

Molecular dynamics simulations

What are molecular dynamics simulations?

Numerical approaches which follow time evolutions of a system by integrating the equation of motion of the particles

They can be used to study

- thermodynamic properties
- dynamical behavior
- non-equilibrium properties

Molecular dynamics

Solving Newton's equations of motions of N particles

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i$$

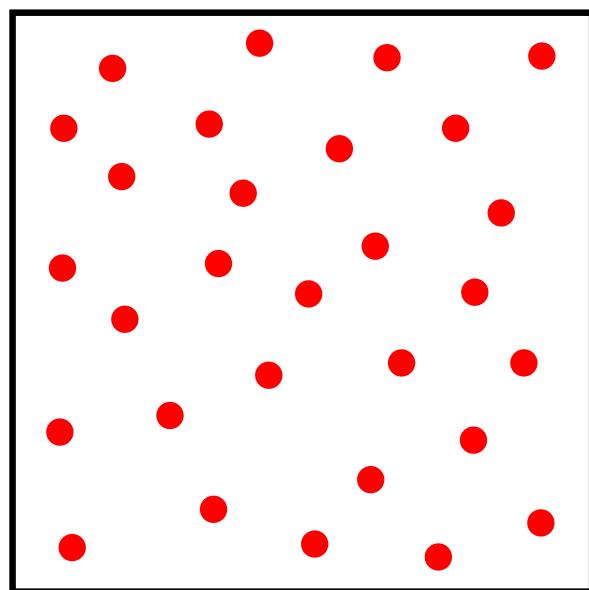
→ trajectory in $6N$ -dimensional phase space

$$(\mathbf{r}_1(t), \dots, \mathbf{r}_N(t), \dot{\mathbf{r}}_1(t), \dots, \dot{\mathbf{r}}_N(t))$$

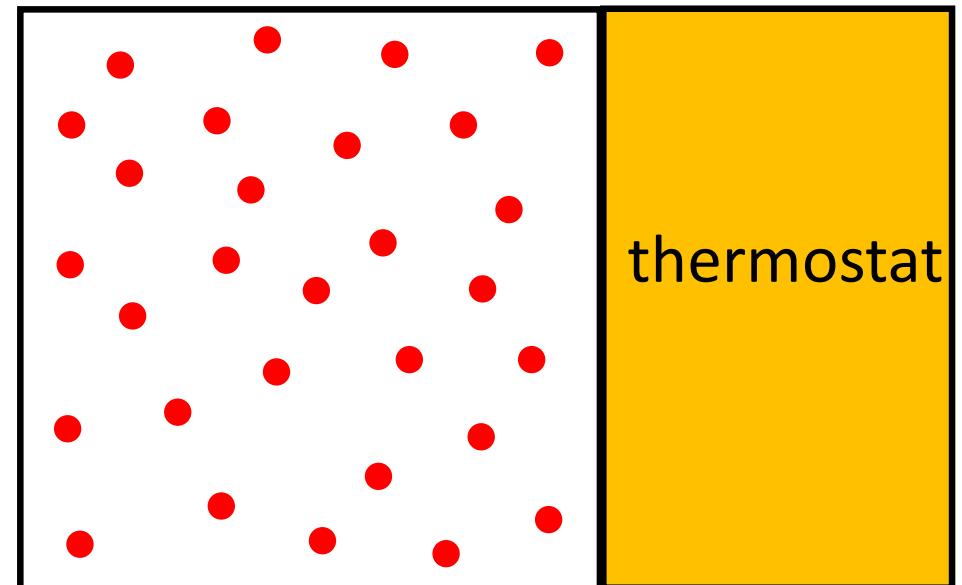
After an equilibration time, we measure the properties of the system

Molecular dynamics and statistical mechanics

$$(\mathbf{r}_1(t), \dots, \mathbf{r}_N(t), \dot{\mathbf{r}}_1(t), \dots, \dot{\mathbf{r}}_N(t))$$



NVE
microcanonical ensemble



NVT
canonical ensemble

Molecular dynamics and statistical mechanics

Work in the microcanonical ensemble

Initial conditions $\{\mathbf{r}_i(t = 0)\}, \{\dot{\mathbf{r}}_i(t = 0)\} \rightarrow E$ which is conserved



$$(\mathbf{r}_1(t), \dots, \mathbf{r}_N(t), \dot{\mathbf{r}}_1(t), \dots, \dot{\mathbf{r}}_N(t))$$

Can we study thermodynamic properties? Can we define T ?

