

Lecture #9: Machine learning for molecular simulation

Previously on

- Graph neural networks
- Message passing
- Permutation invariance

Goals/Agenda

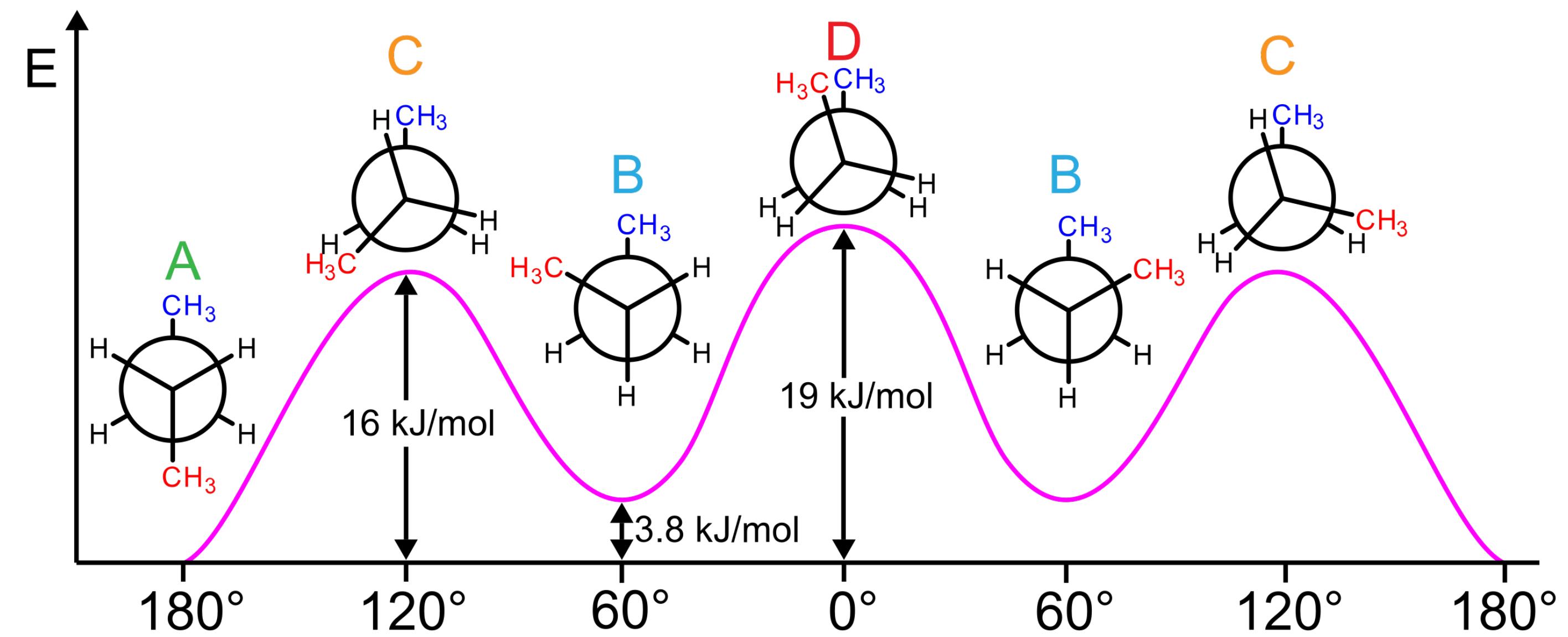
- Molecular dynamics basics
- Interatomic potential
 - Energy and forces
- ML interatomic potentials (MLIPs)
 - Generating data
 - Fitting and validation
 - Equivariance
- Universal MLIPs

Zero-temperature density functional theory calculations

- Static density functional theory calculations yields the thermodynamic properties at 0 K
- We iteratively optimize the geometry until the forces/energy converge

However

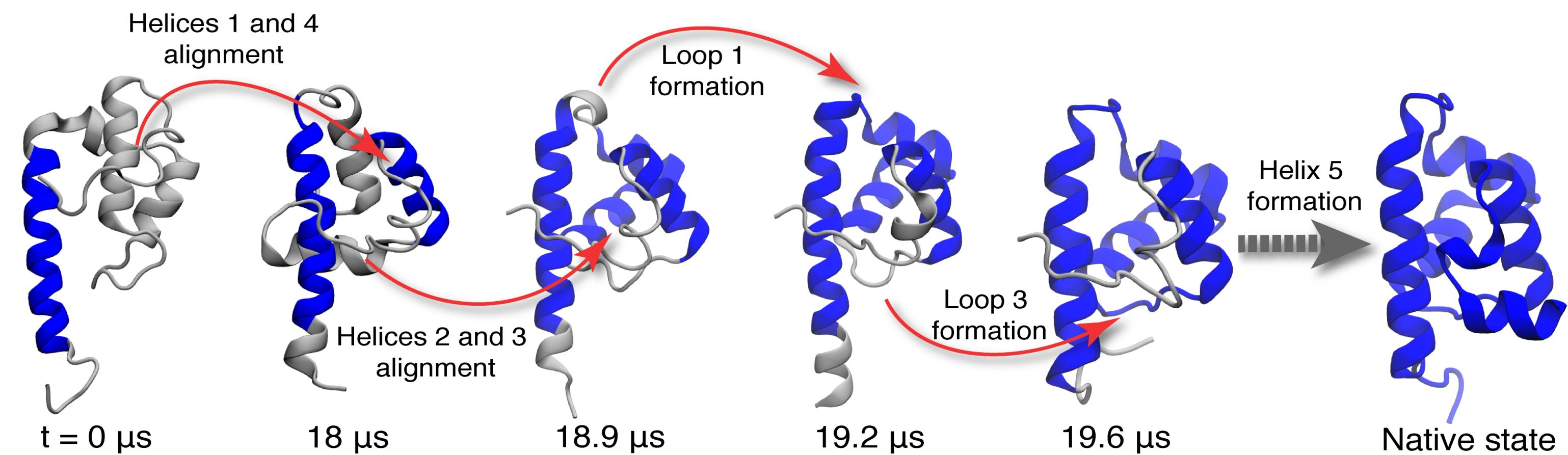
- Sometimes the configurational space is enormous
 - conformers
- Sometimes thermal effects matter
 - phase transition
- Sometimes the rate of some events needs to be estimated
 - diffusion



