



Paris International School on Advanced Computational Materials Science 2021

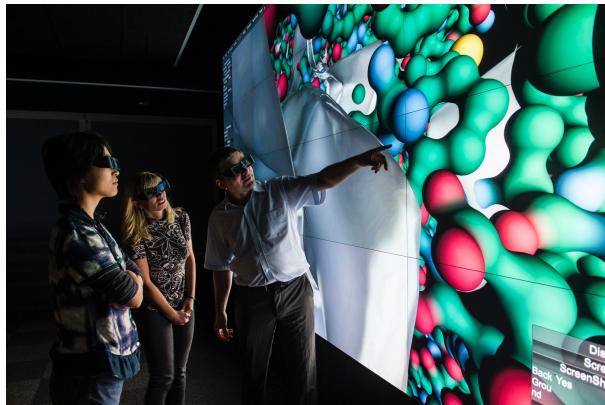
#PISACMS2021

Course 3: Classical Simulations

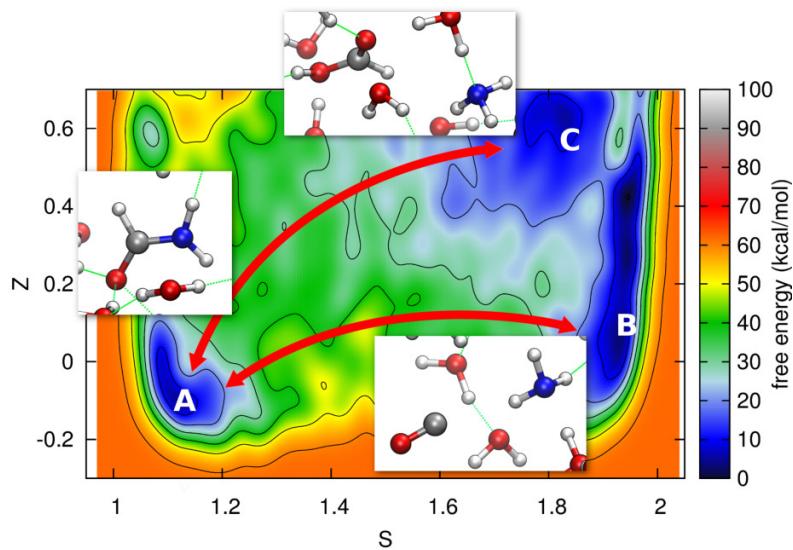
Mathieu Salanne, PHENIX laboratory

<http://www.phenix.cnrs.fr/spip.php?article20>

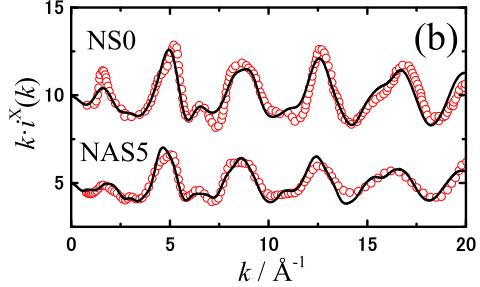
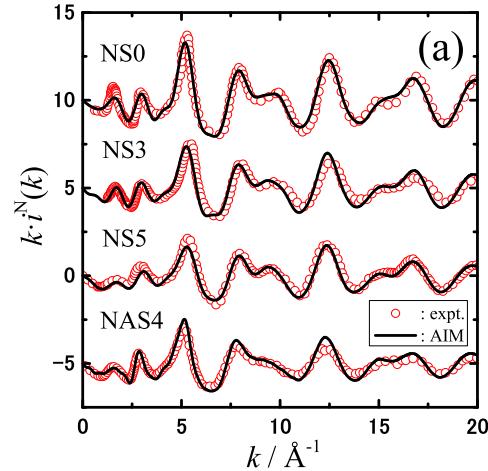
Objectives of molecular simulations



