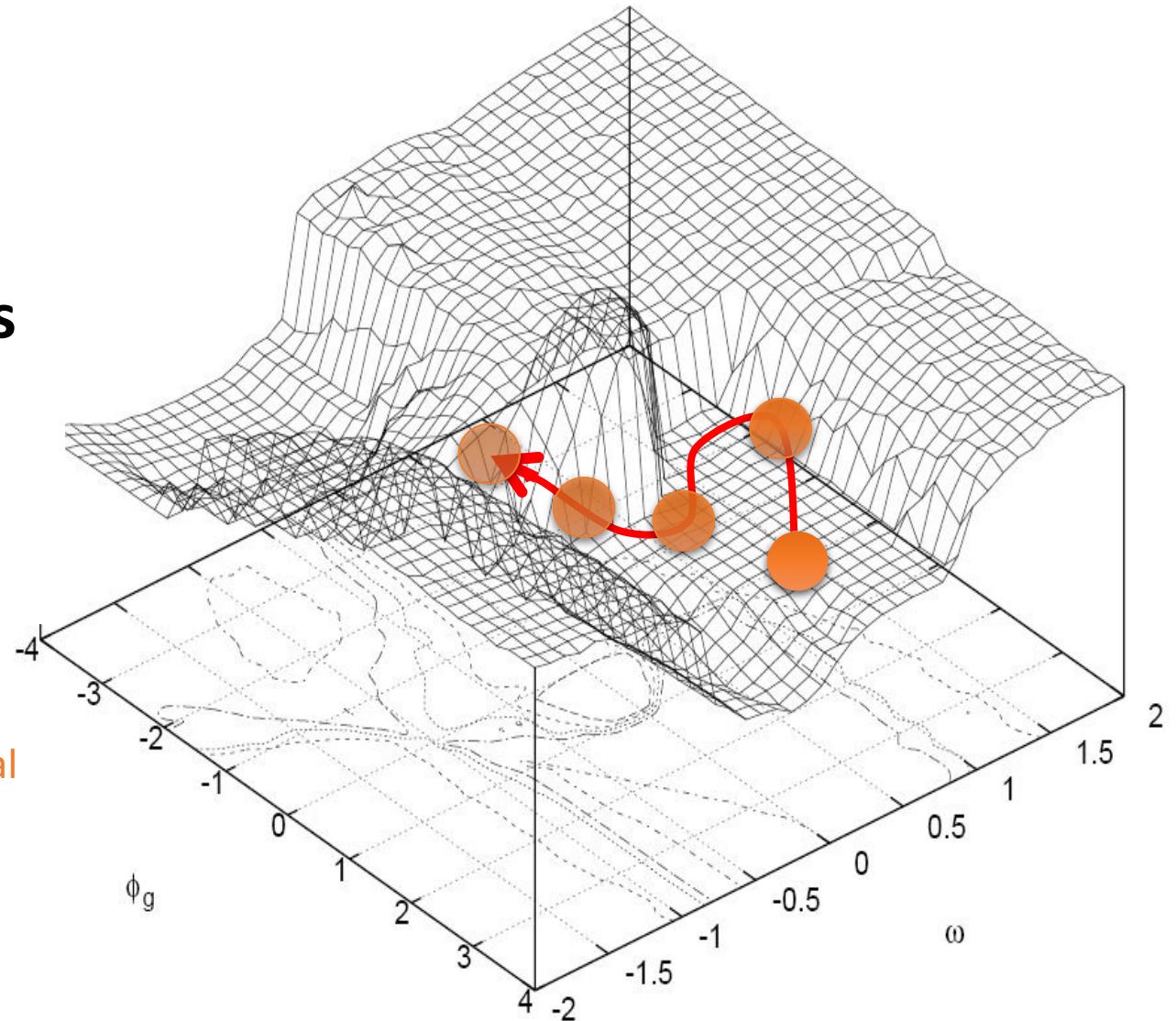
non-bonded

# 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:

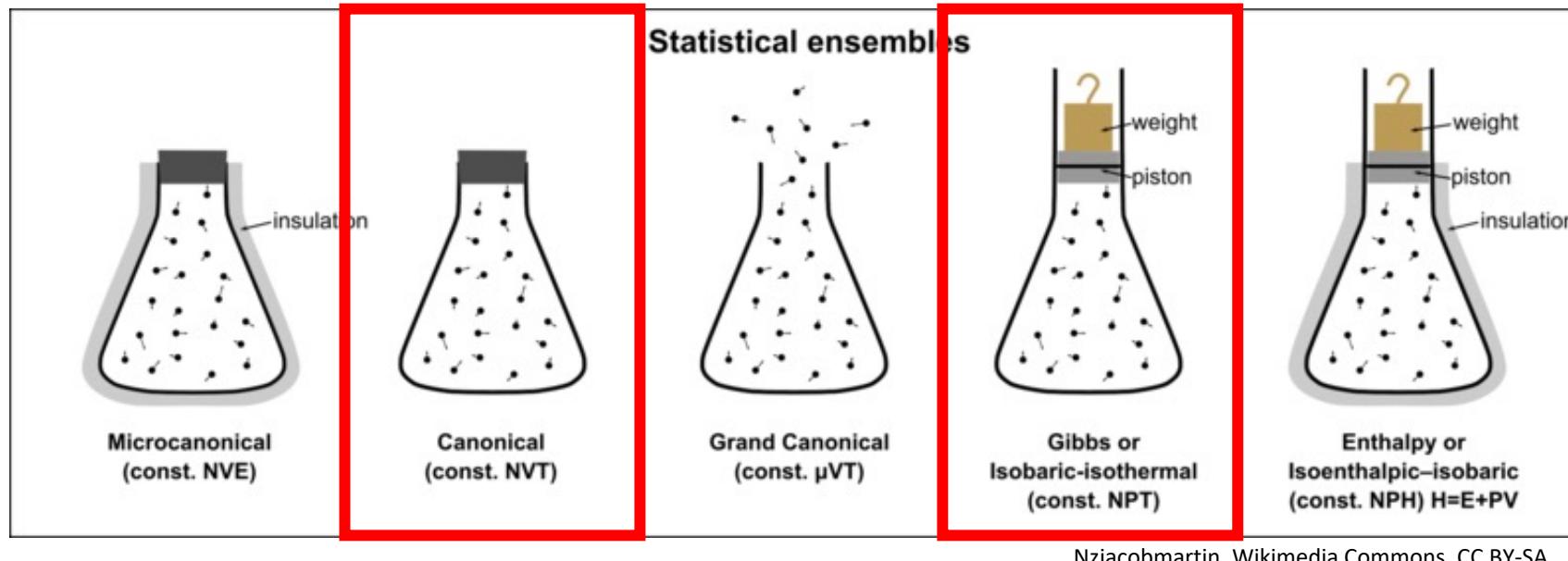
$$\frac{\text{acceleration}}{\text{mass}} = \mathbf{F}_i \quad \mathbf{F}_i = -\frac{\partial E}{\partial \mathbf{r}_i}$$

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

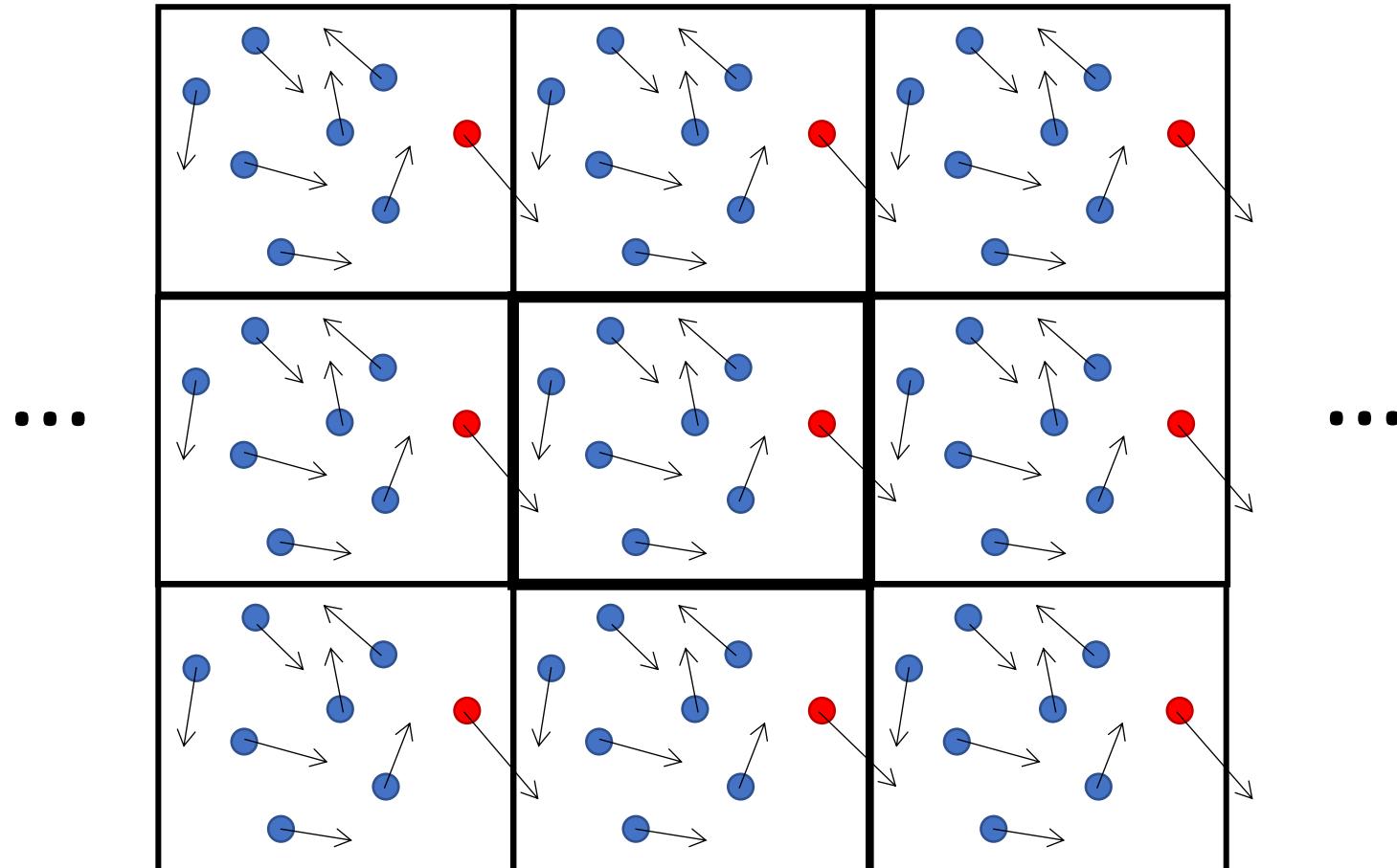
***barostats*** (scaling positions) – constant P

