

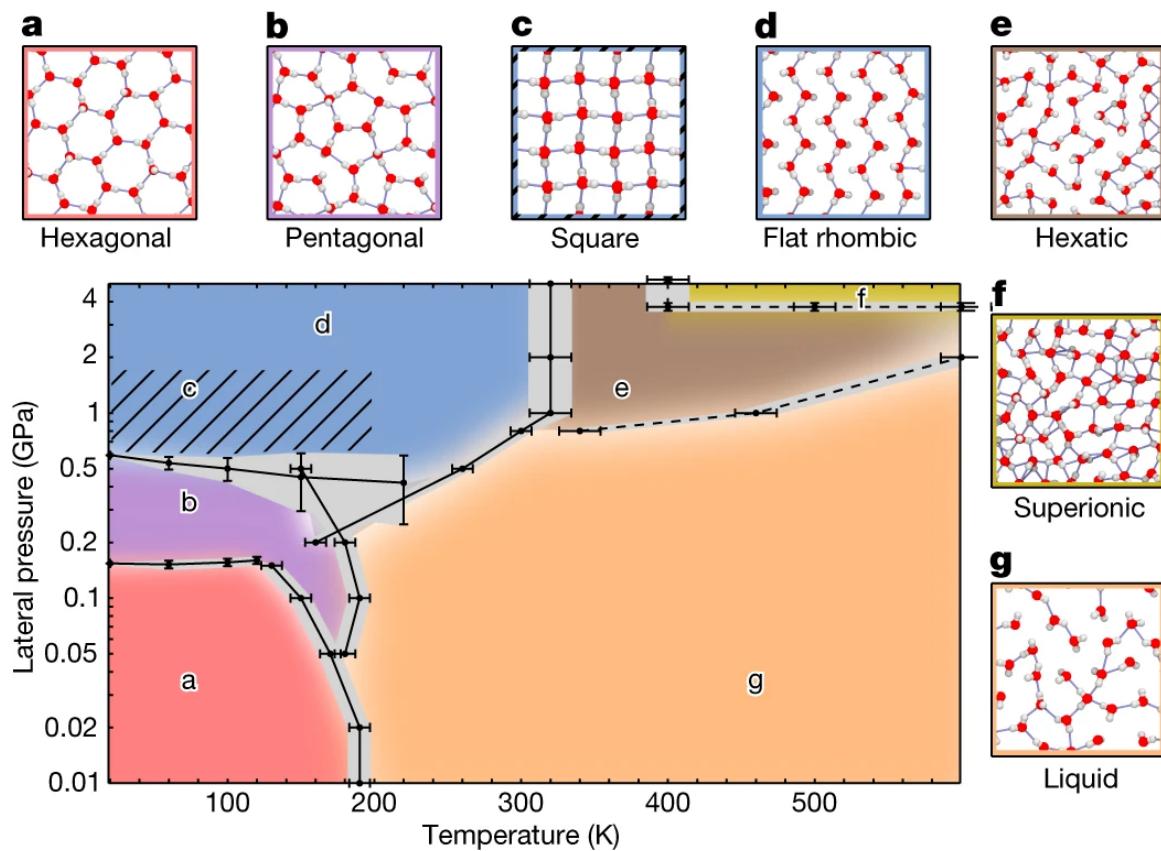


Hands-on 5. MD 1_basic

▼ What can we see using Molecular dynamics (MD)?