Molecular dynamics

...is used to study the dynamics of atomic systems

- i.e. evolution at finite temperature



Basics of molecular dynamics

The net force acting on particle is directly proportional to its acceleration:

$$F_i = m_i \frac{\partial^2 r_i}{\partial t^2}$$

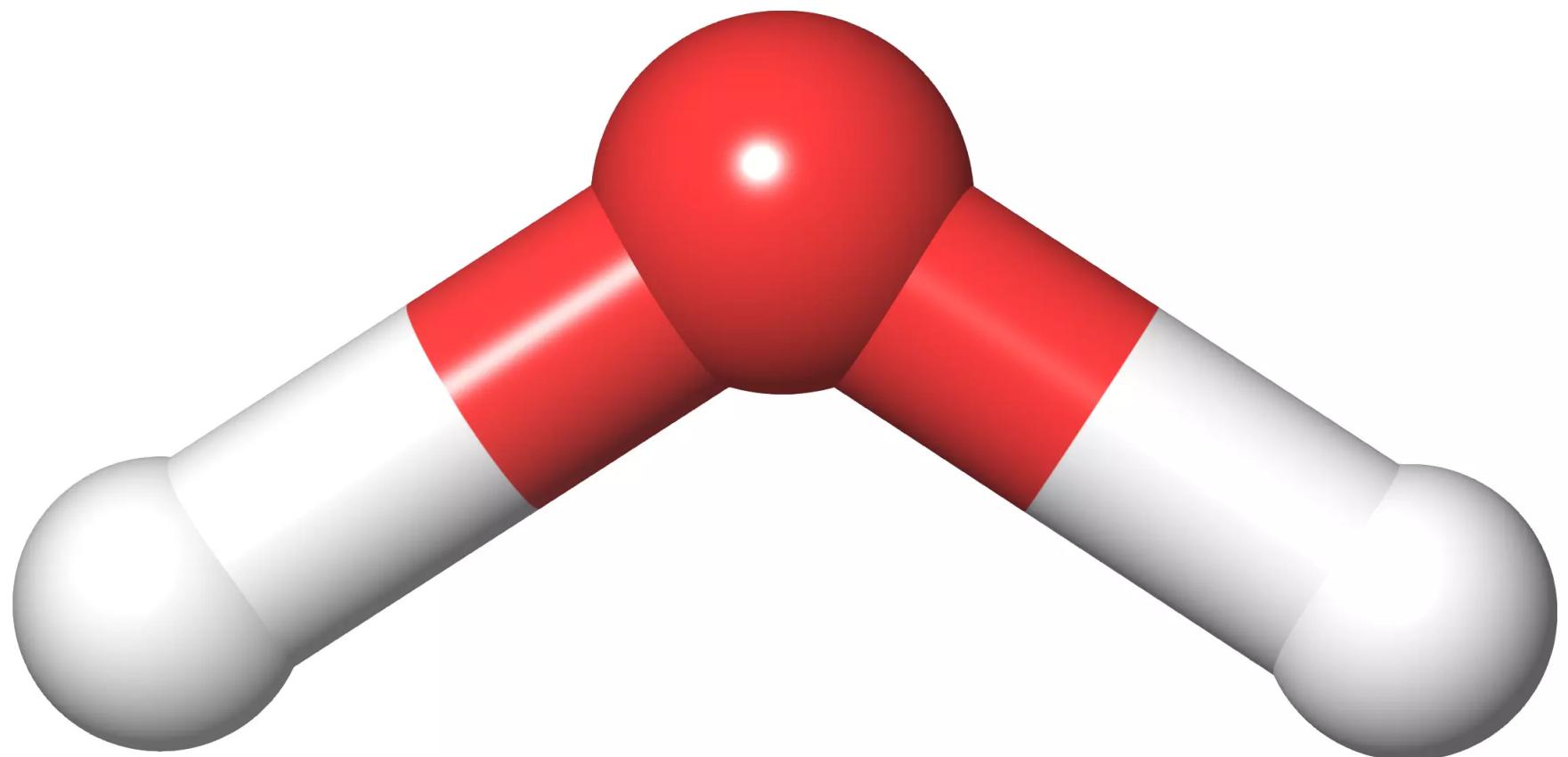
At the same time:

$$F_i = - \frac{\partial V}{\partial r_i}, \text{ where } V \text{ is the potential}$$

energy (surface), $V(R)$

$R = R(r_1, \dots, r_i)$ - is the state of the system, i.e. its geometry

$$\mathbf{r}_1 = (x_1, y_1, z_1)$$



$$\mathbf{r}_2 = (x_2, y_2, z_2)$$

$$\mathbf{r}_3 = (x_3, y_3, z_3)$$

Integrating Newton's laws of motion

- We want to find $r_i(t)$, i.e. $R(t)$
- We **can't** find it analytically for more than two interacting particles (see [three-body problem](#))
- We **can** solve it numerically