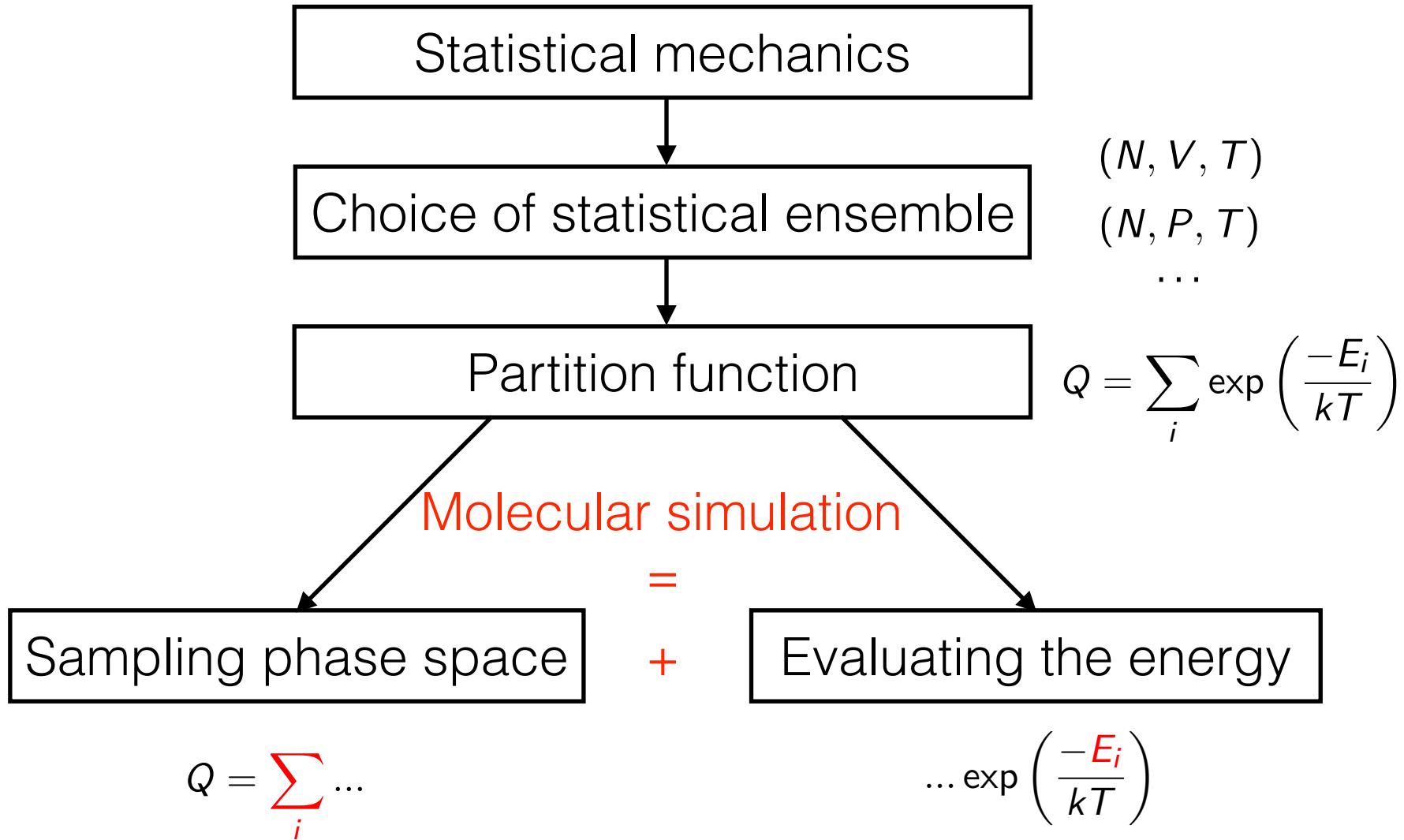
Visualization

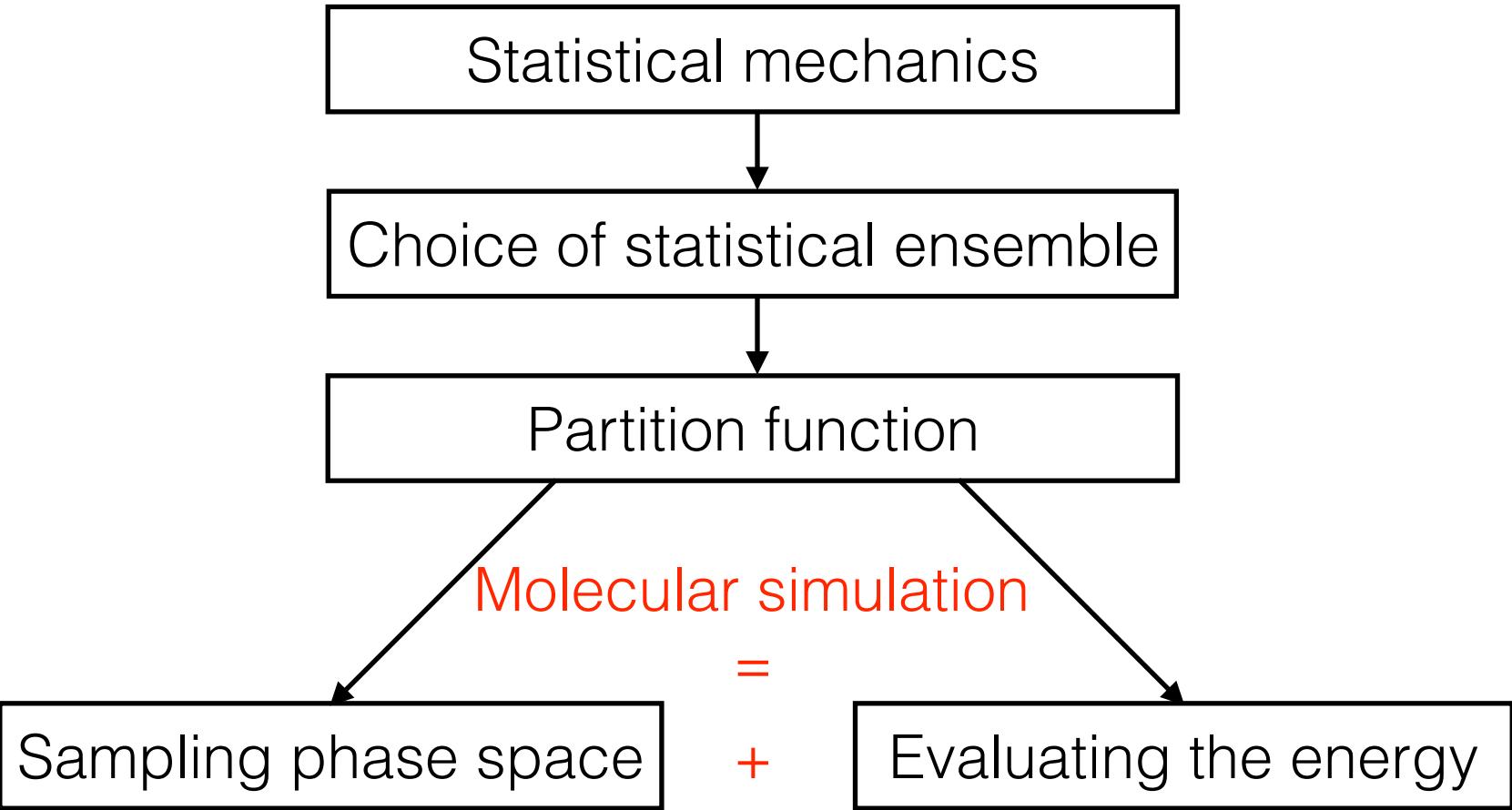


Prediction



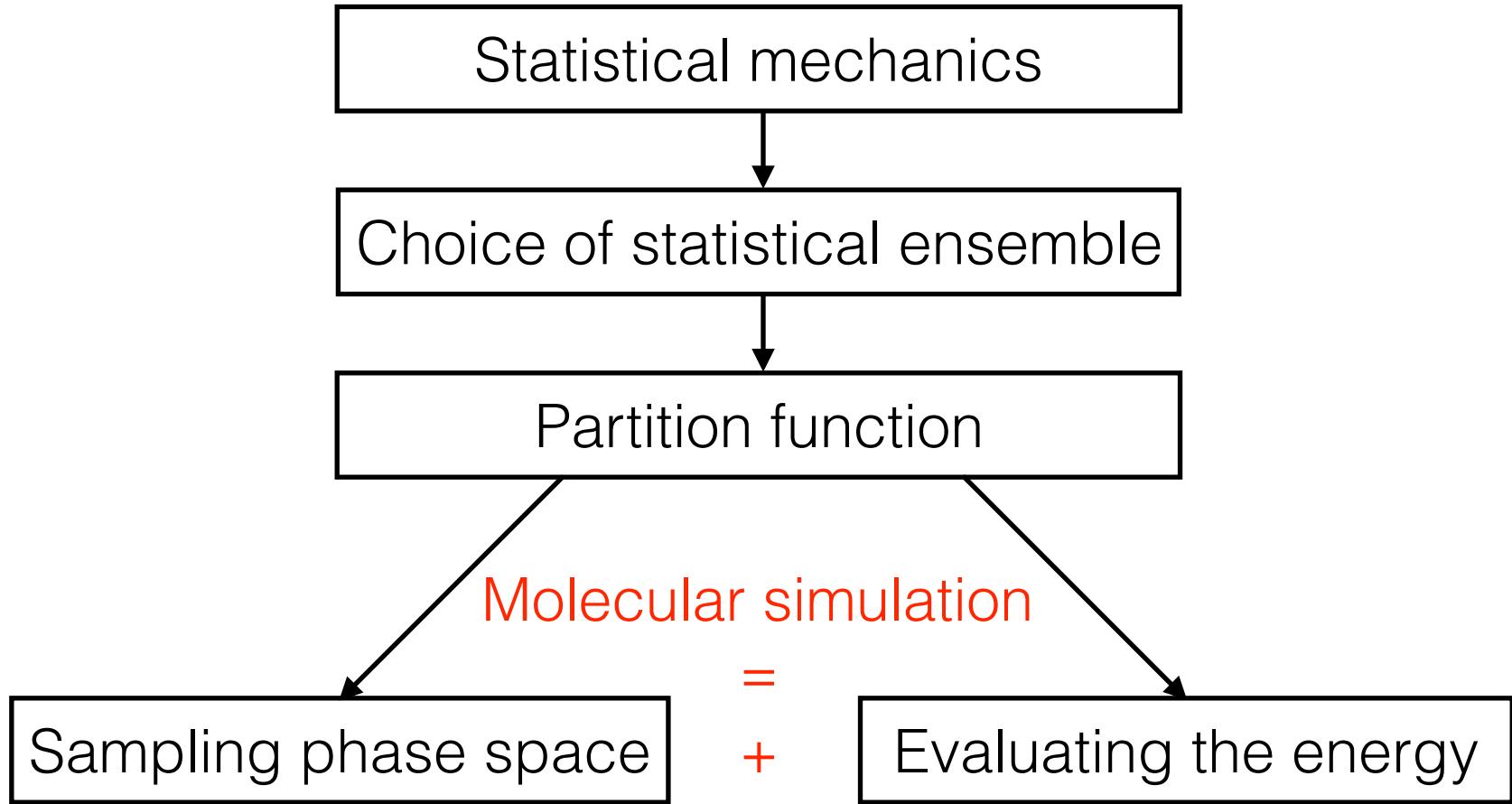
Interpretation





- Single-point calculation
- Energy minimization
- Integrating Newton's equation
(molecular dynamics = MD)
- Stochastic sampling
(Monte Carlo = MC)

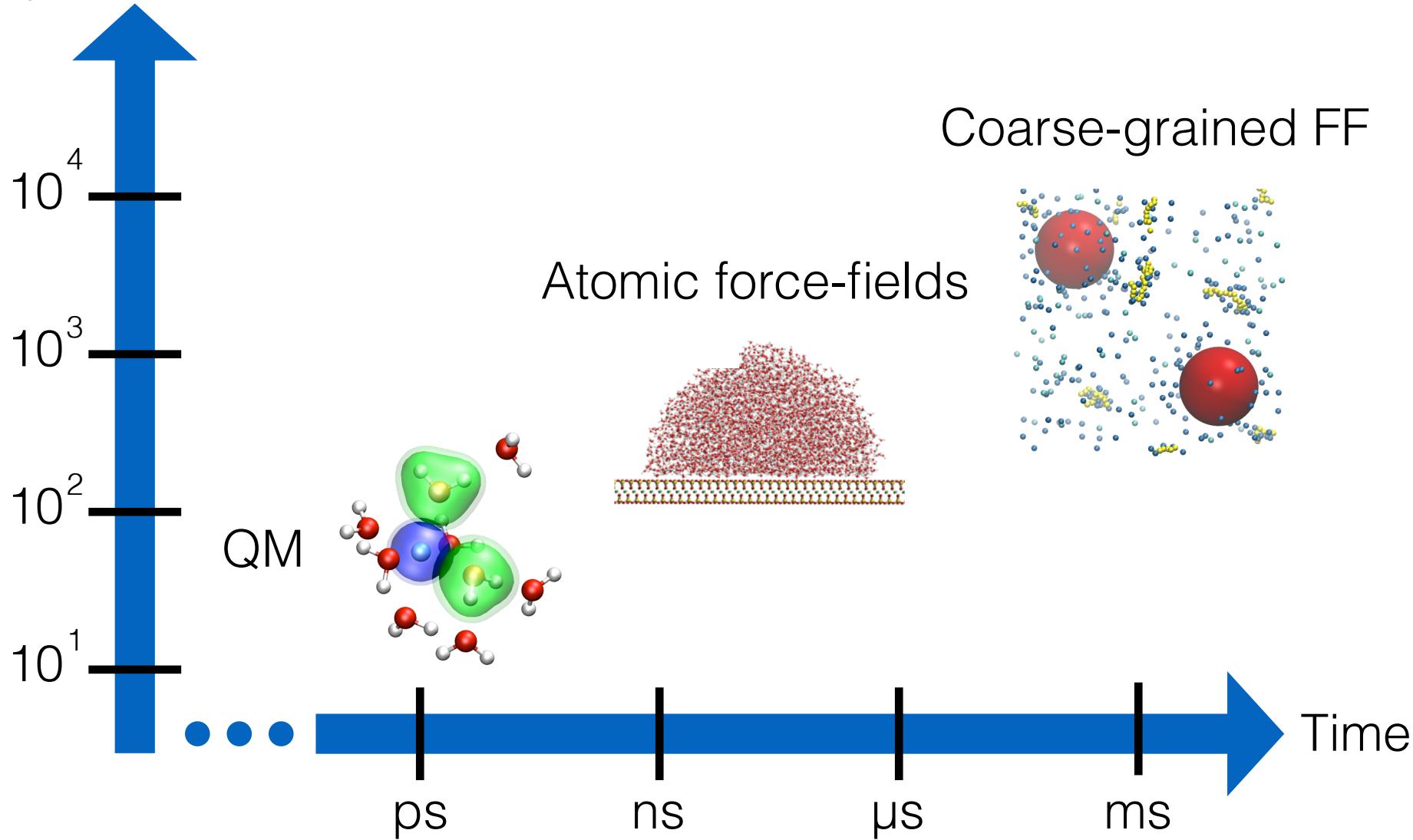
- Quantum methods
 - Hartree-Fock & post HF
 - Density Functional Theory
 - Quantum Monte Carlo
- Classical force fields



- Single-point calculation
- Energy minimization
- Integrating Newton's equation
(molecular dynamics = MD)
- Stochastic sampling
(Monte Carlo = MC)
- Quantum methods
Hartree-Fock & post HF
Density Functional Theory
Quantum Monte Carlo
- Classical force fields

Time/lengthscales

System size (atoms)



Sampling phase space

Monte Carlo

$$\mathcal{P} \propto \exp\left(-\frac{E}{kT}\right)$$

Random moves

Many statistical
ensembles

Non local sampling

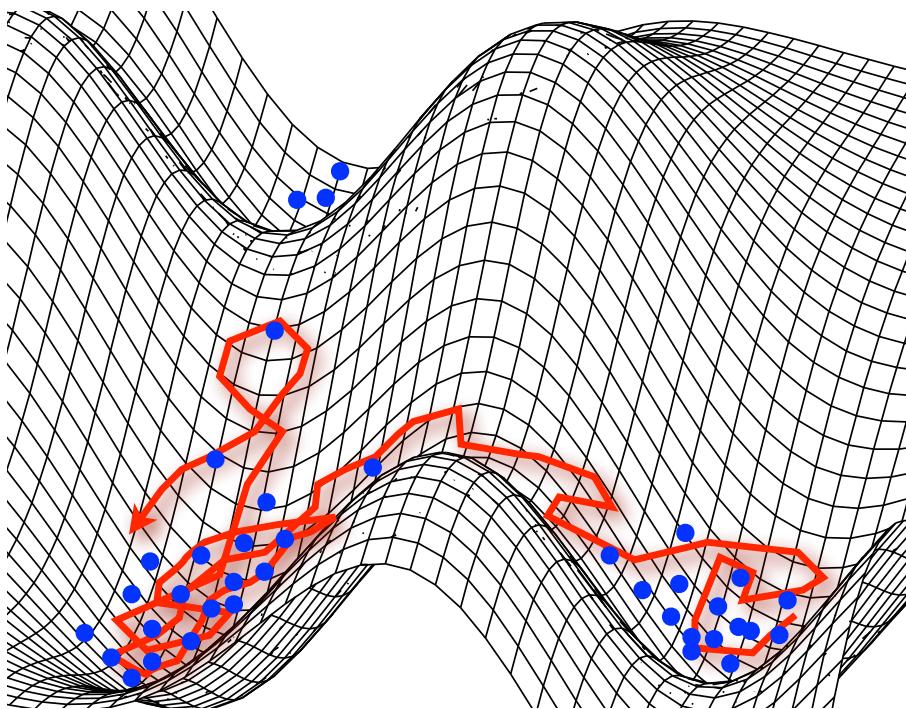
Molecular
dynamics

$$m\ddot{\mathbf{r}} = -\frac{\partial U}{\partial \mathbf{r}}$$

Trajectories

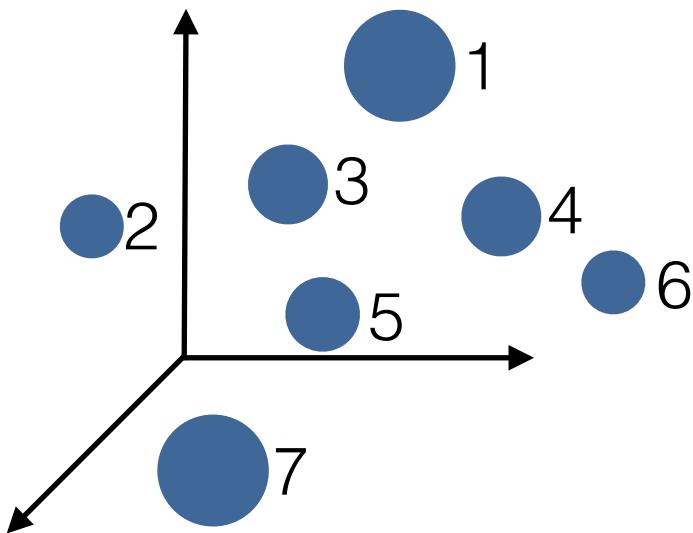
Dynamical
processes

Collective moves



Molecular dynamics: Verlet algorithm

$$\mathbf{r}_1 = (x_1, y_1, z_1); \dot{\mathbf{r}}_1 = (\dot{x}_1, \dot{y}_1, \dot{z}_1)$$



Newton's equation of motion: $m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i = -\frac{\partial \mathcal{U}}{\partial \mathbf{r}_i}$

Impossible to solve analytically

Molecular dynamics: Verlet algorithm

Taylor expansion of the positions at $t + \Delta t$:

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \dot{\mathbf{r}}(t)\Delta t + \frac{1}{2!}\ddot{\mathbf{r}}(t)\Delta t^2 + \frac{1}{3!}\dddot{\mathbf{r}}(t)\Delta t^3 + \mathcal{O}(\Delta t^4)$$

$\mathbf{r}(t)$, $\dot{\mathbf{r}}(t)$ are known

$\ddot{\mathbf{r}}(t)$ calculated using Newton's equation

$\dddot{\mathbf{r}}(t)$ unknown

—————> error of order $\mathcal{O}(\Delta t^3)$

Molecular dynamics: Verlet algorithm

Taylor expansion of the positions at $t + \Delta t$:

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \dot{\mathbf{r}}(t)\Delta t + \frac{1}{2!}\ddot{\mathbf{r}}(t)\Delta t^2 + \frac{1}{3!}\dddot{\mathbf{r}}(t)\Delta t^3 + \mathcal{O}(\Delta t^4)$$

Taylor expansion of the positions at $t - \Delta t$:

$$\mathbf{r}(t - \Delta t) = \mathbf{r}(t) - \dot{\mathbf{r}}(t)\Delta t + \frac{1}{2!}\ddot{\mathbf{r}}(t)\Delta t^2 - \frac{1}{3!}\dddot{\mathbf{r}}(t)\Delta t^3 + \mathcal{O}(\Delta t^4)$$



$$\mathbf{r}(t + \Delta t) + \mathbf{r}(t - \Delta t) = 2\mathbf{r}(t) + \frac{1}{2!}\ddot{\mathbf{r}}(t)\Delta t^2 + \mathcal{O}(\Delta t^4)$$

$$\longrightarrow \mathbf{r}(t + \Delta t) = 2\mathbf{r}(t) - \mathbf{r}(t - \Delta t) + \frac{1}{2!}\ddot{\mathbf{r}}(t)\Delta t^2 + \mathcal{O}(\Delta t^4)$$

Molecular dynamics: Verlet algorithm

For the velocities :

$$\mathbf{r}(t + \Delta t) - \mathbf{r}(t - \Delta t) = 2\dot{\mathbf{r}}(t)\Delta t + \mathcal{O}(\Delta t^2)$$



$$\dot{\mathbf{r}}(t) = \frac{\mathbf{r}(t + \Delta t) - \mathbf{r}(t - \Delta t)}{2\Delta t} + \mathcal{O}(\Delta t^2)$$

- Error of the order of $\mathcal{O}(\Delta t^2)$
- Need to know the positions at $t + \Delta t$