Particle thermalize via the interactions

Molecular dynamics and statistical mechanics

We will work in the microcanonical ensemble

BUT, if the particles interact AND you have many particles,

we can introduce the concept of temperature

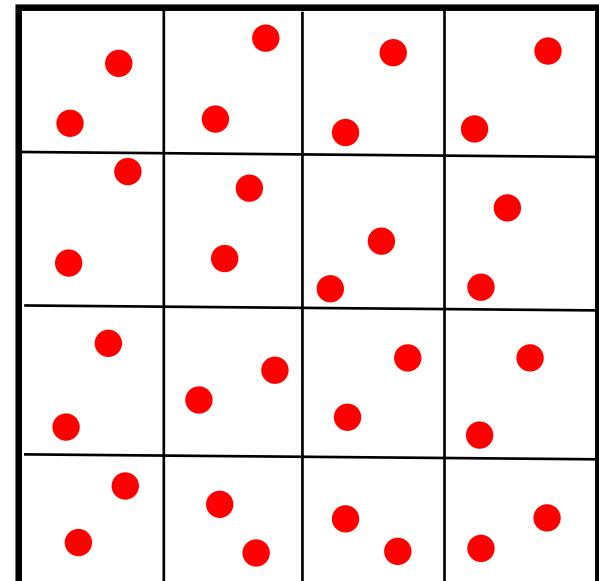
You can view your system as composed of

subsystems embedded in a bath

→ each subsystem will thermalize

(recall Stat. Phys. and how you went from micro to canonical ensemble)

NVE



Molecular dynamics and statistical mechanics

Measuring a quantity A in a molecular dynamics simulation

- Compute the instantaneous value

$$A(t) = A(\mathbf{r}_1(t), \dots, \mathbf{r}_N(t), \dot{\mathbf{r}}_1(t), \dots, \dot{\mathbf{r}}_N(t))$$

- Discard an equilibration period τ_e
- Compute the time average as $\langle A \rangle = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau A(t) dt$

→
$$\langle A \rangle = \frac{1}{N_{\text{steps}}} \sum_{t=1}^{N_{\text{steps}}} A(t)$$

Basic quantities

N particles $\rightarrow \mathbf{r}_1, \dots, \mathbf{r}_N$ and $\mathbf{v}_1, \dots, \mathbf{v}_N$

Kinetic energy

$$K = \sum_{i=1}^N \frac{m_i}{2} \mathbf{v}_i^2$$

Potential energy

$$V = V_{\text{int}}(\mathbf{r}_1, \dots, \mathbf{r}_N) + \sum_{i=1}^N u_{\text{ext}}(\mathbf{r}_i)$$

Forces

$$\mathbf{F}_i = -\nabla_i V_{\text{int}}(\mathbf{r}_1, \dots, \mathbf{r}_N) - \nabla_i u_{\text{ext}}(\mathbf{r}_i)$$

Total energy

$$E = K + V$$

Other properties

N particles $\rightarrow \mathbf{r}_1, \dots, \mathbf{r}_N$ and $\mathbf{v}_1, \dots, \mathbf{v}_N$

Temperature

$$\langle K \rangle = \frac{3N}{2} T \rightarrow T = \frac{2}{3N} \langle K \rangle$$

Distribution of velocities $P(v)$

this week

Thermodynamic properties: Pressure and pair distribution function
next week

Dynamical quantities: We would need more time ...

Classical molecular dynamics

$$V_{\text{int}}(\mathbf{r}_1, \dots, \mathbf{r}_N) \quad ?$$

Classical molecular dynamics with model interatomic potentials
(constructed with help of experiments or quantum calculations)