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

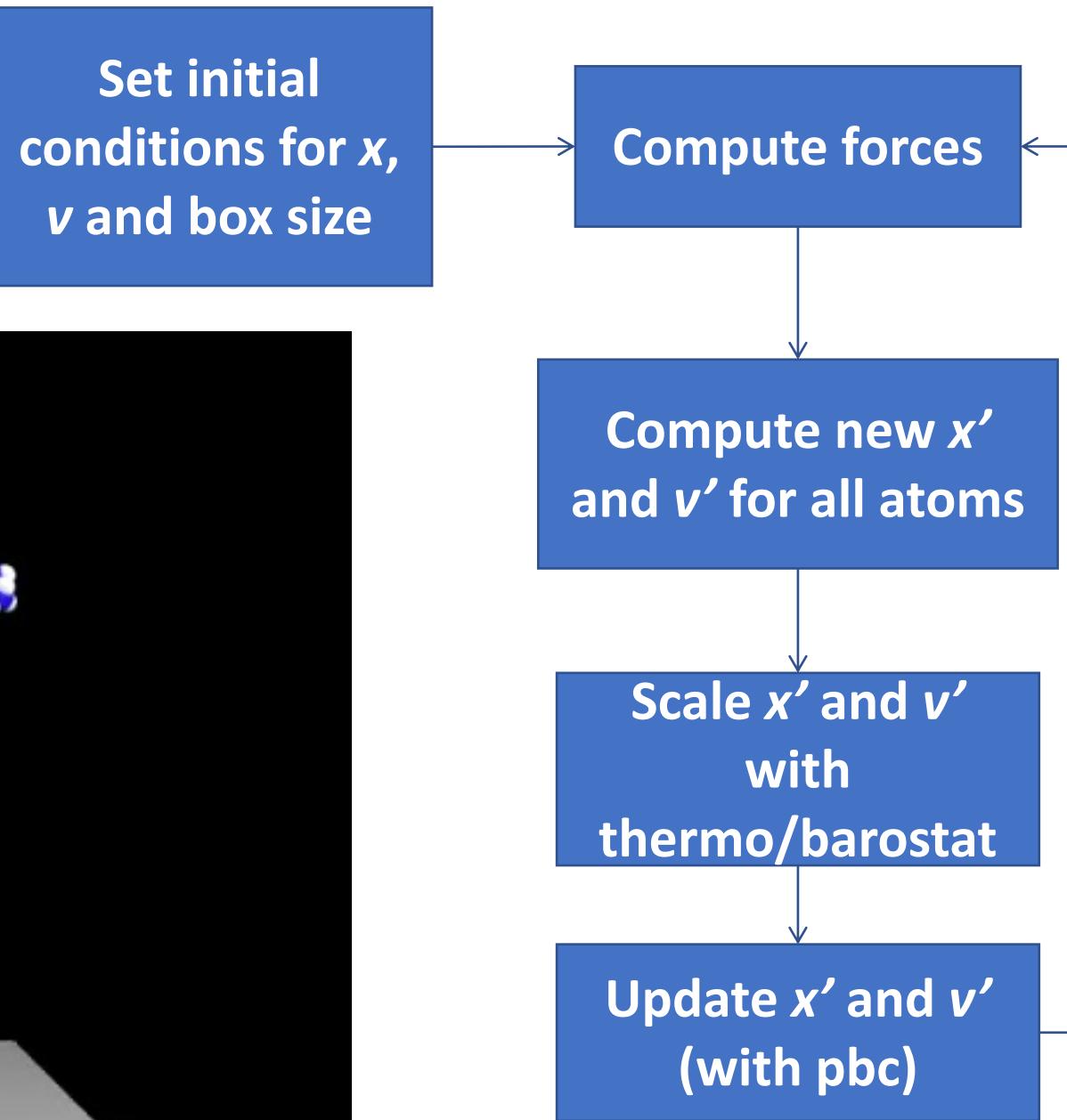
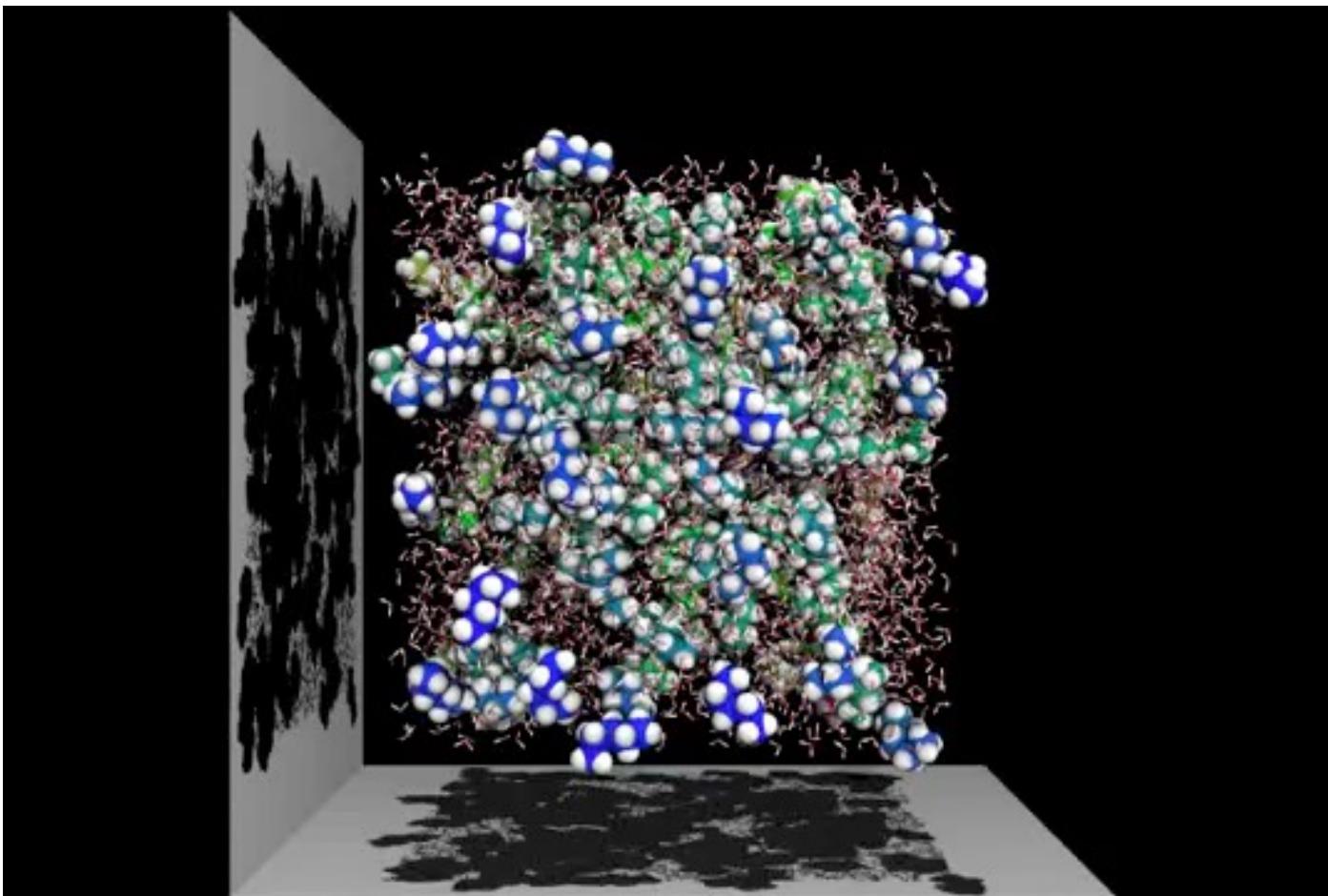
# Is the simulation box finite?

