Institut Pprime

Research in physics and engineering

A lecture on molecular dynamics

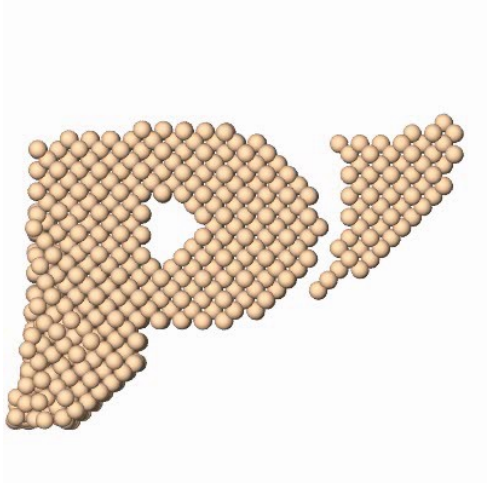
L. Pizzagalli

Outline

- Definition, history, applications, scales and limits
- The theory and the basics
- Interaction potentials
- Setup: initial conditions, boundaries and controls
- Associated techniques for configuration space exploration
- Scales and data issues
- Overcoming space and time scale issues
- Resources

What is molecular dynamics?

- Molecular Dynamics (MD) is a numerical simulation technique aiming at modeling the evolution of an ensemble of particles as a function of time
- In a MD simulation, the classical equation of motion governing the microscopic time evolution of a many-body system are solved numerically subject to boundary conditions appropriate for the geometry or symmetry of the system. (Tuckerman and Martyna)

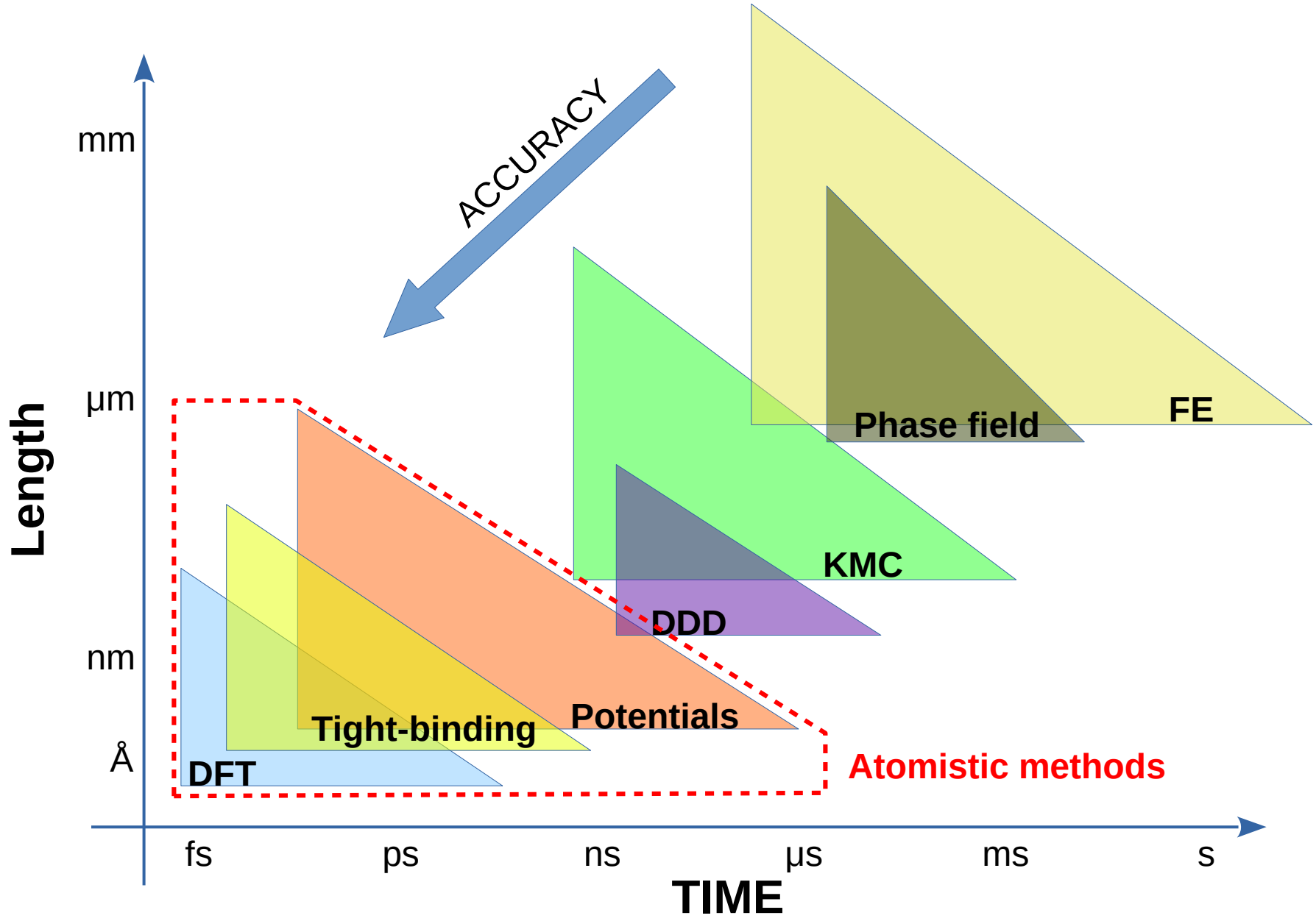


Two main uses:

Dynamical evolution of a system → non-equilibrium behavior, transport, transition

Thermodynamics → equilibrium properties

Time and space scales



A bit of history

The first MD simulation by Fermi / Pasta / Ulam / Tsingou
64 atoms !

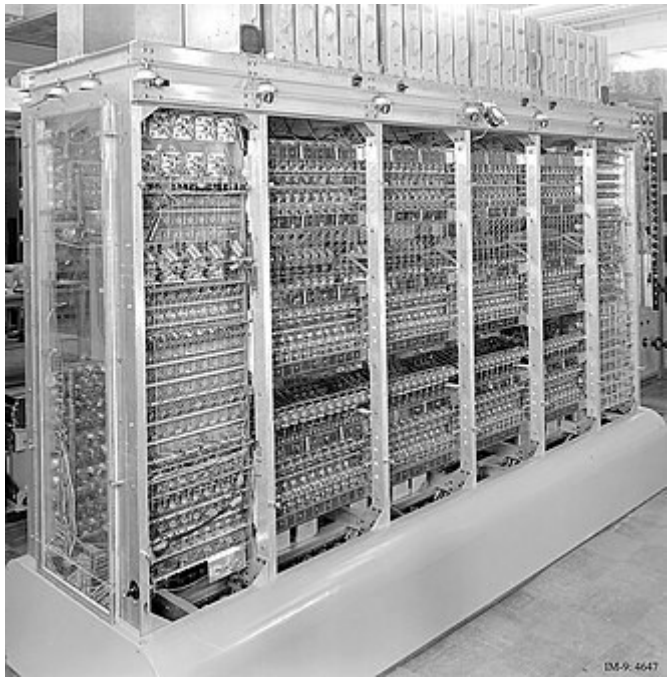
Not the first atomistic simulation (Monte Carlo, 1953)

STUDIES OF NON LINEAR PROBLEMS

E. FERMI, J. PASTA, and S. ULAM
Document LA-1940 (May 1955).

ABSTRACT.

A one-dimensional dynamical system of 64 particles with forces between neighbors containing nonlinear terms has been studied on the Los Alamos computer MANIAC I. The nonlinear terms considered are quadratic, cubic, and broken linear types. The results are analyzed into Fourier components and plotted as a function of time.



Maniac I, Los Alamos

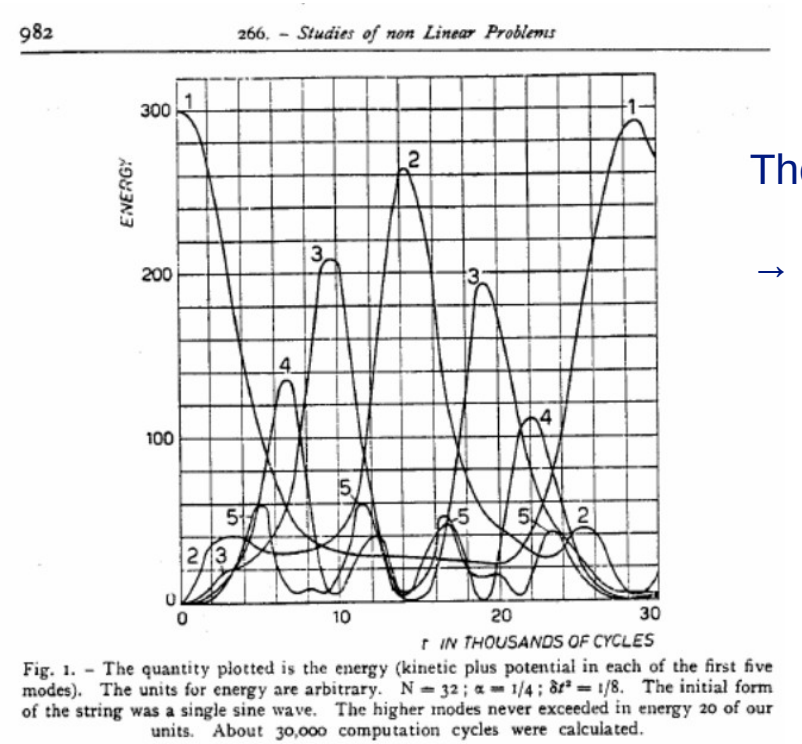
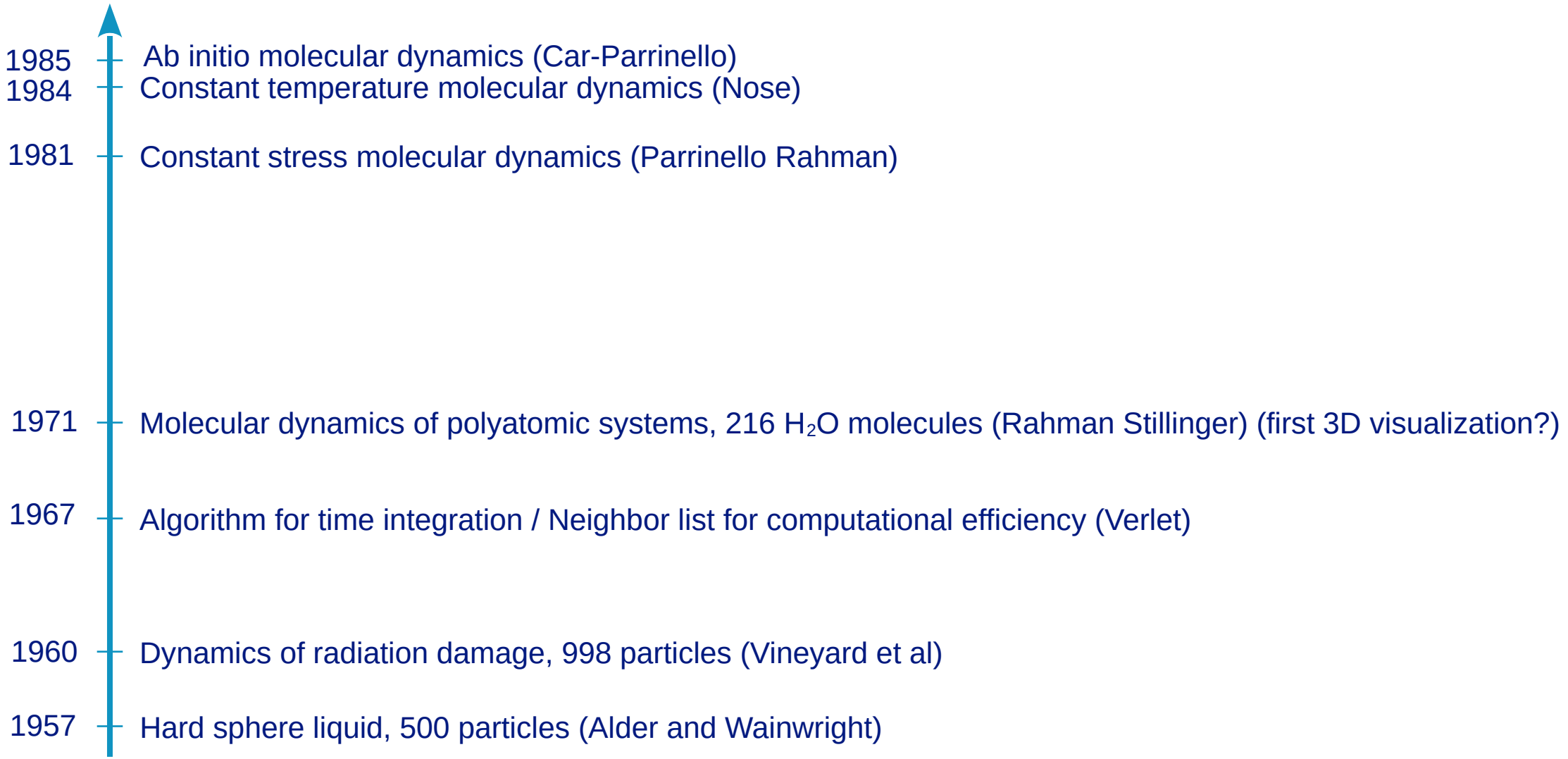