→ One can simulate many millions particles for many 100 ns

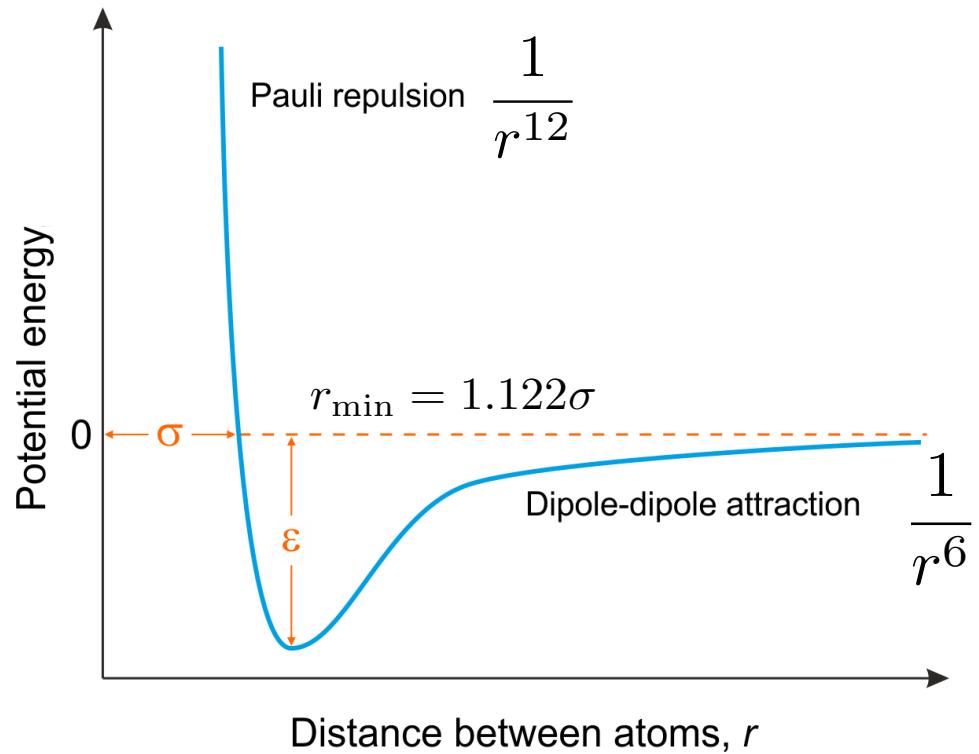
Alternative? Ab initio molecular dynamics

Forces from quantum simulations → Few 100 particles for several ps

Lennard Jones interatomic potential

Simple pair potential

$$V(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{i=1}^N \sum_{j>i} u(|\mathbf{r}_i - \mathbf{r}_j|)$$