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

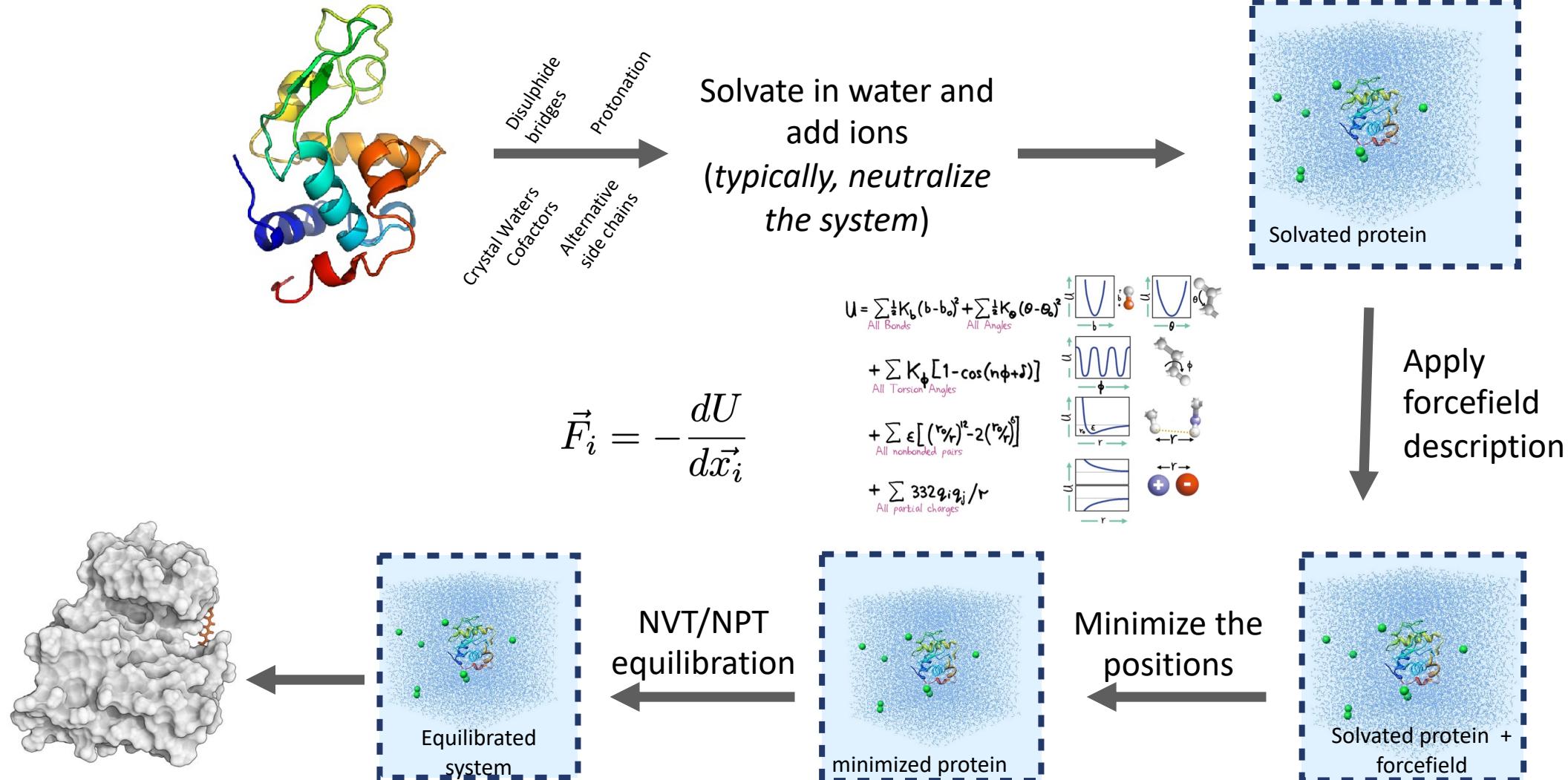
For **boundary effects** use wall, PBC in xy-direction, vacuum in NVT, ...

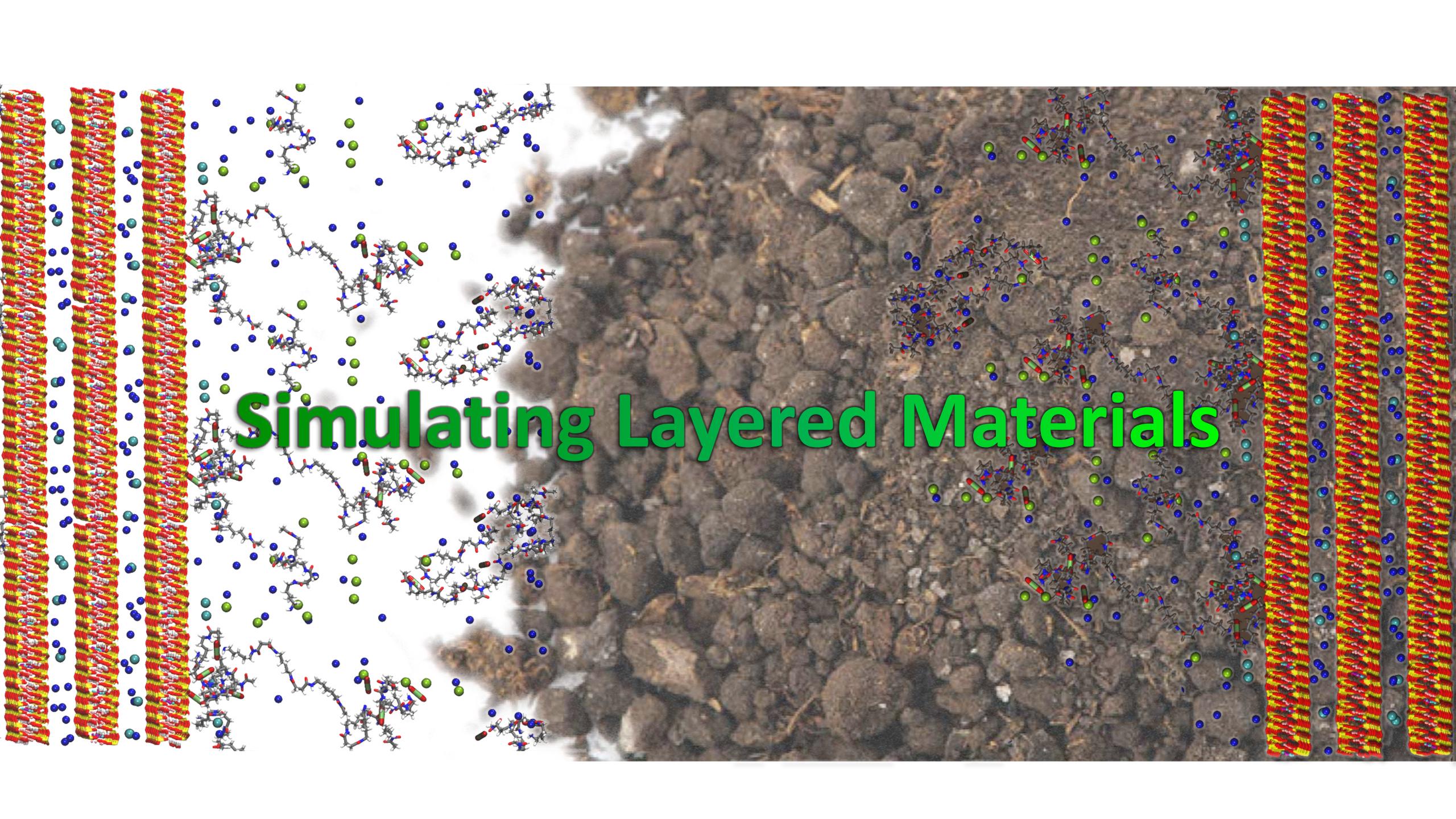


In each simulation timestep...



