



國立清華大學

化學工程學系

National Tsing Hua University  
Department of Chemical Engineering

# 2022 Summer School

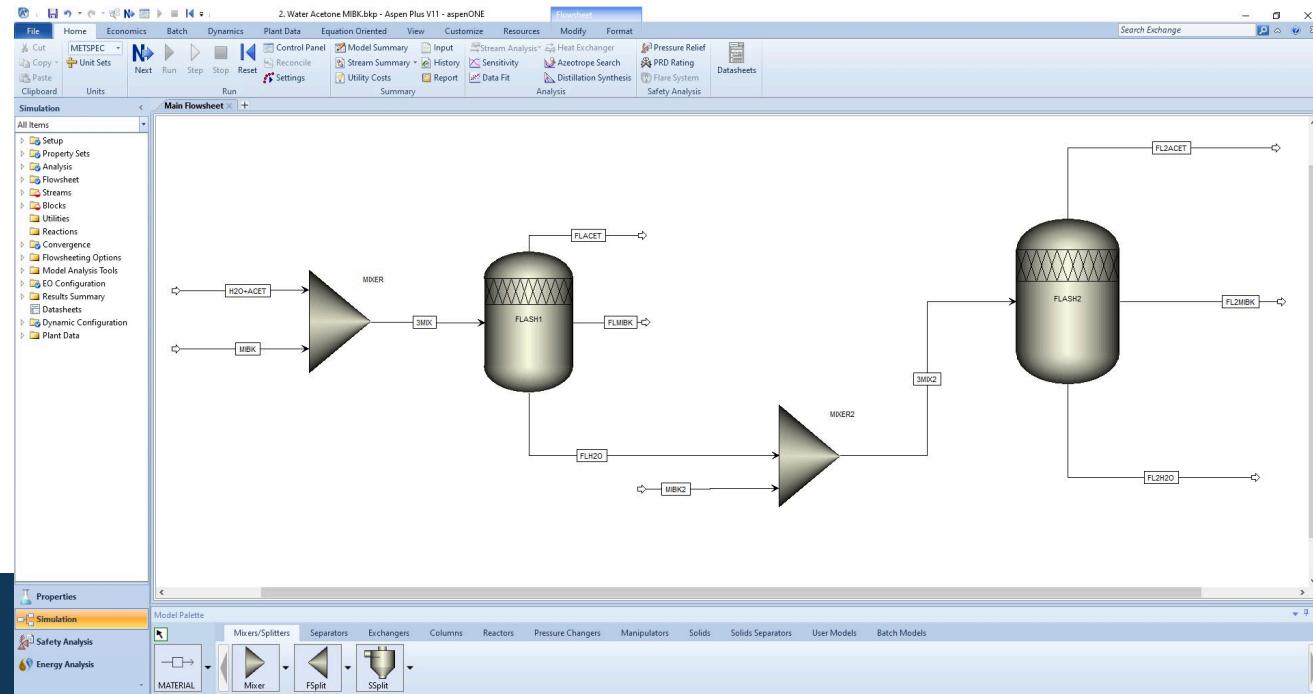
## Electronic Structure Calculations Using GFN2-xTB

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# **Week 1. Introduction to Computational Chemistry/Materials**