Fig. 1. – The quantity plotted is the energy (kinetic plus potential in each of the first five modes). The units for energy are arbitrary. $N = 32$; $\alpha = 1/4$; $\delta t^2 = 1/8$. The initial form of the string was a single sine wave. The higher modes never exceeded in energy 20 of our units. About 30,000 computation cycles were calculated.

Thermalization not always achieved!

→ No ergodicity

A bit of history: milestones



A bit of history: size milestones

2019 — 10^9 atoms (one entire gene)

2013 — 4.125×10^{12} atoms

2006 — 3×10^{11} atoms

2004 — 10^{10} atoms

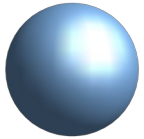
- Maximum size depends on the computational resources
- Maximum size depends on the simulation time and interaction potentials
- Large systems involves other issues

Plastic deformation of tantalum
268 millions atoms
~ 85 x 169 x 338 nm^3

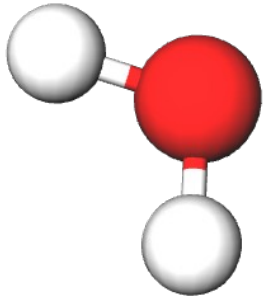
A. Zepeda-Ruiz et al., Nature 550, 7677 (2017)

Why “molecular” and not atomistic?

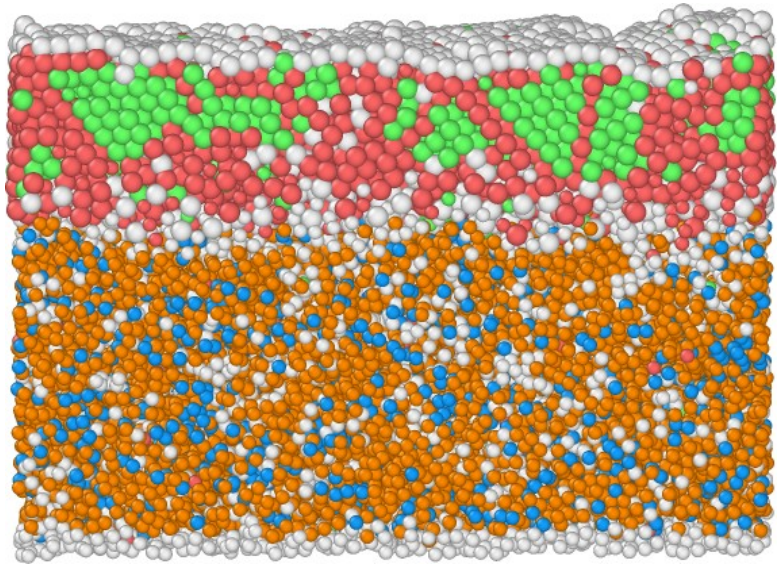
Alder and Wainwright (1957)
Hard sphere model as the unit



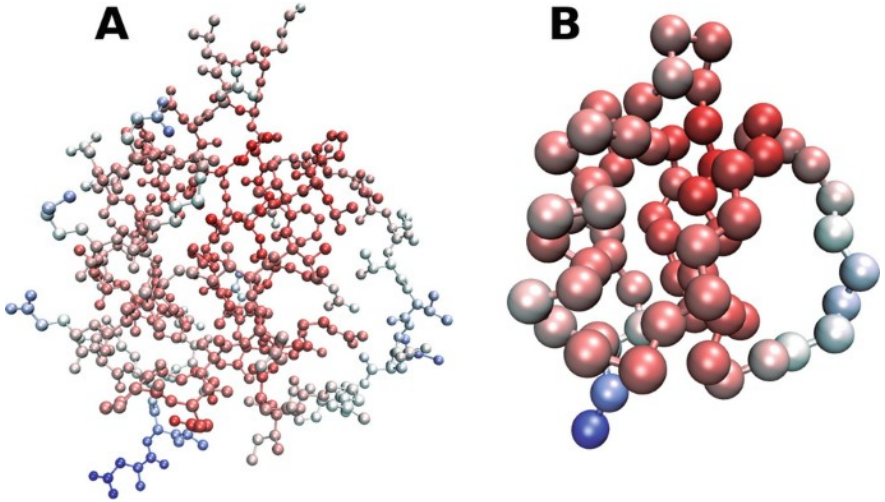
Rahman Stillinger (1971)
Water molecule as the unit



Atoms !!!



A bead (representing a molecule, or a part of it, or a part of a polymer, etc…) as the unit

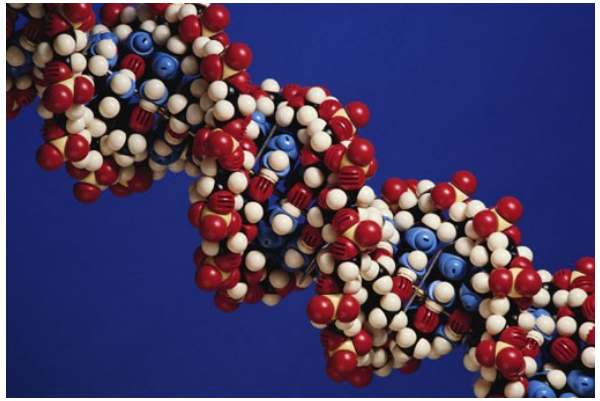


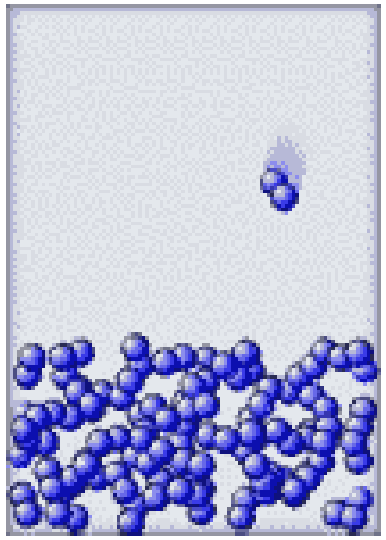
Contessoto et al (2022)
https://doi.org/10.1007/978-1-0716-1716-8_16

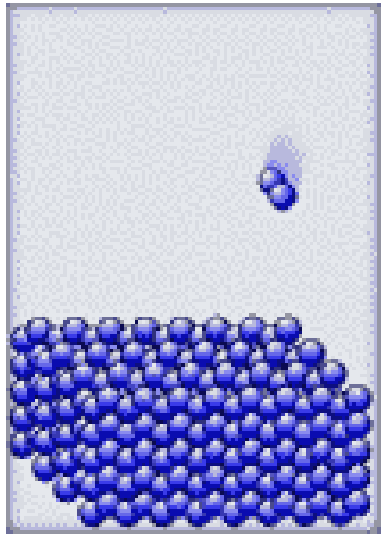
The term ‘Molecular’ comes from the historical context, and the first uses of molecular dynamics (liquids, chemistry)

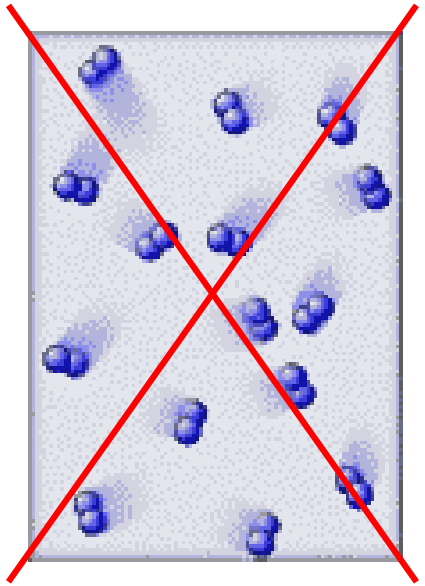
Systems that can be simulated

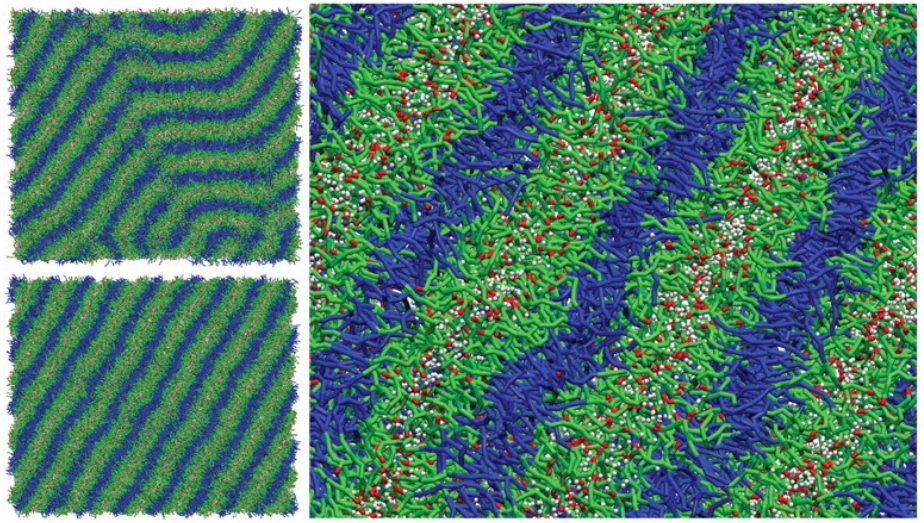
- Liquids
- Solids (crystals, disordered, heterostructures)
- Molecular crystals
- Molecules
- Complex fluids
- ~~Gas~~