Finite difference method

The shape of $V(R)$ is known at the given moment t

The acceleration for each particle is given by:

$$a_i = \frac{F_i}{m_i} = -\frac{1}{m_i} \frac{\partial V}{\partial r_i} \text{ eq. (1)}$$

- 1) Initialize velocities
- 2) Select a small timestep δt (it should correctly describe the changes in your system)
- 3) Calculate forces
- 4) Integrate eq. (1) within $(t, t + \delta t)$ window to get velocities $v_i(t + \delta t)$
- 5) Update coordinates using calculated velocities for each particle $r_i = r_i + \delta t v_i$
- 6) Repeat 2-4 steps N times
- 7) Analyze the discrete trajectory obtained

Quantum chemistry (ab initio) molecular dynamics (AIMD)

The potential energy surface is calculated using quantum chemistry methods

- Pros
 - “Exact”
 - Yields electronic structure
- Cons
 - Small systems can be studied (~100 atoms) - **very expensive**
 - Poor statistics
 - Artificial size-effects for periodic systems
 - Short time scales (~100 ps)
 - Poor statistics

We want to move from quantum mechanics:

$$H(\{Z, \mathbf{R}\}) \xrightarrow{\Psi} E$$

To some surrogate model:

$$F(\{Z, \mathbf{R}\}, W) \xrightarrow{\mathbf{W}} E^*$$

Where F is a learnable function:

$$\min_W \sum_i (E_i - E_i^*)^2$$

Classical MD

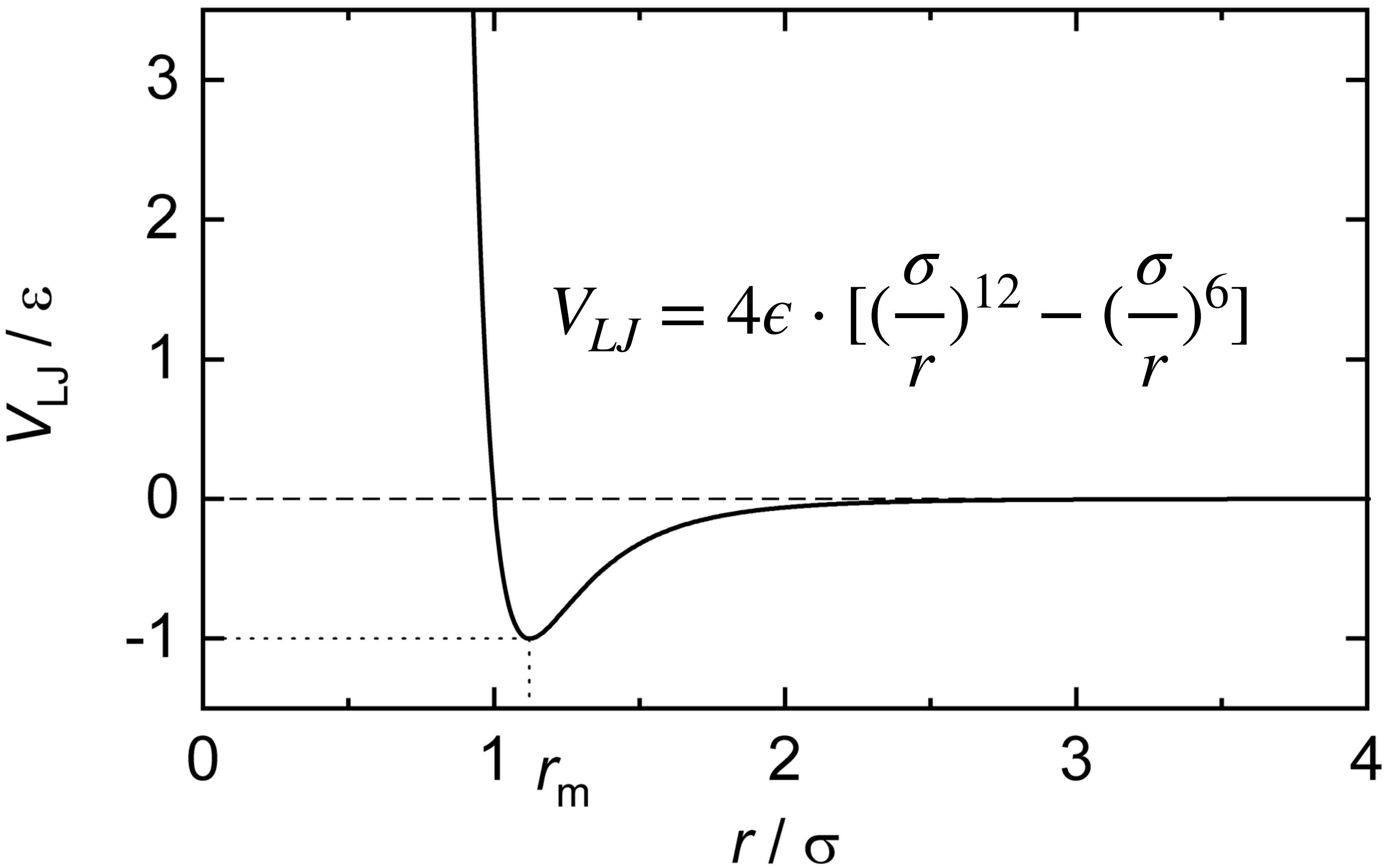
Some "empirical" functional relationship $F(W, R) = V(R)$, W - parameters of the model