# Molecular dynamics require multiple steps for the setup of simulations

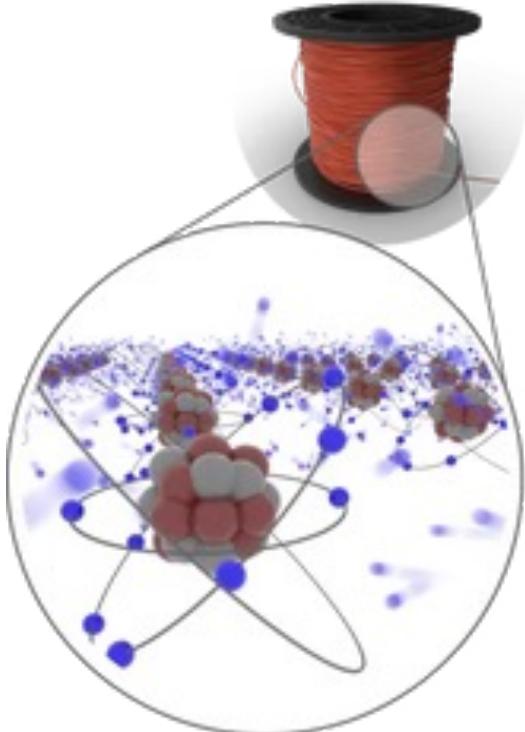




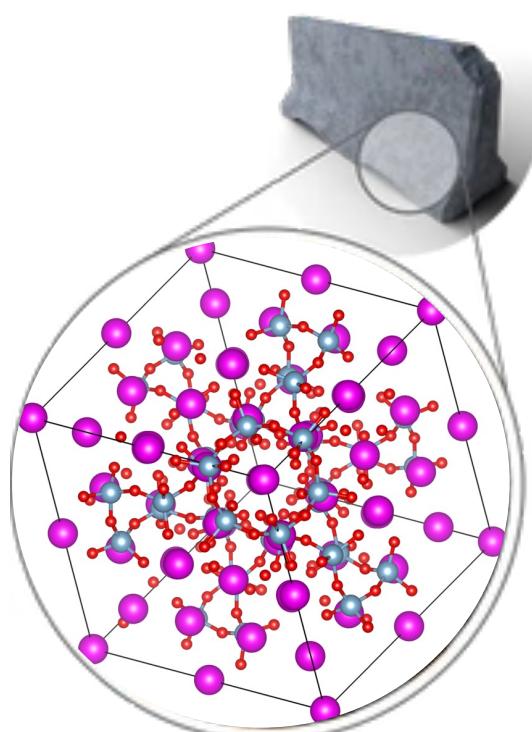
# Simulating Layered Materials

# Materials at the Nanoscale

Electric wire



Concrete wall



Rubber tire



Conducting electricity with free electrons of the metals

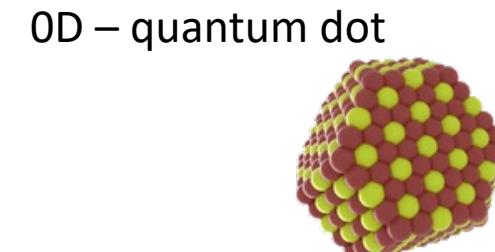
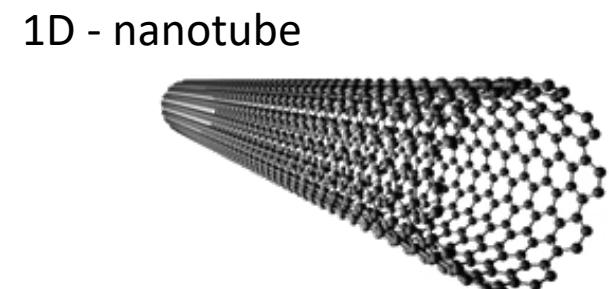
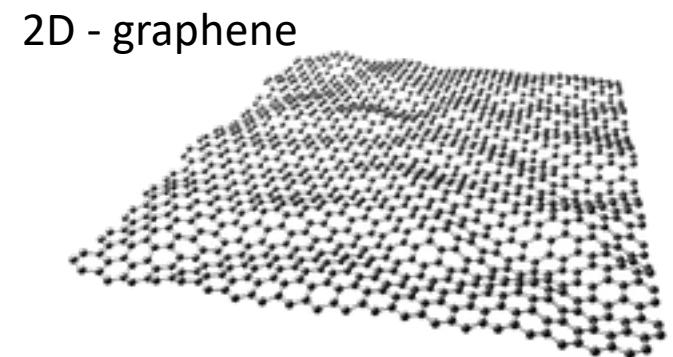
Cement holds together gravel and sand, creating an aggregate material

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

# Dimensionality of materials

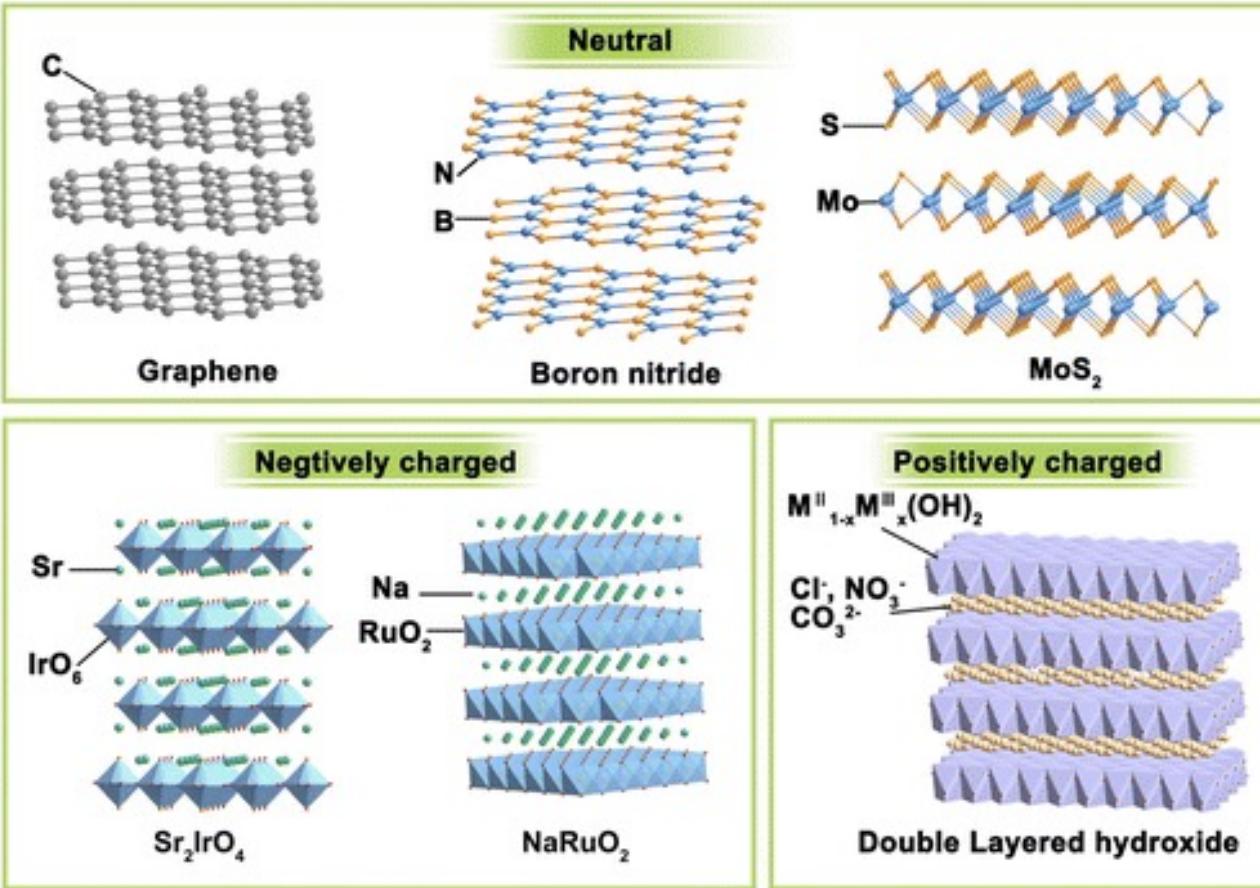
Nanoscopic dimension – where a scale is in nanometers in size, i.e., structure is at an atomic level.

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



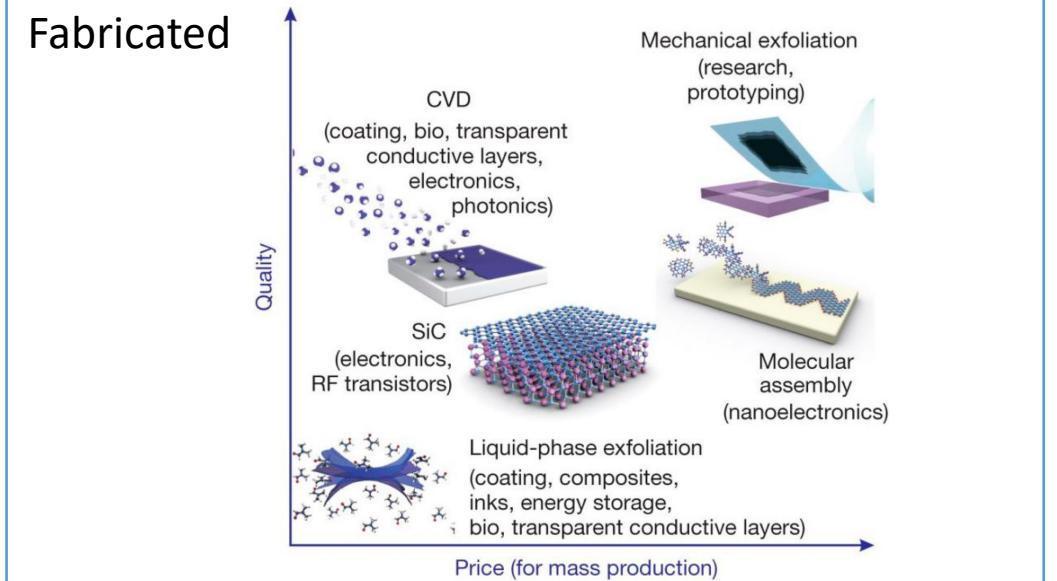
# Why are layered materials of interest?