—————> Problem for thermostatting

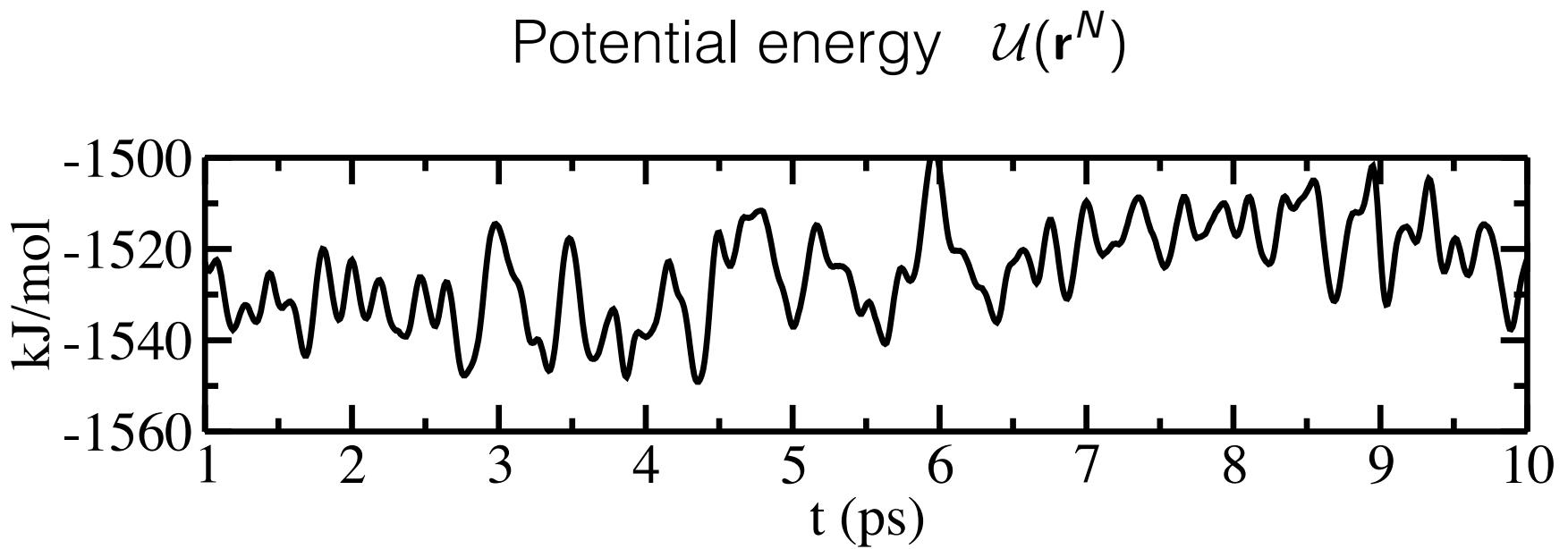
Velocity Verlet

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \dot{\mathbf{r}}(t)\Delta t + \frac{1}{2!}\ddot{\mathbf{r}}(t)\Delta t^2 + \mathcal{O}(\Delta t^4)$$

$$\dot{\mathbf{r}}(t + \Delta t) = \dot{\mathbf{r}}(t) + \frac{\ddot{\mathbf{r}}(t) + \ddot{\mathbf{r}}(t + \Delta t)}{2}\Delta t + \mathcal{O}(\Delta t^2)$$

Most widely used algorithm in MD packages

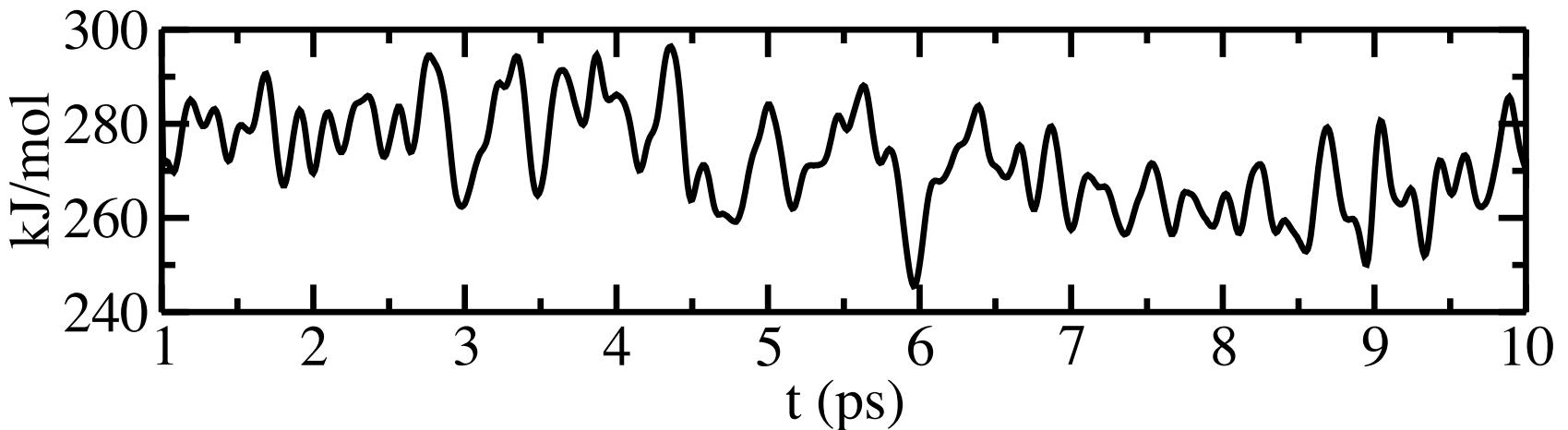
Energy conservation



System: 256 Argon atoms

Energy conservation

Kinetic energy $\mathcal{K}(\dot{\mathbf{r}}^N) = \sum_{i=1}^N \frac{1}{2} m_i \dot{\mathbf{r}}_i^2$



System: 256 Argon atoms

Energy conservation

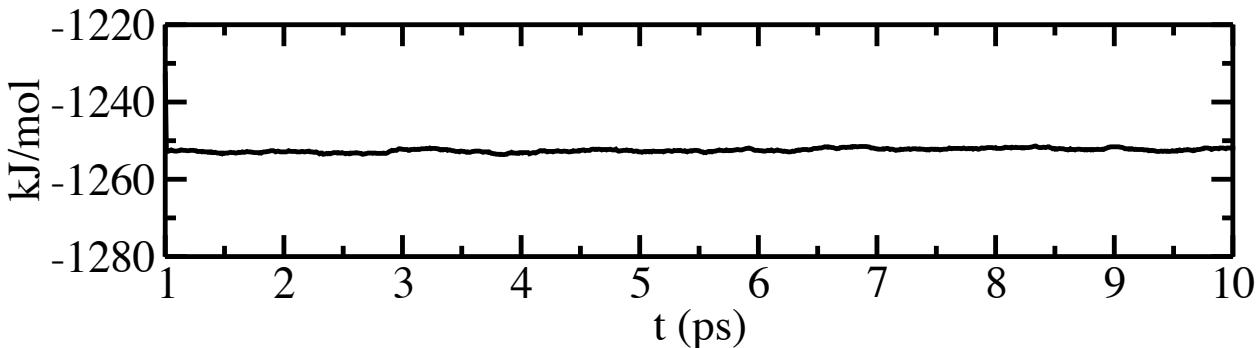
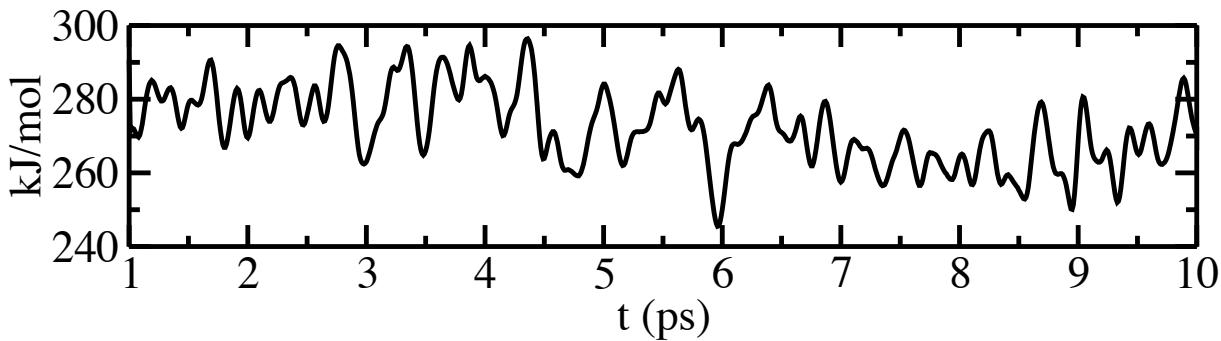
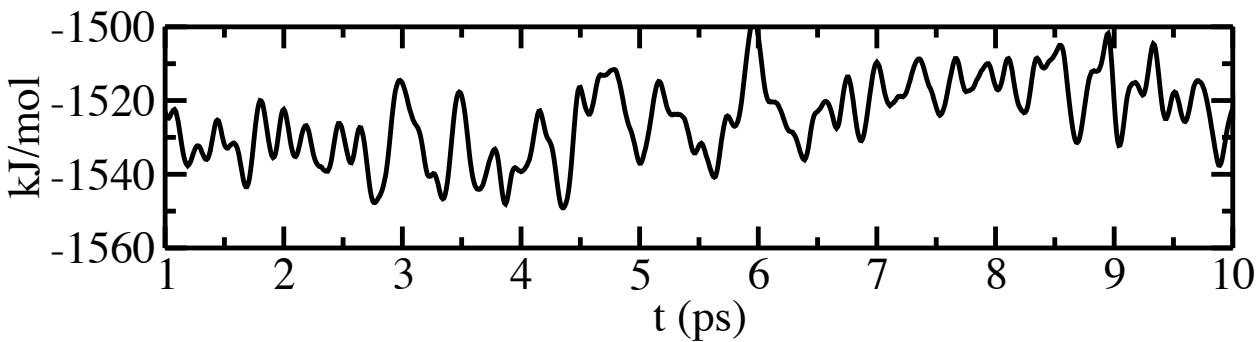
Potential energy

+

Kinetic energy

=

Total energy



Thermodynamic ensembles in MD

(N, V, E) Straightforward

(N, V, T) With a thermostat

(N, P, T) With a barostat

(μ, \check{V}, T) Impossible

Berendsen thermostat

Instantaneous temperature: $\mathcal{T}(t) = \frac{1}{3kN} \sum_{i=1}^N m_i \dot{\mathbf{r}}_i^2$

External heat bath at fixed temperature: $\frac{d\mathcal{T}}{dt} = \frac{1}{\tau} (T_0 - \mathcal{T}(t))$

Velocities scaled at each step: $\dot{\mathbf{r}}_{\text{new}}(t) = \lambda \dot{\mathbf{r}}_{\text{old}}(t)$

Scaling factor: $\lambda = \left[1 + \frac{\Delta t}{\tau} \left(\frac{T_0}{\mathcal{T}(t)} - 1 \right) \right]^{1/2}$

Does not sample correctly the canonical ensemble

—————> Useful for equilibration

Nosé-Hoover thermostat

Add friction term to Newtonian equations of motion

$$\ddot{\mathbf{r}}_i = \frac{\mathbf{F}_i}{m_i} - \chi \dot{\mathbf{r}}_i$$

which is dynamical and responds to temperature fluctuation

$$\dot{\chi} = \frac{1}{Q} \left[\sum_{i=1}^N m_i \dot{\mathbf{r}}_i^2 - 3NkT \right]$$

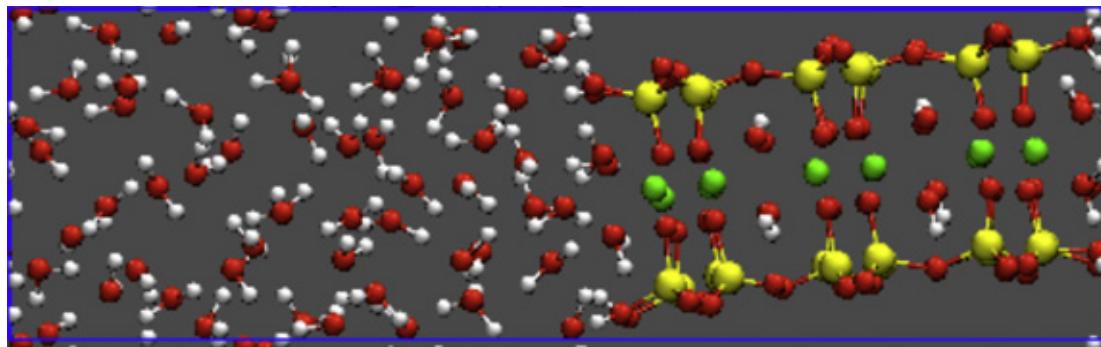
—————> Q is an effective mass(inertia) for the friction

Total energy for the extended system:

$$\mathcal{H}_{\text{NH}} = \mathcal{H} + \frac{Q}{2} \chi^2 + 3NkT \int \chi dt$$