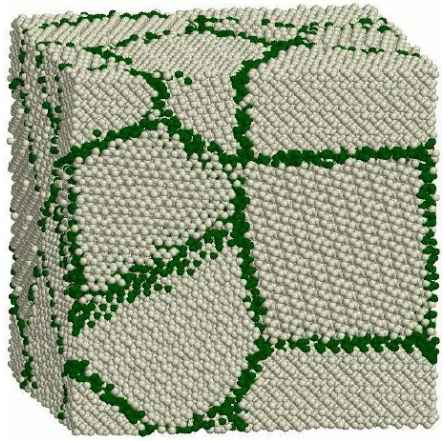




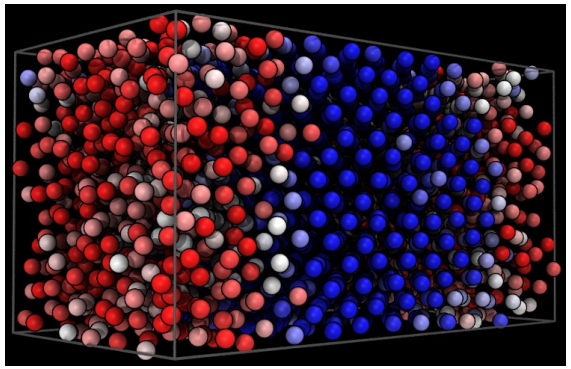


Klein and W. Shinoda, Science (2008)

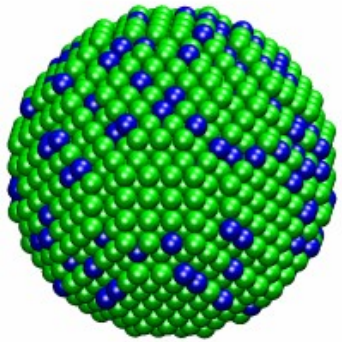
Systems that can be simulated



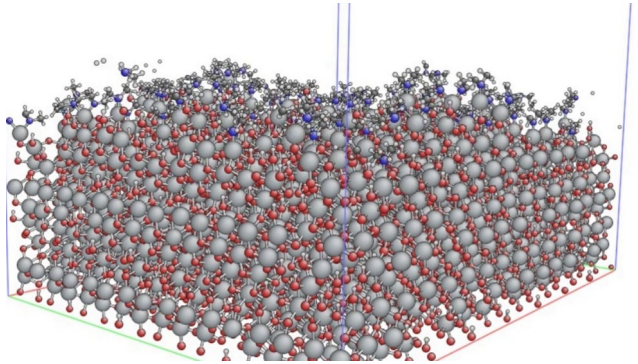
Ultra nanocrystalline diamond



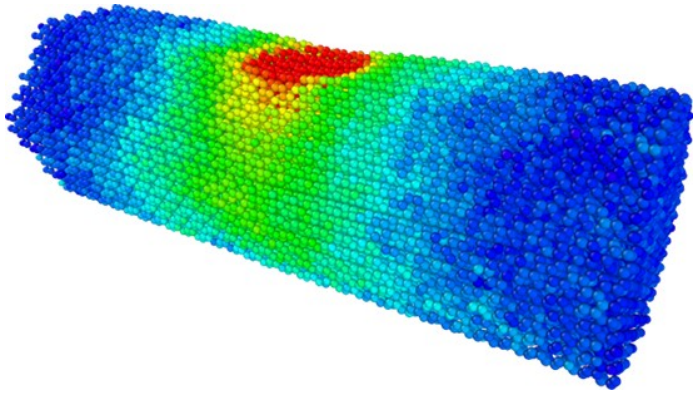
Solid-liquid interface



FeNi nanoparticle



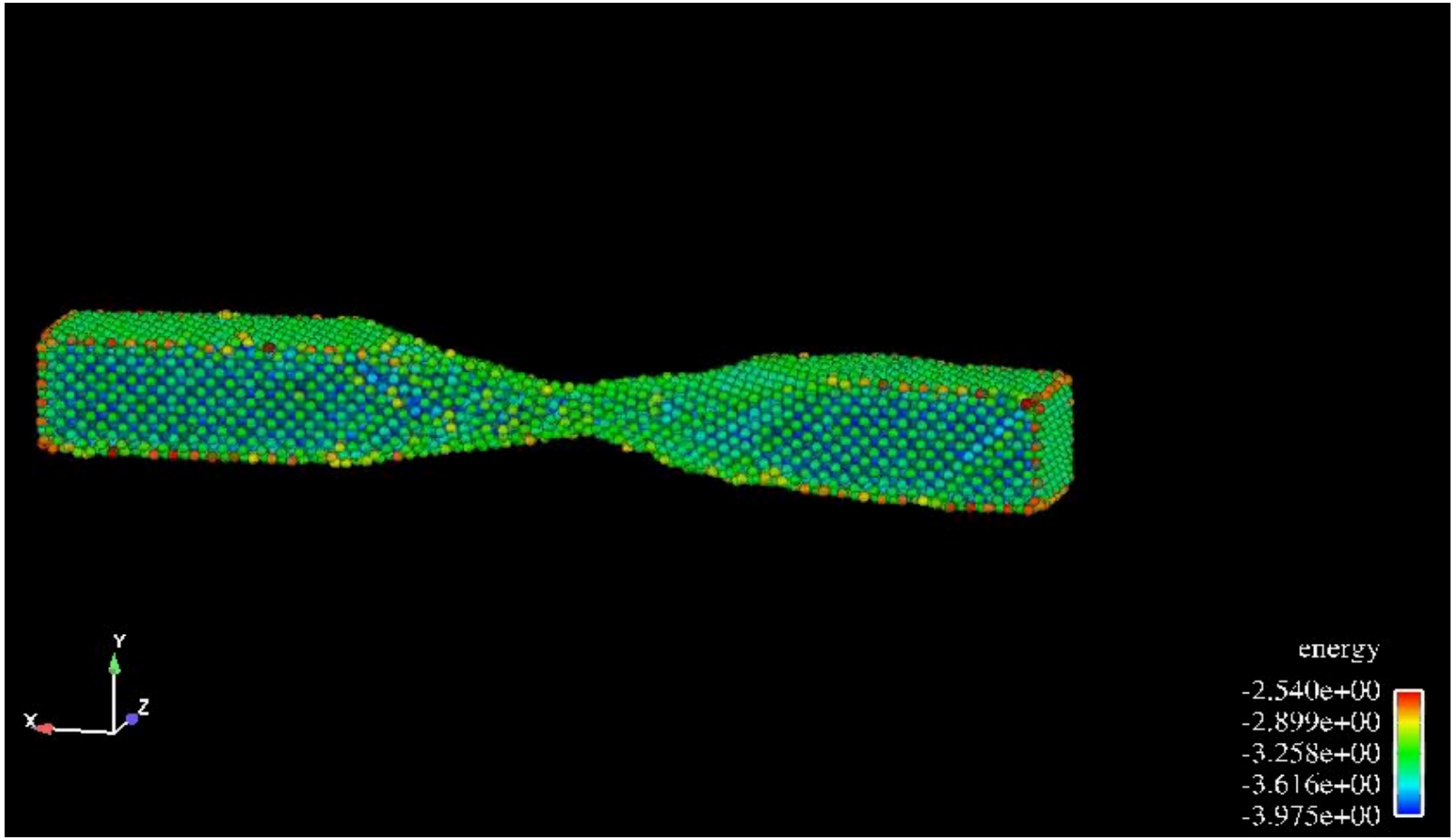
Hafnium dioxide growth



Nanoindentation of ZnO nanowire

Examples

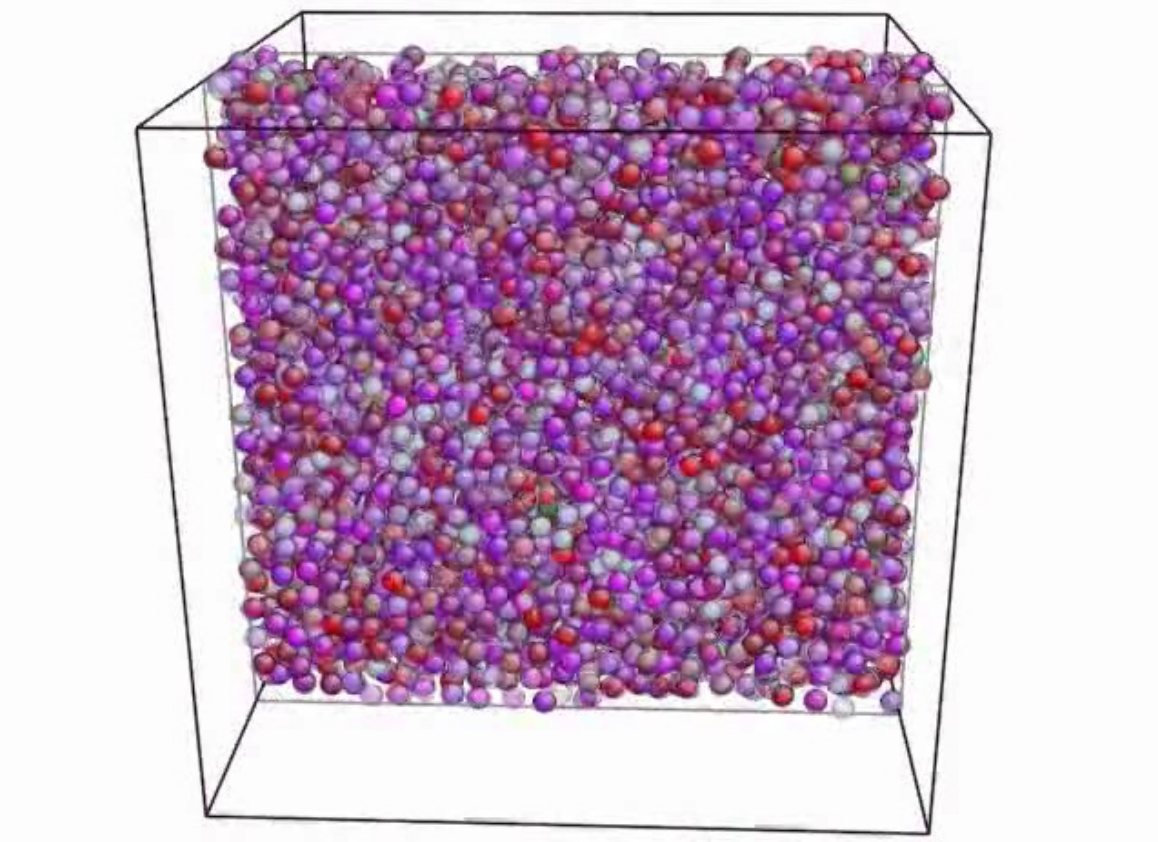
Au nanowire formation and extension



H. S. Park and J. A. Zimmerman, Phys Rev B, 72, 054106 (2005)

Examples

Cavitation in a liquid metal



T. T. Bazhirov, G. E. Norman, and V. V. Stegailov, JPCM, 20, 114113 (2008)

Examples

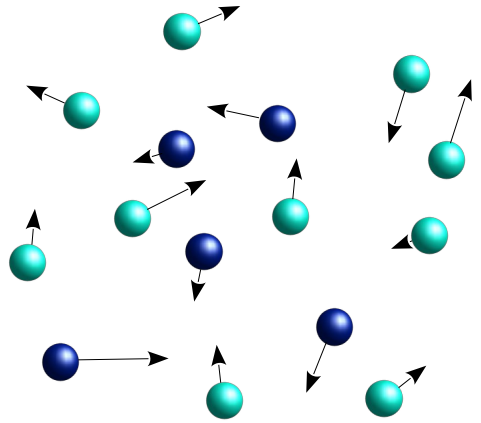
Compression of nanopillars made of pyrocarbons