- *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

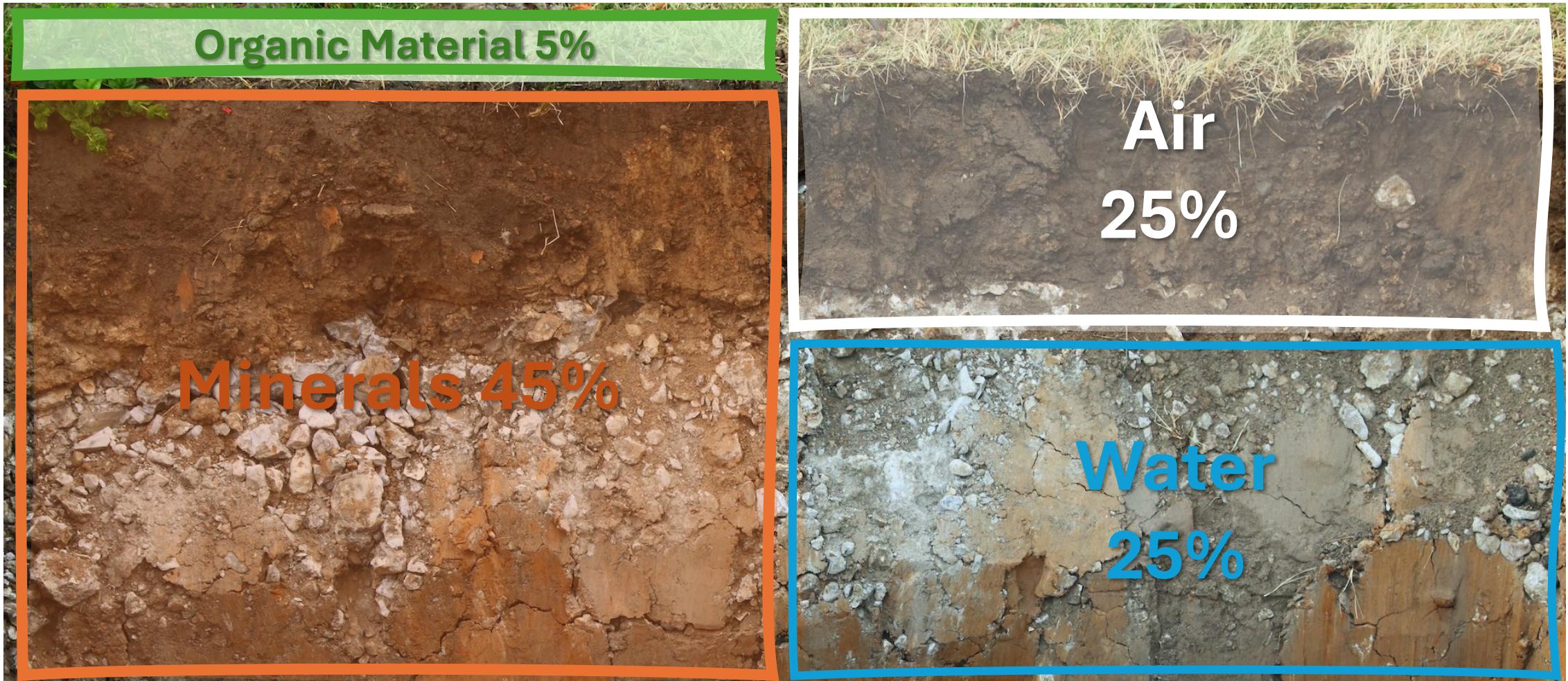


Layered double hydroxide

# The Soil



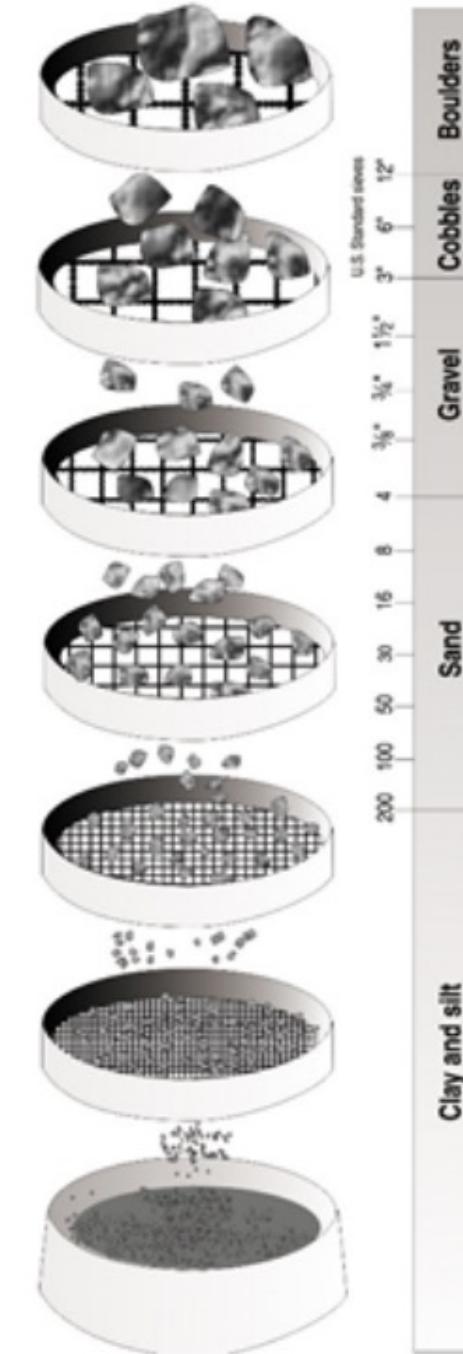
# The Soil



# Minerals in the Soil



# Minerals in the Soil

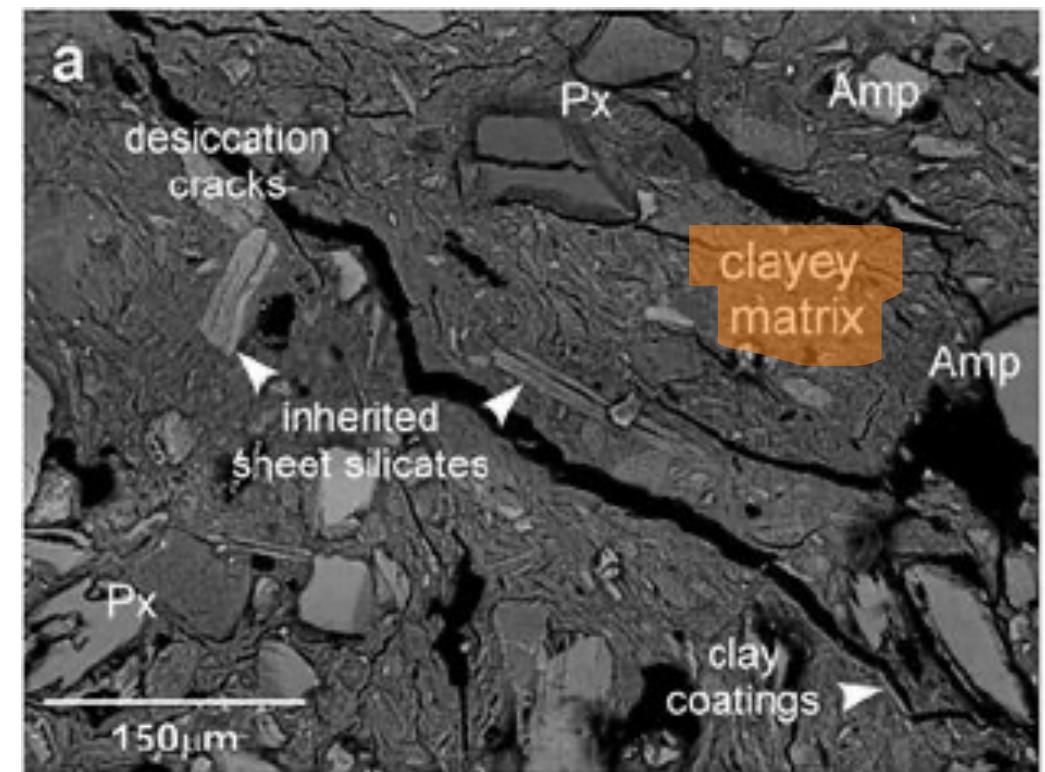


**Sand  
40%**

**Silt  
40%**

**Clay  
10%**