It is a conserved quantity: $\frac{d\mathcal{H}_{\text{NH}}}{dt} = 0$

Periodic boundary conditions



Periodic boundary conditions

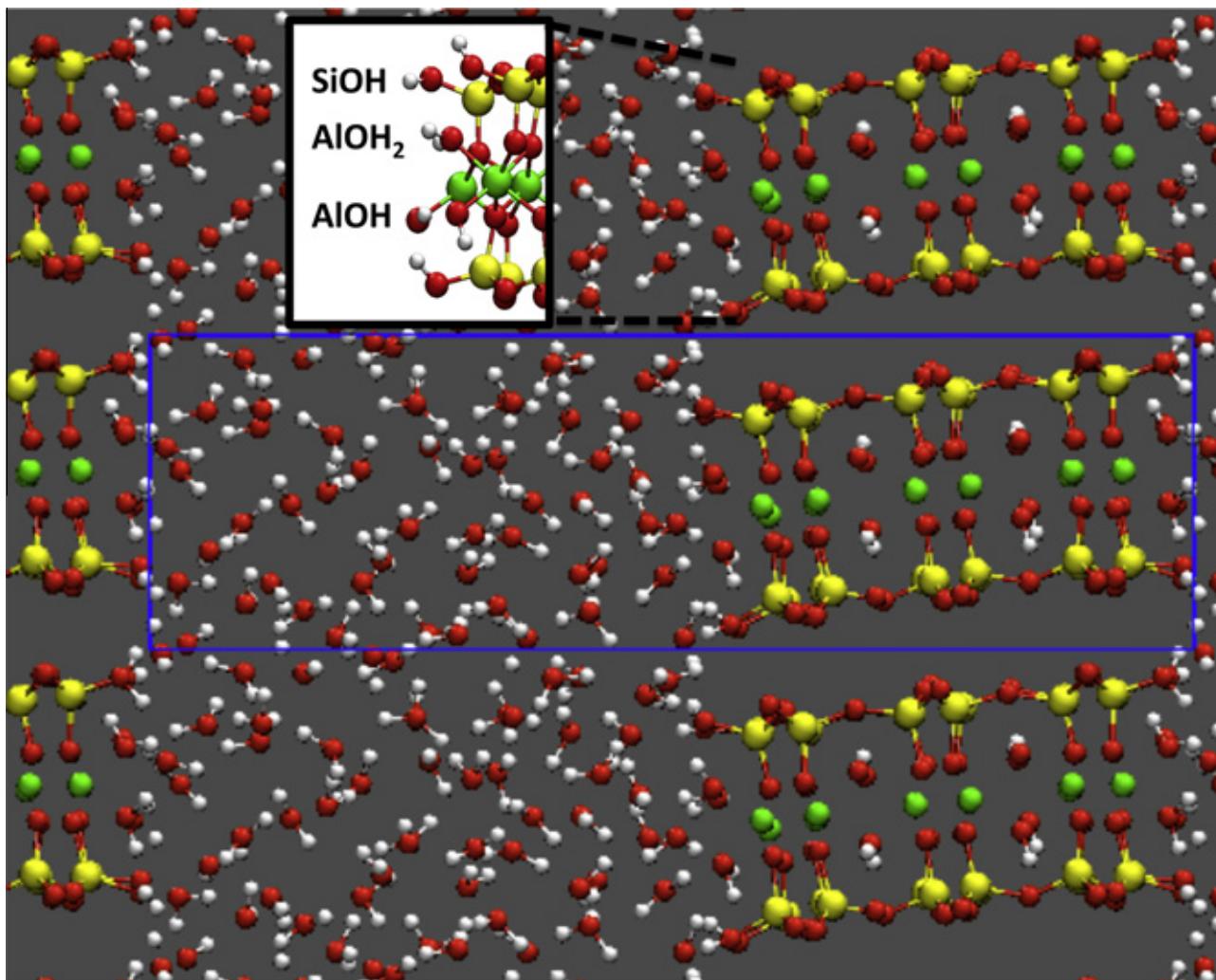
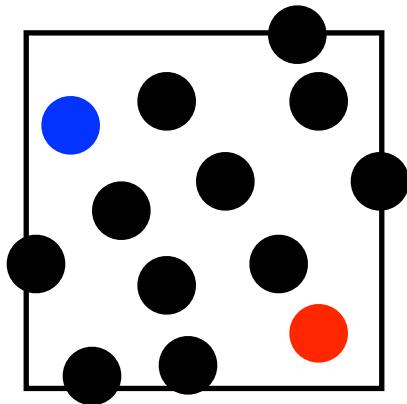
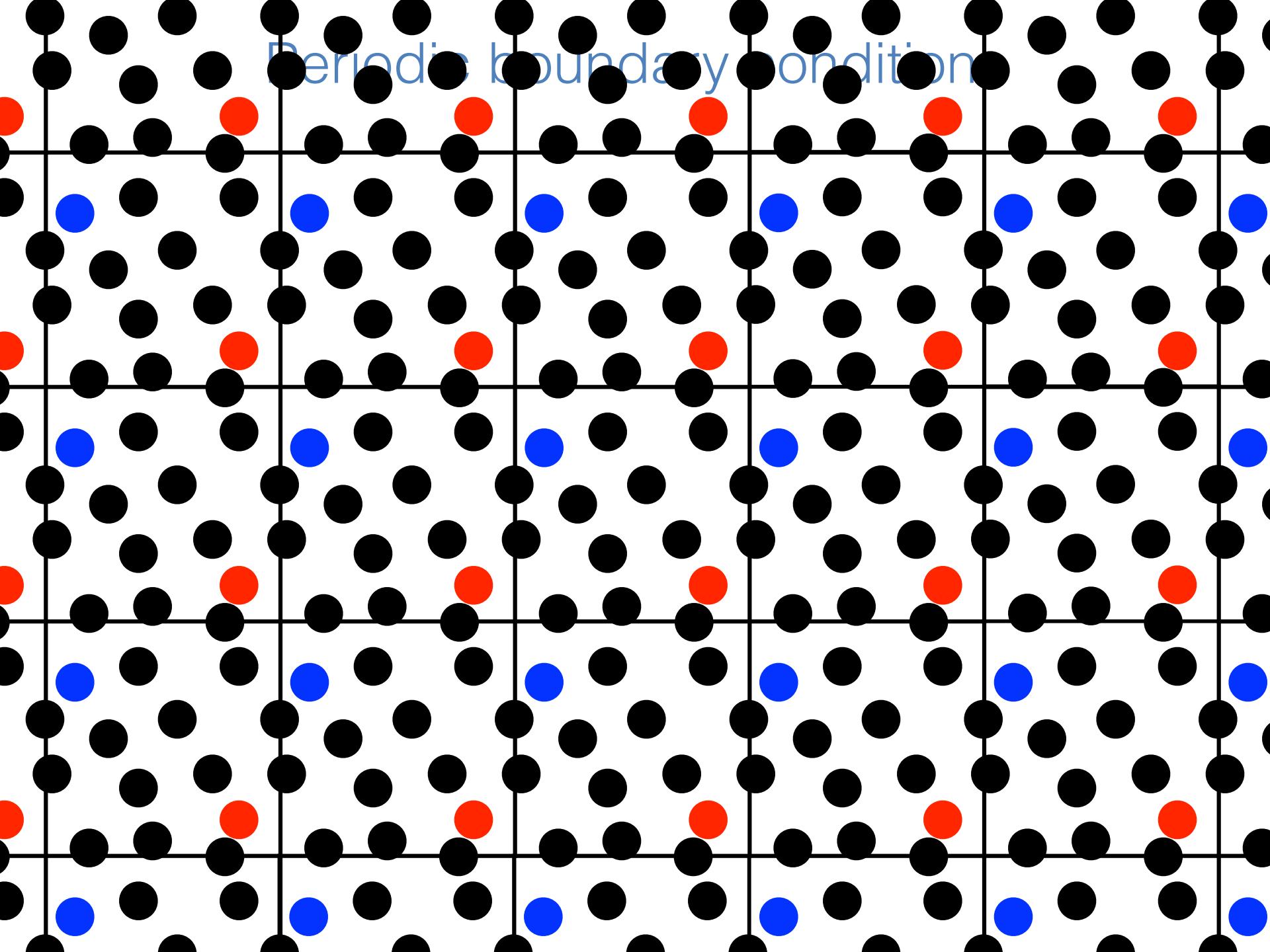