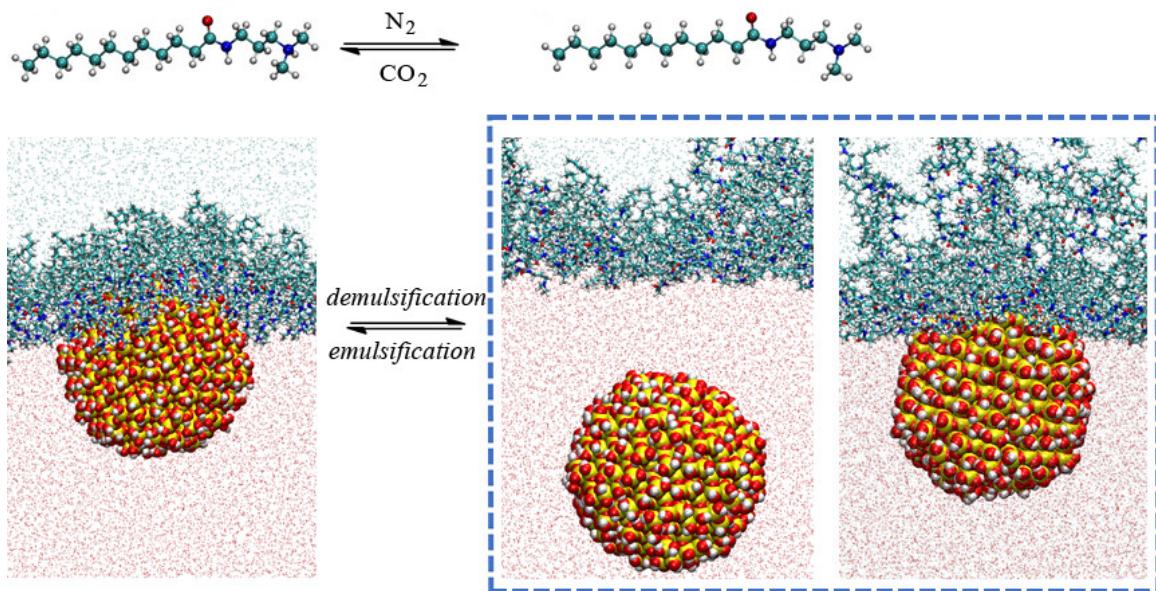
▼ Finding thermodynamically stable structure under realistic condition

- Optimized water structure



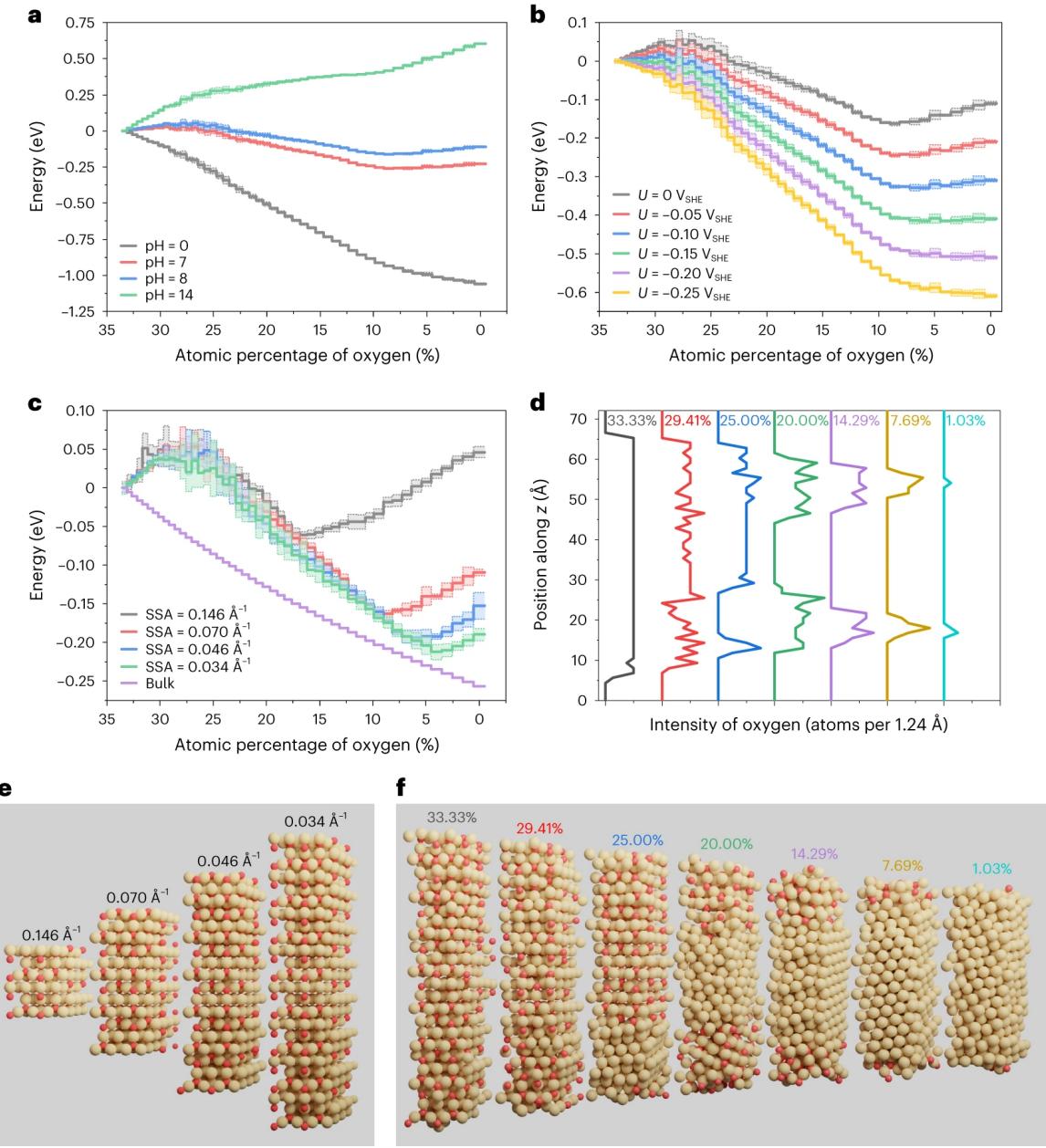
<https://www.nature.com/articles/s41586-022-05036-x/>