- Pros
 - Large scale simulations (10^3 - 10^6 atoms)
 - Long time simulations (~10 nanoseconds)
 - $\times 10^2$ - 10^8 faster compared to DFT
 - Interpretable
- Cons
 - No electronic structure
 - Approximate - may fail
 - Difficult to select a "proper" law (shape of F)
 - The shape of $F(W, R)$ depends on the chemical bonding/coordination
 - no universal approach

Example

Lennard-Jones potential

- Works well for noble gases



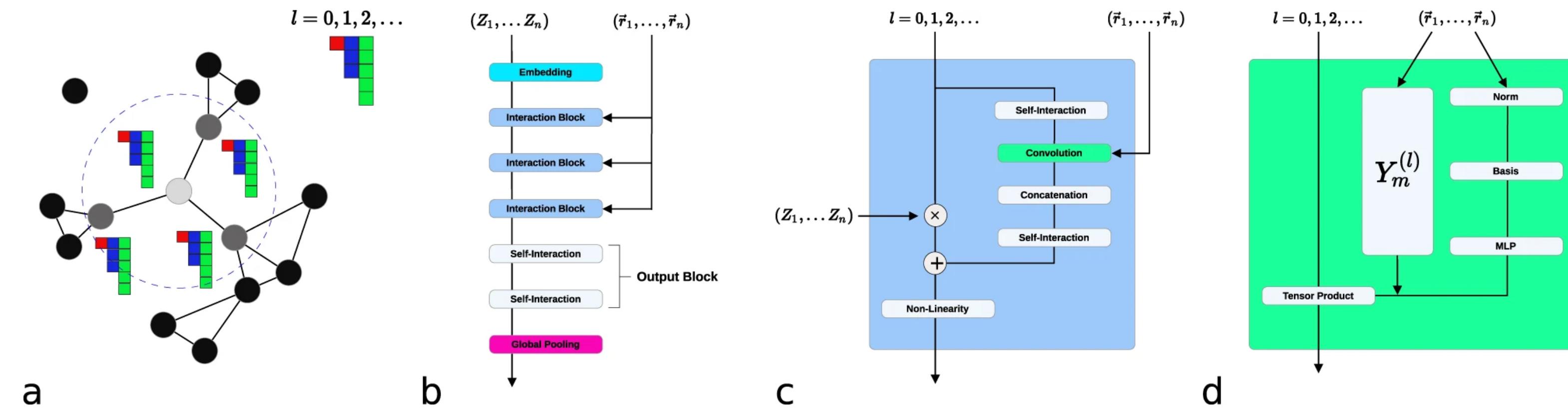
Machine learning assisted MD

Some ML model $F(W, R) = V(R)$, W - parameters of the model

- Pros
 - Large scale simulations (10^3 - 10^6 atoms)
 - Long time simulations (~10 nanoseconds)
 - $\times 10^2$ - 10^3 faster compared to DFT
 - Easy to fit/refit
 - Universal approach to any type of chemical bonding
 - Provides energies and forces with near-DFT accuracy
- Cons
 - No electronic structure
 - Approximate - may fail
 - Difficult to interpret, slower compared to classical MD

Examples

- ML potentials
 - Gaussian approximation potential (GAP)
 - Atomic cluster expansion (ACE)
 - Smooth overlap of atomic positions (SOAP)
 - Moment tensor potentials (MTP)
- GNNs
 - Nequip/Allegro
- NNs
 - The Behler-Parrinello Neural Network



Energy calculations with interatomic potentials

- The potential energy is calculated as the sum of atomic potential energies (site energies)

$$E_{pot} = \sum_{i \in N_{atoms}} E_{i,atomic}$$

- Forces are calculated as follows

$$\vec{F}_i = -\nabla_i E_{pot}$$

Fitting (training) interatomic potentials

- For a **given system**
 - We run AIMD at elevated temperatures to sample atomic configurations
- The dataset
 - Geometries: $\{R_n\}$
 - Energies: $\{E_n(R_n)\}$
 - Forces: $\{F_{i,\alpha}(R_n)\}$
- Loss function

$$\mathcal{L} = \lambda_E \|\hat{E} - E\|^2 + \lambda_F \frac{1}{3N} \sum_{i=1}^N \sum_{\alpha=1}^3 \left\| -\frac{\partial \hat{E}}{\partial r_{i,\alpha}} - F_{i,\alpha} \right\|^2$$

- The hat symbol denotes predictions

We want a fast and accurate universal model

- Can we develop a fast model generalizable to various types of chemical bonding, composition, and structure for predicting total energy?

