

Hylleraas school 2025

3 – MD algorithms

Molecular Dynamics: basic ideas

Methodology:

- Treatment of atoms and molecules as a dynamical system
- Study of the time-evolution by numerical integration of the equations of motion

Gain:

- Realistic description of microscopic events $\rightarrow$ kinetics
- Link to macroscopic ensemble properties (ergodic theorem) $\rightarrow$ thermodynamics

$$\langle \mathcal{O} \rangle = \frac{1}{Q} \int \cdots \int \mathcal{O}(\{\mathbf{r}, \mathbf{p}\}) e^{-\frac{E(\{\mathbf{r}, \mathbf{p}\})}{kT}} d\Gamma = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau \mathcal{O}(t) dt$$

- Straightforward implementation of non-equilibrium phenomena
- **Only apply the boundary conditions of interest**, the thermodynamic ensemble *builds up automatically*

MD : what can we do with it?

- Molecular dynamics is primarily a **statistical sampling** method

$$\langle \mathcal{O} \rangle = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau \mathcal{O}(t) dt$$

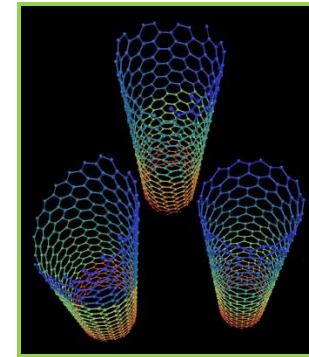
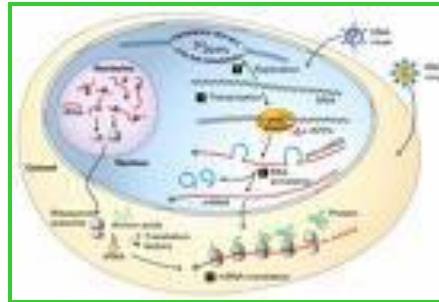
- It requires numerical algorithms to integrate the pertinent equations of motion

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{R}, t) = \hat{H} \Psi(\mathbf{R}, t) \quad \mathbf{F} = m\mathbf{a} \quad \frac{D\mathbf{u}}{Dt} = \frac{1}{\rho} \nabla \cdot \boldsymbol{\sigma} + \mathbf{g}$$
$$-\nabla V(\mathbf{R}) = m \frac{\partial^2 \mathbf{R}}{\partial t^2}$$

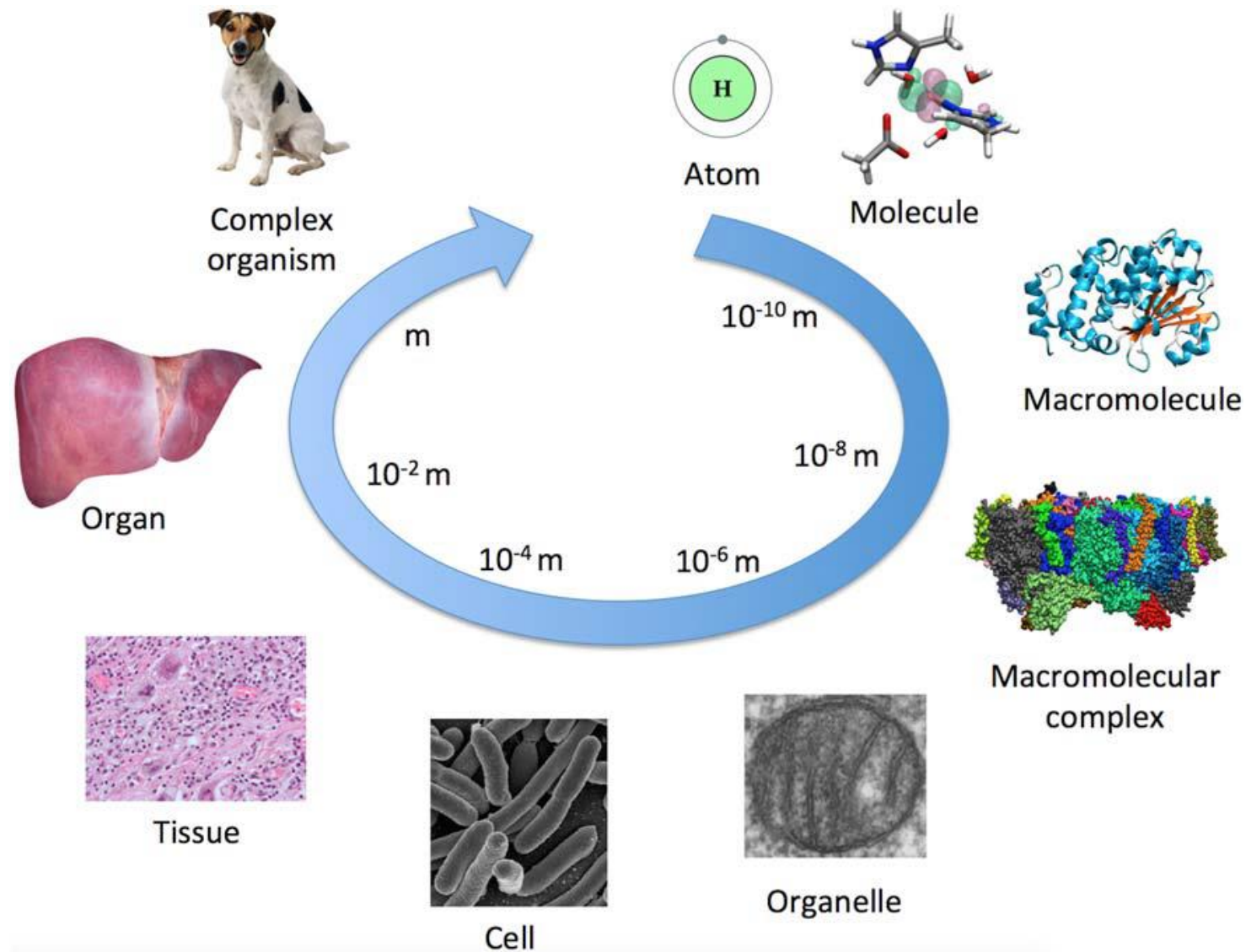
- The costs of such operations depend dramatically:
 - On how complicated it is to evaluate the forces
 - On the number of systems that we study simultaneously
 - On the characteristic times required for proper sampling

What we can do (... in theory)

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{R}, t) = \hat{H} \Psi(\mathbf{R}, t)$$



What we face (...in practice!)



Ab-initio Molecular Dynamics

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{R}, t) = \hat{H} \Psi(\mathbf{R}, t)$$

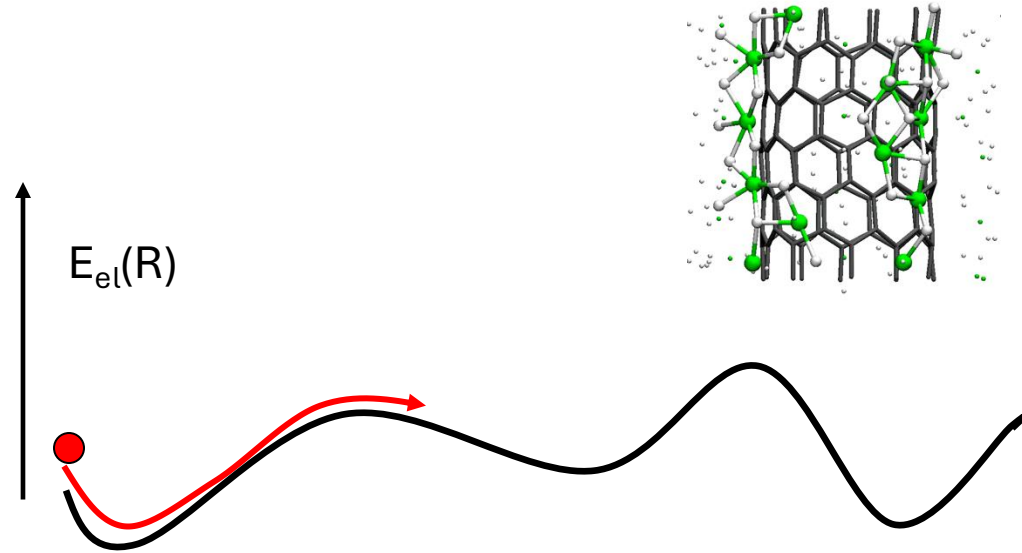
- Born-Oppenheimer approximation
- Car-Parrinello dynamics
- BO dynamics

Requires solution of the time-independent Schrödinger equation for electrons at fixed nuclear positions $\mathbf{R}$:

$$\hat{H}_{el} \varphi(r; R) = E_{el} \varphi(r; R)$$

Nuclei are treated as classical particles $\rightarrow F(R) = -\nabla E_{el}(R)$
(Hellman-Feynman th.)

The nuclear motion is derived by numerical integration of equations of motion



Integration of the Equations of Motion

- Discretise time $\rightarrow \Delta t$
- Taylor-expand atom positions

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \frac{\partial \mathbf{r}(t)}{\partial t} \Delta t + \frac{1}{2} \frac{\partial^2 \mathbf{r}(t)}{\partial t^2} \Delta t^2 + \mathcal{O}(\mathbf{r}^{(III)})$$

Integration of the Equations of Motion

$$\begin{aligned}\mathbf{a}(t) &= \frac{\mathbf{F}(t)}{m} = \frac{1}{m}[-\nabla V(\mathbf{r}(t))] \\ \mathbf{v}(t) &= ???\end{aligned}$$

Impossible to propagate iteratively over time!!