- Understanding nanoparticle solvation in oil-water interface



<https://pubs.acs.org/doi/10.1021/acs.langmuir.3c00949>

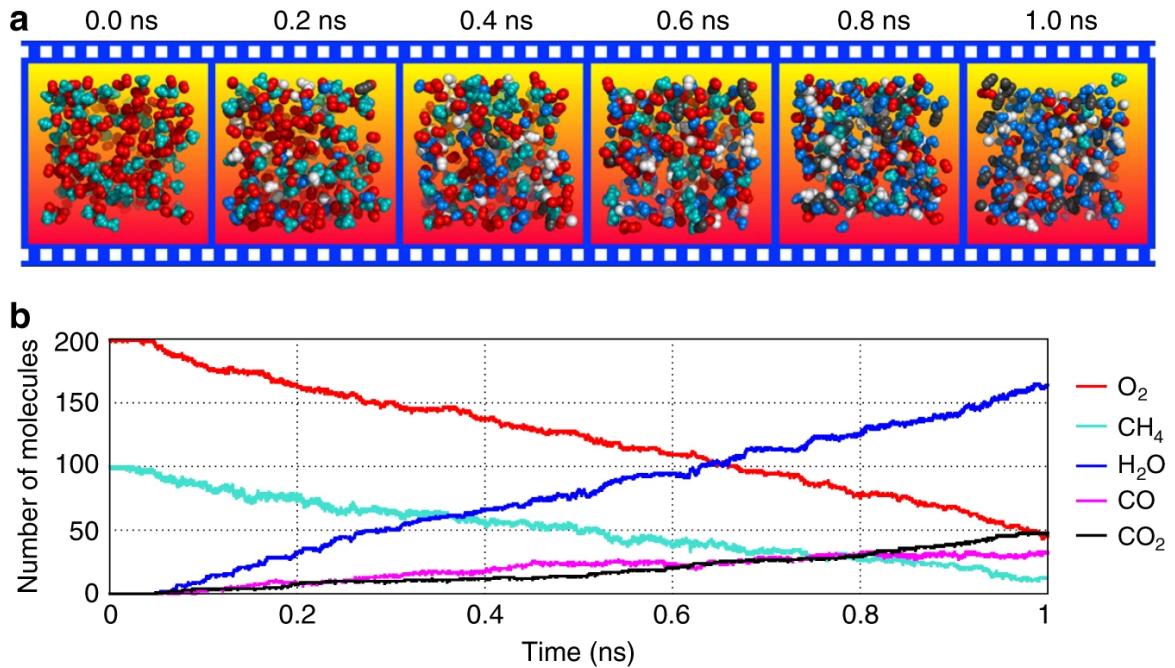
- Understanding oxidation of Copper in applied potential regime