# What are computer simulations?

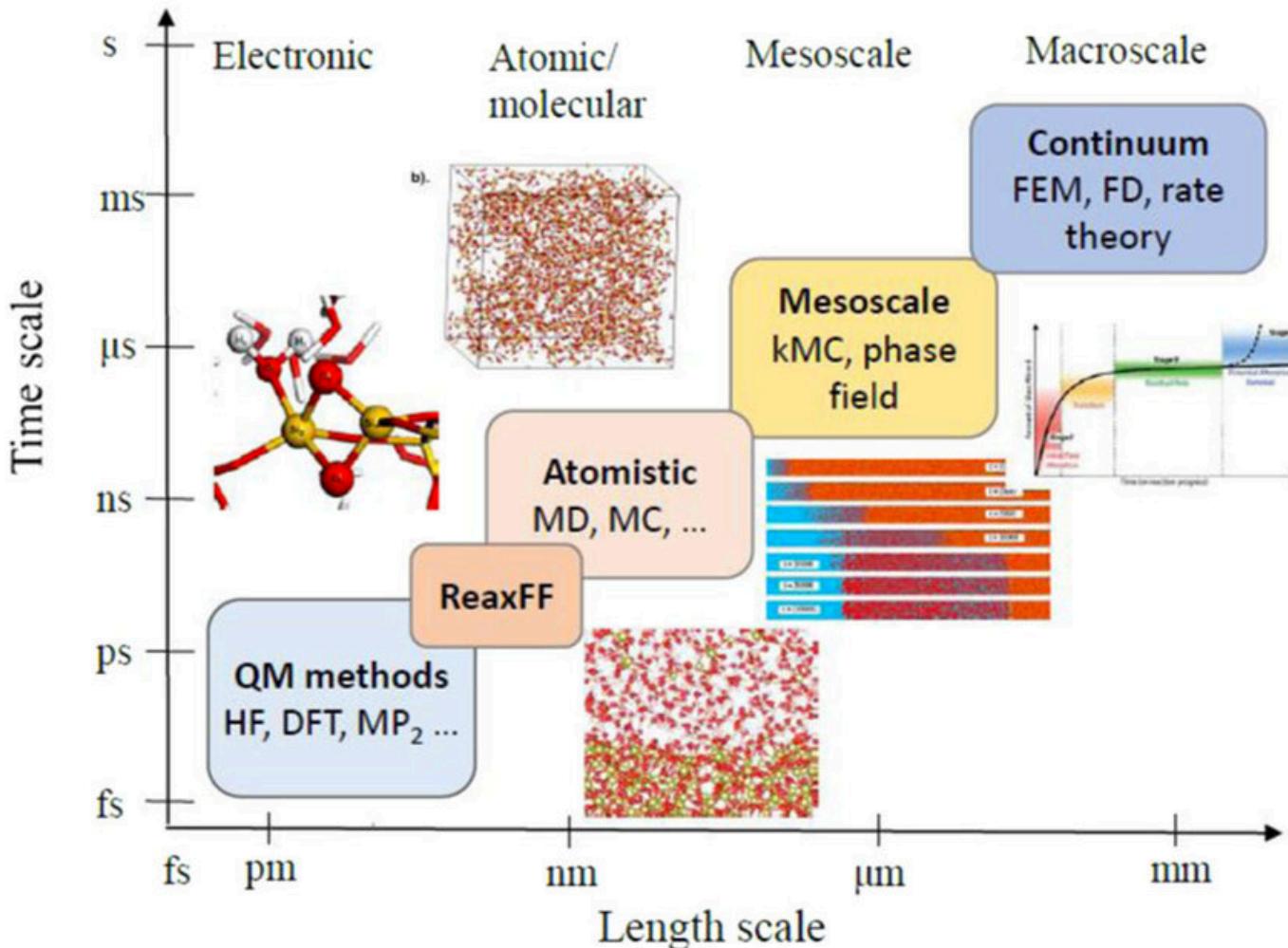
The process of **mathematical modelling**, performed on a **computer**, which is designed to predict the behavior of, or the outcome of, a real-world or physical system.



## Aspen Plus

Conservation law, transport phenomenon, classical thermodynamics and chemical rate equations.