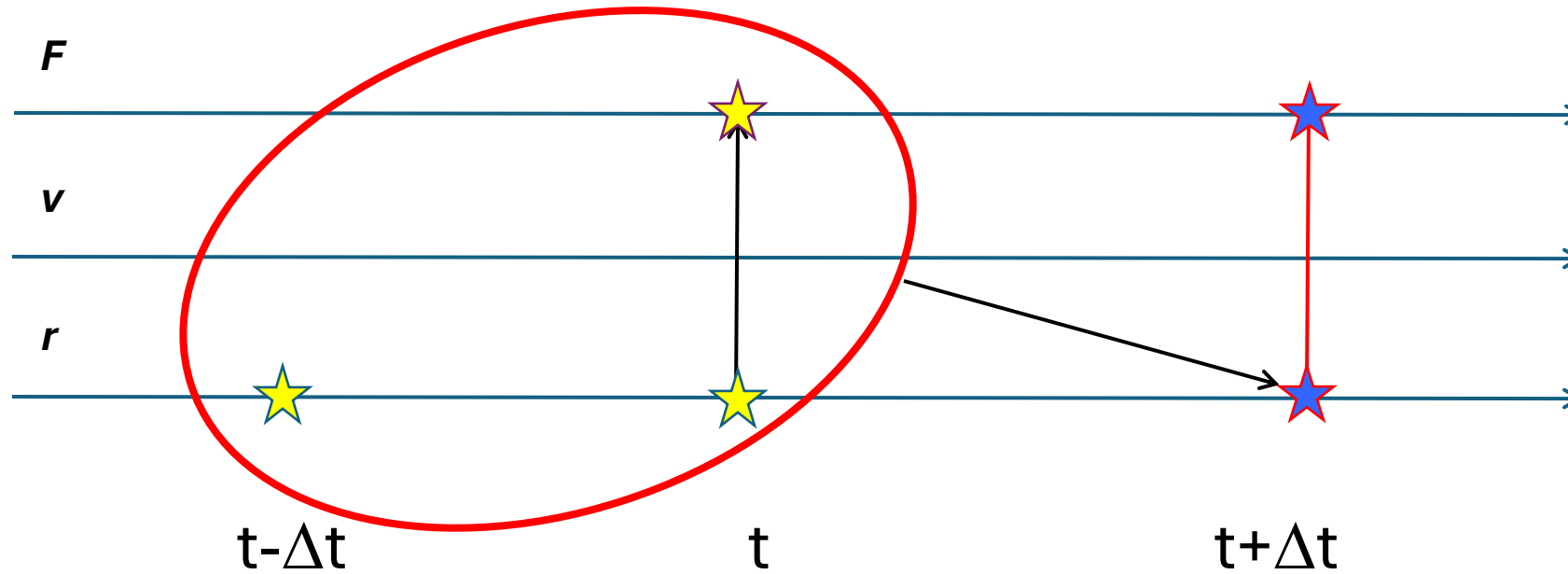
Verlet Algorithm

Verlet (1967):

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \frac{\partial \mathbf{r}(t)}{\partial t} \Delta t + \frac{1}{2} \frac{\partial^2 \mathbf{r}(t)}{\partial t^2} \Delta t^2 + \mathcal{O}(\mathbf{r}^{(III)})$$

$$\mathbf{r}(t + \Delta t) = 2\mathbf{r}(t) - \mathbf{r}(t - \Delta t) + \frac{\mathbf{F}(t)}{m} \Delta t^2$$

Verlet Algorithm



$$\mathbf{r}(t + \Delta t) = 2\mathbf{r}(t) - \mathbf{r}(t - \Delta t) + \frac{\mathbf{F}(t)}{m} \Delta t^2$$

Verlet Algorithm

Verlet (1967):

$$\mathbf{r}(t + \Delta t) = 2\mathbf{r}(t) - \mathbf{r}(t - \Delta t) + \frac{\mathbf{F}(t)}{m} \Delta t^2$$

We can estimate the velocities over an interval of $2\Delta t$:

$$\mathbf{v}(t) = \frac{1}{2\Delta t} [\mathbf{r}(t + \Delta t) - \mathbf{r}(t - \Delta t)]$$

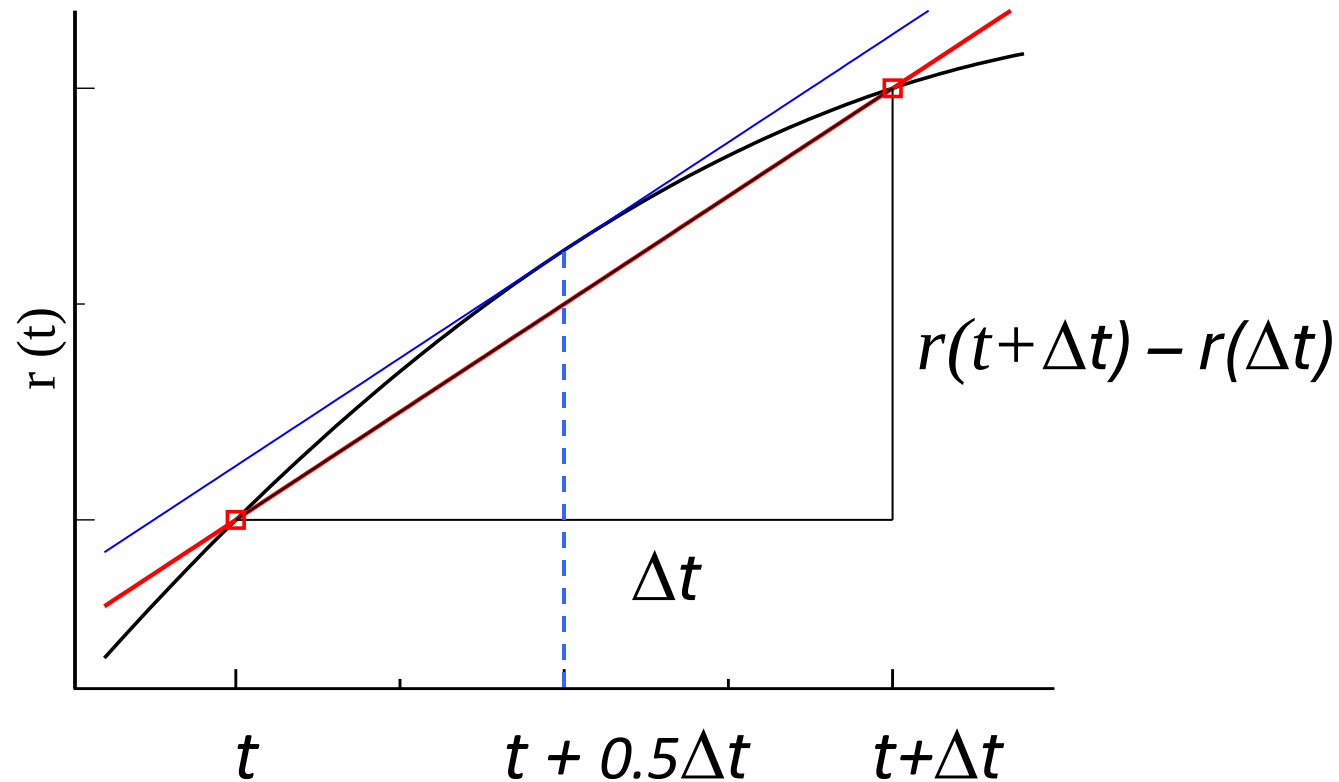
Velocities do not enter into the chain-algorithm for the propagation of the equations of motion

→ We do not have direct control over the kinetic energy (i.e. the Temperature) of the system.

Beyond the Verlet Algorithm

Knowledge of two consecutive values in time for a variable yields to a good estimate for its derivative at a mid-point:

$$v\left(t + \frac{1}{2}\Delta t\right) = \frac{1}{\Delta t}[\mathbf{r}(t + \Delta t) - \mathbf{r}(t)]$$

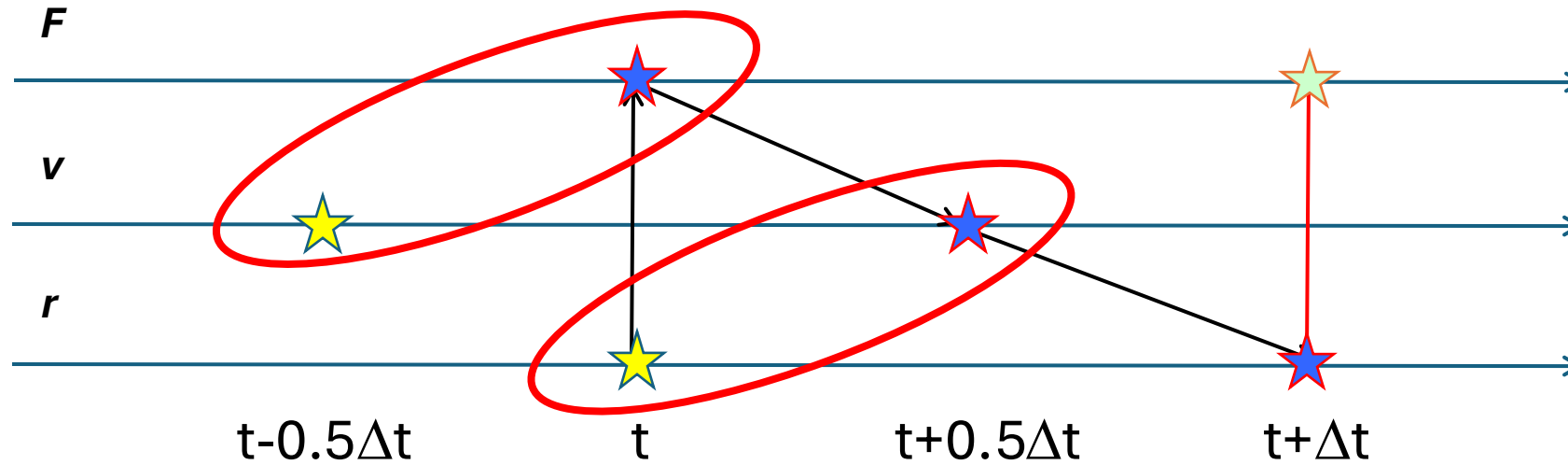


Leap-Frog Algorithm

(Hockney and Eastwood 1988)

$$\begin{aligned} \boldsymbol{v} \left(t + \frac{1}{2} \Delta t \right) &= \frac{1}{\Delta t} [\boldsymbol{r}(t + \Delta t) - \boldsymbol{r}(t)] \\ \boldsymbol{a}(t) &= \frac{1}{\Delta t} \left[\boldsymbol{v} \left(t + \frac{1}{2} \Delta t \right) - \boldsymbol{v} \left(t - \frac{1}{2} \Delta t \right) \right] \end{aligned}$$