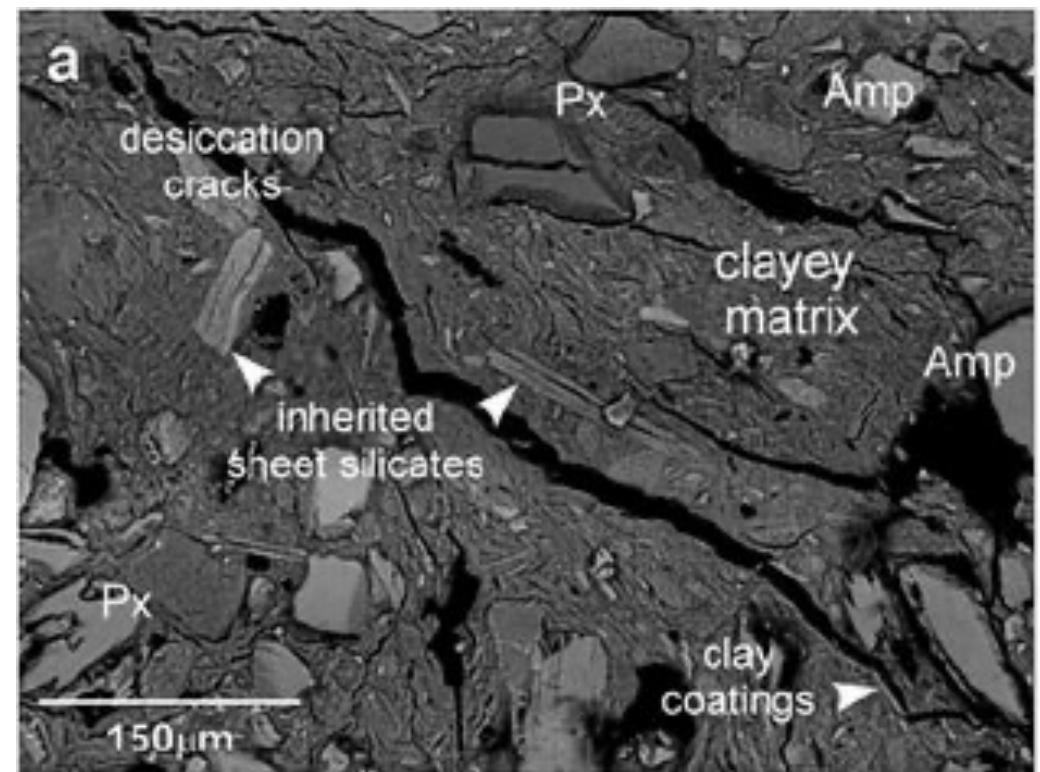
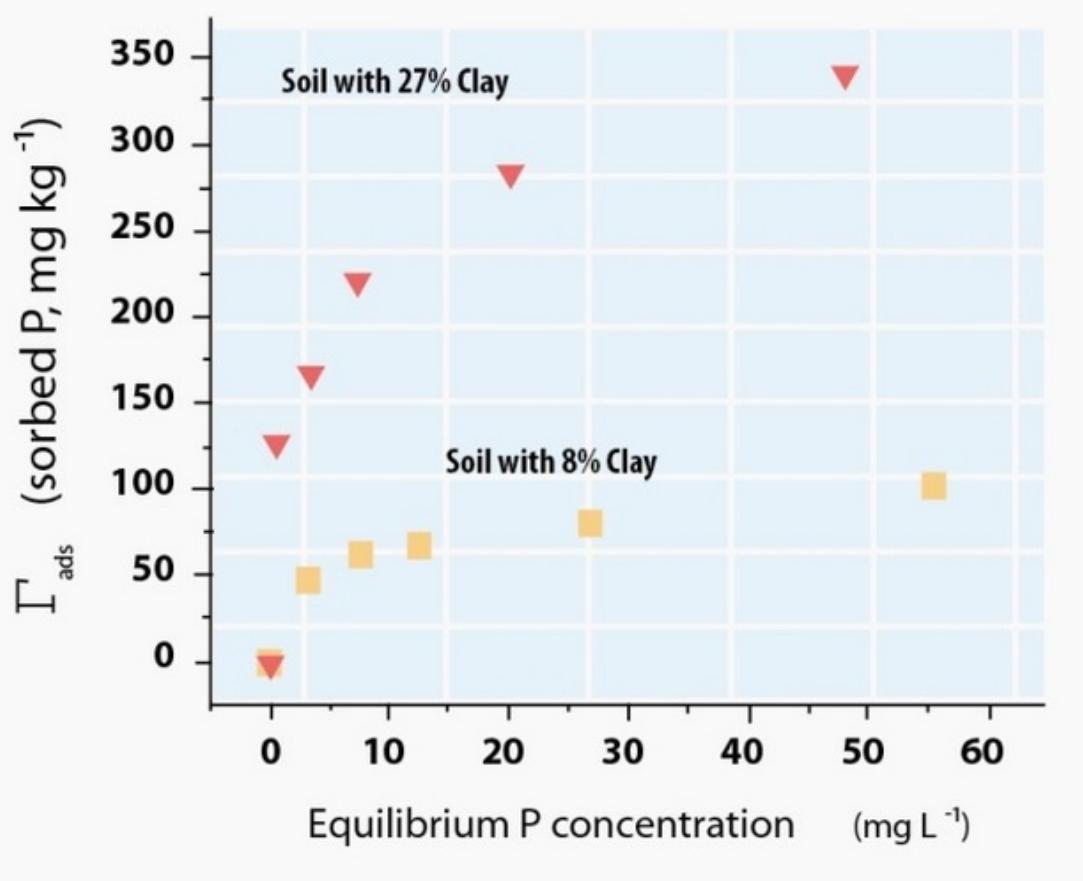
# Minerals in the Soil



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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## Phosphorus sorption by different soils

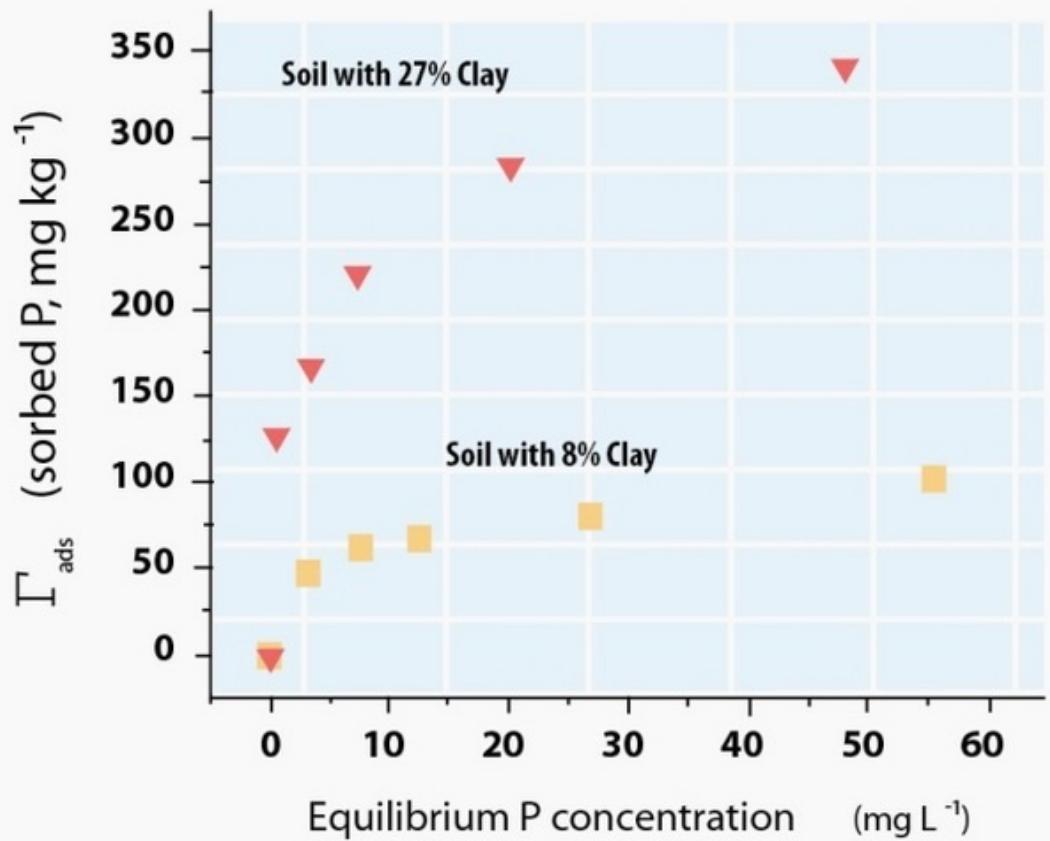
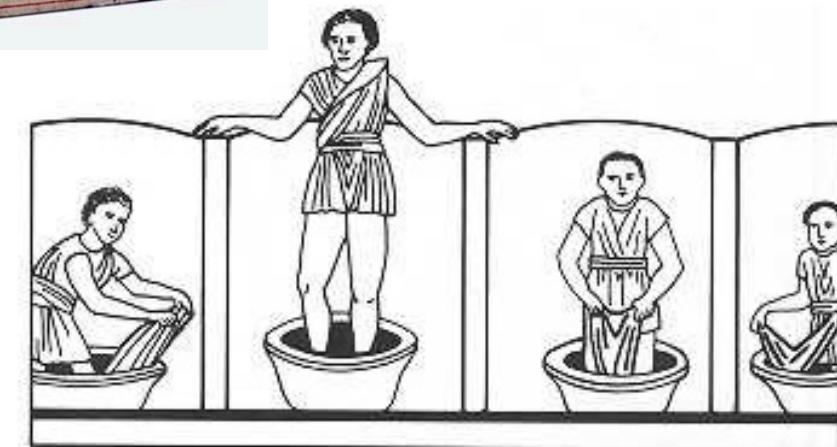