L. Pizzagalli, J. Durinck, P. Lafourcade, JM. Leyssale, to be published

The theory and the basics

The theory: Newtonian mechanics

We have a set of N particles defined by their positions, their velocities and their mass: $\mathbf{r}_i,\ \mathbf{v}_i = \dot{\mathbf{r}}_i,\ m_i$



The system's dynamic is described by the Newton's 2nd law of motion $m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i$

$\mathbf{F}_i$ is the sum of all forces exerted on particle i . It depends only on particles positions (and not on velocities)

To obtain the dynamics, we need to solve N decoupled differential equations

The theory: Hamiltonian mechanics

The Newton's 2nd law of motion can be expressed with Hamiltonian mechanics

$$\mathcal{H}\left(\{\mathbf{r}\},\{\mathbf{p}\}\right)=\sum_{i}^{N}\frac{\mathbf{p}_i^2}{2m_i}+U\left(\{\mathbf{r}\}\right) \qquad \mathbf{p}_i=m_i\mathbf{v}_i=m_i\dot{\mathbf{r}}_i \qquad \mathbf{F}_i=-\frac{\partial U}{\partial \mathbf{r}_i}$$

$$\dot{\mathbf{p}}_i=-\frac{\partial \mathcal{H}}{\partial \mathbf{r}_i}=-\frac{\partial U}{\partial \mathbf{r}_i}=\mathbf{F}_i$$

$$\dot{\mathbf{r}}_i=\frac{\partial \mathcal{H}}{\partial \mathbf{p}_i}=\frac{\mathbf{p}_i}{m_i}$$

$$\Rightarrow \qquad \ddot{\mathbf{r}}_i=\frac{\dot{\mathbf{p}}_i}{m_i}=\frac{\mathbf{F}_i}{m_i}$$

The time evolution in phase space is defined by $\left(\{\mathbf{r}\},\{\mathbf{p}\}\right)$

There are 6N independent variables (usually a bit less depending on initial conditions)

The theory: Energy and momentum conservation

$$\frac{d\mathcal{H}}{dt} = \sum_i^N \left[\frac{\partial \mathcal{H}}{\partial \mathbf{r}_i} \dot{\mathbf{r}}_i + \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i} \dot{\mathbf{p}}_i \right]$$

$$\dot{\mathbf{r}}_i = \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i} \qquad \dot{\mathbf{p}}_i = -\frac{\partial \mathcal{H}}{\partial \mathbf{r}_i}$$

$$\rightarrow \quad \frac{d\mathcal{H}}{dt} = \sum_i^N \left[\frac{\partial \mathcal{H}}{\partial \mathbf{r}_i} \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i} - \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i} \frac{\partial \mathcal{H}}{\partial \mathbf{r}_i} \right] = 0$$

The Hamiltonian (the energy) is a constant

An important consequence is that energy is conserved during the system dynamic evolution (isolated system)

The total linear and angular momenta are conserved during dynamic evolution

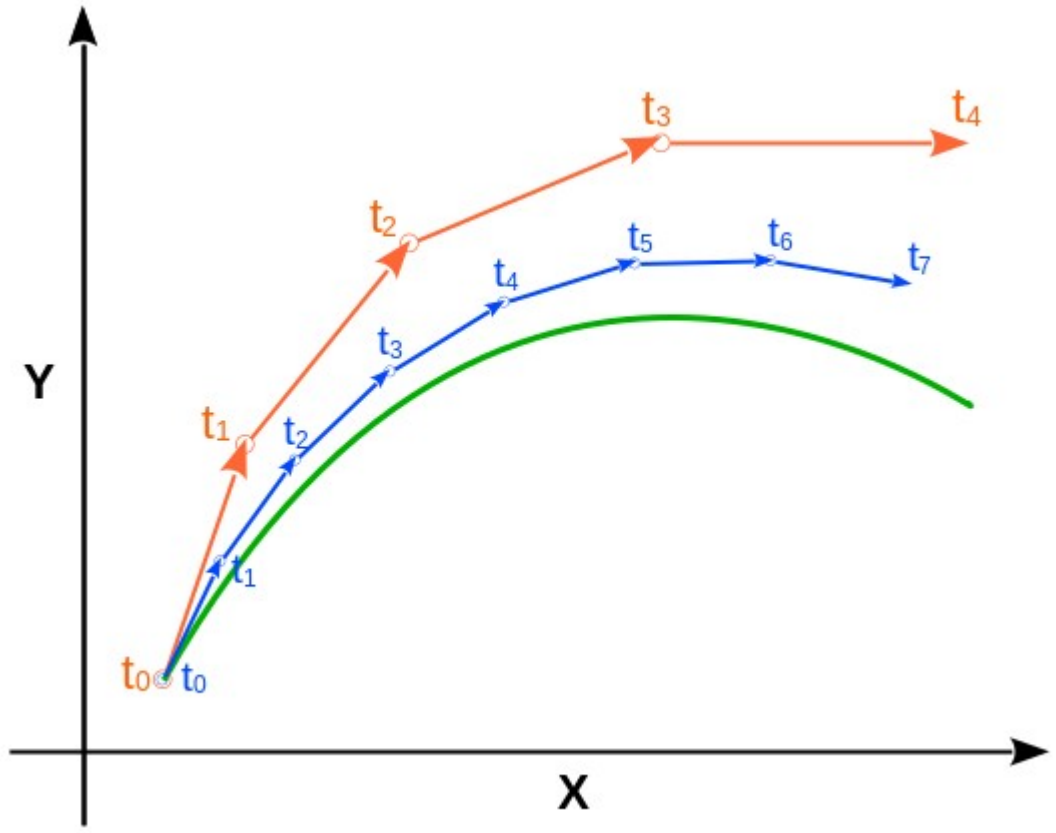
Solving the equation of dynamics

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

An analytical solution is not possible

Numerical integration requires time discretization

The integration accuracy critically depends on the timestep δt



The chosen δt should be small in order to obtain physically accurate trajectories simulation

BUT δt defines the time scale of the simulation, and we want it to be as large as possible

The best compromise depends on multiple factors (temperature, particles mass, nature of the physical interactions)

Timestep optimization

Should be done at the start of a ‘new’ study

δt should be as large as possible, with an ‘accurate’ trajectory, and conserving the total

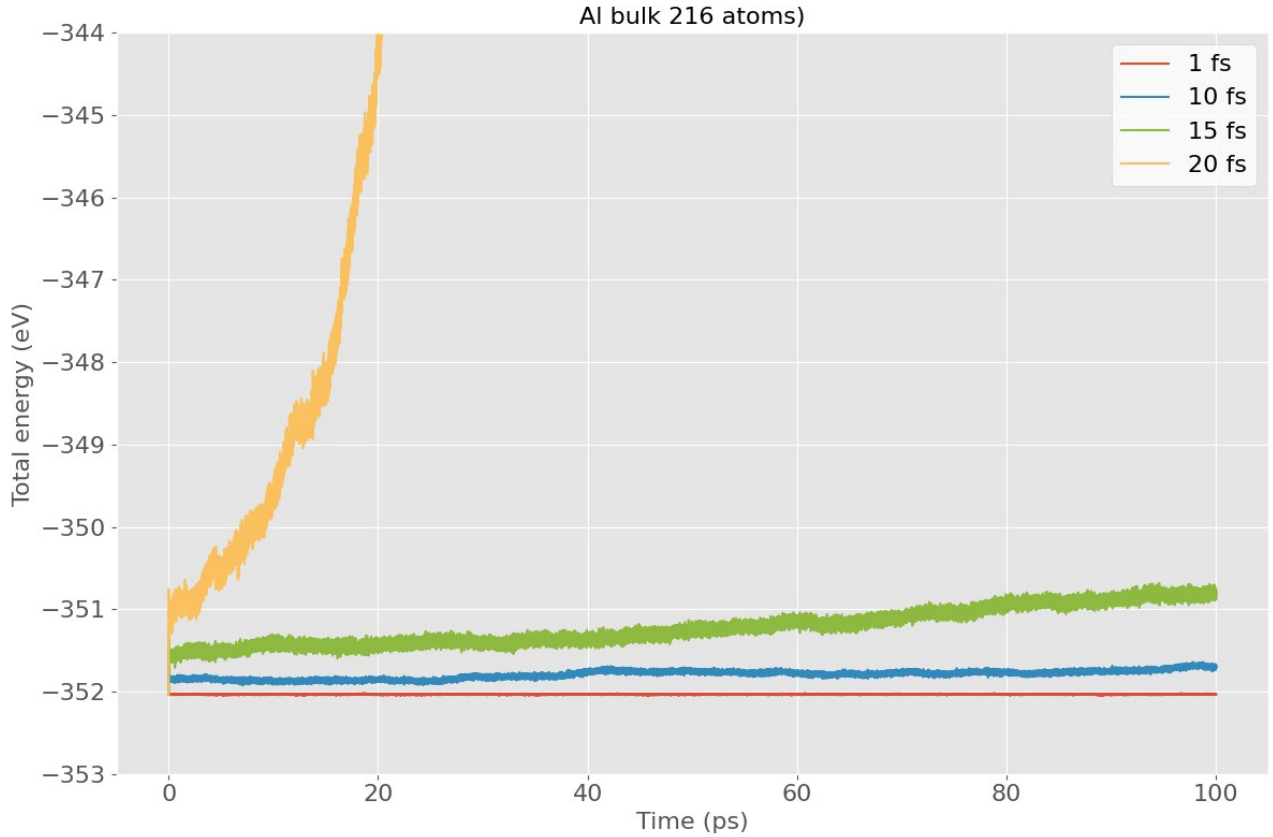
It depends on the nature of the interaction, the mass of atoms, the temperature, the total duration

As a rule of thumb, $\delta t \lesssim \frac{1}{10\omega_D} \sim 2-4$ fs

RMS energy fluctuation $\langle \Delta E^2 \rangle^{\frac{1}{2}} \propto \delta t^2$ (Verlet)

RMS energy fluctuation $\frac{\langle \Delta E^2 \rangle^{\frac{1}{2}}}{E} \lesssim 10^{-4}$