Leap-Frog Algorithm



$$\mathbf{v} \left(t + \frac{1}{2} \Delta t \right) = \mathbf{v} \left(t - \frac{1}{2} \Delta t \right) + \frac{\mathbf{F}(t)}{m} \Delta t$$

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \mathbf{v} \left(t + \frac{1}{2} \Delta t \right) \Delta t$$

- + Velocities enter into the algorithm
- They are evaluated at mid-steps

Velocity Verlet Algorithm

(Swope et al. 1982)

Position propagation of the Verlet fixes the error at the 4th order of the derivative.
Let's build an algorithm for the velocities with the same order

$$\frac{\partial \mathbf{a}(t)}{\partial t} = \frac{\partial^2 \mathbf{v}(t)}{\partial t^2} = \frac{1}{\Delta t} [\mathbf{a}(t + \Delta t) - \mathbf{a}(t)]$$

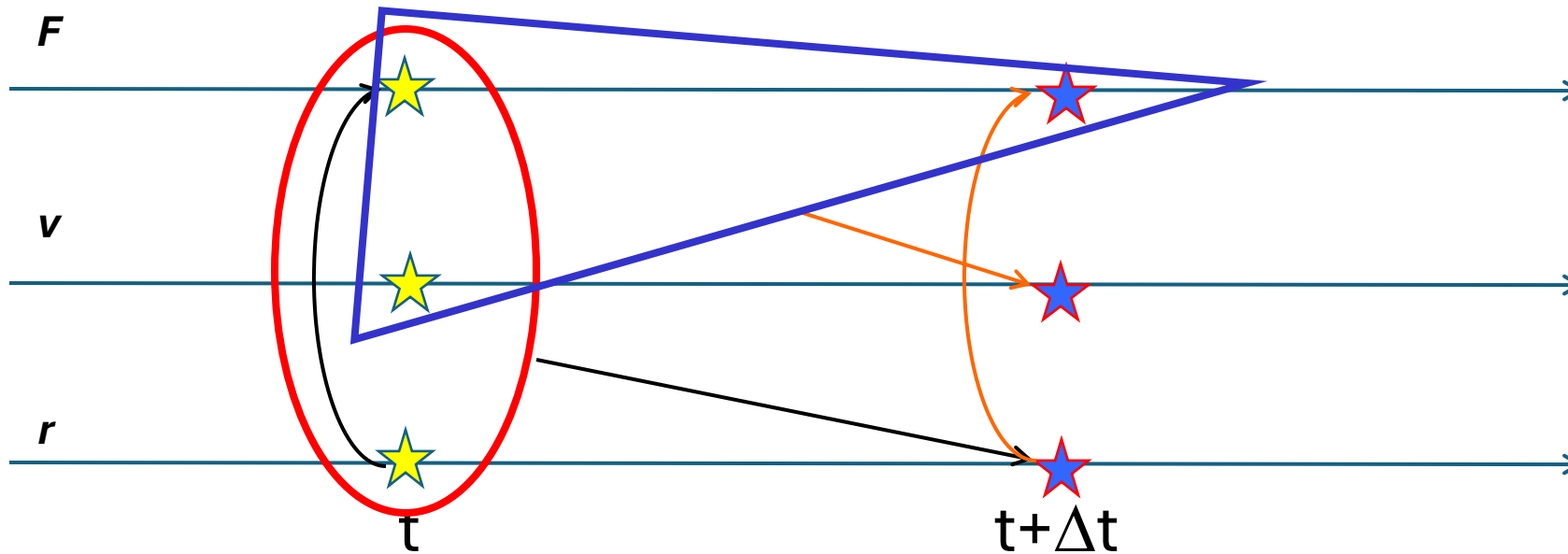
Velocity Verlet Algorithm

$$\begin{aligned}\frac{\partial \mathbf{a}(t)}{\partial t} &= \frac{\partial^2 \mathbf{v}(t)}{\partial t^2} = \frac{1}{\Delta t} [\mathbf{a}(t + \Delta t) - \mathbf{a}(t)] \\ \mathbf{v}(t + \Delta t) &= \mathbf{v}(t) + \mathbf{a}(t)\Delta t + \frac{1}{2\Delta t} [\mathbf{a}(t + \Delta t) - \mathbf{a}(t)]\Delta t^2 = \mathbf{v}(t) + \frac{1}{2} [\mathbf{a}(t + \Delta t) + \mathbf{a}(t)]\Delta t\end{aligned}$$

$$\mathbf{v}(t + \Delta t) = \mathbf{v}(t) + \frac{1}{2m} [\mathbf{F}(t + \Delta t) + \mathbf{F}(t)]\Delta t$$

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \mathbf{v}(t)\Delta t + \frac{1}{2m} \mathbf{F}(t)\Delta t^2$$

Velocity Verlet Algorithm



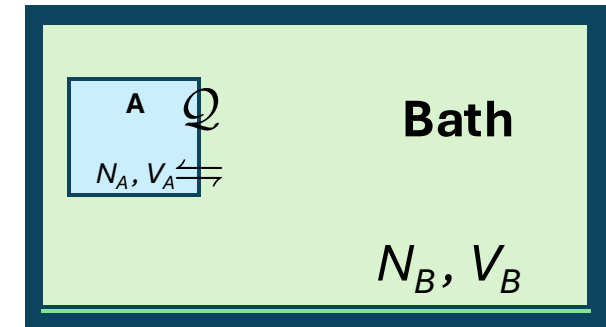
$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \mathbf{v}(t)\Delta t + \frac{1}{2m}\mathbf{F}(t)\Delta t^2$$

$$\mathbf{v}(t + \Delta t) = \mathbf{v}(t) + \frac{1}{2m}[\mathbf{F}(t + \Delta t) + \mathbf{F}(t)]\Delta t$$

++ Both positions and velocities are known at the same time,
and they are both used for time propagation

Thermodynamic ensembles

- Integration of EoM $\rightarrow$ conservation of the energy $\rightarrow$ sampling the microcanonical ensemble (NVE) (*easy*)
- Canonical ensemble (NVT)
 - Mimicking the presence of the external bath
 - Perturbation of the EoM (*complex*)
- Hierarchy of algorithms according to the type of perturbation imposed:
 - Strong coupling
 - Weak coupling
 - Stochastic
 - Extended Lagrangian



Weak coupling: Berendsen thermostat

- The internal temperature of system, at “constant temperature” conditions, is **NOT CONSTANT!**

$$\frac{3}{2}NkT(t) = \sum_{i=1}^N \frac{p_i^2(t)}{2m_i} \Rightarrow T(t) = \frac{2}{3Nk} K(t)$$

$$\sigma(K) \propto \sqrt{N} \Rightarrow \sigma(T) \propto \frac{1}{\sqrt{N}}$$

You can demonstrate this using the formulas:

$$\sigma^2(x) = \langle x^2 \rangle - \langle x \rangle^2$$

$$\langle \mathcal{O} \rangle = \frac{1}{Q} \int \cdots \int \mathcal{O}(\{\mathbf{r}, \mathbf{p}\}) e^{-\frac{E(\{\mathbf{r}, \mathbf{p}\})}{kT}} d\Gamma$$

Fluctuations of the kinetic energy

$$\sigma^2(x) = \langle x^2 \rangle - \langle x \rangle^2$$

$$\begin{aligned}\sigma^2(K) &\propto \frac{1}{Q} \iint \left(\sum_{i=1}^N p_i^2 \right)^2 e^{-\beta K} d^{3N}p - \left(\frac{1}{Q} \iint \sum_{i=1}^N p_i^2 e^{-\beta K} d^{3N}p \right)^2 \\&= \sum_{i=1}^N \frac{1}{Q} \iint p_i^4 e^{-\beta K} d^{3N}p + \frac{2}{Q} \sum_{i < j} \iint p_i^2 p_j^2 e^{-\beta K} d^{3N}p - \left(\frac{N}{q} \iint p^2 e^{-\beta p^2/2m} d^3p \right)^2 \\&= N \langle p^4 \rangle + N(N-1) \langle p^2 \rangle \langle p^2 \rangle - N^2 \langle p^2 \rangle^2 = N \left(\langle p^4 \rangle - \langle p^2 \rangle^2 \right) \\&\Rightarrow \sigma(K) \propto \sqrt{N} \quad \Rightarrow \sigma(T) \propto \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}}\end{aligned}$$

Weak coupling: Berendsen thermostat

Weak coupling strategy

Adding perturbation to the EoM due to heat-flow equation:

$$\frac{\partial T}{\partial t} = -\frac{1}{\tau}(T - T_0)$$

$$\begin{aligned}\frac{T(t + \Delta t) - T(t)}{\Delta t} &= \frac{T_0 - T(t)}{\tau} & T(t + \Delta t) &= \frac{T_0 - T(t)}{\tau} \Delta t + T(t) \\ & & &= T(t) \left[1 + \frac{\Delta t}{\tau} \left(\frac{T_0}{T(t)} - 1 \right) \right]\end{aligned}$$

$$\frac{1}{2}mv^2(t + \Delta t) = \frac{1}{2}mv^2(t) \left[1 + \frac{\Delta t}{\tau} \left(\frac{T_0}{T(t)} - 1 \right) \right]$$

Algorithm: at every MD step, the all the velocities are rescaled according to the factor λ :

$$v'(t) = \lambda v(t); \quad \lambda = \sqrt{1 + \frac{\Delta t}{\tau} \left[\frac{T_0}{T(t)} - 1 \right]}$$

Sampling catastrophe

- The Berendsen algorithm punishes local fluctuations of the temperature, which are, in fact, correct.
- Moreover, it does not respect detailed balance, and energy conservation:

$$v'(t) = \lambda v(t); \quad \lambda = \sqrt{1 + \frac{\Delta t}{\tau} \left[\frac{T_0}{T(t)} - 1 \right]}$$

$$T_0 = \alpha p_0^2$$

$$p_0 \pm \Delta p$$

← random collision

$$T - T_0 \propto (p_0 \pm \Delta p)^2 - p_0^2 = \Delta p^2 \pm 2p_0 \Delta p$$

Scaling factor larger for positive fluctuations than for negative ones

→ The algorithm subtracts kinetic energy to fluctuating DoF (vibrations!)