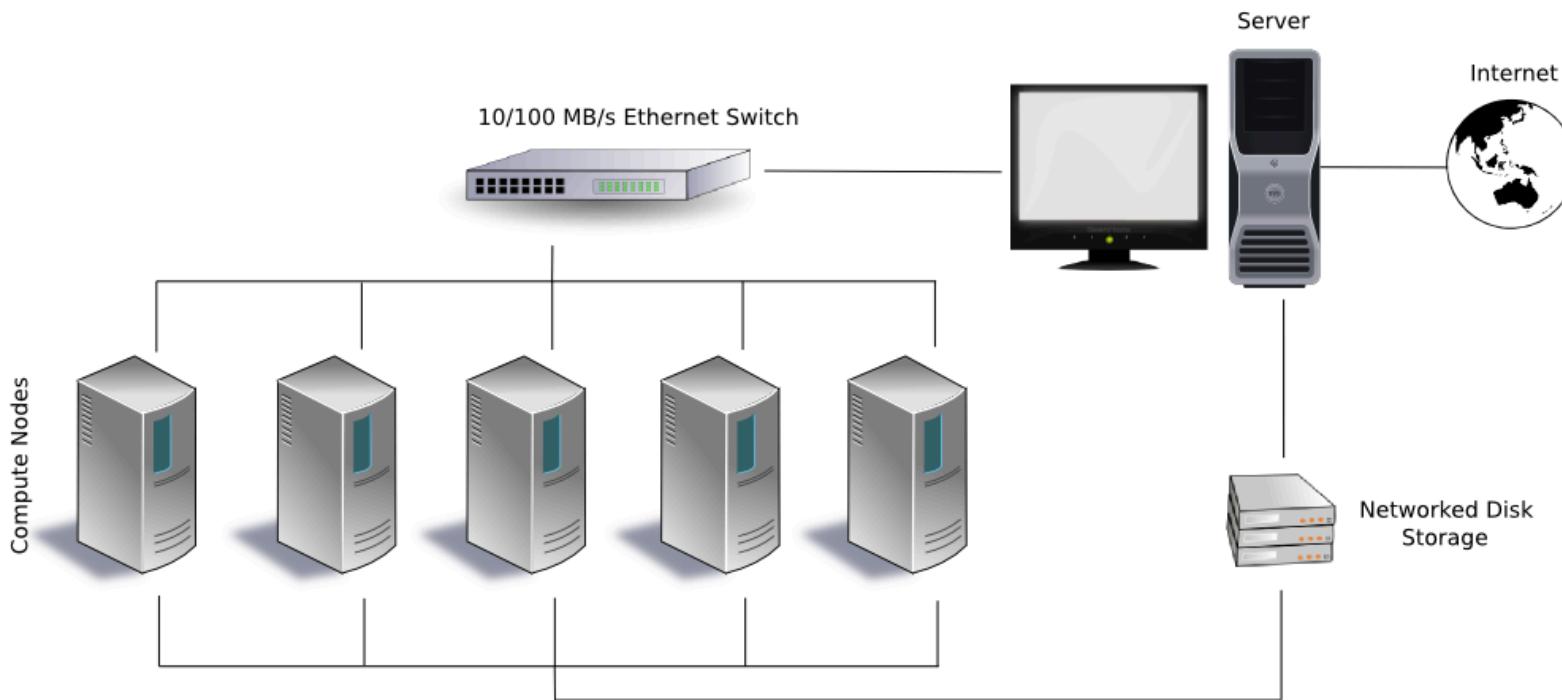
# What are computer simulations?



- Computer + software
- Scale matters!
  - Time
  - Length
- Methods
- Structural inputs

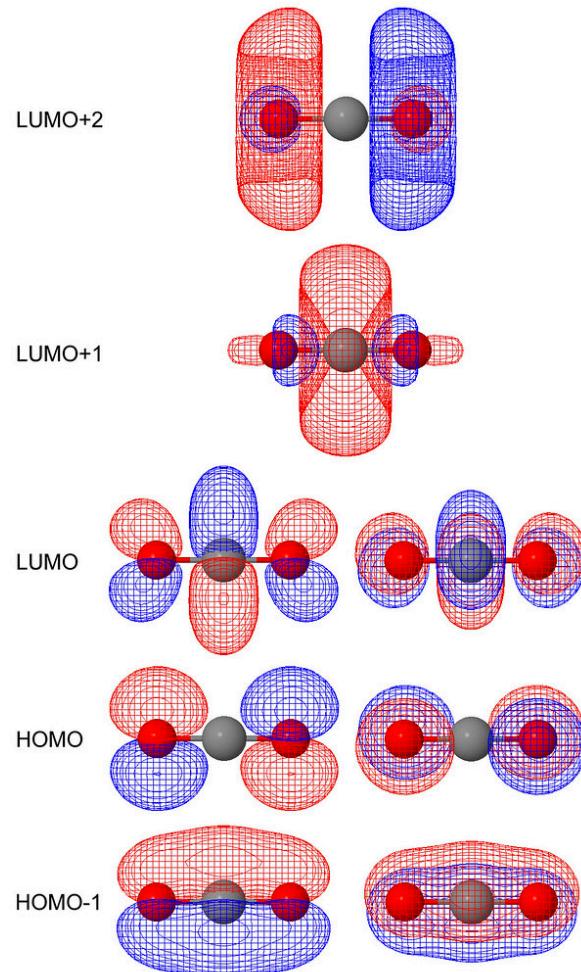
# What types of computers do we use?