Figure from Tazi, Geochim. Cosmochim. Acta, 2012

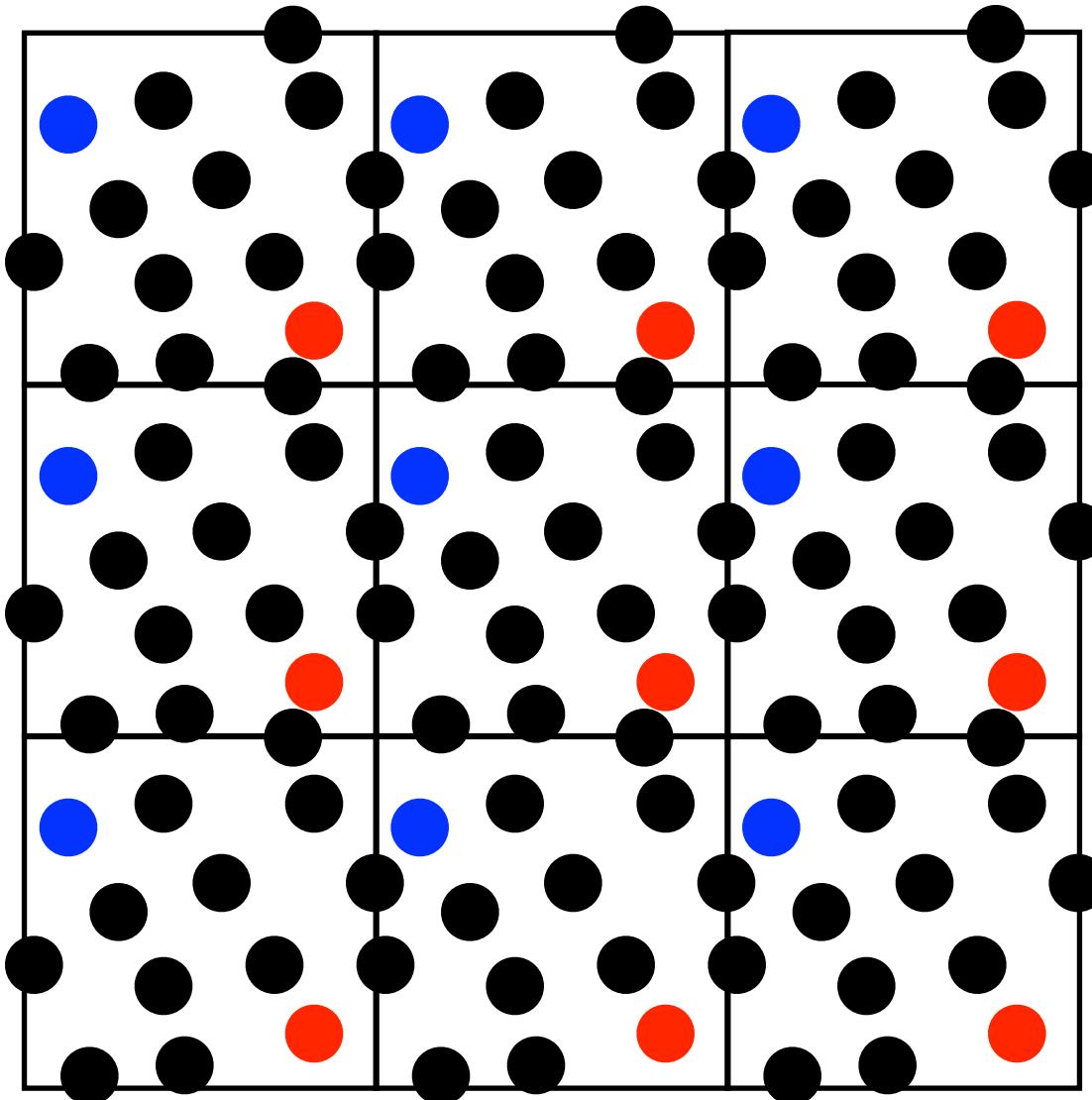
Periodic boundary conditions



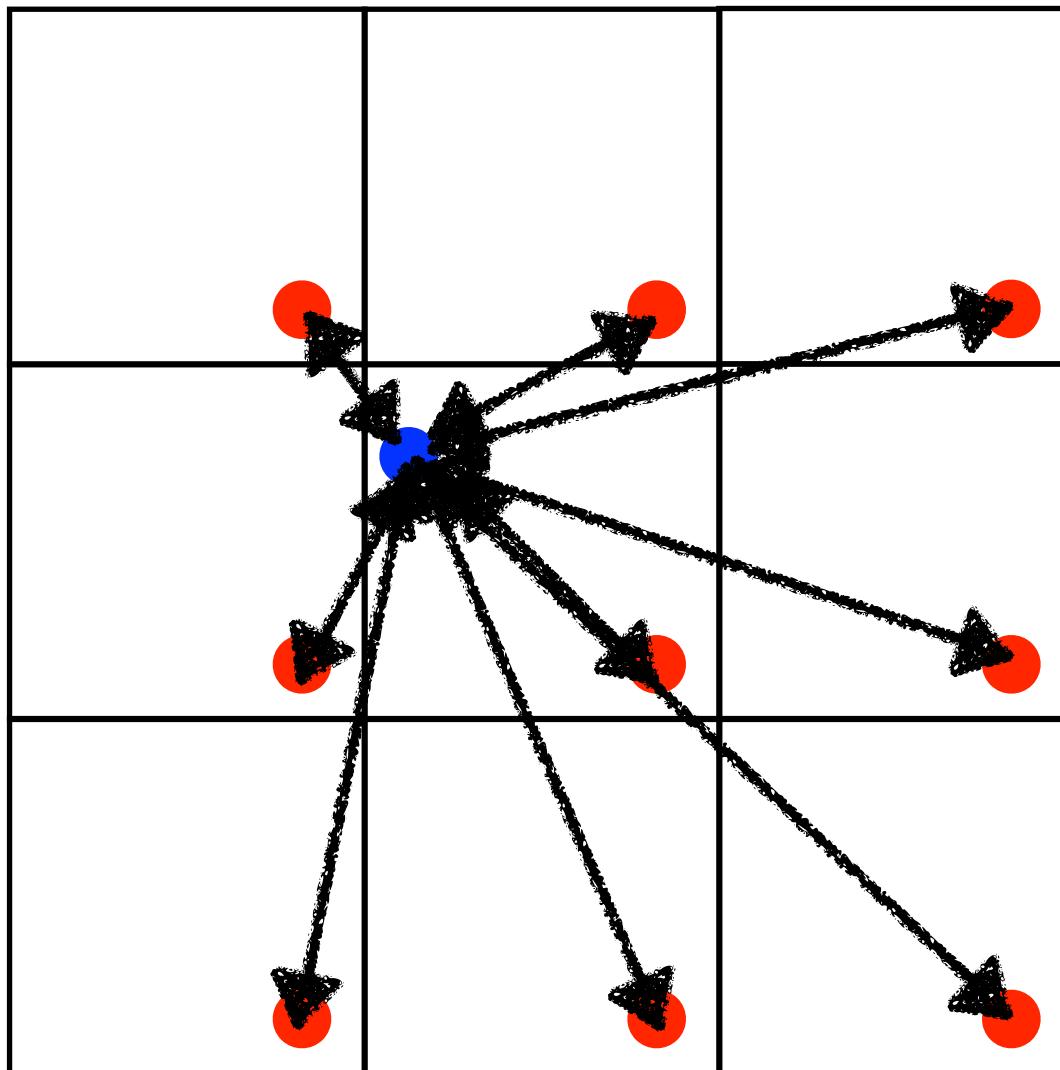
Periodic boundary condition



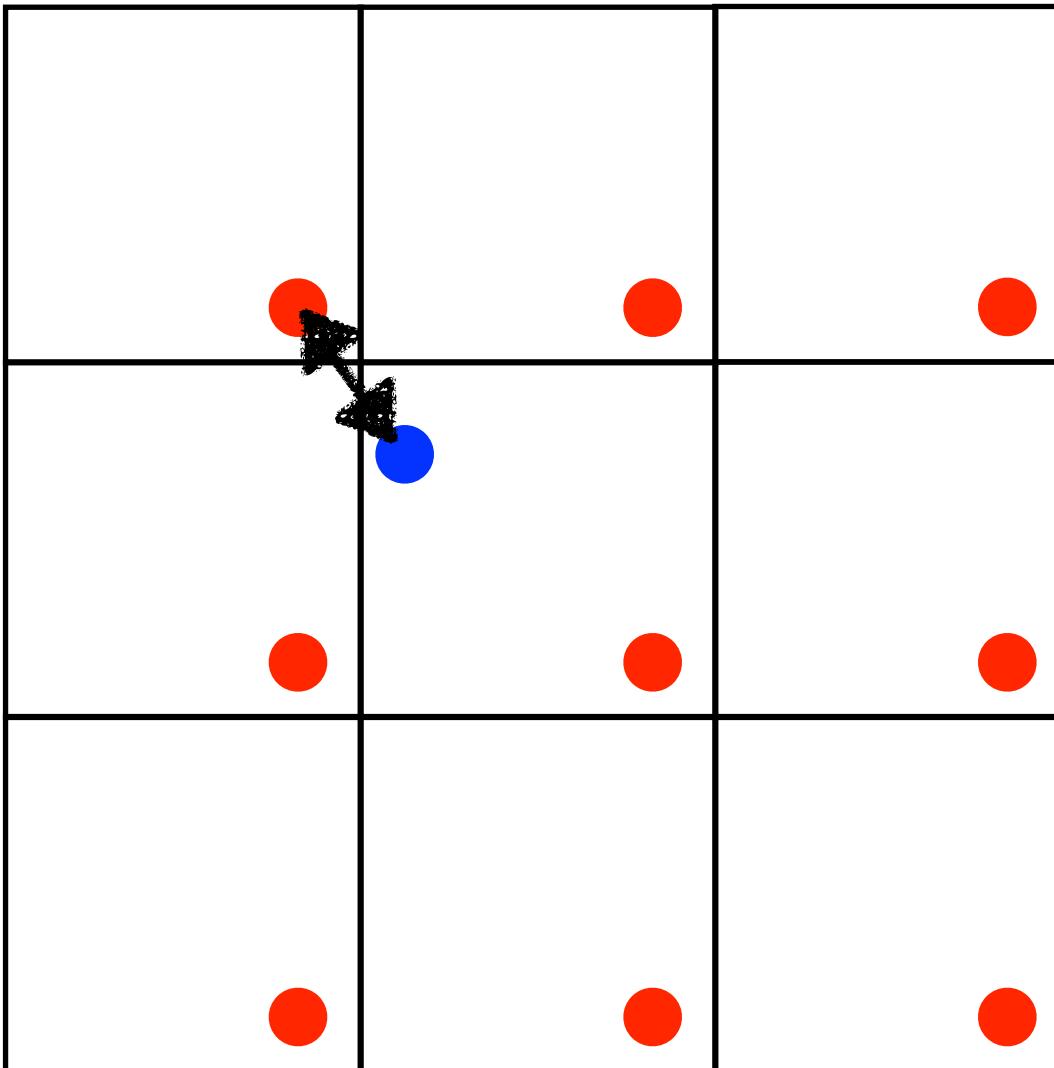
Periodic boundary conditions



Periodic boundary conditions

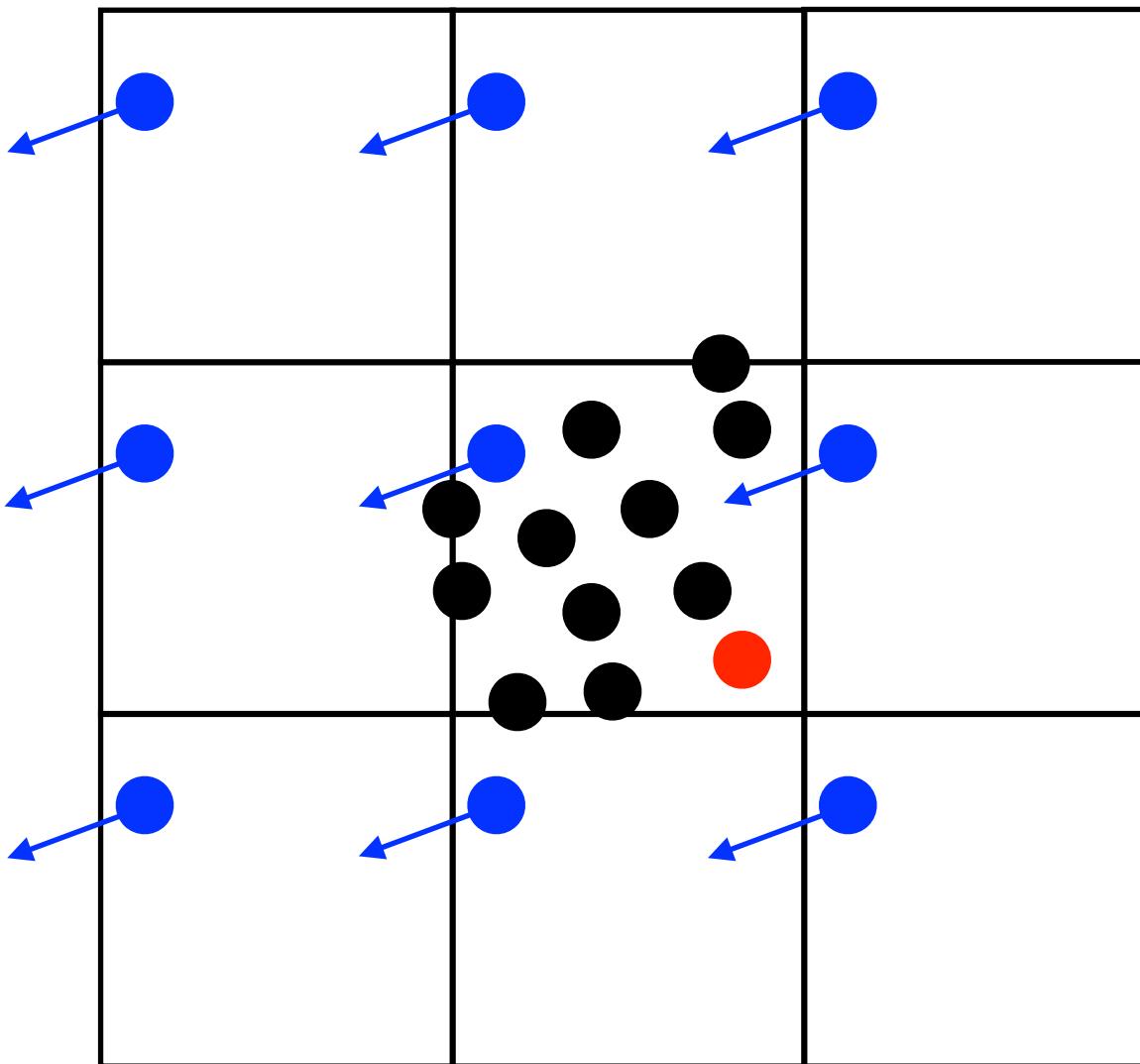


Periodic boundary conditions

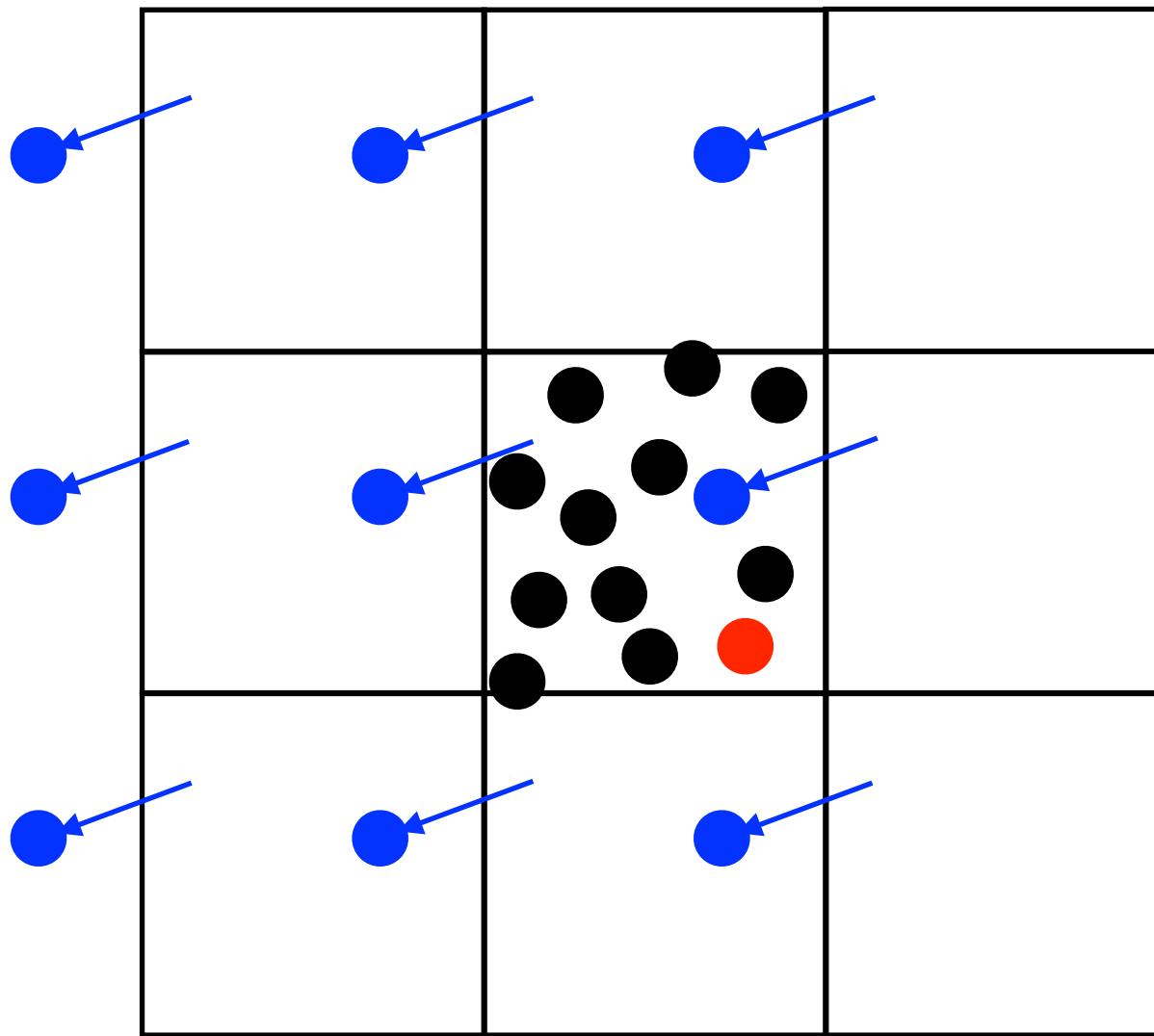


Minimum image convention

Periodic boundary conditions



Periodic boundary conditions



Constant number of atoms in the cell

Lagrangian mechanics

Lagrangian for a system consisting of n generalized degrees of freedom:

$$\mathcal{L}(\mathbf{q}^N, \dot{\mathbf{q}}^N) = \mathcal{K}(\dot{\mathbf{q}}^N) - \mathcal{U}(\mathbf{q}^N)$$