Flying ice cube artifact!!

Discussion time!!

Using the heat flow equation leads to the ice cube paradox.

Why is it so???

(No maths, it's a conceptual problem)

Fixing the Berendsen thermostat:

Canonical Sampling by Velocity Rescaling (Bussi-Donadio-Parrinello Thermostat)

- Heat-flow equation is a macroscopic, deterministic equation $\frac{\partial T}{\partial t} = -\frac{1}{\tau}(T - T_0)$
- Emergent behaviour from stochastic microscopic motion

We need to reintroduce stochastic noise into the equations!

→ When particles hits the bath, they will be randomly (ac-/de-)celerated

$$\lambda_{tot} = \sqrt{1 + \underbrace{\frac{\Delta t}{\tau} \left[\frac{T_0}{T(t)} - 1 \right]}_{\text{Heat flow}} + \underbrace{\sqrt{\frac{4}{3N} \frac{T_0}{T(t)} \frac{\Delta W}{\sqrt{\tau}}}}_{\text{Stochastic factor}}}$$

← White noise

Computational Feasibility of MD

All MD algorithms require

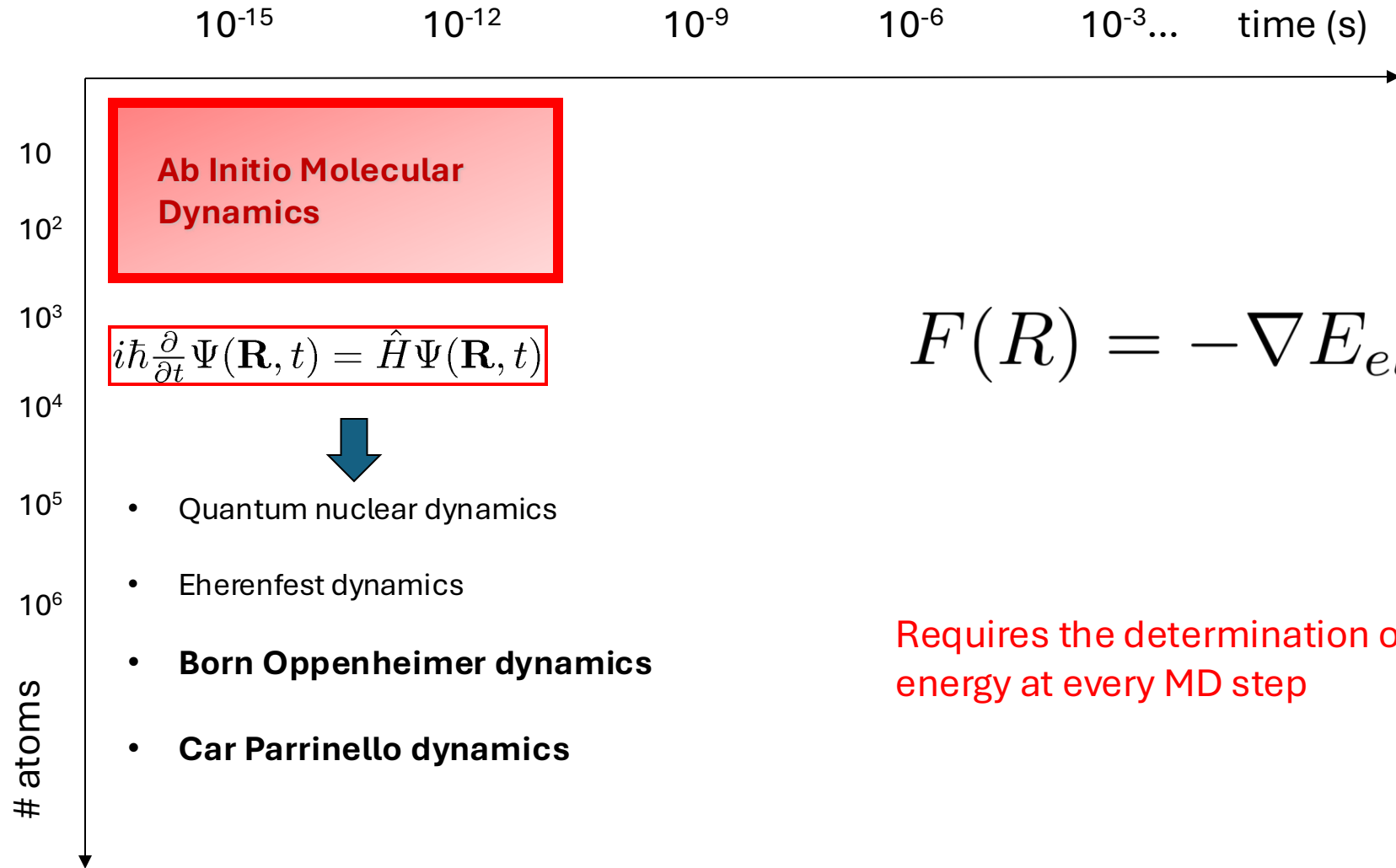
- 1 – discretization of the time-step Δt
- 2 – the calculation of the forces on all atoms at time t :

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \mathbf{v}(t)\Delta t + \frac{1}{2m}\mathbf{F}(t)\Delta t^2$$

$$\mathbf{v}(t + \Delta t) = \mathbf{v}(t) + \frac{1}{2m}[\mathbf{F}(t + \Delta t) + \mathbf{F}(t)]\Delta t$$

The limitations on the time-step, and the computational costs for the calculations of the forces determine **the feasible sizes and times** for a molecular dynamics simulation.

MD: boundaries and beyond



$$F(R) = -\nabla E_{el}(R)$$

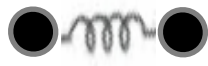
Requires the determination of the electronic energy at every MD step

Computational costs of MD

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + v(t)\Delta t + \frac{1}{2m}\mathbf{F}(t)\Delta t^2$$

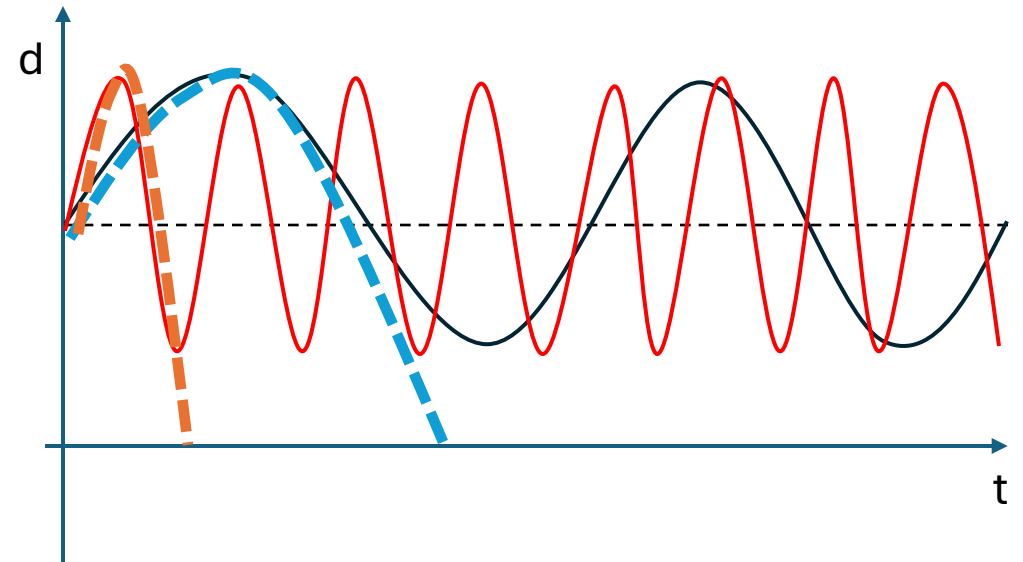
2nd order polynomial

- Cost of the individual operations (calculation of the forces) per one MD step
- Total number of steps $N_{steps} = \frac{\mathcal{T}}{\Delta t}$



Timestep determined by the fastest vibration in the system

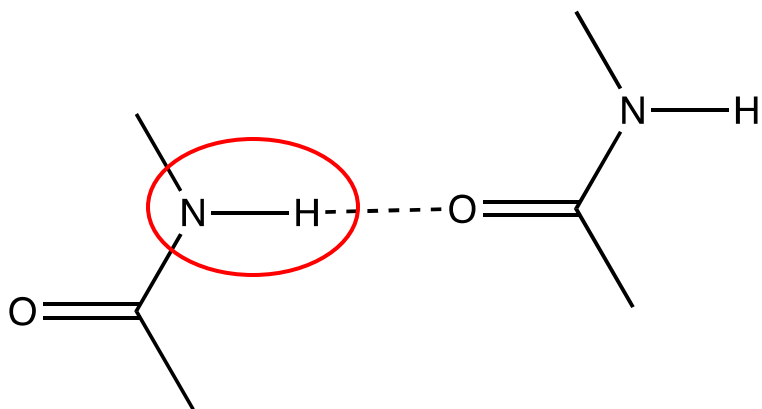
X-H bonds!!!!



SHAKE algorithm (and offsprings...): constrain bonds with H to their equilibrium values → increase Δt

Why/when constraining bonds?

- When you are not interested in that dynamics, AND:
- **Adiabatic separation:** harmonic oscillators with different frequencies do not couple



Fast vibration! Intra-/inter-molecular moieties feel the average position of the H atom.