Usual values in material science are 0.5 – 2 fs



Verlet algorithm

$$\mathbf{r}_i(t+\delta t) = \mathbf{r}_i(t) + \dot{\mathbf{r}}_i(t)\delta t + \frac{\ddot{\mathbf{r}}_i(t)\delta t^2}{2} + \frac{\dddot{\mathbf{r}}_i(t)\delta t^3}{6} + \mathcal{O}(\delta t^4)$$

$$\mathbf{r}_i(t-\delta t) = \mathbf{r}_i(t) - \dot{\mathbf{r}}_i(t)\delta t + \frac{\ddot{\mathbf{r}}_i(t)\delta t^2}{2} - \frac{\dddot{\mathbf{r}}_i(t)\delta t^3}{6} + \mathcal{O}(\delta t^4)$$

$$\mathbf{r}_i(t+\delta t) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t-\delta t) + \ddot{\mathbf{r}}_i(t)\delta t^2 + \mathcal{O}(\delta t^4)$$

Cancellation 1st and 3rd order
→ better accuracy than simple Taylor

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

$$\mathbf{r}_i(t_0+\delta t) = \mathbf{r}_i(t_0) + \dot{\mathbf{r}}_i(t_0)\delta t + \frac{\ddot{\mathbf{r}}_i(t_0)\delta t^2}{2} + \mathcal{O}(\delta t^3)$$

Probably the most famous
First use by Jean-Baptiste Delambre (1791)

Accuracy is $\mathcal{O}(\delta t^4)$ by step, but leads to a total accuracy of $\mathcal{O}(\delta t^2)$ by accumulation

Velocity Verlet algorithm

$$\mathbf{r}_i(t+\delta t) = \mathbf{r}_i(t) + \dot{\mathbf{r}}_i(t)\delta t + \frac{\ddot{\mathbf{r}}_i(t)\delta t^2}{2}$$

$$\dot{\mathbf{r}}_i(t+\delta t) = \dot{\mathbf{r}}_i(t) + \frac{\ddot{\mathbf{r}}_i(t) + \ddot{\mathbf{r}}_i(t+\delta t)}{2}\delta t$$

$$\mathbf{r}_i(t+\delta t) = \mathbf{r}_i(t) + \dot{\mathbf{r}}_i(t)\delta t + \frac{\ddot{\mathbf{r}}_i(t)\delta t^2}{2}$$

$$\mathbf{F}_i(t+\delta t) \rightarrow \ddot{\mathbf{r}}_i(t+\delta t) = \frac{\mathbf{F}_i(t+\delta t)}{m_i}$$

$$\dot{\mathbf{r}}_i(t+\delta t) = \dot{\mathbf{r}}_i(t) + \frac{\ddot{\mathbf{r}}_i(t) + \ddot{\mathbf{r}}_i(t+\delta t)}{2}\delta t$$

More simple than ‘normal’ Verlet algorithm

Often used in code

Same global error than normal Verlet, i.e $\mathcal{O}(\delta t^2)$

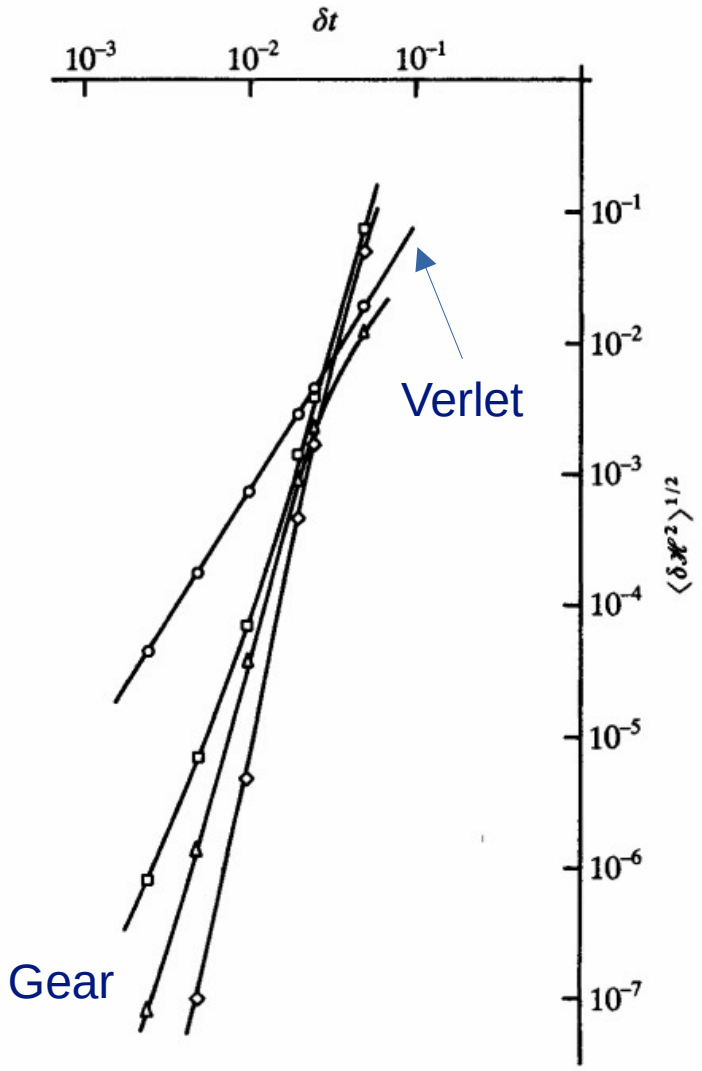
Other algorithms

- Leapfrog integrator: a variant of Verlet algorithm (Hockney 1970)
- Beeman's algorithm: another variant of Verlet algorithm (Beeman 1976)
- Gear predictor – corrector algorithm (1966)
- r-Respa : reversible reference system propagator algorithm (Tuckerman 2000)
- And several others...

A good algorithm is fast, allows for large δt, is as accurate as possible, allows for energy and momentum conservation, and is time reversible

The accuracy is different for all algorithms, but in practice it is simpler to play with δt

Velocity Verlet is the most used in literature (simple and efficient)



Allen and Tildesley (1987)

Algorithm in practice...

Input

$\{\mathbf{r}_i(t_0), \mathbf{v}_i(t_0)\}$

Potential energy calculation from positions

$\mathrm{E}_{\mathrm{pot}}(\{\mathbf{r}_i(t)\})$

Forces calculation either directly or as derivatives of the potential energy

$$\mathbf{F}_i(t) = -\frac{\partial \mathrm{E}_{\mathrm{pot}}(t)}{\partial \mathbf{r}_i(t)}$$

Numerical integration Verlet algorithm (or others)

$$\ddot{\mathbf{r}}_i(t) = \frac{\mathbf{F}_i(t)}{m_i}$$

$\{\mathbf{r}_i(t+\delta t), \mathbf{v}_i(t+\delta t)\}$

Output

- Trajectories (positions and velocities) of all particles
- Total energy
- Forces

A molecular dynamics run in practice

1 - Define the interactions between particles (the potential)

2 - Define the boundary and control conditions

3 - Set the initial state (initial positions, initial velocities)

4 - Run the simulation

5 - Analyze the output

Interaction potentials

Classical interatomic potentials

- Idea: describe the interactions between atoms using models (empirical or not)
- Proposed well before the first molecular dynamics simulations
- Used in the first molecular dynamics simulations (1957)
- Often called force-field methods in chemistry

$$E = f_1(\{R_\alpha\}) + f_2(\{R_\alpha, R_\beta\}) + f_3(\{R_\alpha, R_\beta, R_\gamma\}) + \dots$$

Self-energy (often = 0) Pair energy Angular energy Higher order terms

- All the physics is included in the functions f_i
- Forces obtained as the derivatives (numerical or analytical) of the energy

Lennard-Jones potential (1924-1931)

$$E = \sum_{R_{\alpha\beta}} U^{\mathrm{LJ}}(R_{\alpha\beta}) \qquad U^{\mathrm{LJ}}(R_{\alpha\beta}) = 4\epsilon \left[\left(\frac{\sigma}{R_{\alpha\beta}} \right)^{12} - \left(\frac{\sigma}{R_{\alpha\beta}} \right)^{6} \right]$$

Ion-ion repulsion

van der Waals attraction

- Pair contributions only
- One of the oldest and simplest potential, extensively studied, and still largely used as a model potential for model system
- Computationally very efficient (only power, with the repulsion term as the square of the attraction one)
- Physical meaning of the attraction term
- Potential developed for liquids and for vdW solids (but used in many other cases)

Other standard pair potentials

$$U^{\mathrm{Morse}}(R_{\alpha\beta}) = \epsilon\, e^{\rho_0\left(1-\frac{R_{\alpha\beta}}{r_0}\right)}\left(e^{\rho_0\left(1-\frac{R_{\alpha\beta}}{r_0}\right)}-2\right)$$ Morse potential (1929)

$$U^{\mathrm{Buck}}(R_{\alpha\beta}) = Ae^{-R_{\alpha\beta}/B} - \frac{C}{R_{\alpha\beta}^6}$$ Buckingham potential (1938)

$$U^{\mathrm{Mie}}(R_{\alpha\beta}) = C\epsilon\left[\left(\frac{\sigma}{R_{\alpha\beta}}\right)^n - \left(\frac{\sigma}{R_{\alpha\beta}}\right)^m\right]$$ Mie potential (1903)

- Work extremely well for weakly bonded systems
- Computationally fast
- Poor reliability for modelling surface, melting, phase transitions of strongly bonded solids (metals, covalent, oxides)
- Physical meaning of the attraction term
- Potential developed for liquids and for vdW solids (but used in many other cases)

The Stillinger-Weber potential

- An example of potential designed for materials with covalent bonds

$$E = f_2\left(\{R_i, R_j\}\right) + f_3\left(\{R_i, R_j, R_k\}\right)$$

$$f_2\left(\{R_i, R_j\}\right) = A\varepsilon\left[B\left(\frac{\sigma}{R_{ij}}\right)^p - \left(\frac{\sigma}{R_{ij}}\right)^q\right]\exp\left(\frac{\sigma}{R_{ij} - a\sigma}\right)$$

$$f_3\left(\{R_i, R_j, R_k\}\right) = h(R_{ij}, R_{ik}, \theta_{jik}) + h(R_{ij}, R_{jk}, \theta_{ijk}) + h(R_{ik}, R_{jk}, \theta_{ikj})$$

$$h(R_{ij}, R_{ik}, \theta_{jik}) = \lambda\varepsilon\left[\cos\theta_{jik} + \frac{1}{3}\right]^2 \exp\left(\frac{\gamma\sigma}{R_{ij} - a\sigma}\right)\exp\left(\frac{\gamma\sigma}{R_{ik} - a\sigma}\right)$$

- Originally designed for silicon (zinc-blende structure)
- Penalty energy for bending the bonds
- More parameters than for pair potentials (9 for silicon)
- Available sets of parameters for many materials

F. Stillinger et al., Phys. Rev. B (1985)

Many-body potentials

- The bonds strength depends on the local atomic environment

EAM potentials (like ‘EMT’, ‘glue’ model)

Daw, Foiles, and Baskes, Mat. Sci. Rep. 9 (1993) 251-310

$$E = \sum_{\alpha} F(\rho_\alpha) + \frac{1}{2}\sum_{\alpha \neq \beta} \Phi(R_{\alpha\beta}) \qquad \rho_\alpha = \sum_{\beta \neq \alpha} \rho_\beta^a (R_{\alpha\beta})$$