Architecture of a cluster



# QM methods / *ab-initio* methods

molecular orbitals (MOs) of  $\text{CO}_2$



- *Ab-initio* means from the beginning
  - No empirical parameters
- Solve QM **eigen value problems**
  - Wavefunction  $\hat{H}\Psi = E\Psi$
  - All properties of systems (energy, molecular dipole, electron density, electrostatic potential...)
- **Wavefunction**-based method vs **DFT**

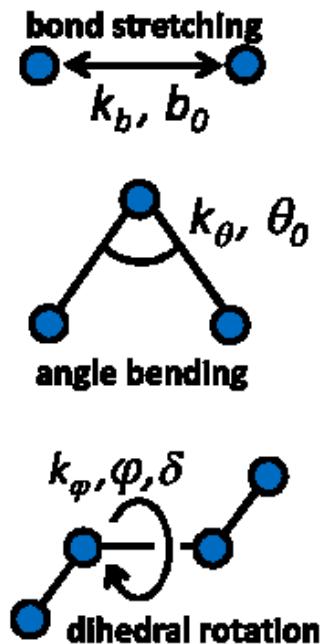
# (All-atom) forcefield approaches

Describe interactions between atoms (objects) using mathematical functions.

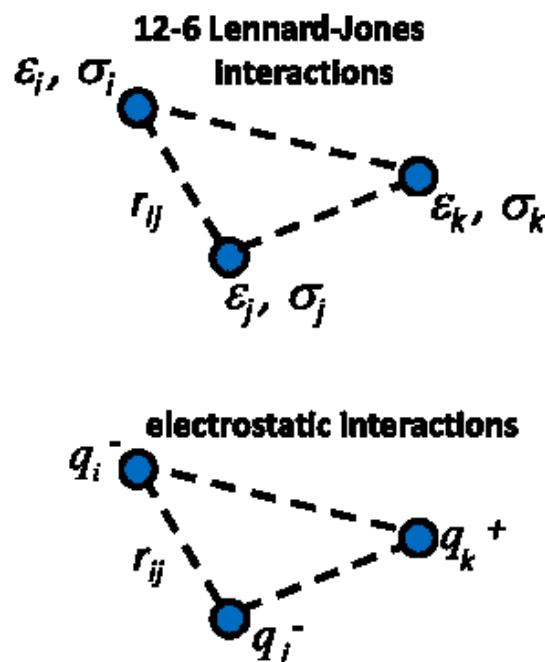
## Force Field Equation

$$PE = \sum k_b (b - b_o)^2 + \sum_{\text{angle}} k_\theta (\theta - \theta_o)^2 + \sum_{\text{dihed}} k_\phi [1 + \cos(n\phi - \delta)] + \sum_{L-J} 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \sum_{\text{Coulomb}} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}$$