Simulations of bulk condensed systems

$$\hat{V}(R) \rightarrow \sum_{i < j} \hat{V}(R_{ij})$$

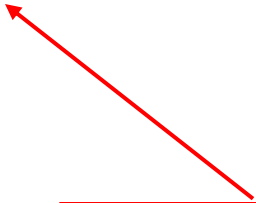
Quantum mechanical molecular Hamiltonian:

The potential energy is a sum of two-body terms

$$E_{el}(R) \approx \sum_i V(\mathbf{R}_i) + \frac{1}{2} \sum_{ij} V(\mathbf{R}_{ij}) + \frac{1}{3!} \sum_{ijk} V(\mathbf{R}_i, \mathbf{R}_j, \mathbf{R}_k) + \dots$$

Empirical mechanical potential by many body expansion... but most of the time:

$$V_{MM}(R) \approx \sum_{i < j} V(R_{ij}) + V_{bonded}$$

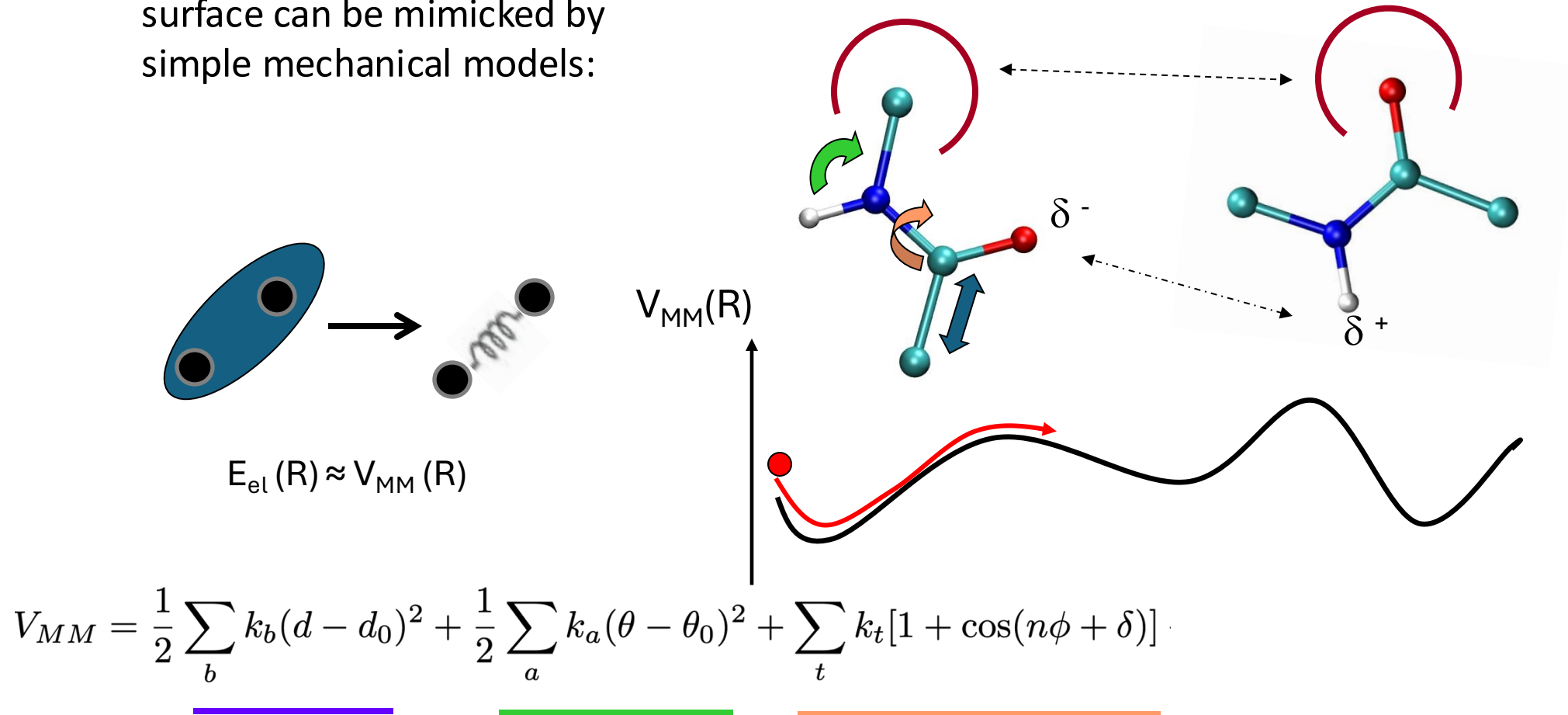


Neural network potentials!!!

V_{bonded} : local interaction between atoms connected in a molecular moiety,
designed ad hoc to keep the detailed chemical structure in place

Classical Molecular Dynamics: force fields

The electronic potential energy surface can be mimicked by simple mechanical models:



For a historical retrospective about mechanical potentials for biological systems, see:
M. Levitt, Nat. Struct. Biol. 8, 392-393 (2001)

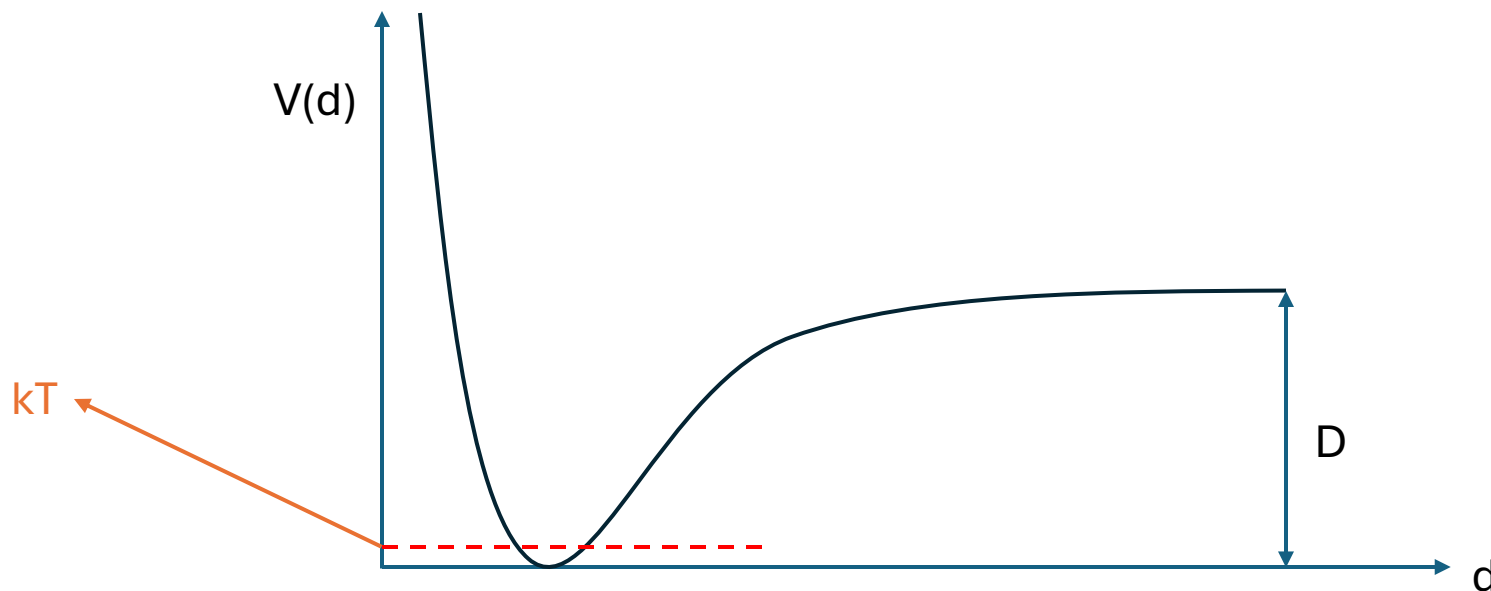
Why does such a brutal approximation work???

$$V_{MM} = \frac{1}{2} \sum_b k_b (d - d_0)^2 + \frac{1}{2} \sum_a k_a (\theta - \theta_0)^2 + \sum_t k_t [1 + \cos(n\phi + \delta)] + \frac{1}{4\pi\epsilon_0} \sum_{i<j} \frac{q_i q_j}{r_{ij}} + \sum_{i<j} \left(\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^6} \right)$$

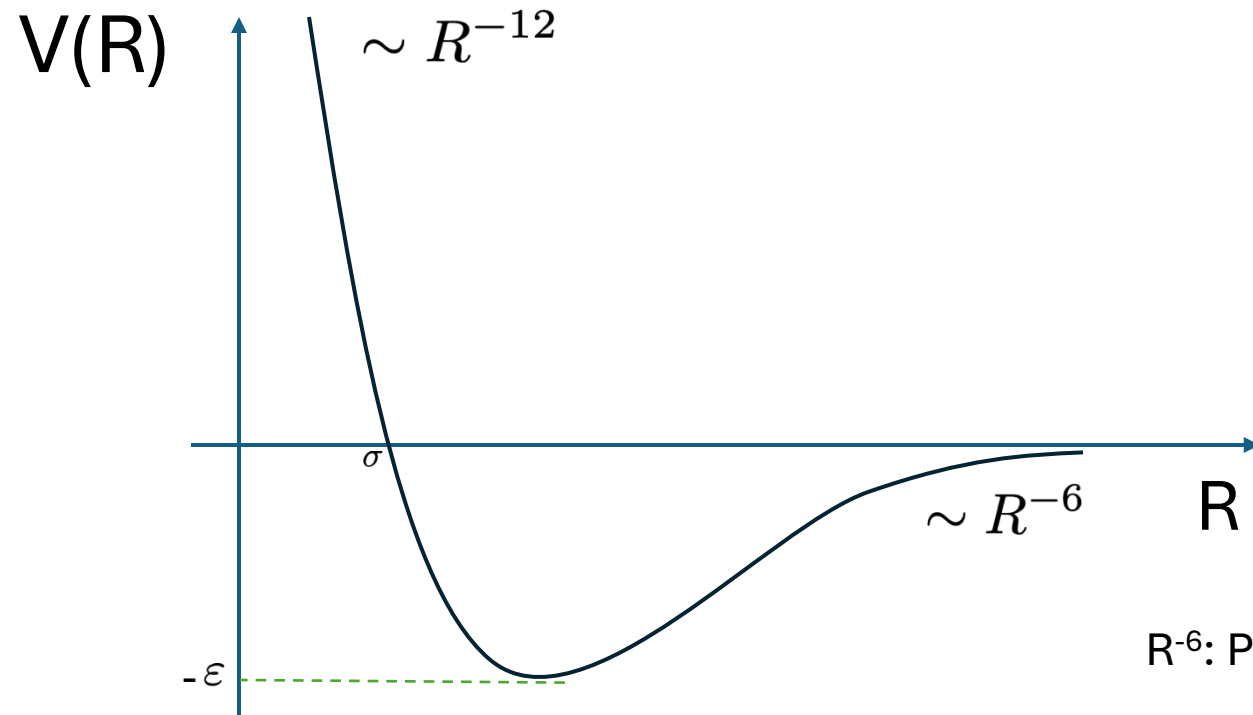
Discussion time!!!