Attractive embedding energy

Ion-ion repulsion

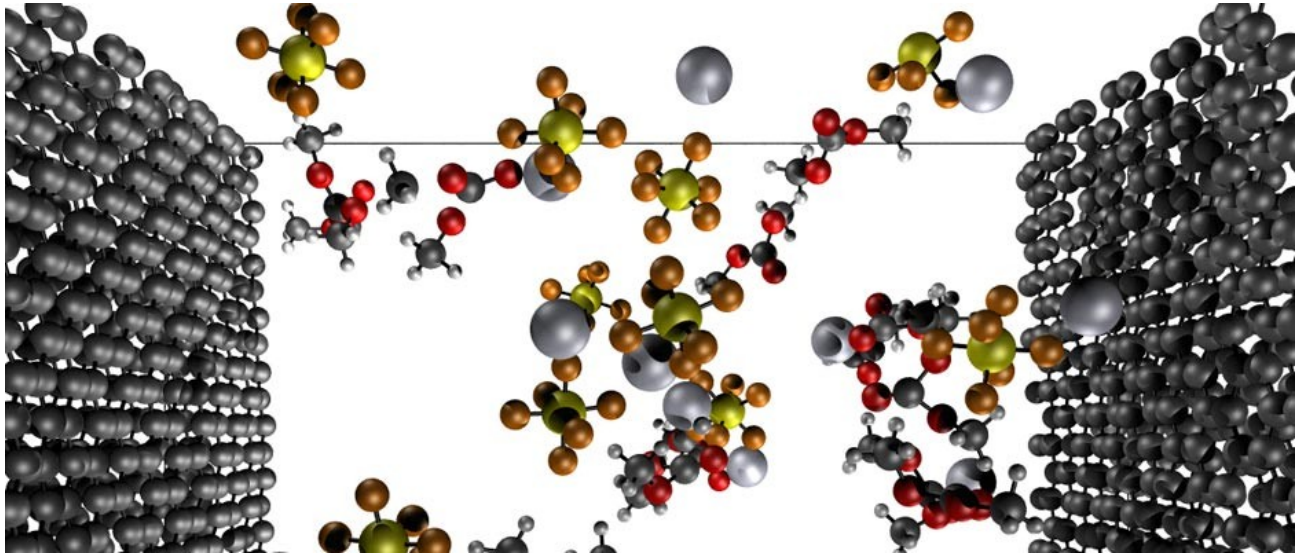
- Extension with bond directionality (for transition metals, semiconductors): MEAM
- It exists hundreds of different potentials:
  - Tersoff (semiconductors)
  - EDIP (semiconductors)
  - AIREBO (C-H)
  - Beck (He)
  - MGPT (transition metals)

And even more sets of parameters

More and more complex potentials

- Potentials designed to model multi-components systems, with a diverse electronic structure
- REAXFF (A.C.T. van Duin, W.A. Goddard, III), Charge-Optimized Many-Body potentials COMB (S. Phillpot)

$$
\begin{aligned}
E_{REAXFF} = \; & E_{bond} + E_{lp} + E_{over} + E_{under} + E_{val} \\
& + E_{pen} + E_{coa} + E_{C2} + E_{triple} + E_{tors} \\
& + E_{conj} + E_{H-bond} + E_{vdWaals} + E_{Coulomb}
\end{aligned}
$$



ReaxFF simulation on a low-density battery electrolyte (PF6/DMC) between two graphite surfaces

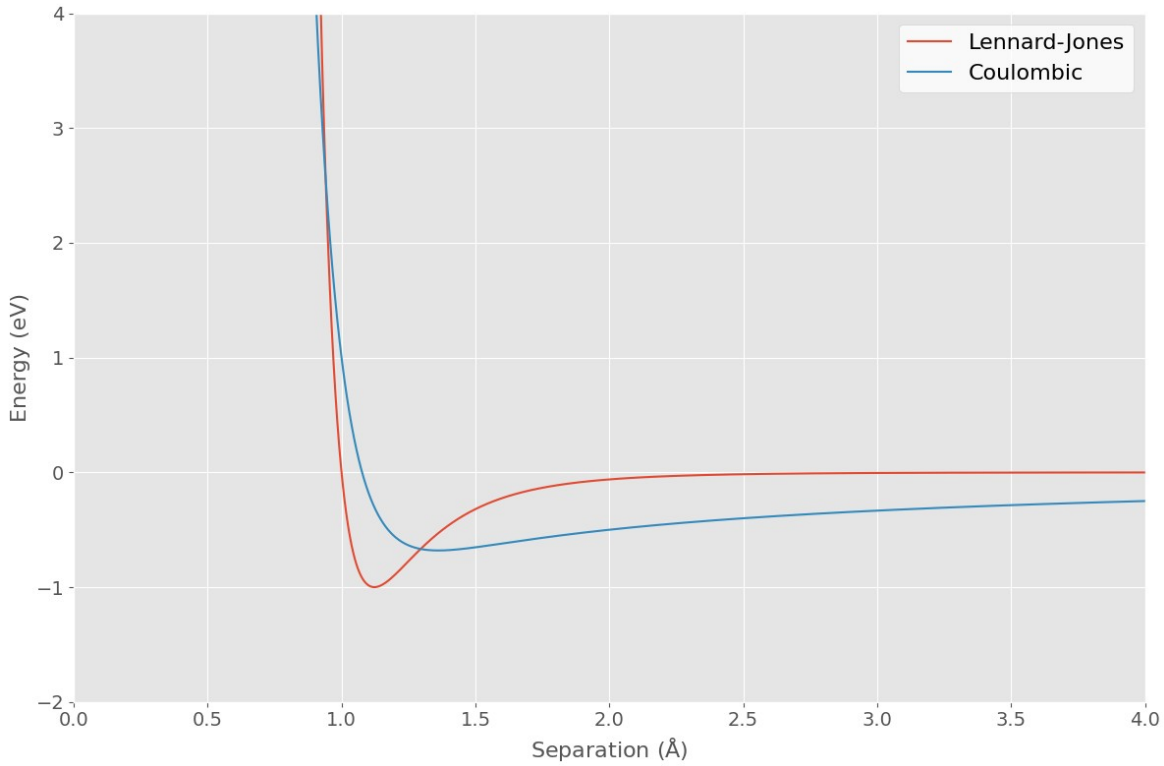
Bedrov, D. et al. J. of Phys. Chem. A 2012, 116, 2978

BUT slow, and also overfitting issues

Interaction cutoff

- In practice, interactions are considered to be negligible beyond a certain threshold (the cutoff, usually 3 Å to 5 Å)
- It determines the number of interacting neighbors and the computational cost (scaling O(N))
- Potential issue with discontinuities at the cutoff (use of smoothing functions)
- Some potentials make use of Coulombic interactions (long range). For instance, ionic materials with charges. In that case, there is no cutoff and interactions between all atoms are computed. The computational cost increases.

$$U^{\mathrm{Coul}}(R_{\alpha\beta}) = \frac{Cq_\alpha q_\beta}{\varepsilon R_{\alpha\beta}} + A\exp\left(\frac{-R_{\alpha\beta}}{\rho}\right)$$



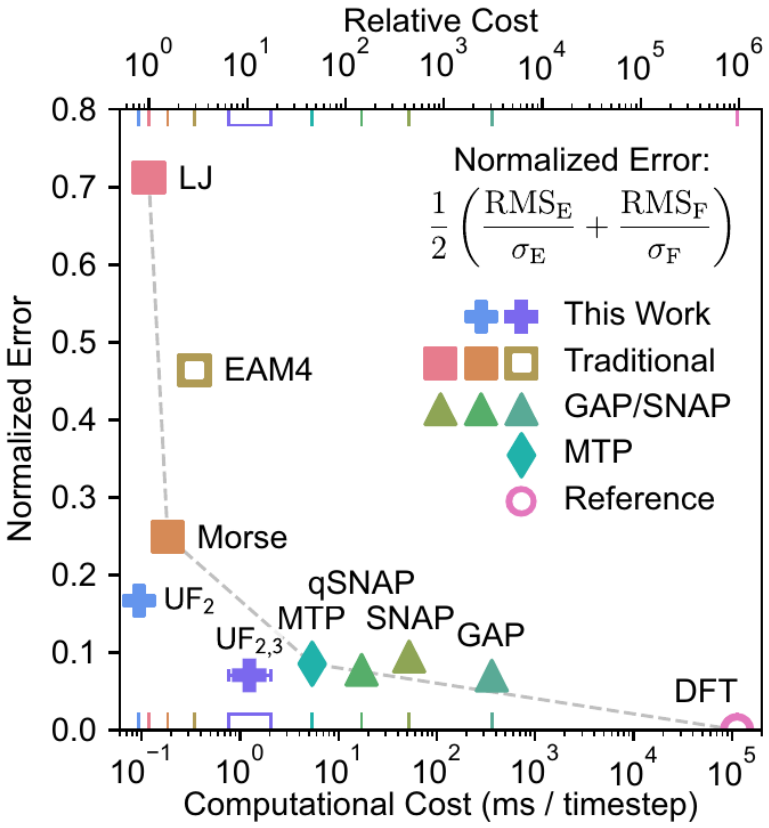
Dealing with long range interactions

- Replace point charges with smeared charge distribution and split between short-range and long-range parts
- Can be dealt with the simple Ewald summation. The scaling is $O(N^{3/2})$
- Faster methods have been developed:
  - Particle mesh Ewald. Charges interpolated on a 3D grid + FFT
  - Particle-particle-particle-mesh (P^3M). The scaling is O(N logN).
  - Multilevel Summation Method (MSM): Several meshes with different resolutions. The scaling is O(N) (but with a substantial additional cost)
  - Fast Multipole Method (FMM): charges interpolation with polynomials. The scaling is also O(N).
  - And probably others I am not aware of...