## Bonded Terms

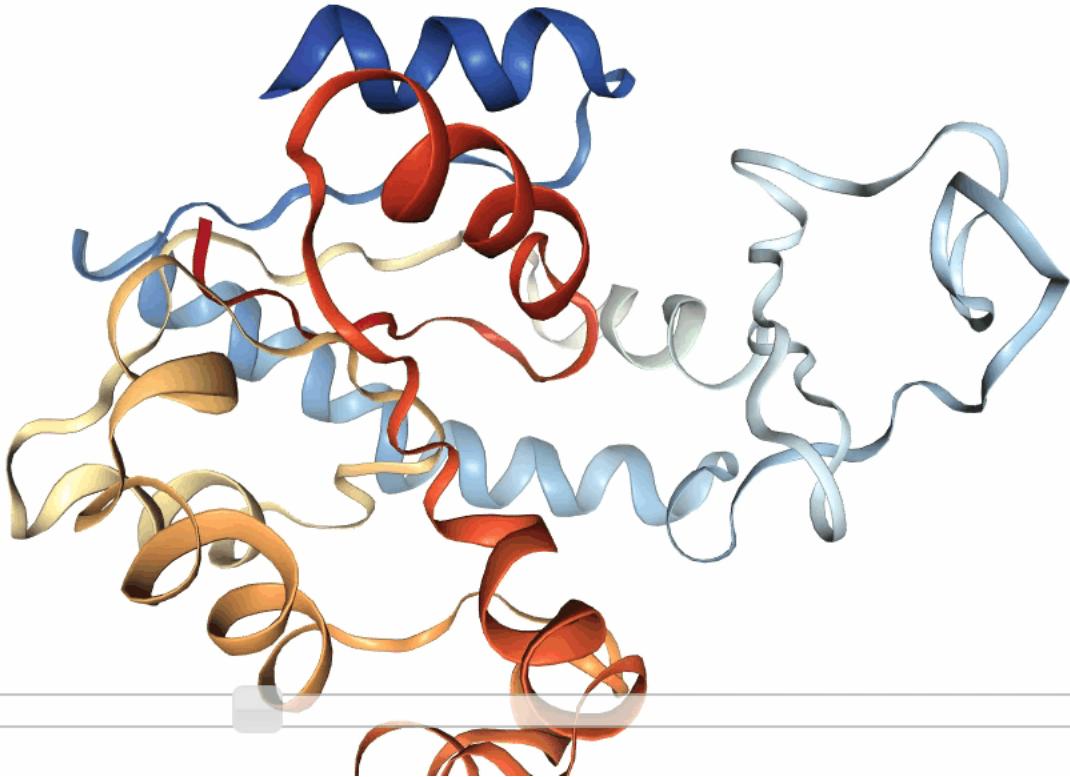


## Nonbonded Terms



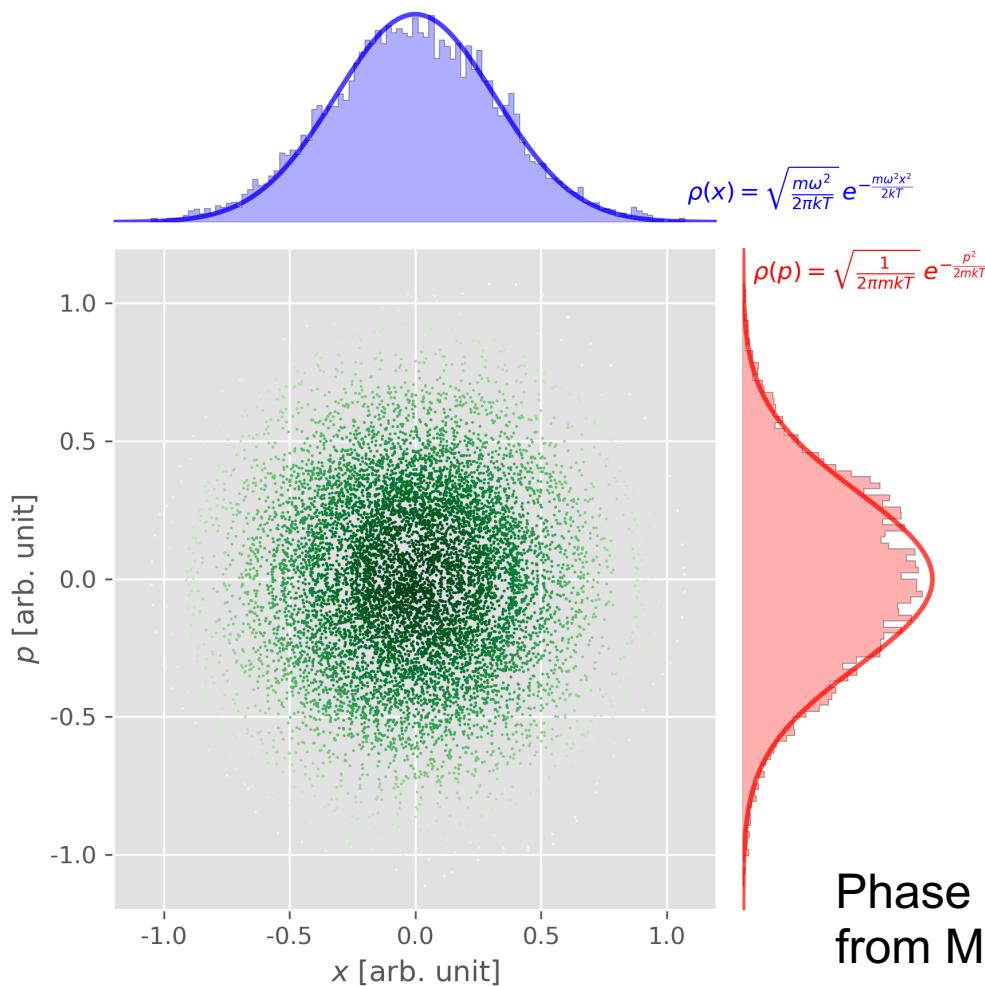
- Bonded and nonbonded
- **Harmonic** approximations
  - Bond breaking?
- Pair interactions
  - Lennard-Jones
  - Point charges