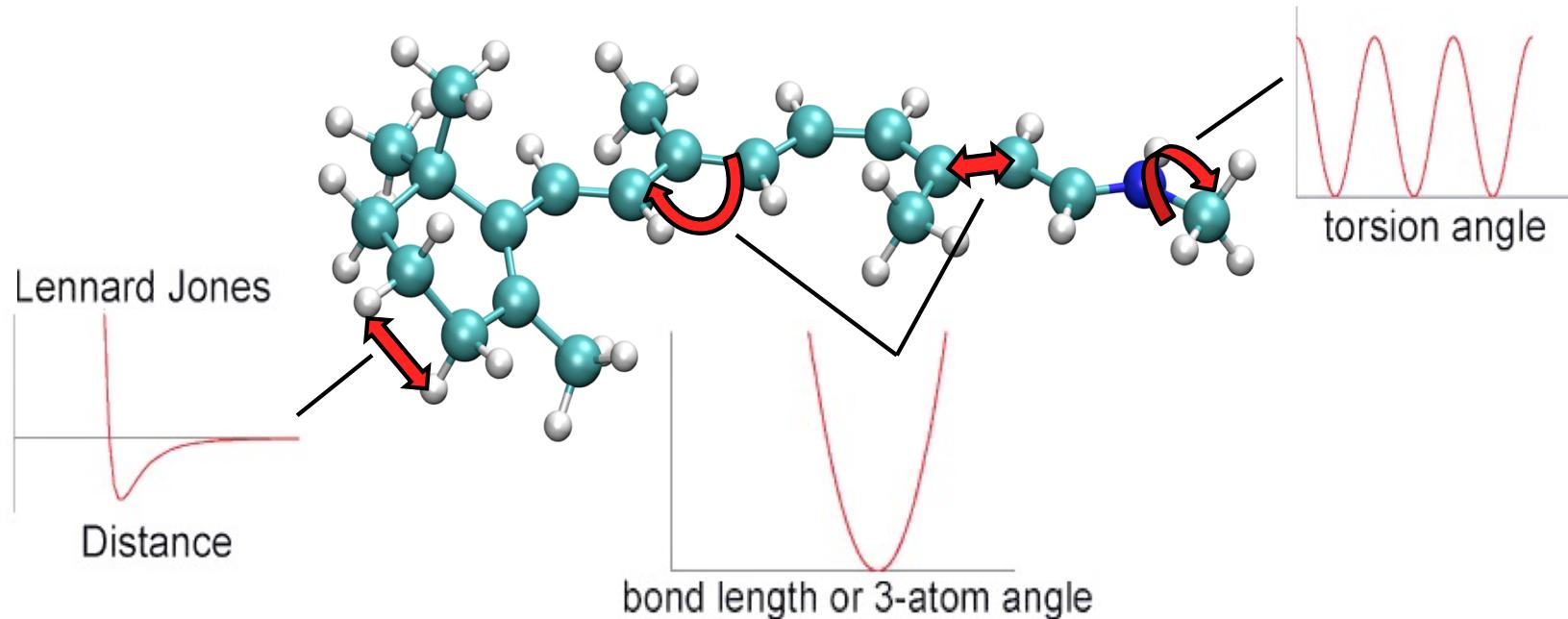


$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

good for rare gases such as Ar

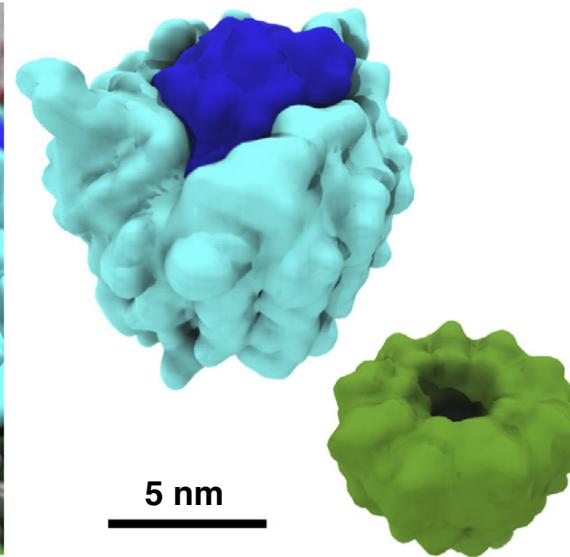
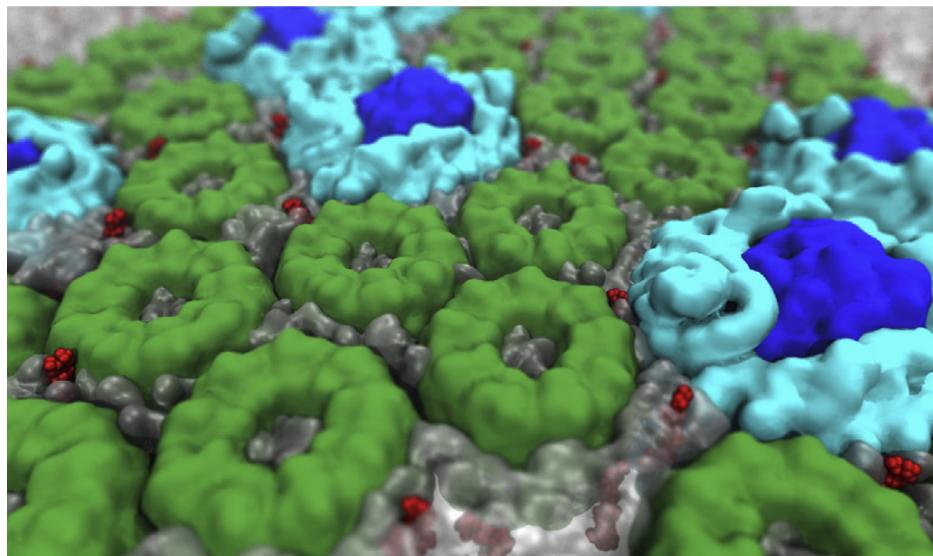
More complicated potentials