$$F(\{Z, \mathbf{R}\}, W) \xrightarrow{W} E^*$$

Universal ML interatomic potentials

GNNs

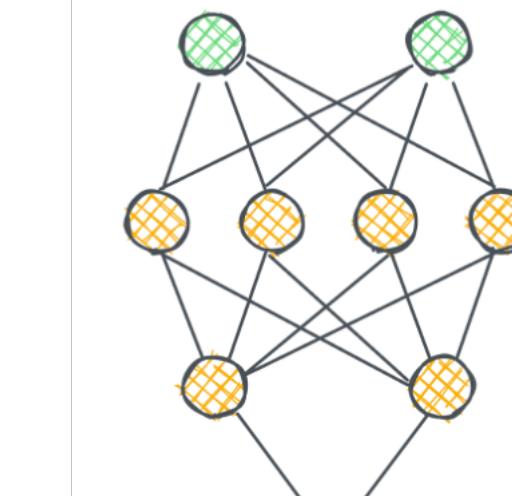
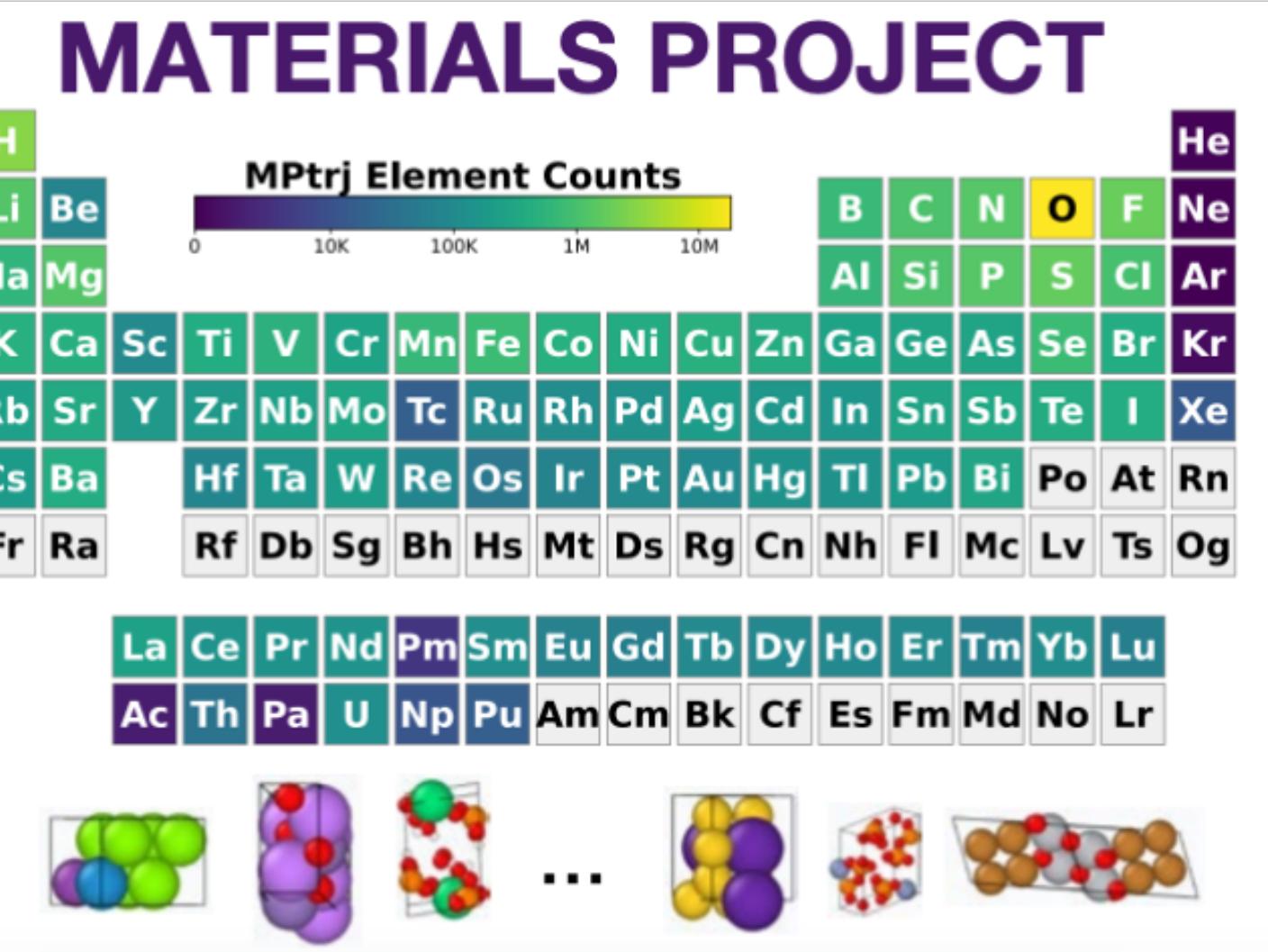
- Trained on large and diverse quantum chemistry datasets
 - The Materials Project (MPTrj), MatPES, Alexandria
- Can be applied to unknown systems
 - For solving downstream tasks

Pros:

- Works out of the box
- Can be refitted (finetuned) with a small amount of data

Cons:

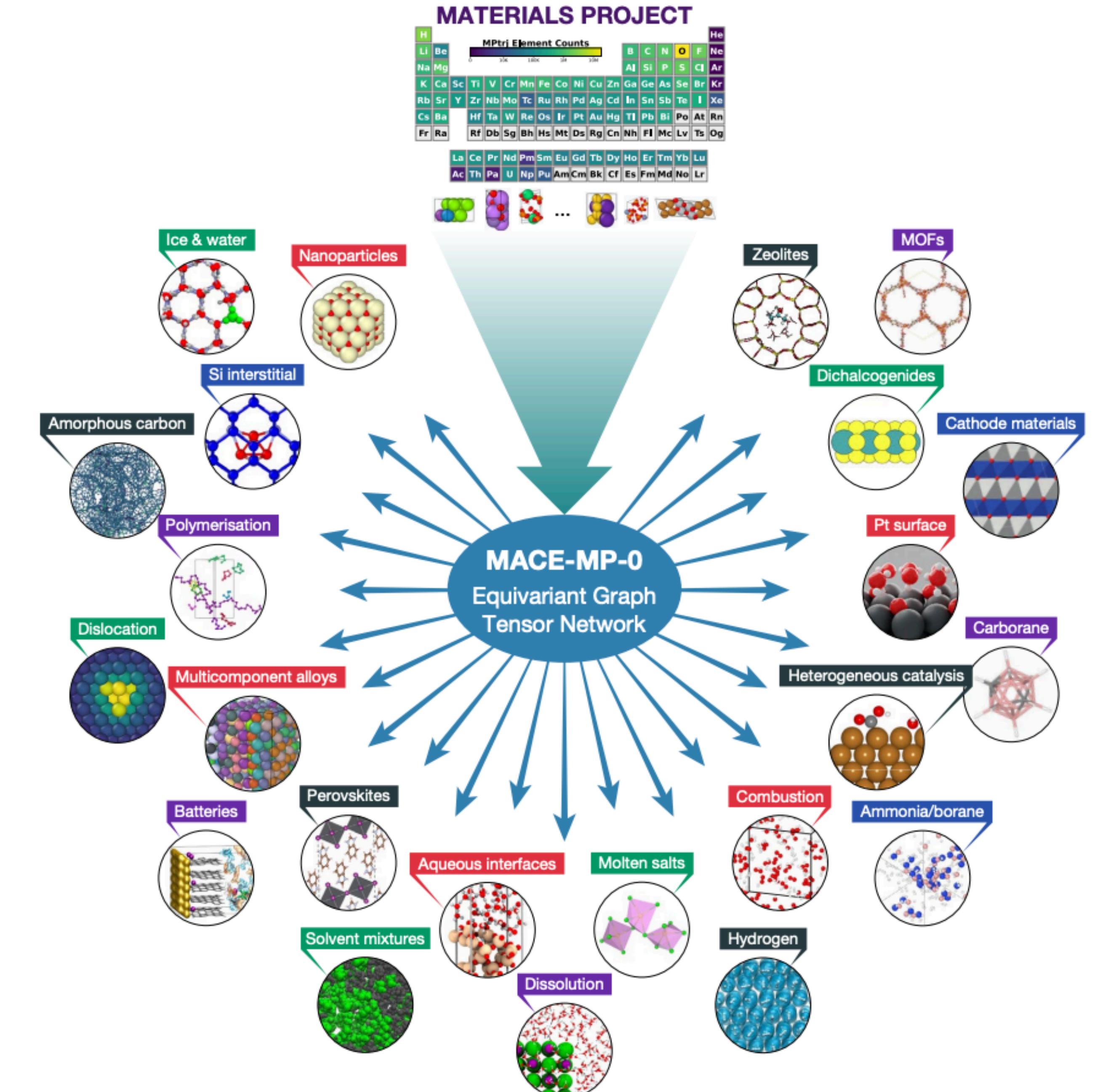
- Universality is debatable. Should be carefully validated before using
- A lot of weights -> slower compared to ML potentials developed for a specific system