# Molecular dynamics simulations



- Evolve the trajectories of systems
  - Newton's equations of motion
- What are required?
  - Initial conditions ( $\vec{r}_0^i$ ,  $\vec{v}_0^i$  for all atoms)
  - **Thermodynamic ensemble** (NVE, NVT, NPT,...)
  - Evaluation of forces (QM or FF)
- Properties
  - **Dynamics and thermodynamics (?)**

# Statistical mechanics



Assumption: if the system is **ergodic**!

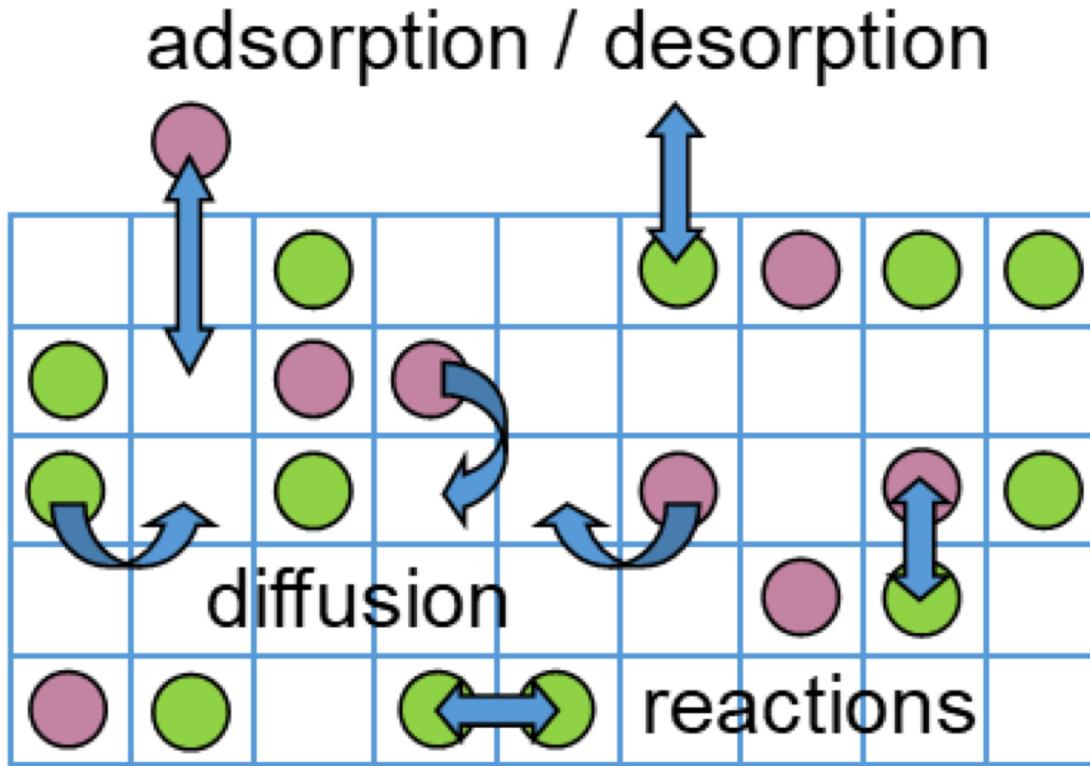
$$A = -k_B T \ln Q_{NVT}$$

$$Q_{NVT} = \frac{1}{h^{3N} N!} \int \int \exp\left[-\frac{1}{k_B T} H(x, p_x)\right] dx dp_x$$

$$A = k_B T \ln \left\langle \exp\left[\frac{1}{k_B T} H(x, p_x)\right] \right\rangle$$

Phase space distribution of 1D harmonic oscillator obtained from MD simulation with the Langevin thermostat.

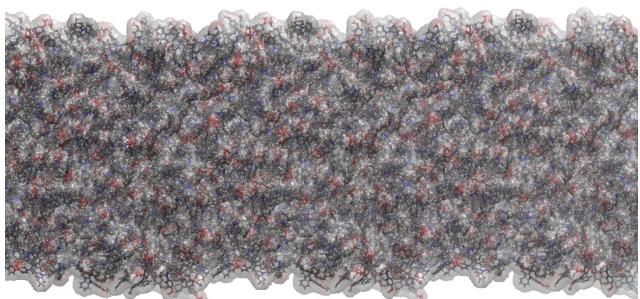
# Kinetic Monte Carlo



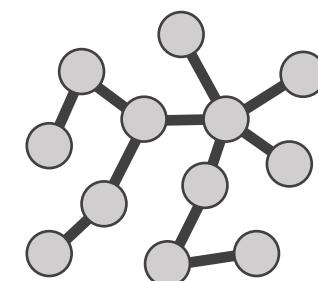
- Mesoscale simulations
- Complicated systems
  - Various events
  - Surface reactions