Kinetic energy Potential energy

Equations of motion with Euler-Lagrange equation:

$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{q}}_i} - \frac{\partial \mathcal{L}}{\partial \mathbf{q}_i} = 0$$

Lagrangian mechanics

For a system consisting of N atoms:

$$\mathcal{L}(\mathbf{r}^N, \dot{\mathbf{r}}^N) = \mathcal{K}(\dot{\mathbf{r}}^N) - \mathcal{U}(\mathbf{r}^N) = \sum_{i=1}^N \frac{1}{2} m_i \dot{\mathbf{r}}_i^2 - \mathcal{U}(\mathbf{r}^N)$$

$$\frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_i} = m_i \ddot{\mathbf{r}}_i \quad \text{and} \quad \frac{\partial \mathcal{L}}{\partial \mathbf{r}_i} = -\frac{\partial \mathcal{U}}{\partial \mathbf{r}_i}$$

so that Euler-Lagrange is equivalent to Newton's equation:

$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_i} - \frac{\partial \mathcal{L}}{\partial \mathbf{r}_i} = 0 \quad \equiv \quad m_i \ddot{\mathbf{r}}_i = -\frac{\partial \mathcal{U}}{\partial \mathbf{r}_i}$$

Constraints with SHAKE algorithm

Extended Lagrangian with constraints:

$$\mathcal{L}^*(\mathbf{r}^N, \dot{\mathbf{r}}^N) = \mathcal{L}(\mathbf{r}^N, \dot{\mathbf{r}}^N) + \sum_{k=1}^n \lambda_k \sigma_k(\mathbf{r}^N)$$

λ_k is a Lagrange multiplier associated to the constraint:

$$\sigma_k(\mathbf{r}^N) = (\xi(\mathbf{r}^N) - \xi_k)$$

For example to fix the distance between a couple of atoms:

$$\sigma_k(\mathbf{r}^N) = (\mathbf{r}_i - \mathbf{r}_j)^2 - d_{ij}^2$$

Constraints with SHAKE algorithm

We now have $\frac{\partial \mathcal{L}}{\partial \mathbf{r}_i} = \mathbf{F}_i - \sum_{k=1}^n \lambda_k \frac{\partial \sigma_k}{\partial \mathbf{r}_i}$



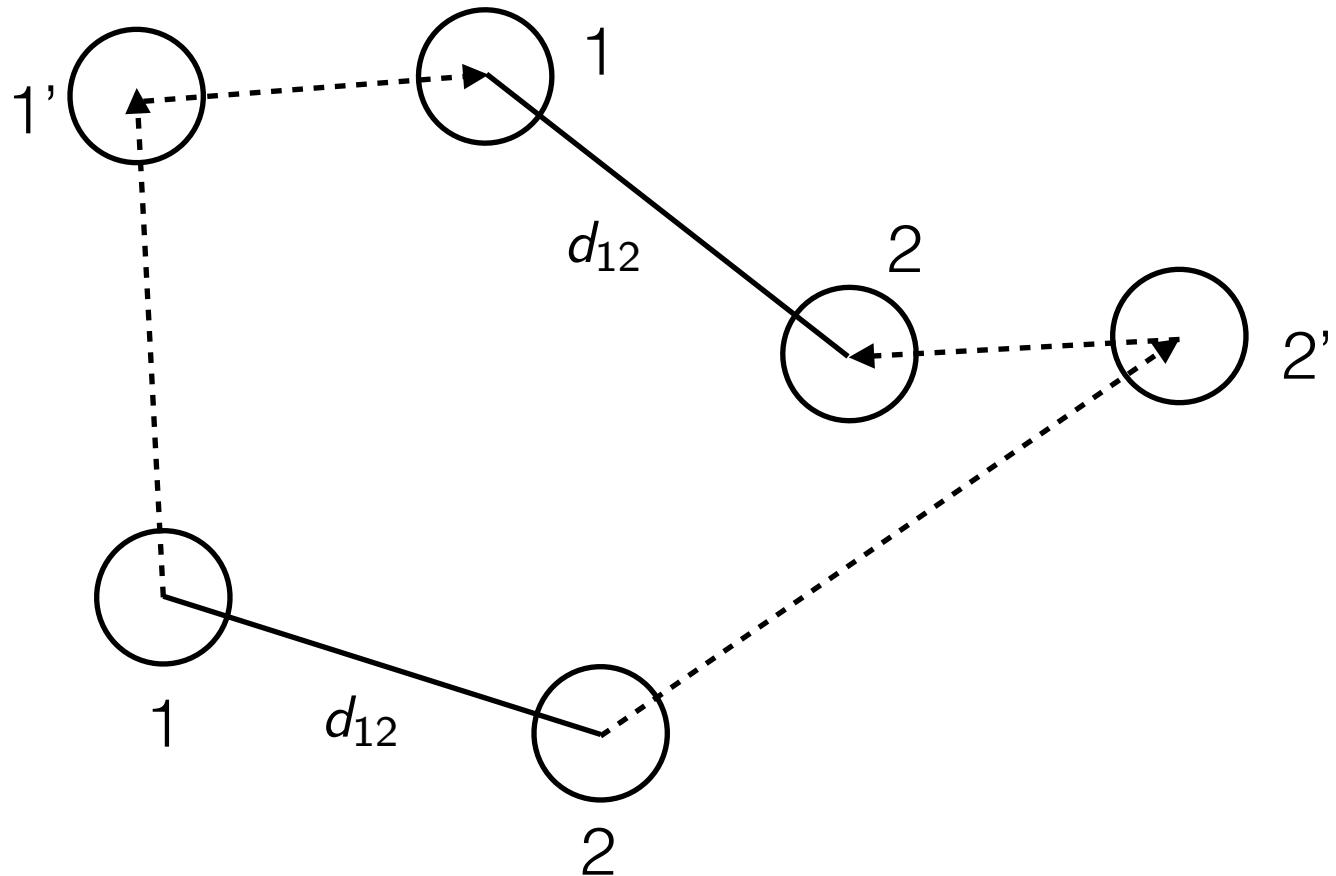
\mathbf{G}_i additional force

The new equation of motion is:

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

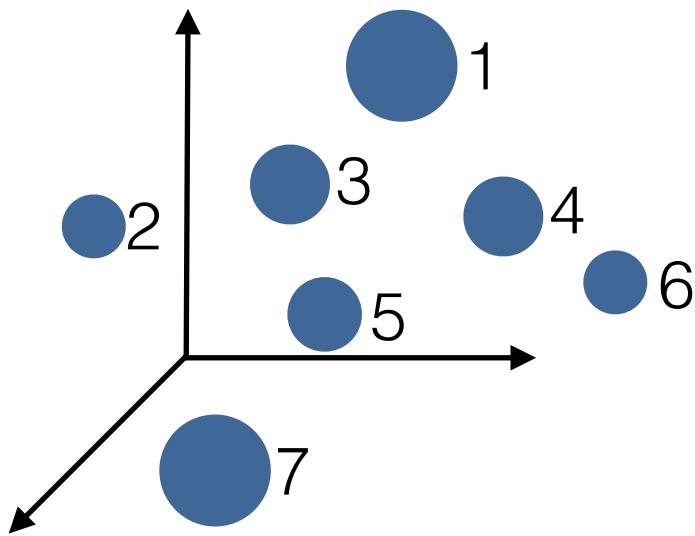
and the conserved quantity does not change

Constraints with SHAKE algorithm



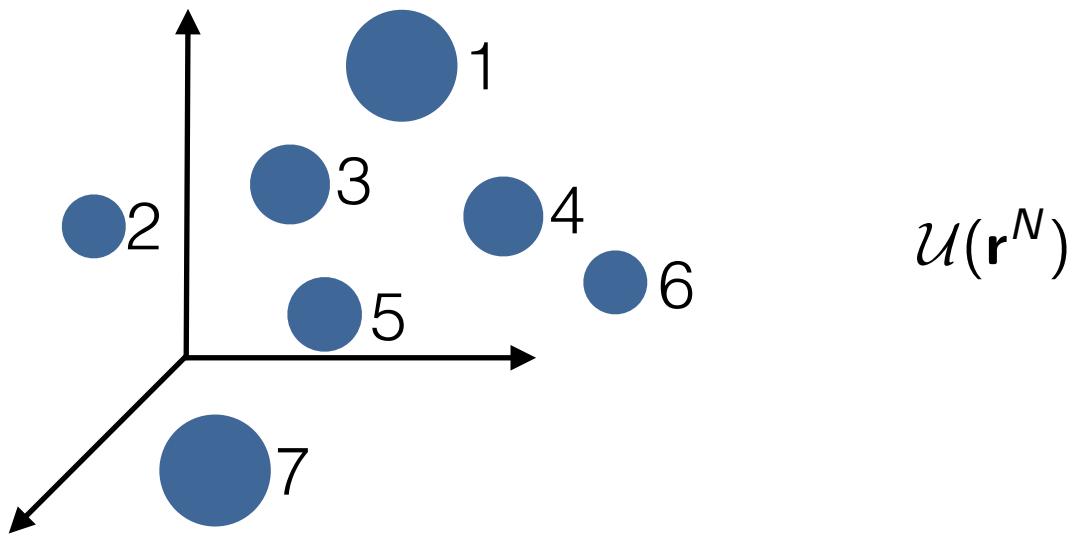
Molecular dynamics: Verlet algorithm

$$\mathbf{r}_1 = (x_1, y_1, z_1); \dot{\mathbf{r}}_1 = (\dot{x}_1, \dot{y}_1, \dot{z}_1)$$

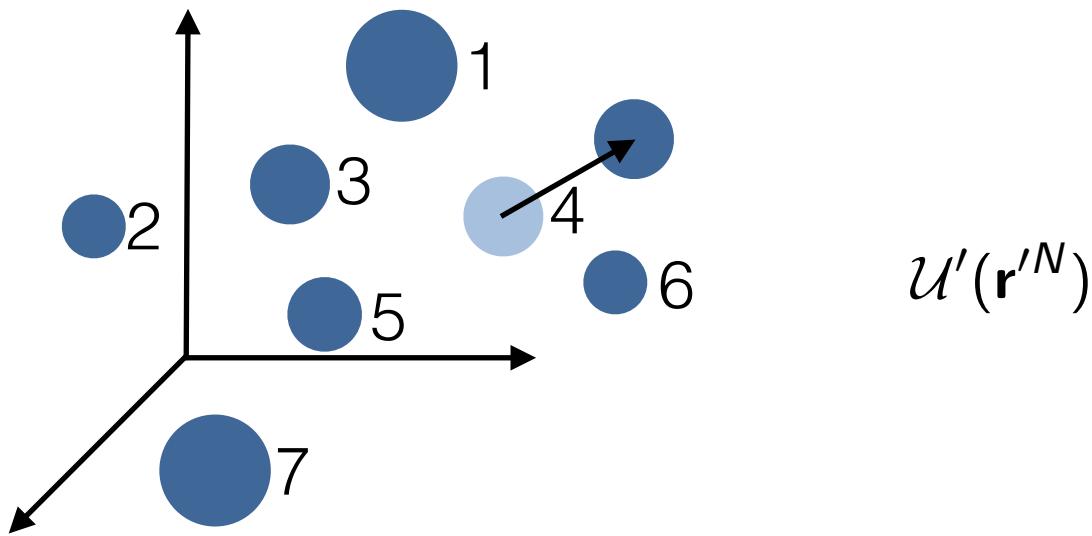


Newton's equation of motion: $m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i = -\frac{\partial \mathcal{U}}{\partial \mathbf{r}_i}$