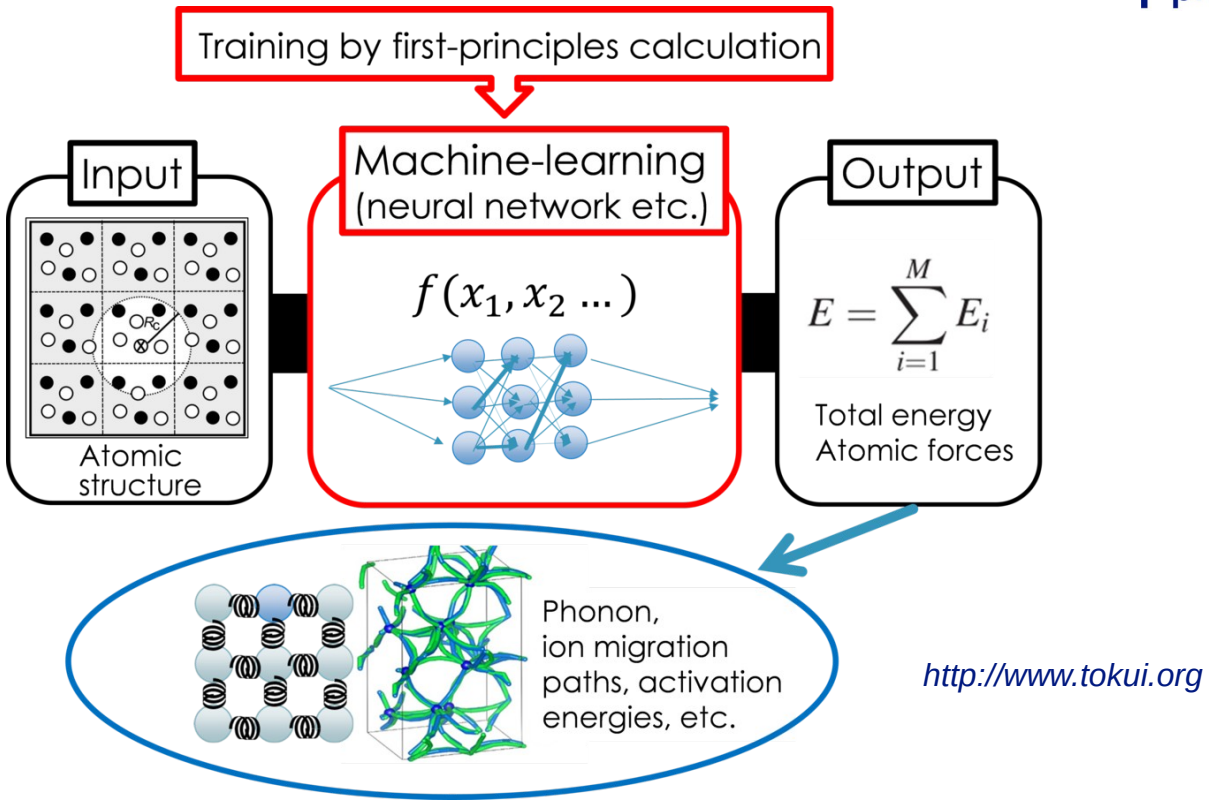
Approximations are made in all case, and an ‘accuracy’ parameter on energy/forces has to be defined

Machine learning interatomic potentials

- AI techniques associated with simplified structural descriptors, non-physical structure-energy mapping
- GAP, MTP, ACE, AGNI, etc...



S.R. Xie et al, npj Computational Materials (2023)



http://www.tokui.org

- Huge progress in accuracy/cost tradeoff in the last few years
- Extremely good for interpolation, much less for extrapolation
  → the 'quality' of the database is crucial

Energy/forces from electronic structure

- Instead of atoms, the matter is considered as composed of ions and electrons
- Ion-ion forces are easy to compute (Coulombic interactions)
- Ionic forces due to electrons can be obtained using the Hellman-Feynmann theorem

$$F_\alpha^{elec} = -\nabla_\alpha E_0 = -\nabla_\alpha \left[\frac{\langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle} \right] = -\frac{\langle \Psi_0 | \nabla_\alpha \mathcal{H} | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle}$$

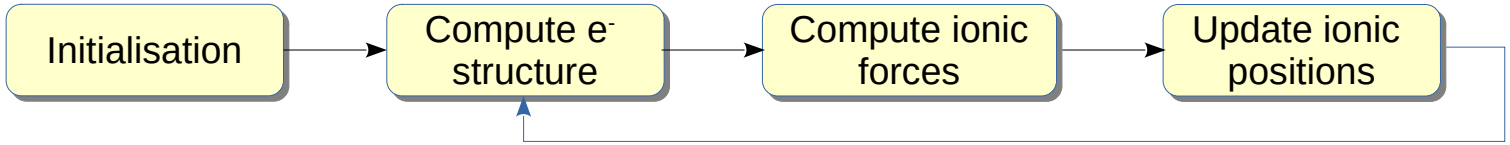
Usual approaches to compute the Hamiltonian (and its derivative) are:

- A tight-binding description (DFTB formalism for instance)
- Density Functional Theory

MD from electronic structure

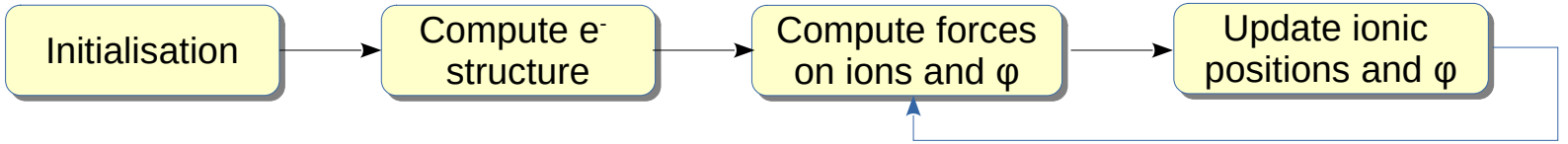
- Two different kind of dynamics

Born-Oppenheimer



Car-Parrinello

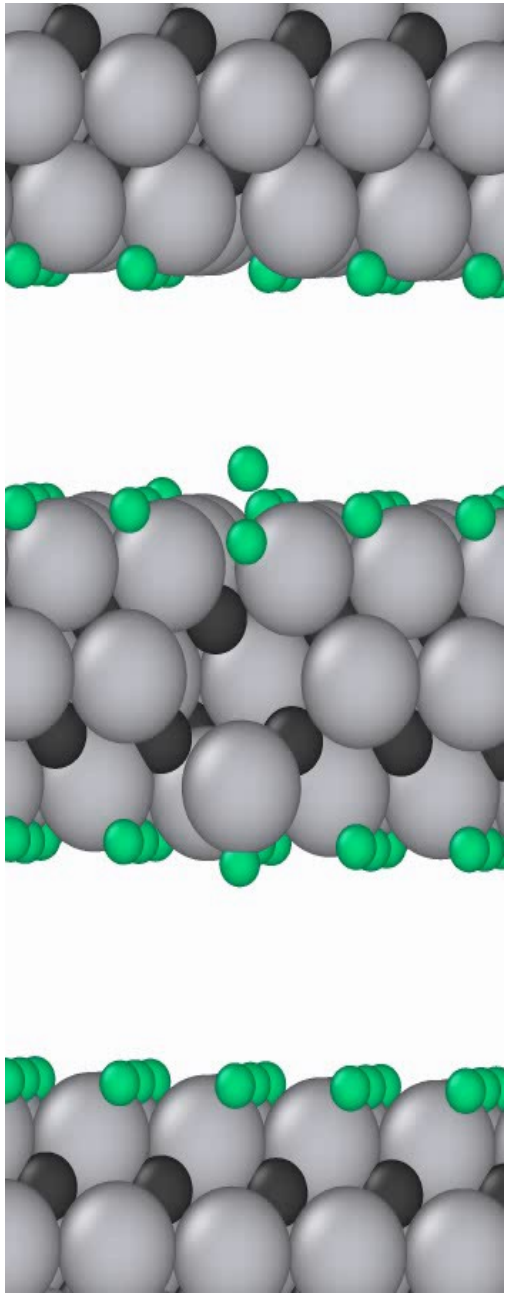
$$\mathcal{L}^{qm} = \sum_{i}^{\text{occ}} \int \mathrm{d}r\, \mu_i \, |\dot{\psi}_i(r)|^2 \; - \; E\left(\{\psi_i\}\right) \; + \; \sum_{ij} \Lambda_{ij} \left(\int \mathrm{d}r\, \psi_i^*(r)\, \psi_j(r) \; - \; \delta_{ij} \right)$$



- Car-Parrinello is faster than Born-Oppenheimer, BUT it is trickier to use, it needs to be coded, and the timestep is at least one order of magnitude lower

MD from electronic structure

- Irradiation of a Mxene: $Ti_3C_2F_2$
- 45 eV transferred to a F atom
- BO Molecular dynamics



Interatomic potentials: conclusion

- One can define four classes of potentials:

  Model potentials: fast, accurate for a limited set of materials, largely used to test models

  Semi-empirical potentials: Often fast and reliable, with a good to moderate accuracy, not available for all materials (especially alloys), not easy to develop new ones

  Machine learning potentials: Higher CPU cost, with excellent accuracy, could be developed for any materials with a relative easiness, reliability needs to be tested

  ‘Electronic structure’ potentials: Very high CPU cost with bad scaling, excellent accuracy and reliability (DFT, lower for DFTB), available for almost all materials (DFT)

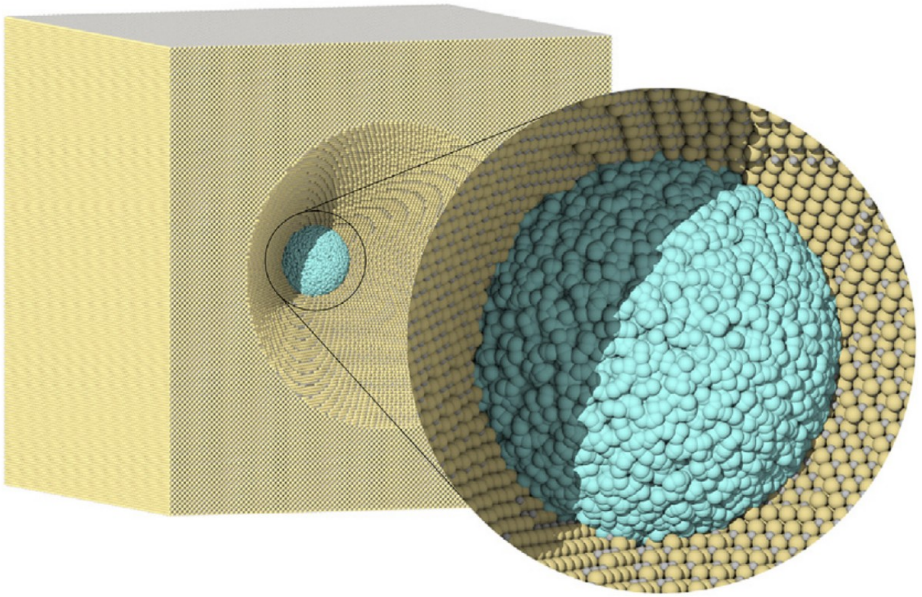
- It is important to know what you can get from the potential (and what you cannot get) → read the literature / make tests
- There is a trade-off to accept between computational cost and accuracy/reliability
- Use the right potential for a given material

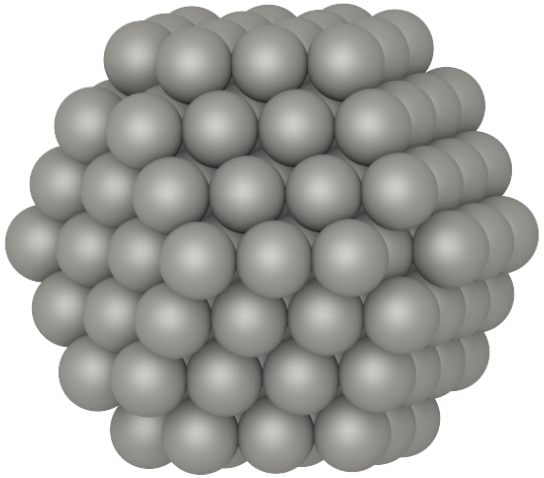
Setup: initial conditions, boundaries and controls