<https://www.nature.com/articles/s41929-024-01132-5/>

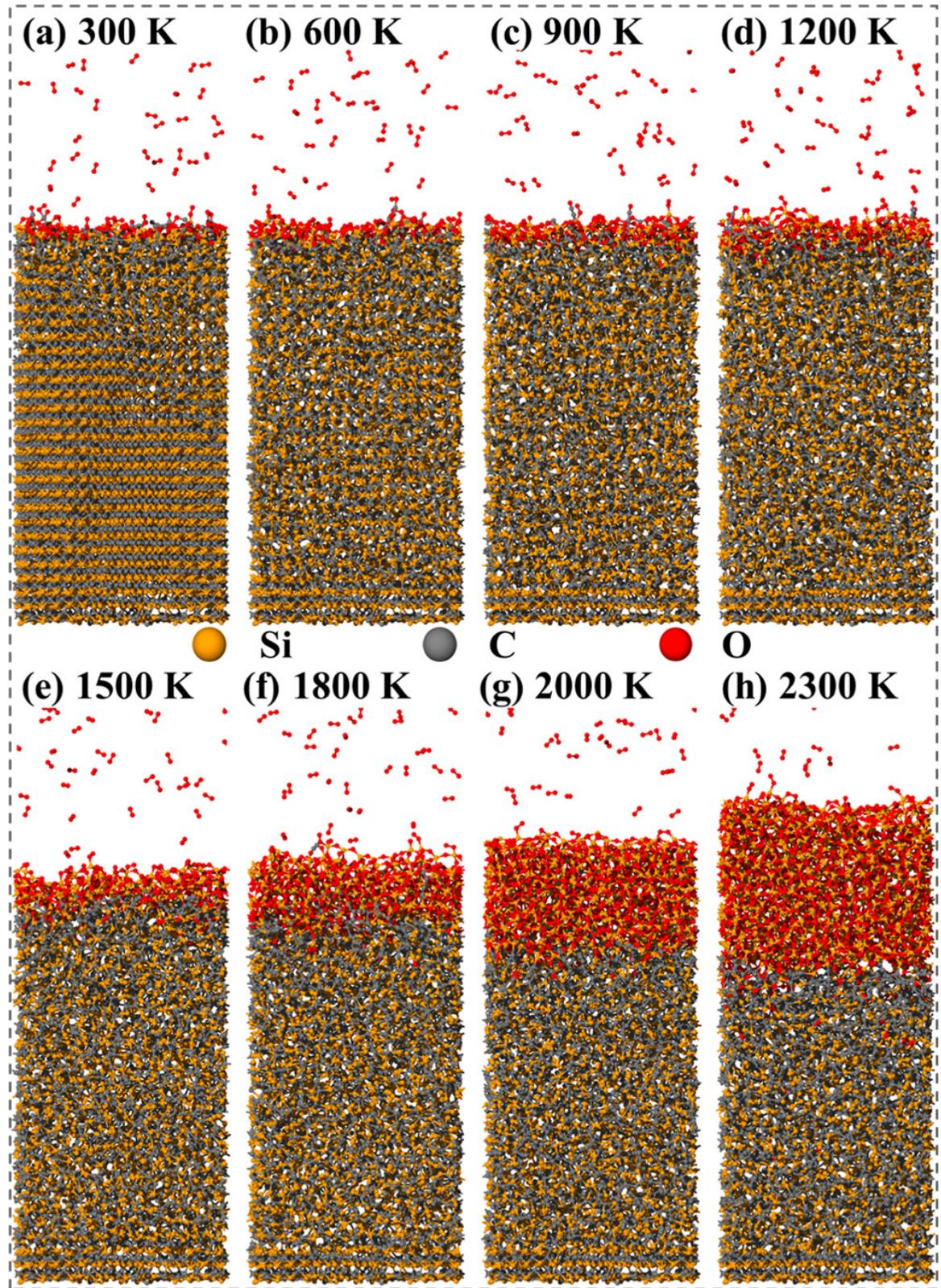
▼ Describing reactions in a realistic manner