Figure from A Thompson & KW Goyne (2012) *Nature Education Knowledge*



**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

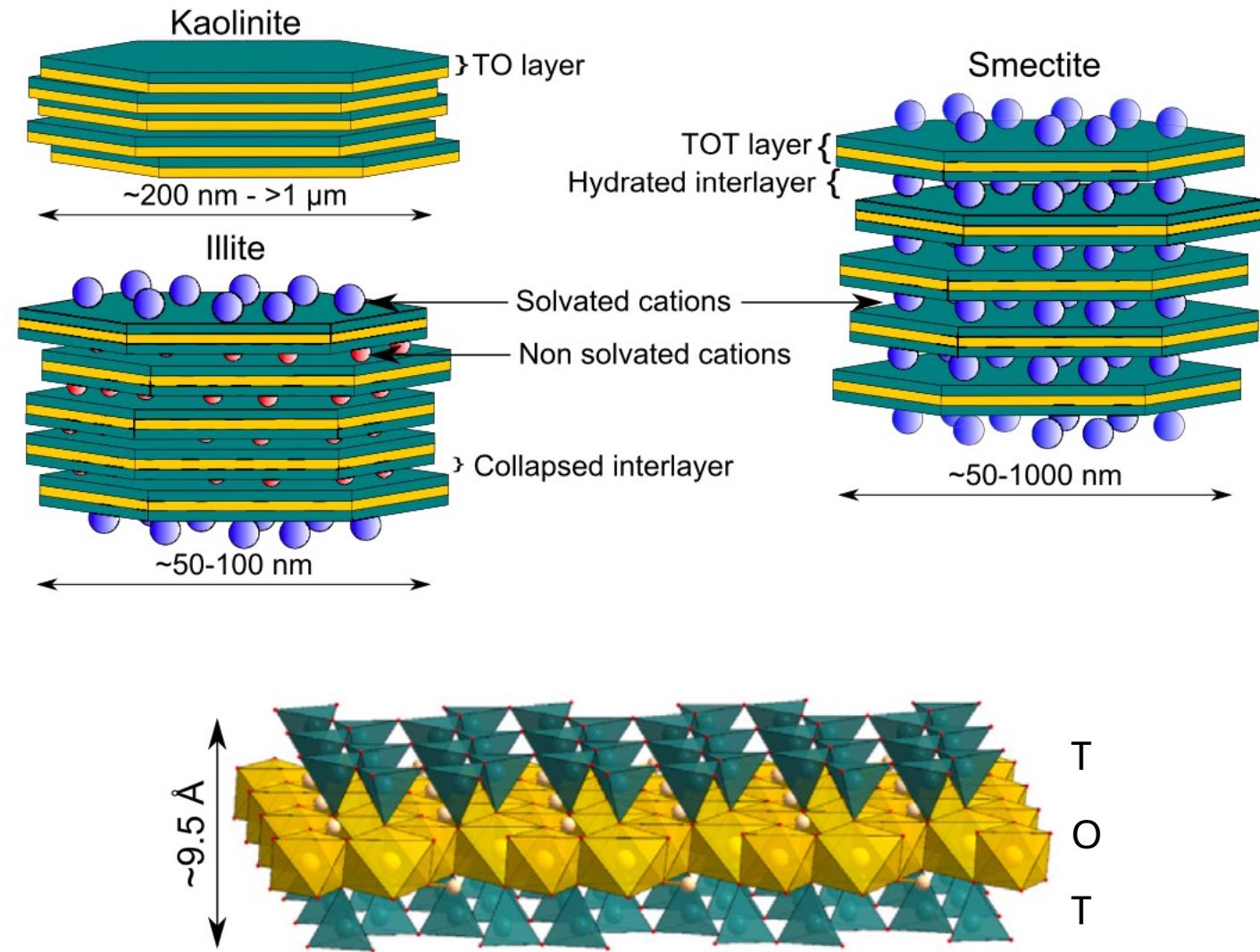
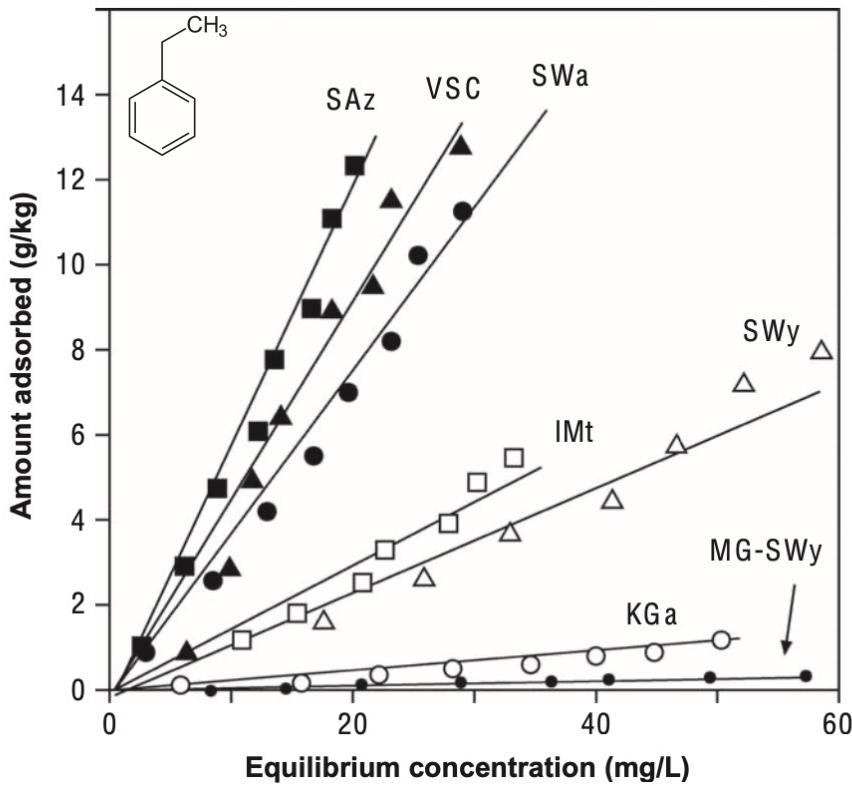
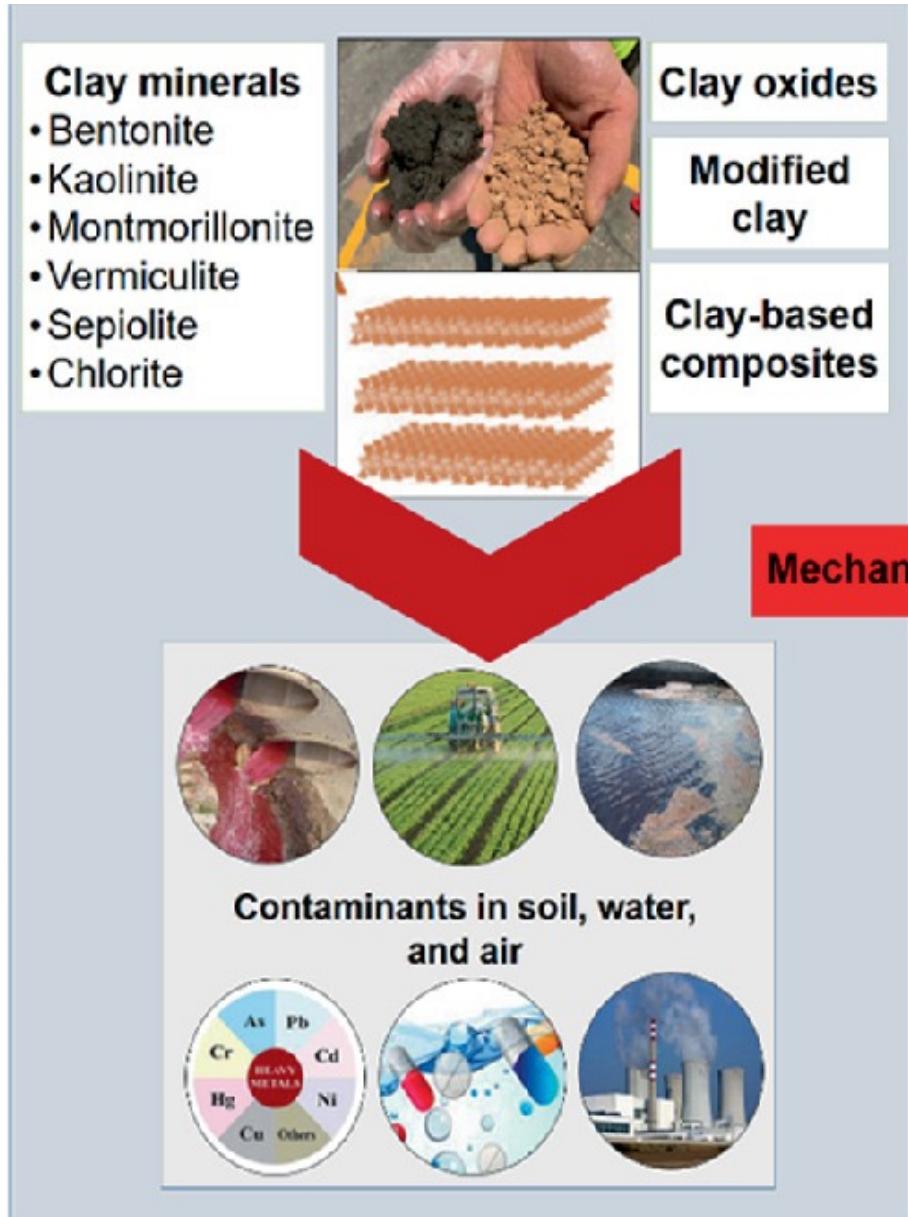