Shouldn't we use better model potentials for bond stretching/bending??

- D (covalent bond) $\sim 200\text{-}400 \text{ kJ mol}^{-1}$
- kT (300 K) $\sim 2 \text{ kJ mol}^{-1}$



True also for Lennard-Jones (aka 6-12) potential



$$V = \frac{A}{R^{12}} - \frac{B}{R^6}$$

$$V = 4\epsilon \left(\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right)$$

R^{-6} : Physically sound (induced dipole-dipole attraction)

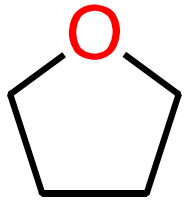
R^{-12} : it's the square of R^{-6} !!!!

Range of a potential

$$\sum_{i < j} V(R_{ij})$$

Non-bonded potentials:

Distance-dependent potentials that act, in principle, on all particle couples

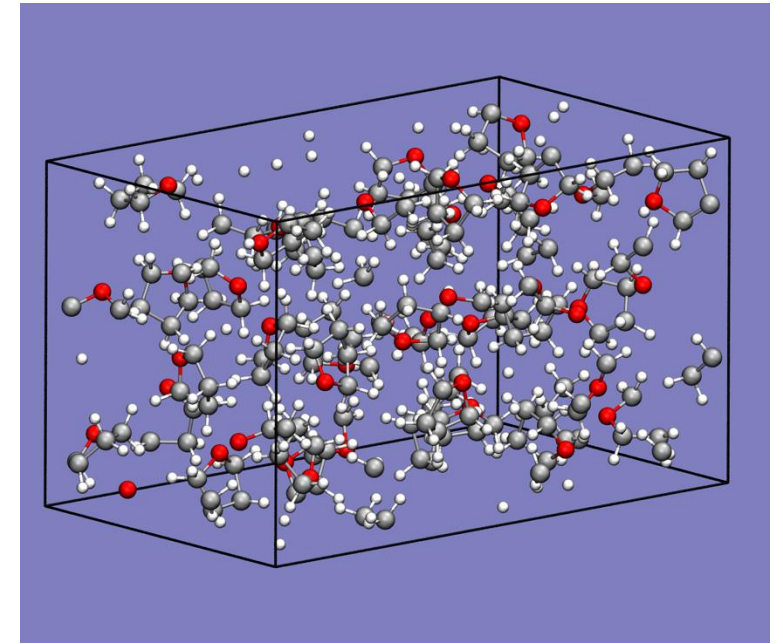


Tetrahydrofuran (organic solvent): 13 atoms per molecule

25 x 15 x 15 Å³ box: at room conditions, ~ 42 molecules → N=546 atoms

$$\frac{N}{2}(N - 1) \text{ terms} \approx 150'000 = \mathbf{1'350'000 \text{ operations}}$$

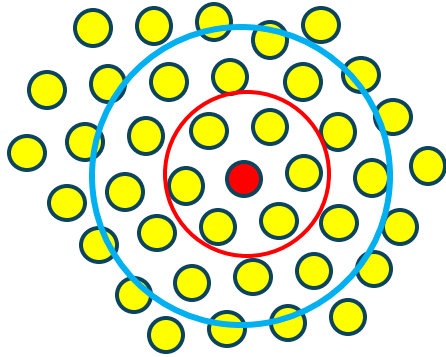
$$R_{ij} = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2} = 9 \text{ operations}$$



The costs of 2-body non-bonded interactions grows $\propto N^2$

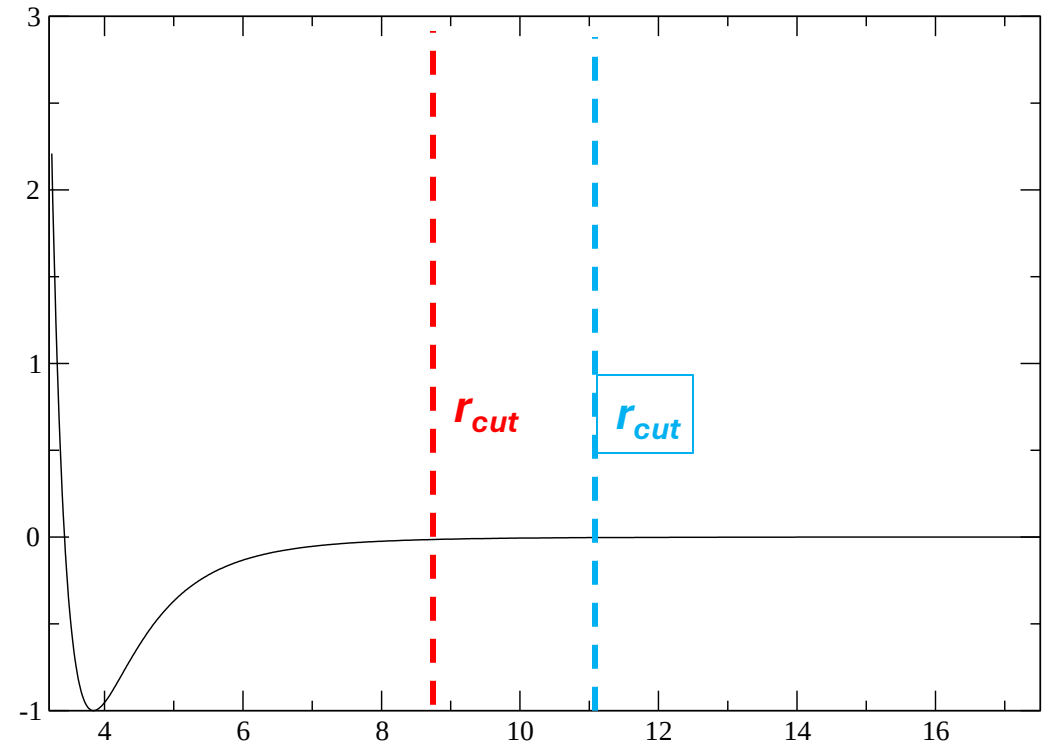
Reducing computational costs

- Distance-dependent potentials fade at long distances: $\lim_{R \rightarrow \infty} V(R) = 0$
- We define a cut-off distance beyond which we can assume that the potential is zero



Build neighbour list, sum over neighbours only:

$$\propto N^2 \rightarrow \propto \eta(r_{cut})N$$



Reducing computational costs

$$\propto N^2 \rightarrow \propto \eta(r_{cut})N$$

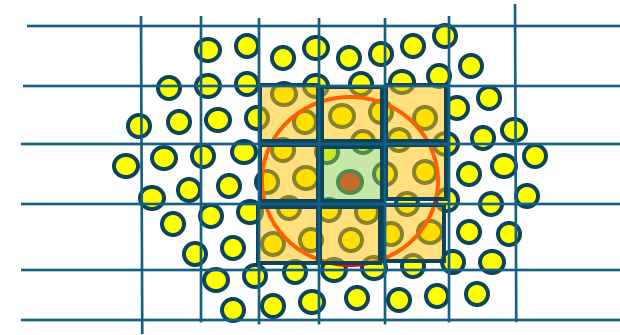
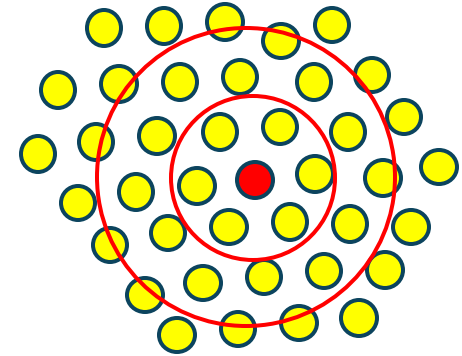
Ok for lattice simulations. **Not ok** for simulations of fluids!

According to their diffusion coefficient, atoms will mix, exiting and entering one another's regions of interaction.