- real-time combustion reaction monitoring



<https://www.nature.com/articles/s41467-020-19497-z>

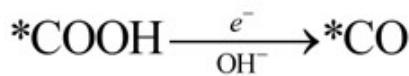
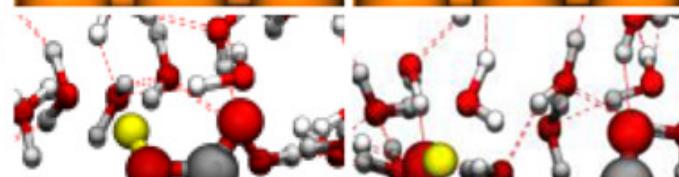
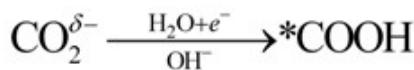
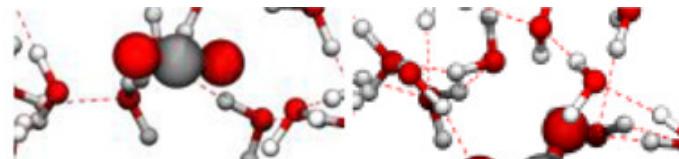
- Oxidation of Silicon carbide



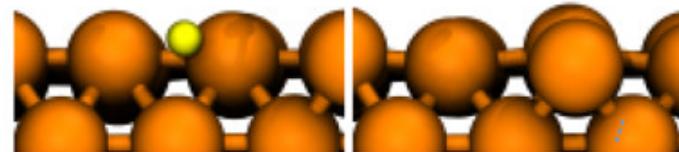
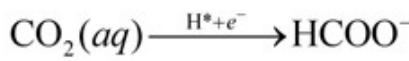
<https://pubs.acs.org/cms/10.1021/acسامي.4c12392>

- CO₂ reduction reaction

*CO formation



Formate(HCOO⁻) formation



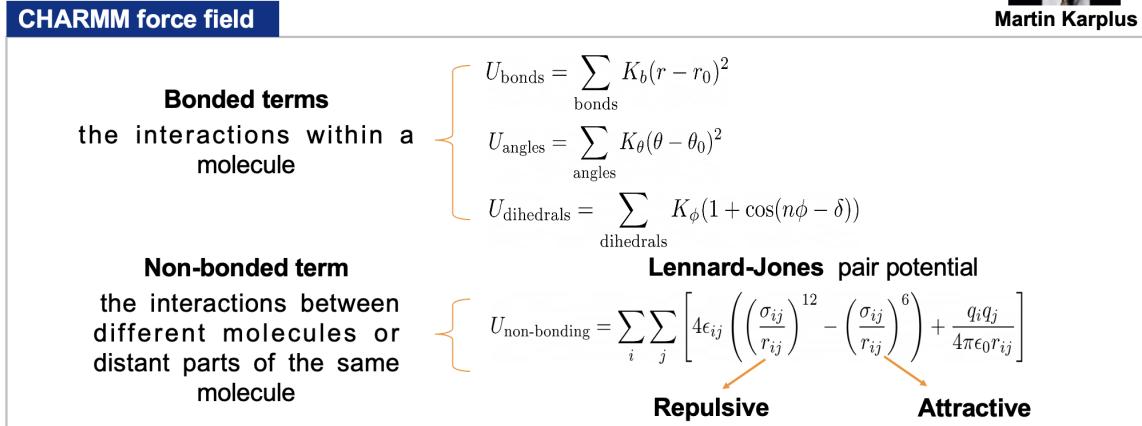
<https://pubs.acs.org/cms/10.1021/jacs.6b08534>

▼ Concept of Force field

$$U(R) = U_{\text{bonds}} + U_{\text{angles}} + U_{\text{dihedrals}} + U_{\text{non-bonding}}$$



Martin Karplus



The **parameters** are typically obtained by fitting to **experimental** data or **DFT** calculations.

A **force field** in classical molecular dynamics (MD) simulations is a mathematical model that describes the potential energy of a system of atoms or molecules. Force fields predict system behavior over time under different conditions (e.g., temperature, pressure).

Common Components:

- **Bond Stretching:** Modeled by harmonic potentials (e.g., Hooke's law).
- **Angle Bending:** Describes deviations from equilibrium angles.
- **Torsional Interactions:** Captures energy changes from bond rotation.
- **Non-Bonded Interactions:** Includes electrostatics (Coulomb) and van der Waals forces (e.g., Lennard-Jones potential).