  - Charge transport
- Rates are needed!
  - Rate expression
  - Calculated from MD or QM

# Multiscale simulations: charge transport

## 1 Generate morphology (MD)



## 2 Transform morphology to network



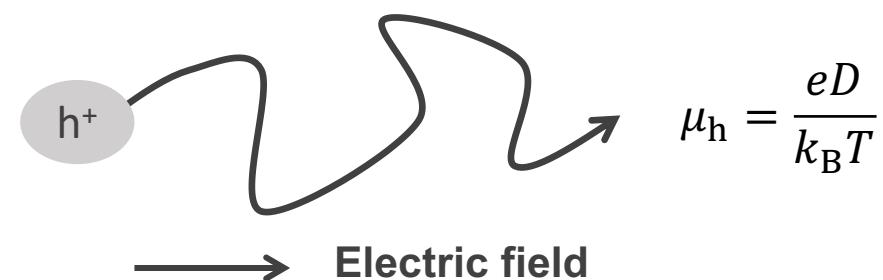
● molecule  
— molecular pair

## 3 Compute charge transfer rate

$$k_{CT} = \frac{2\pi}{h} \frac{1}{\sqrt{4\pi\lambda k_B T}} V^2 \exp \left[ -\frac{(\Delta E + \lambda)^2}{4\lambda k_B T} \right]$$

~3000 molecules and > 20,000 molecular pairs

## 4 Perform kMC simulations



# Readings

- Eigen-value problems and molecular orbitals (basic QC)
  - Molecular Quantum Mechanics 5<sup>th</sup> Ed., Peter Atkins
- Wavefunction method (Hartree-Fock Theory)
  - Chapter 3 / Introduction to Computational Chemistry 3<sup>rd</sup> Ed., Frank Jensen
- DFT
  - An introduction to density functional theory, N. M. Harrison
- Force-field
  - Chapter 2 / Introduction to Computational Chemistry 3<sup>rd</sup> Ed., Frank Jensen