Figure from Jaynes & Boyd (1991). Soil Sci. Soc. Am. J. 55

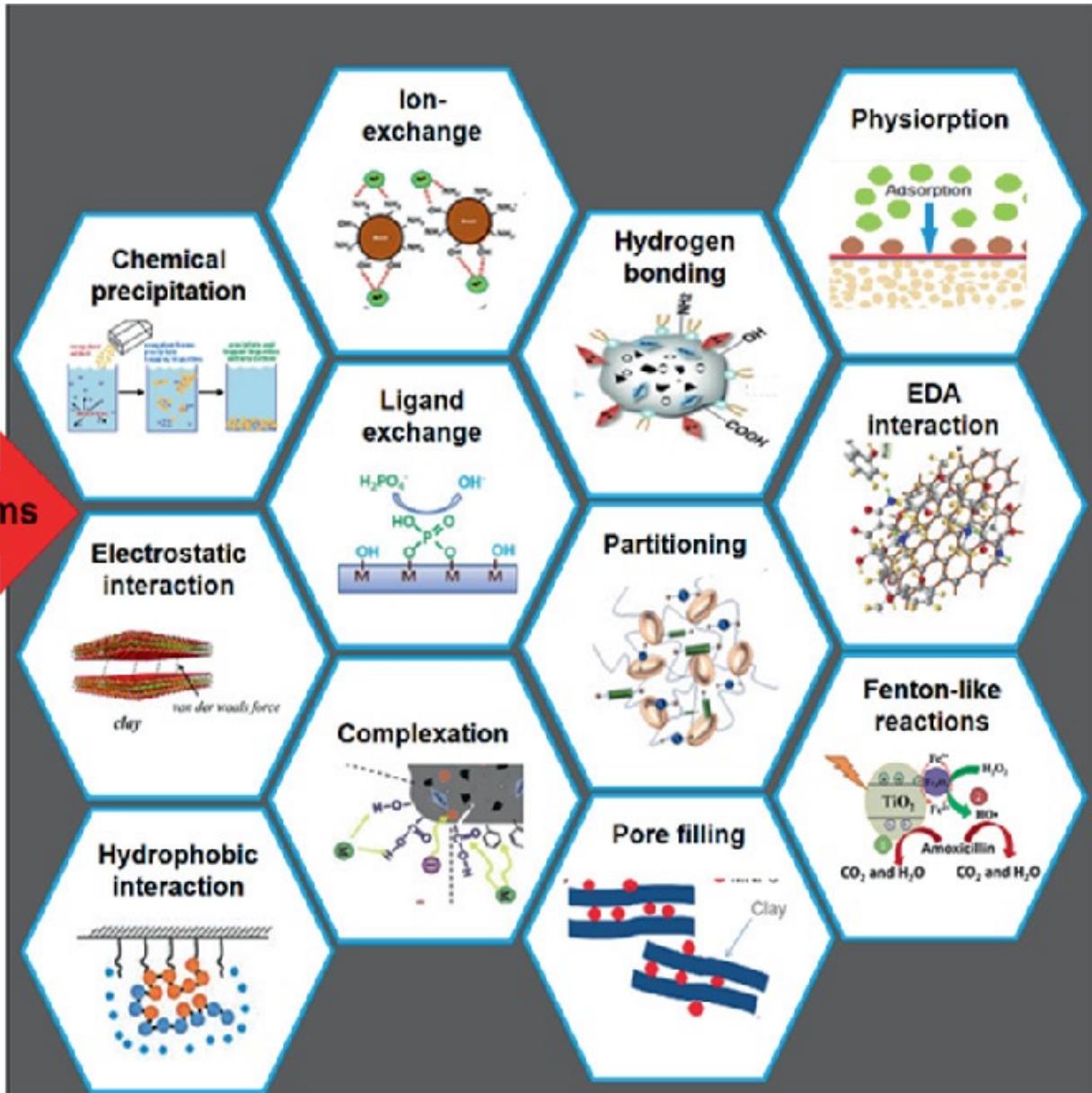
Figure from Developments in Clay Science, Vol. 6C. DOI: 10.1016/B978-0-08-100027-4.00001-2

# Clay minerals for pollution management:

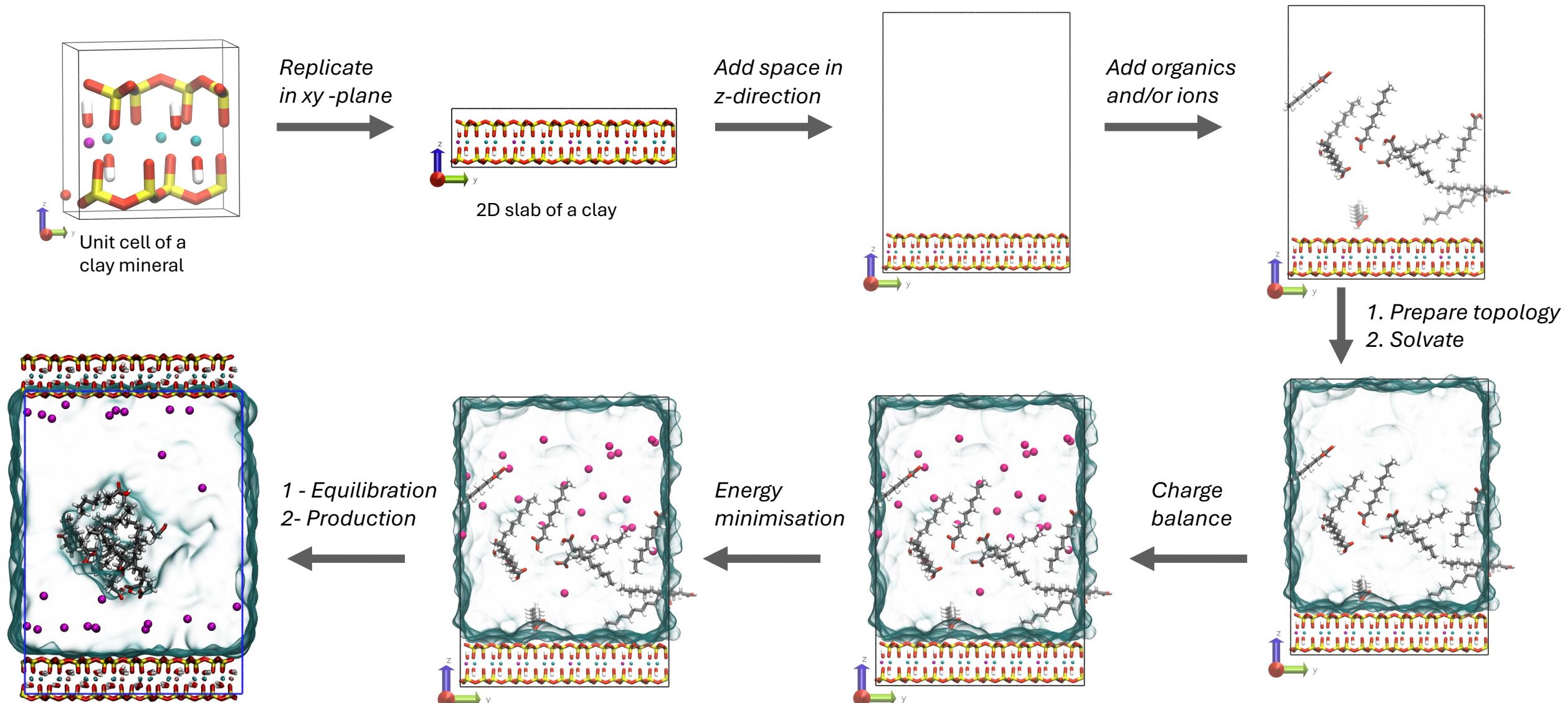
Advanced modifications, composites, nanobased material  
Low cost  
Abundant  
Easy to dispose  
Recyclable



Mechanisms



# How do I start modeling clay mineral system?

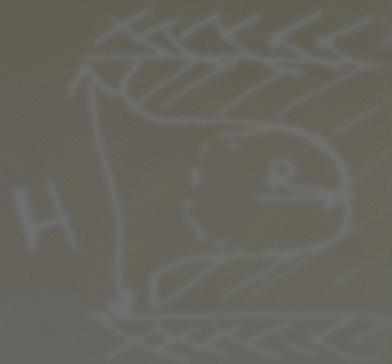


$$\delta_t^2 = \delta_d^2 +$$

$\delta_{\text{sol}}$  - dispersive  
 $\delta_p$  - polar  
 $\delta_n$  - hydrogen

Solvent performance

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



# Questions?