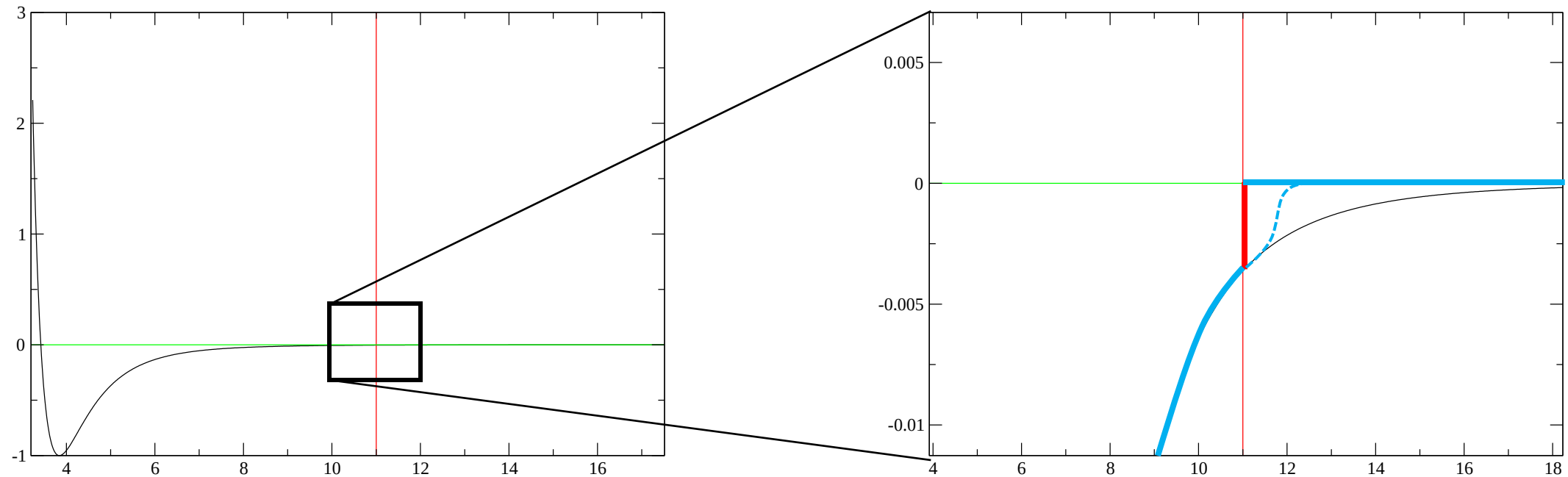
Solution: Building time-dependent pair lists

- Lists of interacting atoms are defined for a number of steps,
- At fixed intervals, neighbour lists are updated. This timestep is computationally costly $\propto N$
 $\propto N^2$

Variety of algorithms to reduce costs for building the pair-lists,
For example, cell-based neighbour search



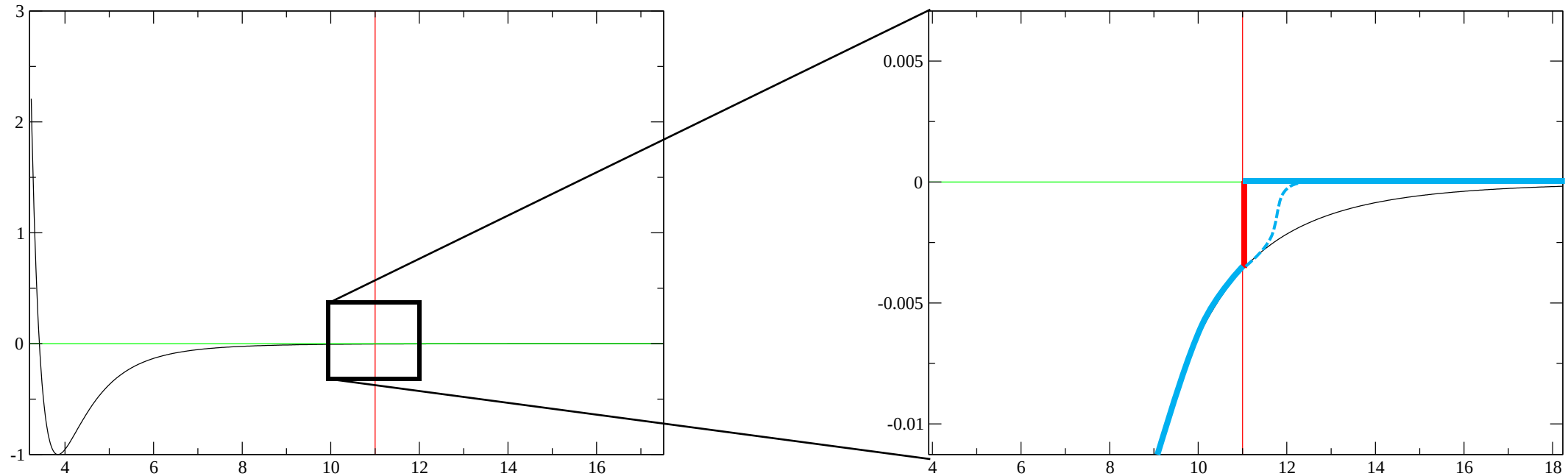
Are we satisfied with cut-off approaches?



Point of discontinuity, non-derivable --> jump in the forces.

Solution: numerical smoothing functions.

Are we satisfied with cut-off approaches?



Point of discontinuity, non-derivable --> jump in the forces.

Solution: numerical smoothing functions.

✓ *Total control on the numerical error, systematic check on convergence*

... or not????

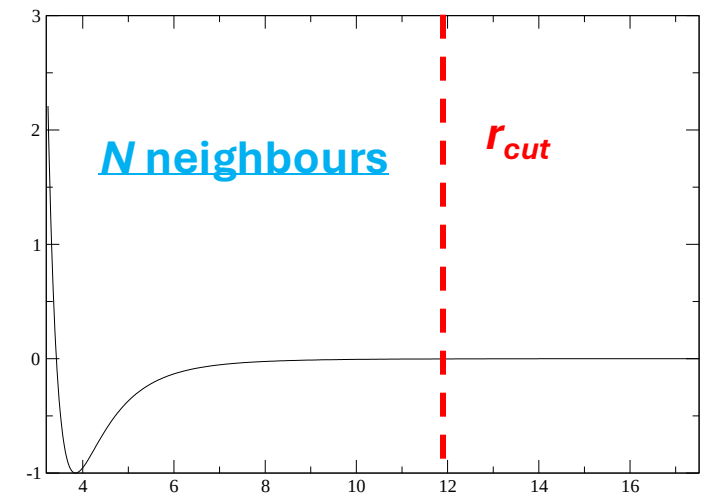
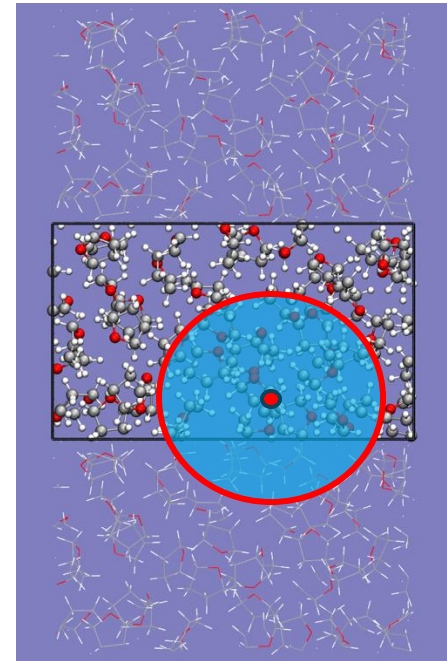
Are we satisfied with cut-off approaches?

- Error control is numerically feasible for finite-size systems.
- This may not be the case for extended systems, for example under PBC

$$\varepsilon_1 = \sum_{n=2}^{\infty} V(R_{1,n}) = \sum_{n=2}^N V(R_{1,n}) + \sum_{n=N+1}^{\infty} V(R_{1,n})$$

$$\varepsilon_1 \approx \sum_{n=2}^N V(R_{1,n}) \quad \text{Numerical approximation of the exact result}$$

$$\Delta\varepsilon = \sum_{n=N+1}^{\infty} V(R_{1,n}) \quad \text{Numerical Error}$$



IF this series converges, then we can systematically reduce it by increasing r_{cut}

Statistical estimate of the cut-off error

For a monoatomic system: $\mathcal{P}(r)$: normalised probability distribution for a particle being at distance r from the reference one.

$$\langle \varepsilon_1 \rangle = 4\pi(N-1) \int_0^\infty V(r) \mathcal{P}(r) r^2 dr$$

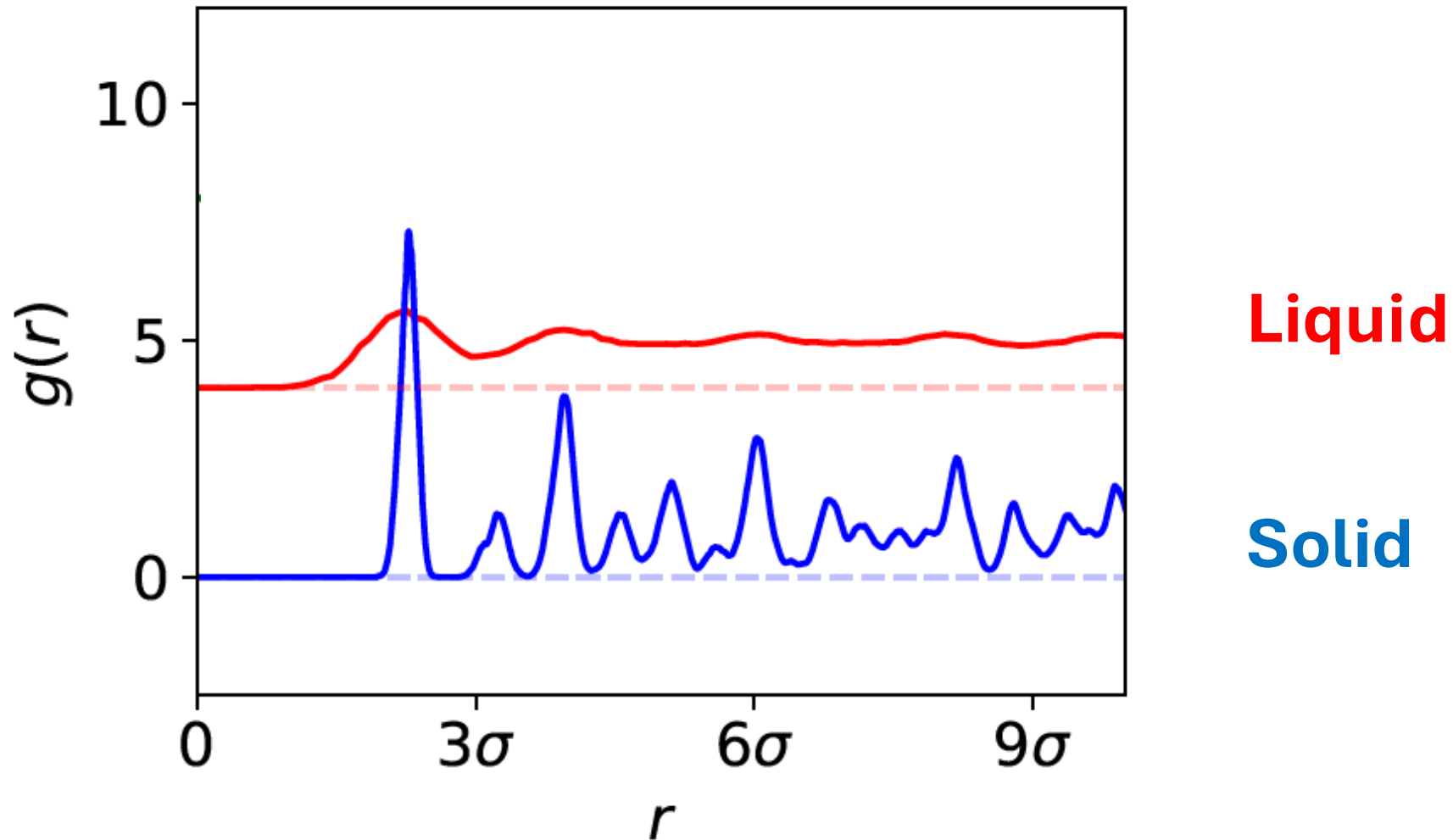
$$\langle \varepsilon_1 \rangle = 4\pi(N-1) \left[\int_0^{r_{cut}} V(r) \mathcal{P}(r) r^2 dr + \int_{r_{cut}}^\infty V(r) \mathcal{P}(r) r^2 dr \right]$$