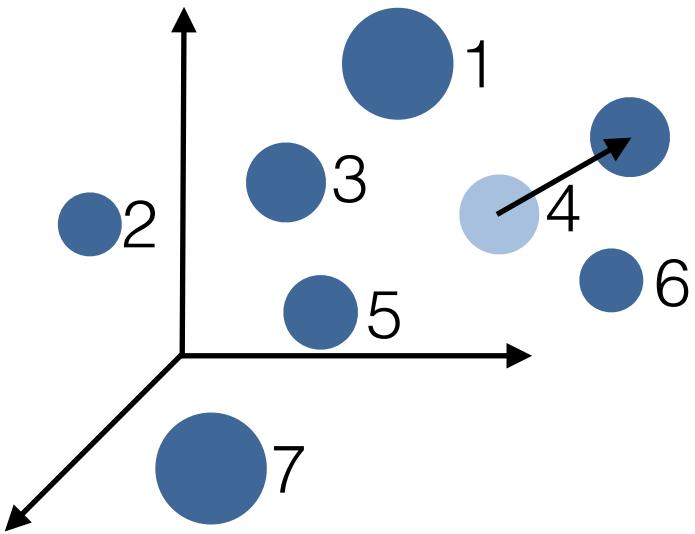
Monte-Carlo: Metropolis algorithm



Monte-Carlo: Metropolis algorithm

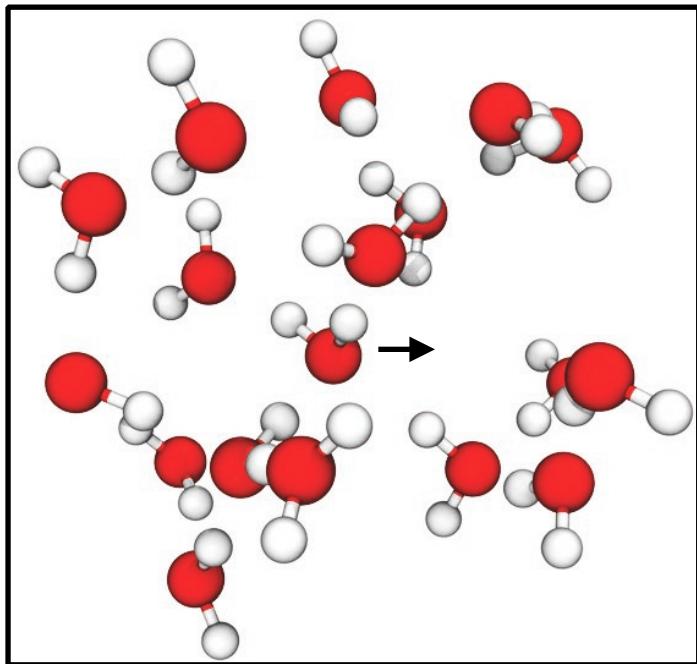


Monte-Carlo: Metropolis algorithm

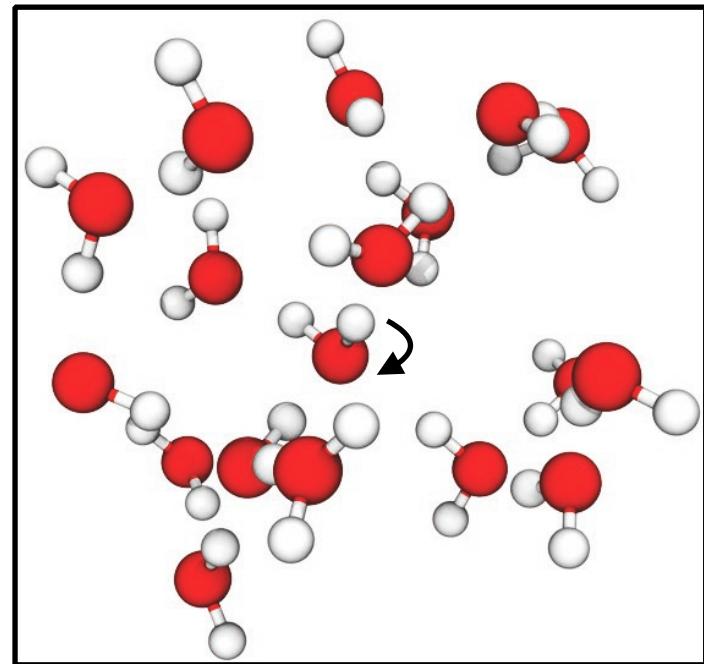


Move is accepted with probability $\mathcal{P} = \min \left(1, \exp\left(-\frac{\mathcal{U}' - \mathcal{U}}{kT}\right) \right)$

Monte-Carlo: Metropolis algorithm



Translation



Rotation

Thermodynamic ensembles in MC

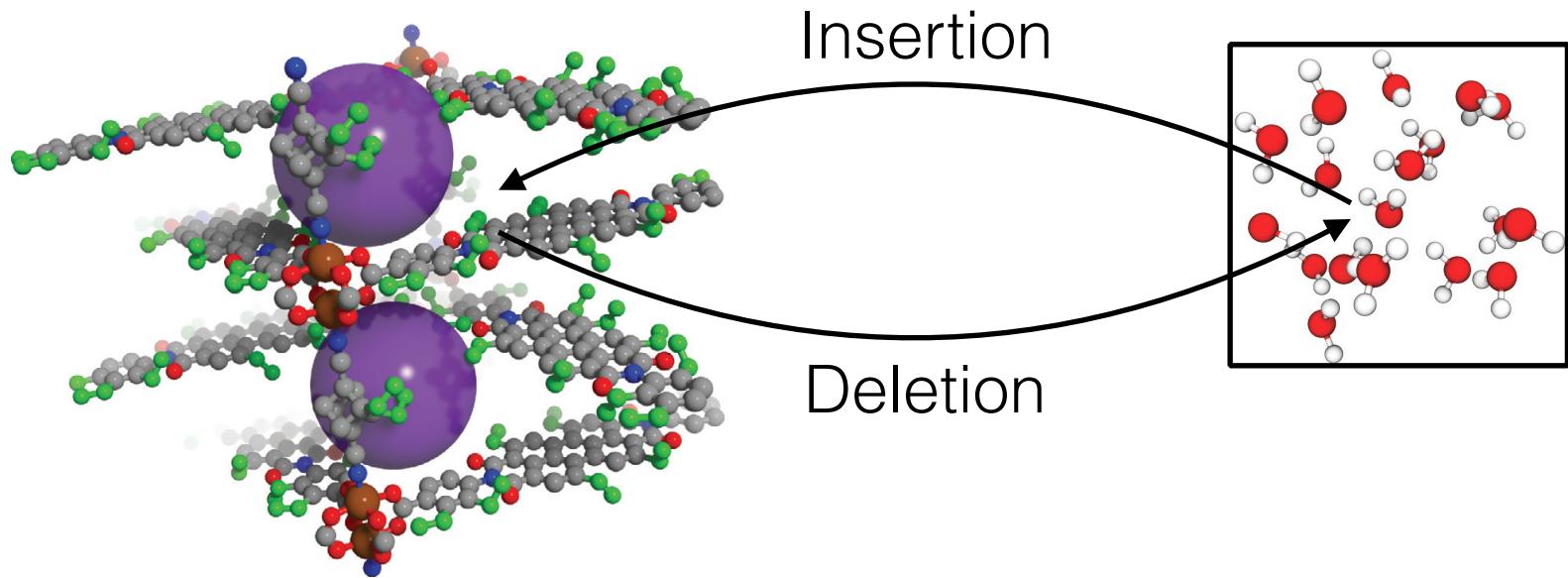
(N, V, E) Impossible

(N, V, T) Straightforward

(N, P, T) With a barostat

(μ, V, T) Possible

Monte-Carlo: Grand canonical ensemble

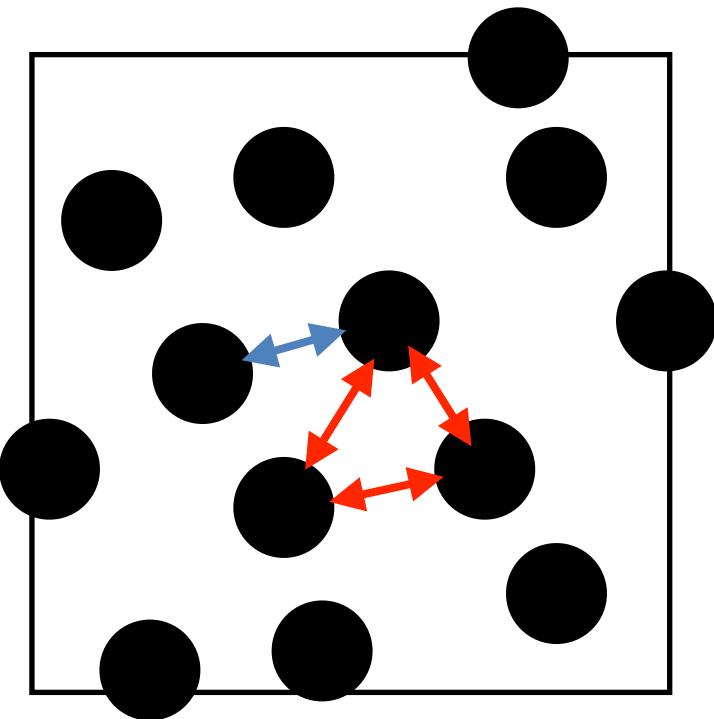


System in equilibrium with a reservoir
at fixed chemical potential

Interactions in condensed matter

- Electron sharing (chemical bonds, metals)
- Coulomb
- Electronic clouds overlap repulsion
- Long-range dispersion
- Induction (polarisation)

Interactions in condensed matter

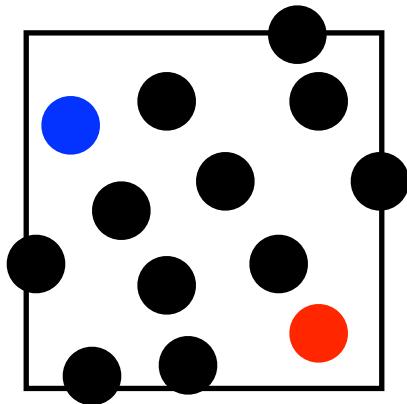


$$\begin{aligned}\mathcal{U}(\mathbf{r}^N) = & \sum_{i < j} U_{ij}^{\text{2-body}}(\mathbf{r}_i, \mathbf{r}_j) \\ & + \sum_{i < j < k} U_{ijk}^{\text{3-body}}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) \\ & + \dots\end{aligned}$$

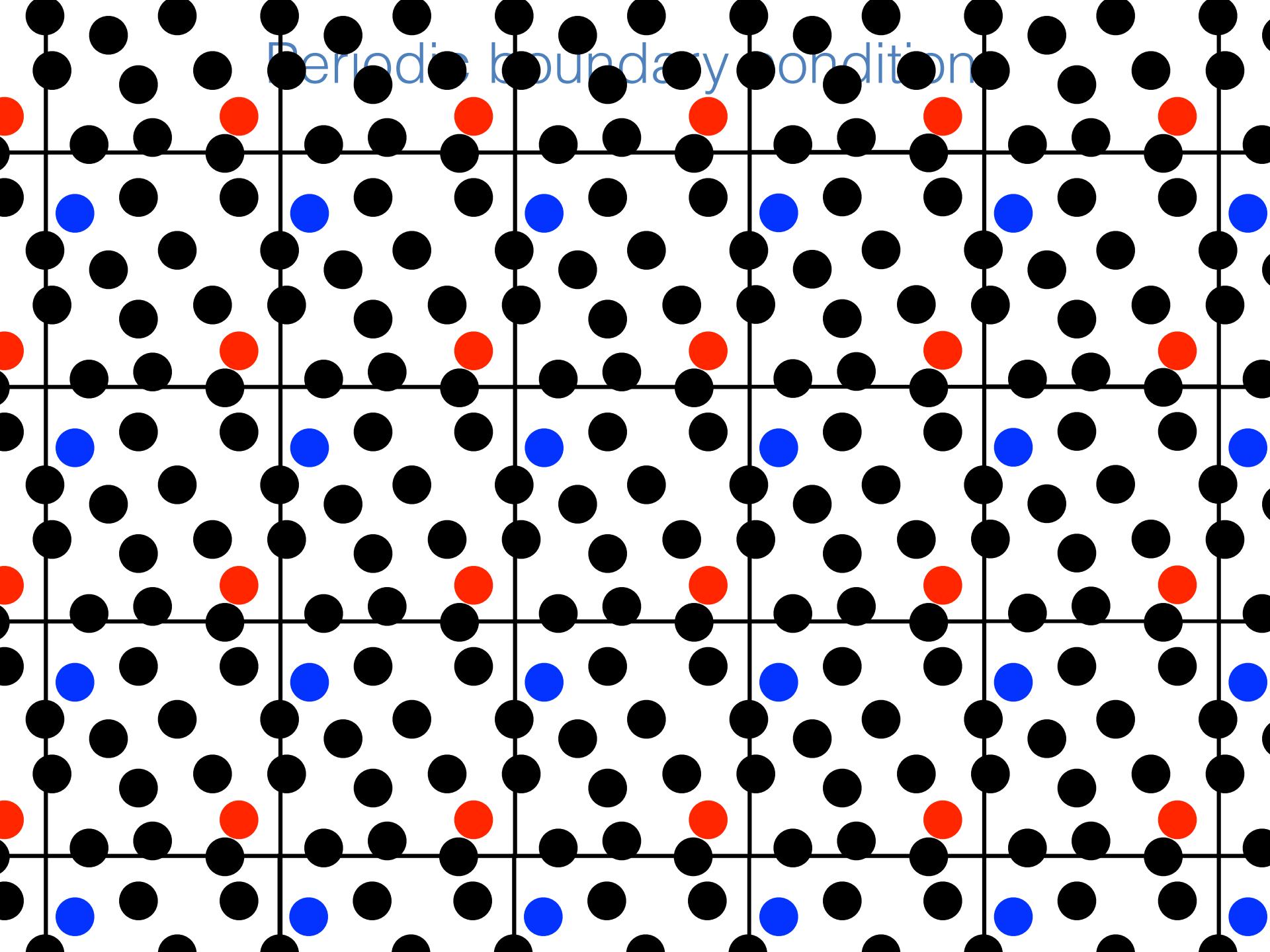
$$\mathcal{U}(\mathbf{r}^N) \approx \sum_{i < j} U_{ij}^{\text{2-body}}(r_{ij}) \quad \text{with} \quad r_{ij} = | \mathbf{r}_i - \mathbf{r}_j |$$