Comparison with DFT Potentials:

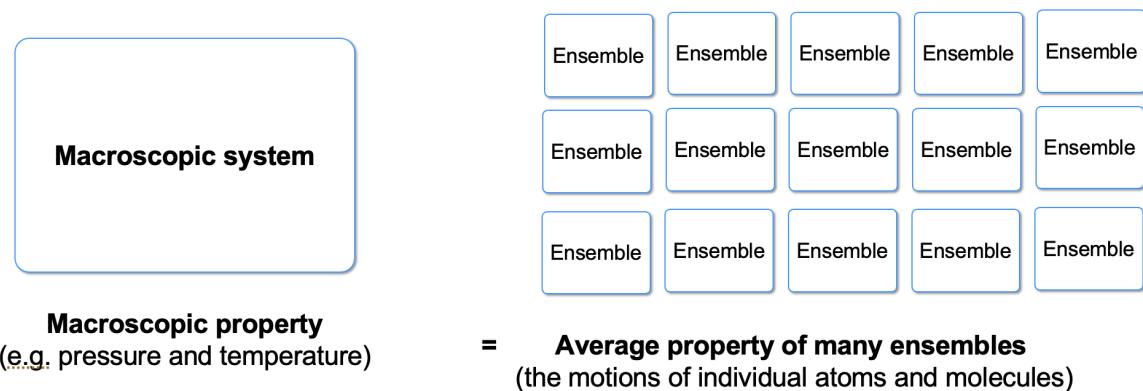
Aspect	Force Field	DFT Potential
Nature	Empirical, classical mechanics	Quantum mechanical, first principles
Accuracy	Less accurate, faster	Highly accurate, slower
Interactions	Predefined functions	Solves electronic structure
Applicability	Large systems, long timescales	Small systems, quantum effects

▼ Philosophical Foundations of MD: Ergodicity and Ensemble Approaches

Ergodicity: Achieving Thermodynamic Equilibrium Through State Exploration

Ergodic theory suggests that, given sufficient time, a system will explore all of its accessible states. However, a single MD simulation may not run long enough to capture the full range of these states. To overcome this limitation, multiple simulations with different initial conditions are often performed. This approach increases the likelihood of sampling a more comprehensive set of the system's possible configurations, providing a better representation of its phase space and moving closer to thermodynamic equilibrium.

Ensemble: a large collection of theoretical copies of a system



Ensemble	Fixed Variables	System Interaction
Microcanonical (NVE)	N, V, E	Isolated, no exchange of energy or particles
Canonical (NVT)	N, V, T	Exchanges energy with surroundings, fixed temperature
Isothermal-Isobaric (NPT)	N, P, T	Exchanges energy and volume, fixed temperature & pressure
Grand Canonical (μ VT)	μ , V, T	Exchanges energy and particles, fixed chemical potential & temperature

Practical Use:

- **Microcanonical ensemble** is good for isolated systems.
- **Canonical ensemble** is commonly used in simulations of systems at constant temperature.
- **Isothermal-Isobaric ensemble** is useful for studying systems at constant pressure, like biological systems or materials under realistic conditions.
- **Grand Canonical ensemble** is useful for open systems where particle number varies, like in adsorption processes or chemical reactions.

▼ Hands-on tutorial explained

Purpose: to get coefficient of linear thermal expansion (CTE, α)

$$\frac{a(T)}{a_{RT}} = 1 + \alpha \cdot T$$

Where:

- $a(T)$ is the lattice constant at temperature T ,
- a_{RT} is the lattice constant at room temperature (let's assume it is at 300 K),
- T is the temperature in Kelvin,
- α is the coefficient of linear thermal expansion.

We are going to run MD simulations of Bulk and cluster of metal element.
FF we are using is EMT potential (Supports the following standard EMT metals:
Al, Cu, Ag, Au, Ni, Pd and Pt.)

K. W. Jacobsen, P. Stoltze, and J. K. Nørskov, Surf. Sci. 366, 394 (1996).

Assignment

Please **select one metal element** from the following: **Al, Cu, Ag, Au, Ni, Pd, or Pt.**

Run an **NPT simulation** (constant Number of atoms, Pressure, and Temperature) at **different temperatures** and calculate the **coefficient of linear thermal expansion (CTE, α)** for the selected metal.

Note: if you want to fit experimental data of Ag, Al, Ni, dont forget to convert Celcius to Kelvin in experiment excel file.