$$F(\{Z, \mathbf{R}\}, W) \xrightarrow{W} E^*$$

Examples

- M3GNet (the first one)
- CHGNet
- MACE
- SevenNet



Take home message

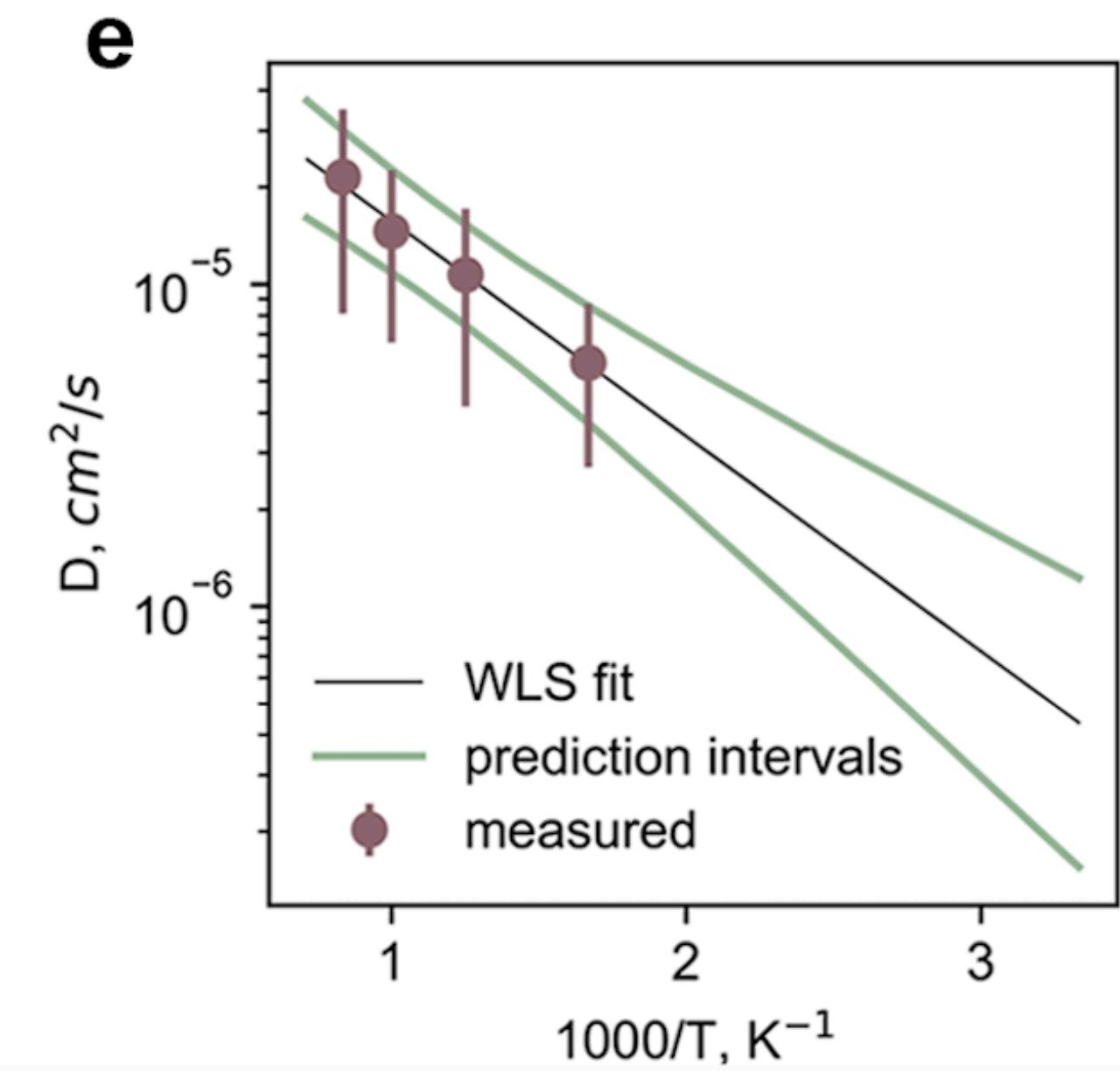
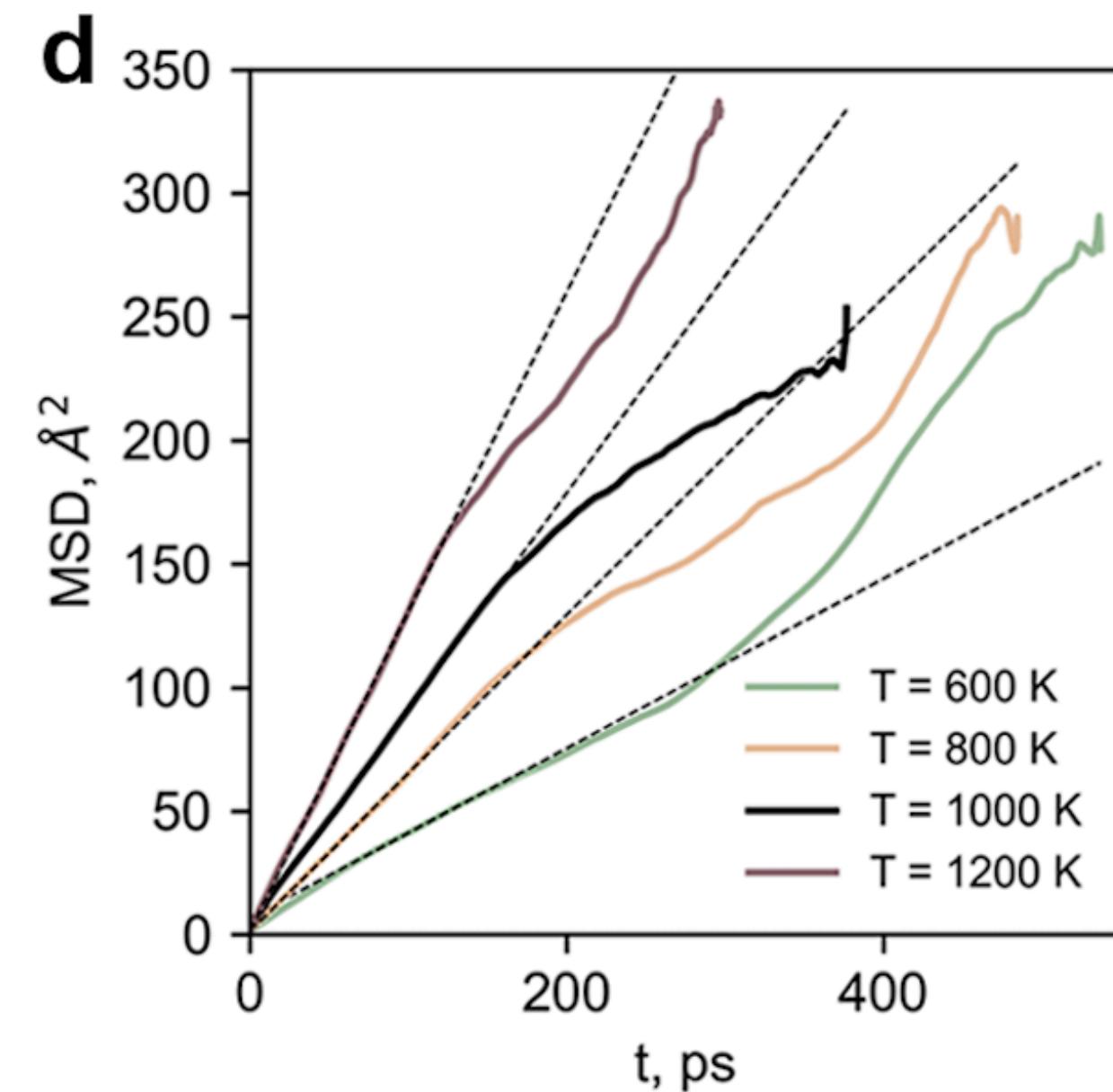
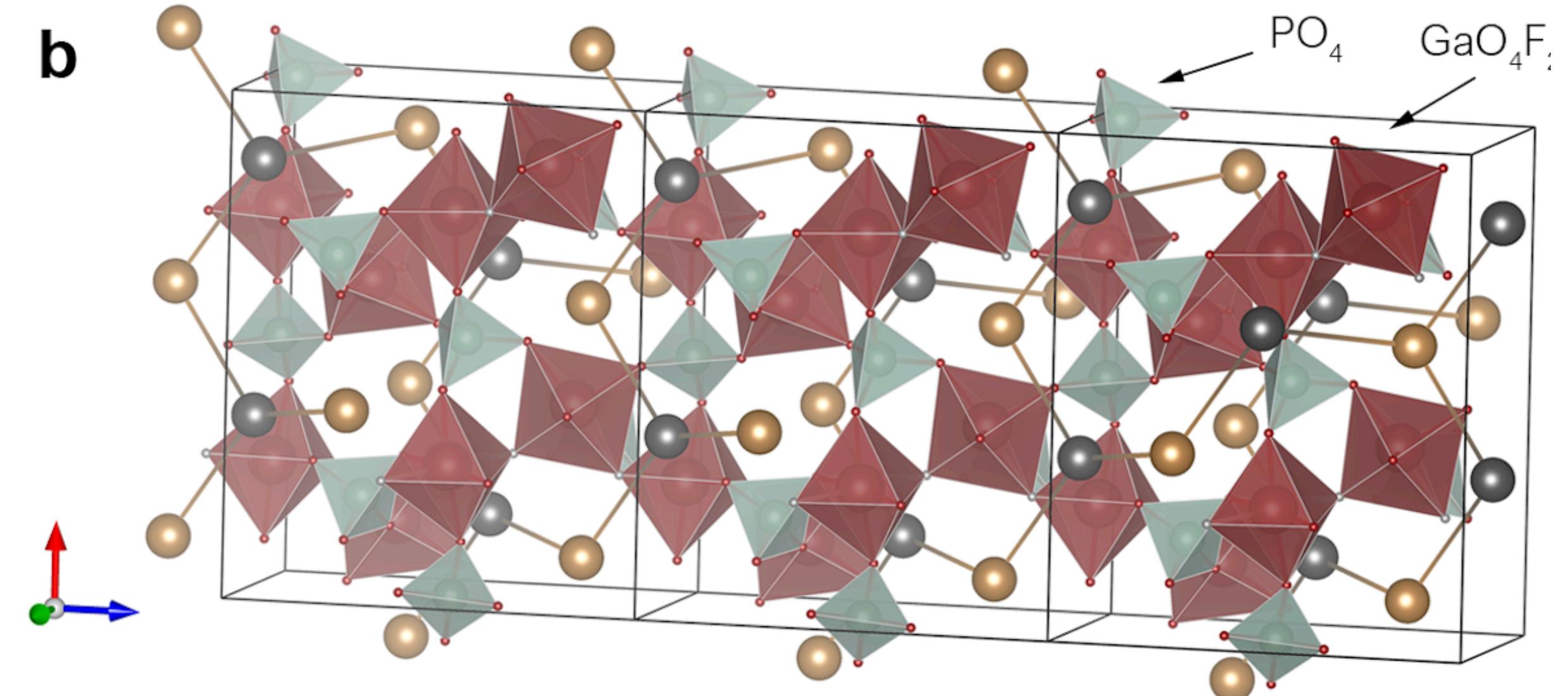
- MD is used to study the evolution of atomic systems at the given conditions
- Machine learning interatomic potentials (MLIPs) are used to accelerate simulations
 - with near-DFT accuracy
- Universal MLIPs are trained on large dataset
 - to solve downstream tasks for a wide range of chemical systems

Ionic conductivity (for the seminar)

"is a measure of a substance's tendency towards ionic conduction.

Ionic conduction is the movement of ions.

The phenomenon is observed in solids and solutions. Ionic conduction is one mechanism of current." ([wiki](#))



Formulas (for the seminar)

MSD vs. dt

$$MSD(\tau) = 6D\tau$$

Arrhenius equation

$$D = D_0 \exp(-E_a/kT)$$

Ionic conductivity

$$\sigma = \frac{\rho e^2 D}{kT}, \text{ where}$$

- ρ is the diffusing particle density (number of ions N , per volume, V , of the system)
- e is the charge of electron
- D is the diffusivity
- k is Boltzman's constant