Force field = Expression for $\mathcal{U}(\mathbf{r}^N)$ + Parameters

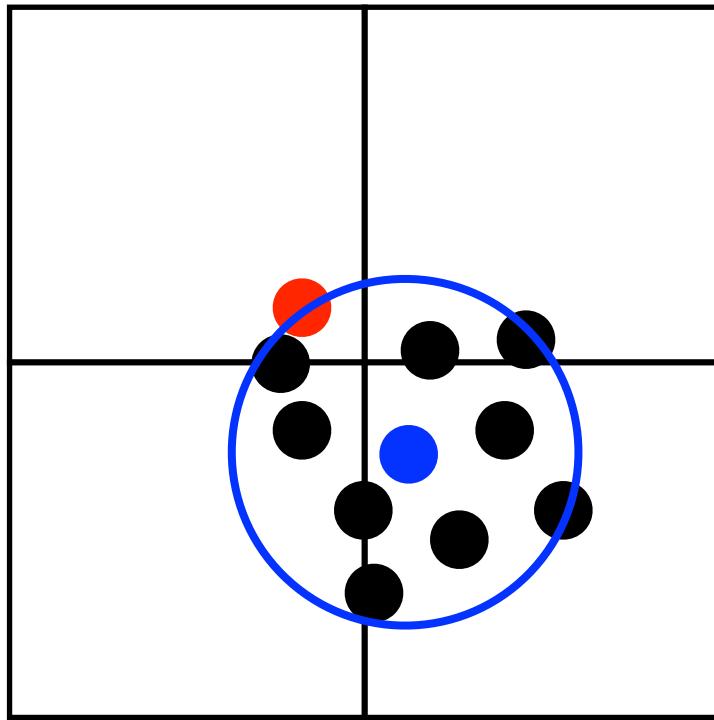
Periodic boundary conditions



Periodic boundary condition



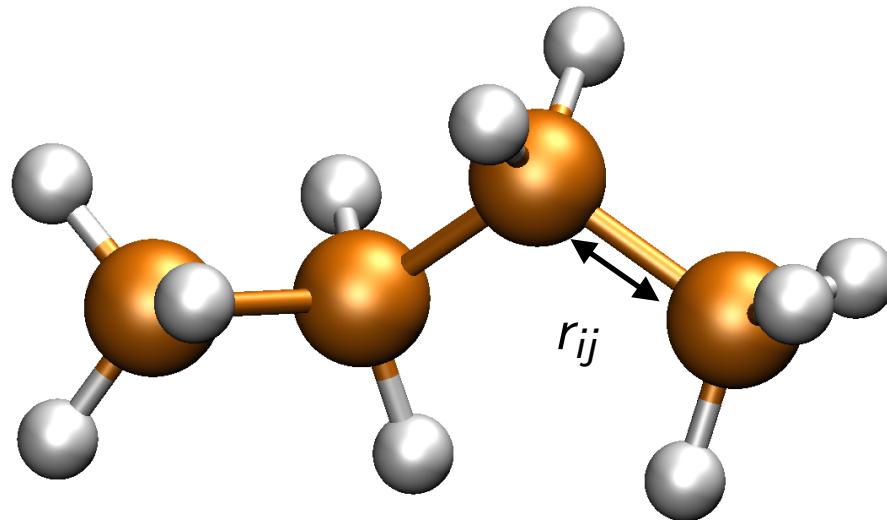
Periodic boundary conditions



Short-ranged potentials: spherical cut-off

Long-ranged potentials: numerical tricks (e.g. Ewald)

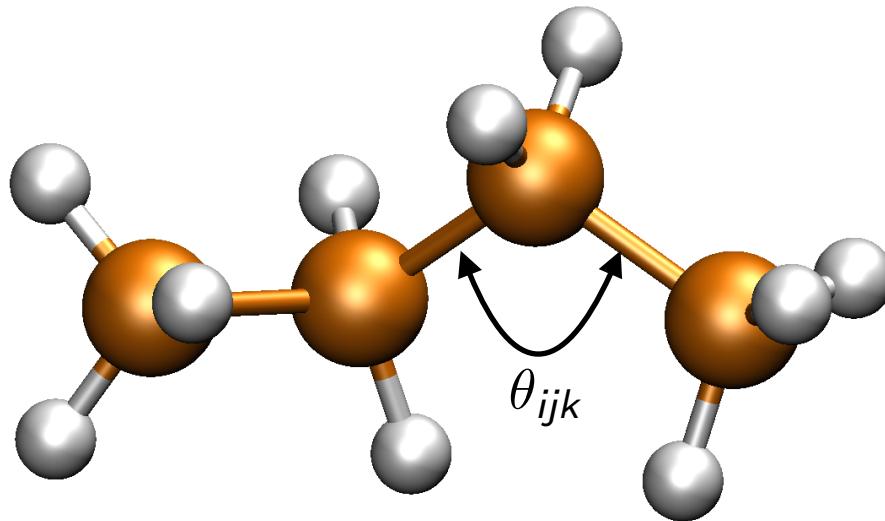
Intramolecular contributions



Spring-like term for the bonds:

$$U_{ij}^{\text{bonds}}(r_{ij}) = \frac{k_{ij}^r}{2} (r_{ij} - r_{ij}^0)^2$$

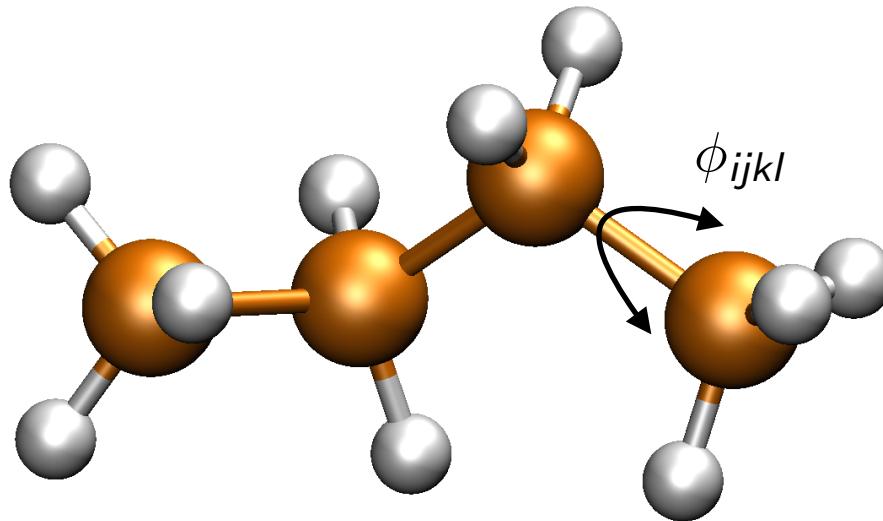
Intramolecular contributions



Spring-like term for the angles:

$$U_{ij}^{\text{angles}}(\theta_{ijk}) = \frac{k_{ijk}^\theta}{2} (\theta_{ijk} - \theta_{ijk}^0)^2$$

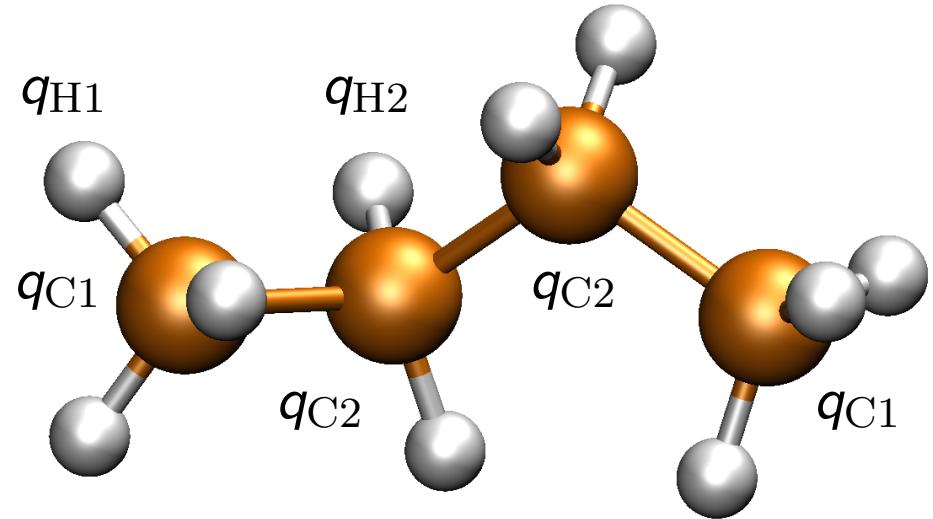
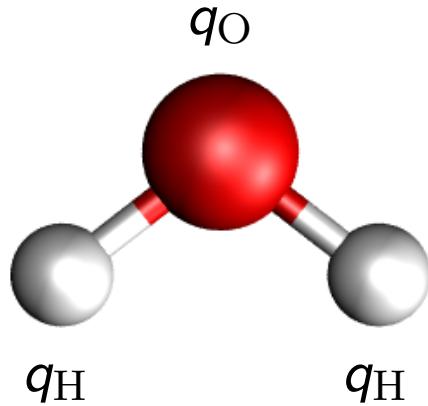
Intramolecular contributions



Contribution due to torsions:

$$U_{ijkl}^{\text{dihedrals}}(\phi_{ijkl}) = \sum_{m=1}^4 \frac{V_{ijkl}^m}{2} [1 + (-1)^m \cos(m\phi_{ijkl})]$$

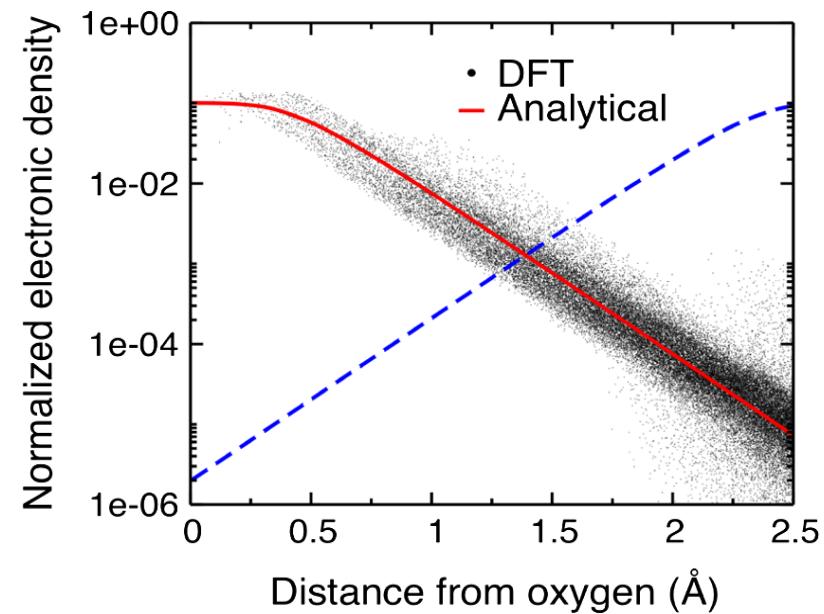
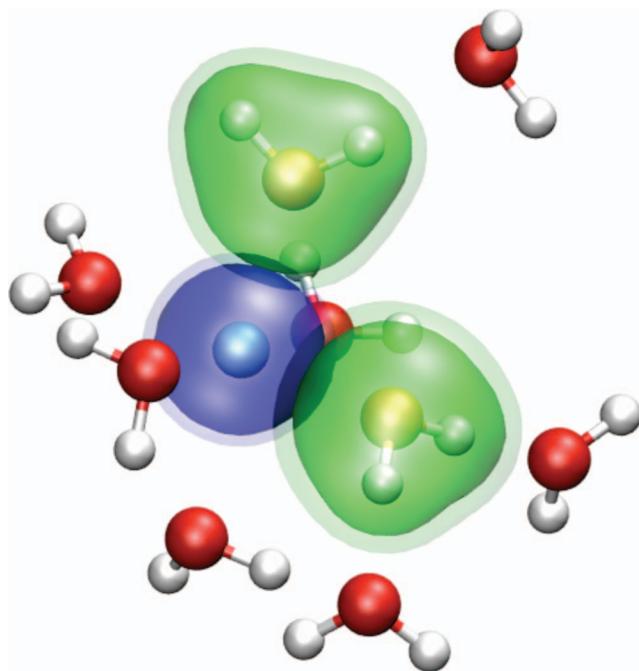
Coulomb interaction



For a neutral molecule $\sum_i q_i = 0$

Pair potential $U_{ij}(r_{ij}) = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j e^2}{r_{ij}} \equiv \frac{q_i q_j}{r_{ij}}$

Overlap repulsion interaction



Main contribution at short range

Overlap repulsion interaction