Typical form of all-atom force fields



Large-scale molecular dynamics simulations

Light harvesting membrane

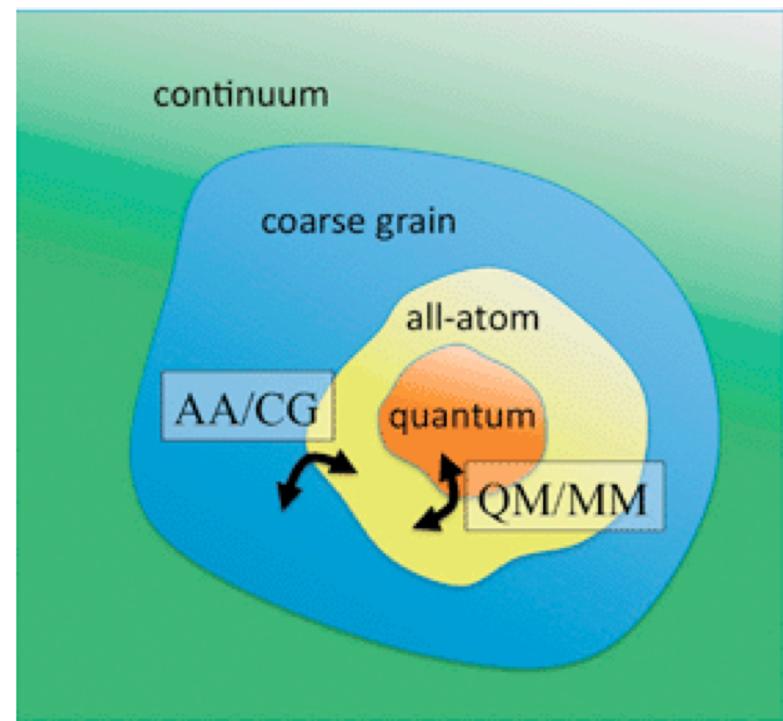
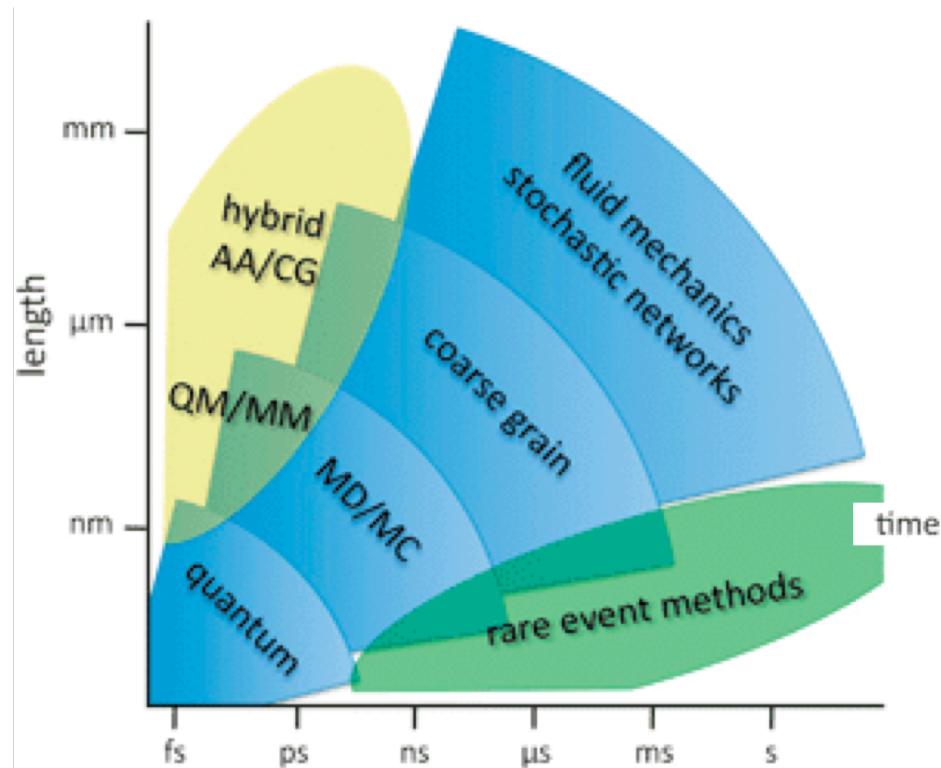


Current Opinion in Structural Biology

Schulten (2015)

22 million atoms for 150 ns

Time and length scales



B. Ensing PCCP (2010)

Let us begin

Enjoy!

Read the notes “A molecular dynamics primer” by Furio Ercolessi