$$\langle \Delta \varepsilon \rangle = 4\pi(N-1) \int_{r_{cut}}^\infty V(r) \mathcal{P}(r) r^2 dr \quad \text{Defining: } g(r) = \frac{d(r)}{d_0} = \nu \frac{(N-1)}{N} \mathcal{P}(r)$$

$$\langle \Delta \varepsilon \rangle = 4\pi d_0 \int_{r_{cut}}^\infty V(r) g(r) r^2 dr$$

Radial distribution (aka pair correlation) function

$$g(r) = \frac{d(r)}{d_0}$$



Physical meaning of $g(r)$

$$g(r) = \frac{d(r)}{d_0} \propto \mathcal{P}(r) \propto e^{-\beta \Delta \mathcal{F}(r)}$$

$$\Delta \mathcal{F}(r) = -k_B T \ln g(r) \quad \text{Potential of mean force (PMF)}$$

PMF: Free energy; mean field potential felt by two interacting particles in the presence of an environment at thermal equilibrium

Potential of mean force - meaning

$$g(r) \propto \mathcal{P}(r) = \frac{4\pi V}{\mathcal{Z}} \int e^{-\beta E(\mathbf{r})} d\mathbf{r}_3 \cdots d\mathbf{r}_N$$

$$\mathcal{F}(r) = -kT \ln g(r) = -kT \ln \frac{4\pi V}{\mathcal{Z}} \int e^{-\beta E(\mathbf{r})} d\mathbf{r}_3 \cdots d\mathbf{r}_N + \text{const}$$

$$-\nabla_r \mathcal{F}(r) = kT \nabla \ln g(r) = -kT \beta \frac{\int \nabla E(\mathbf{r}) e^{-\beta E(\mathbf{r})} d\mathbf{r}_3 \cdots d\mathbf{r}_N}{\int e^{-\beta E(\mathbf{r})} d\mathbf{r}_3 \cdots d\mathbf{r}_N} = \langle -\nabla E(\mathbf{r}) \rangle$$

The **potential of mean force** is a potential which gradient yields the **expectation value of the force** felt by two particles at given distance, subject to the mean-field produced by all the others around them

Back to the cut-off error...

$$\langle \Delta \varepsilon \rangle = 4\pi d_0 \int_{r_{cut}}^{\infty} V(r) g(r) r^2 dr$$

In a condensed system: for $r \gg 1 \Rightarrow g(r) \sim 1$

$$\langle \Delta \varepsilon \rangle \approx 4\pi d_0 \int_{r_{cut}}^{\infty} V(r) r^2 dr$$

Convergence of the integral depends on decay of $V(r) \sim r^{-n}$

For $n > 3$ $\int_{r_{cut}}^{\infty} r^{2-n} dr = \frac{1}{n-3} \frac{1}{r_{cut}^{n-3}}$ ✓ *Error converges, it is reduced by increasing r_{cut}*

Short-range potentials

$$V_{LJ}(r) \sim r^{-6}$$

For $n < 3$ **Error DIVERGES!!! Cut-off schemes are numerically unacceptable**

Long-range potentials

$$V_{Coulomb}(r) \sim r^{-1}$$

For $n = 3$ Border-line, conditional convergence. Numerical estimates problematic

Cohesive energy for molecular dipolar crystals

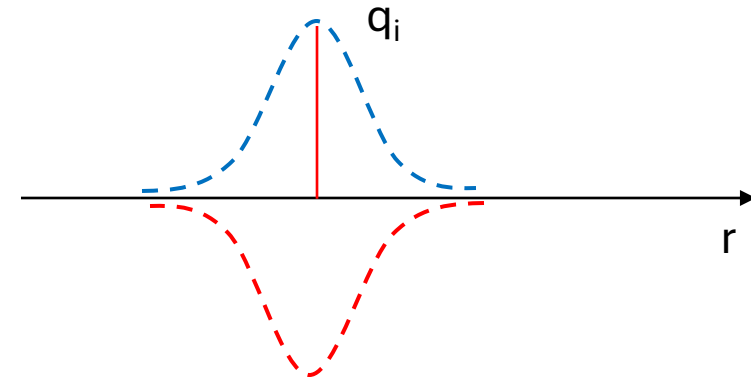
The Ewald method

- Write the electrostatic energy as: $W = \frac{1}{2} \sum_i q_i \psi(\mathbf{r}_i)$
- separate the electrostatic problem in short-range and long-range contributions

$$\psi(\mathbf{r}_i) = \psi_{sr}(\mathbf{r}_i) + \psi_{lr}(\mathbf{r}_i)$$

The two components are built by construction of charge densities

$$\rho(\mathbf{r}) = \rho_{sr}(\mathbf{r}) + \rho_{lr}(\mathbf{r}) = \sum_{i=1}^N q_i [\delta(\mathbf{r} - \mathbf{r}_i) - \mathcal{G}(\mathbf{r} - \mathbf{r}_i)] + \sum_{i=1}^N q_i \mathcal{G}(\mathbf{r} - \mathbf{r}_i)$$



The Ewald method: short–long range

- This globally neutral moiety gives rise to well-behaved high-order multipolar terms that can be evaluated by direct summation and truncation

- This charge density, $\rho_{lr}(\mathbf{r}) = \sum_{i=1}^N q_i \mathcal{G}(\mathbf{r} - \mathbf{r}_i)$ is a well-behaved analytic function.

From Maxwell relations:

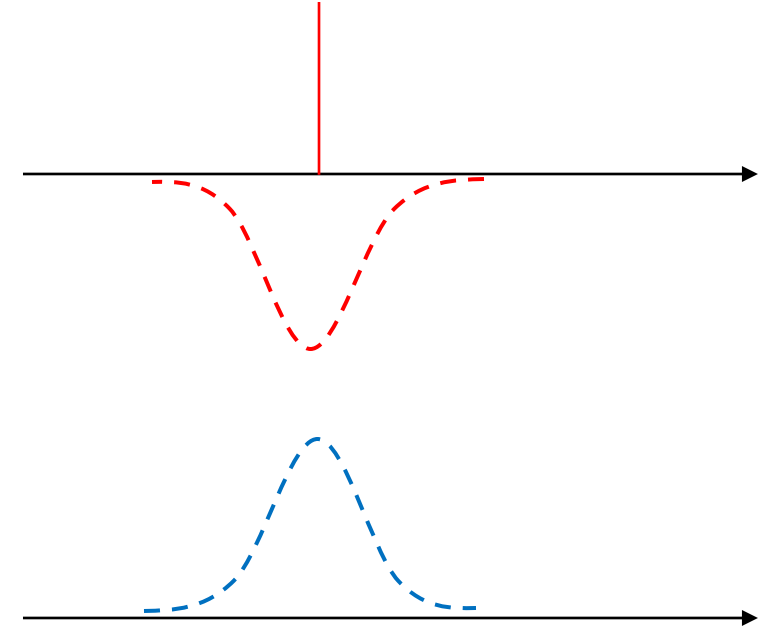
$$\nabla^2 \psi_{lr}(\mathbf{r}) = -\frac{\rho_{lr}(\mathbf{r})}{\epsilon}$$

Let's move in Fourier space:

$$\nabla^2 \int \hat{\psi}(\mathbf{k}) e^{-i\mathbf{k} \cdot \mathbf{r}} d\mathbf{k} = - \int \frac{\hat{\rho}(\mathbf{k})}{\epsilon} e^{-i\mathbf{k} \cdot \mathbf{r}} d\mathbf{k}$$

$$\int k^2 \hat{\psi}(\mathbf{k}) e^{-i\mathbf{k} \cdot \mathbf{r}} d\mathbf{k} = \int \frac{\hat{\rho}(\mathbf{k})}{\epsilon} e^{-i\mathbf{k} \cdot \mathbf{r}} d\mathbf{k}$$

$$\hat{\psi}(\mathbf{k}) = \frac{\hat{\rho}(\mathbf{k})}{\epsilon k^2}$$



Ewald: Long range component

- Thus, the long-range component of the electrostatic potential is simply obtained by two FT operations:

$$\psi_{lr}(\mathbf{r}) = FT^{-1} \left[\frac{FT[\rho_{lr}(\mathbf{r})]}{\epsilon k^2} \right]$$

- The combination of the Ewald method with Fast-Fourier Transform operations on regular grids allows for calculations in PBC scaling with a cost proportional to:
 $\propto N \log N$
- This method is known in the literature as Particle-Mesh Ewald (PME)