Initial positions

The initial atomic positions $\{\mathbf{r}_i(t_0)\}$ need to be defined for each MD simulation

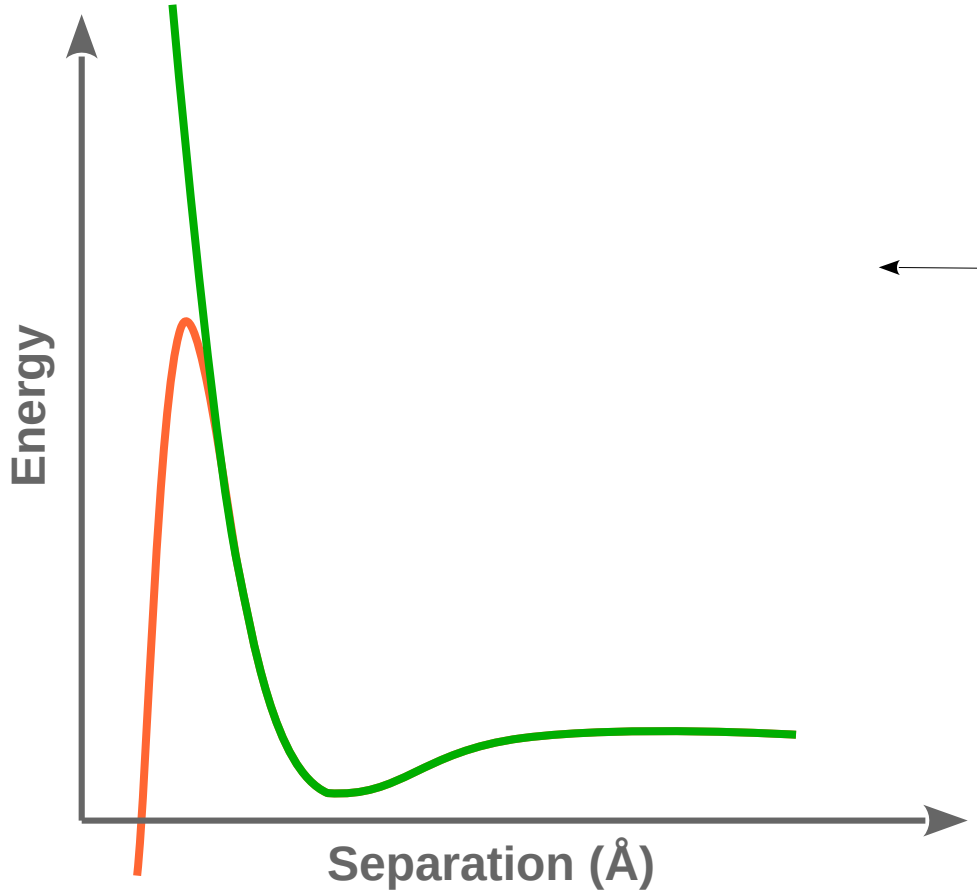
Several tools are available to build simple (pristine crystalline bulk) and complex (heterostructures, porous, defected, etc...) systems : python libraries, Atomsk, MD codes, etc…

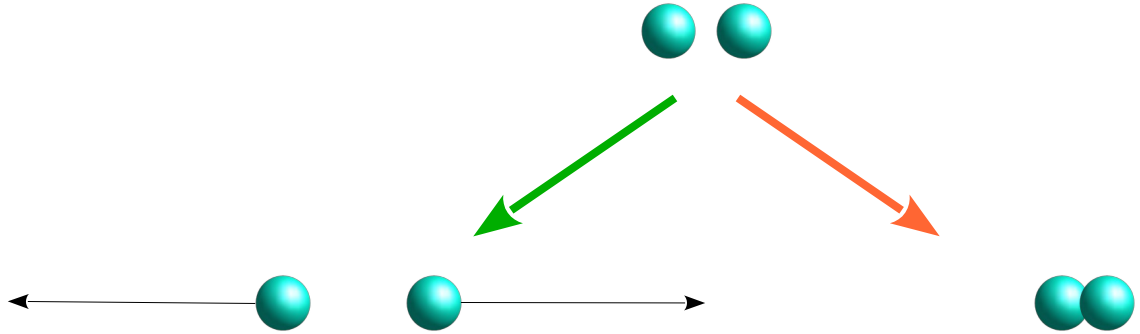




Initial positions: pitfalls

A possible issue arises when two atoms are initially too close (bad construction, bad translation vectors using PBC, random positions)





This is often the fingerprint of an error...

An initial minimization with limited forces can help in a few cases

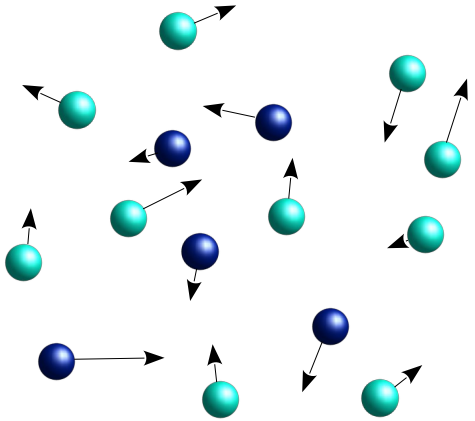
Initial velocities

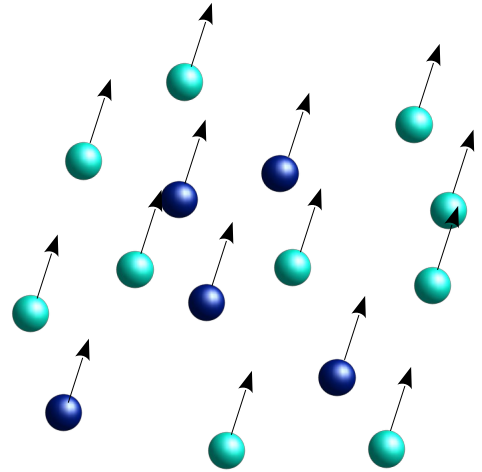
The initial atomic velocities $\{\mathbf{v}_i(t_0) = \dot{\mathbf{r}}_i(t_0)\}$ also need to be defined

The temperature of a MD simulation is computed from atomic velocities, assuming that all atomic motions correspond to a true thermal motion (i.e. for instance all allowed vibrational modes are excited in a solids)

$$\sum_i^N \frac{1}{2} m_i |\dot{\mathbf{r}}_i|^2 = \frac{3}{2} N k_B T$$

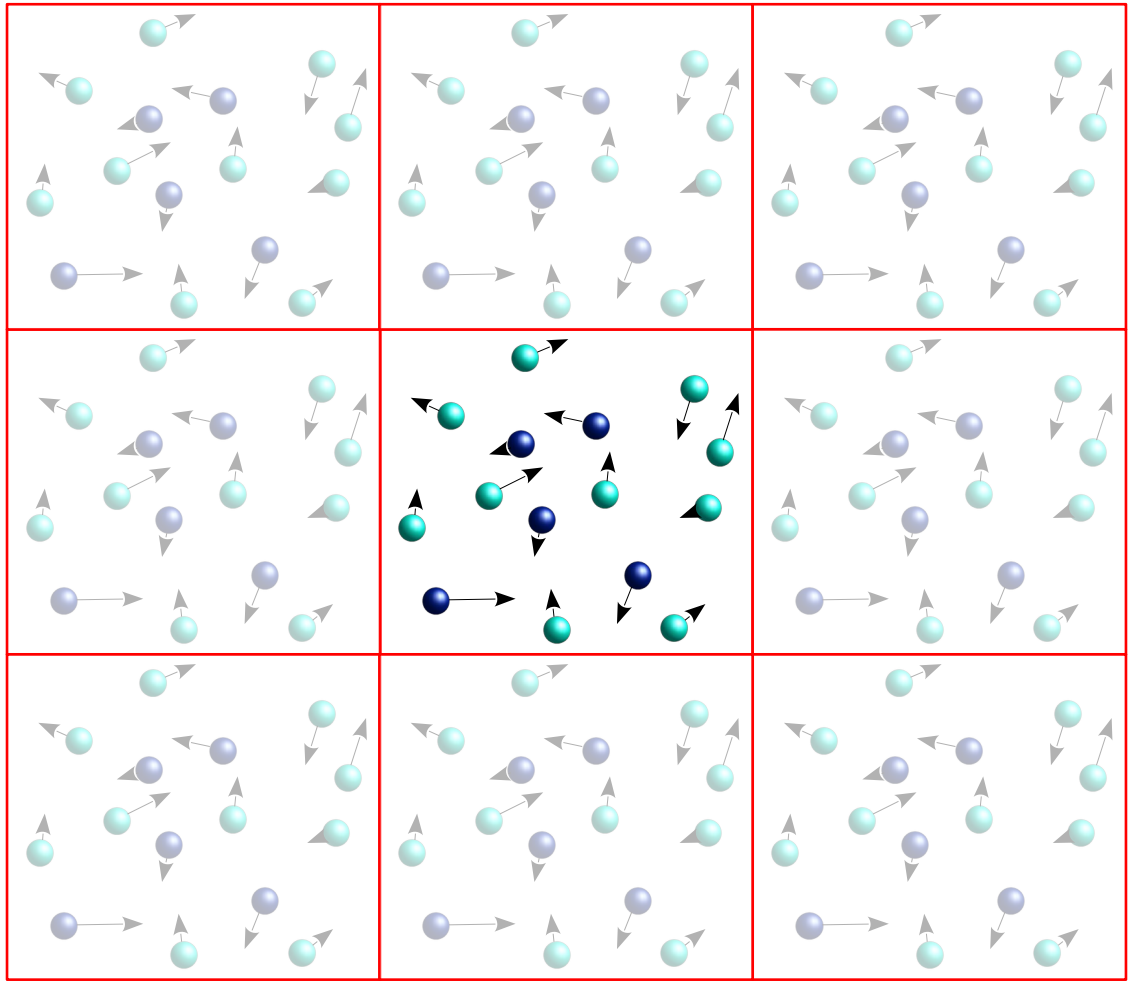
This condition is equivalent to total translation and rotation momenta equal to zero





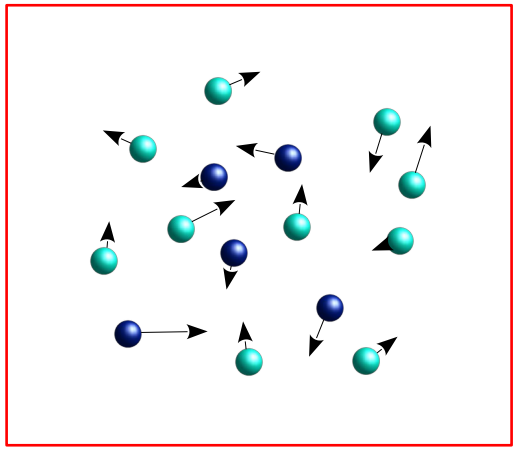
The initial velocities can be set according to a Gaussian distribution centered on the target temperature (with zero momenta) . A thermalisation phase is required to ensure the correct excitation of vibration modes.

Boundary conditions



Periodic boundary conditions (PBC) to model an infinite system

Fixed boundary conditions for finite systems



PBC can be used to model all situations (using enough volume around the system)

NVE ensemble

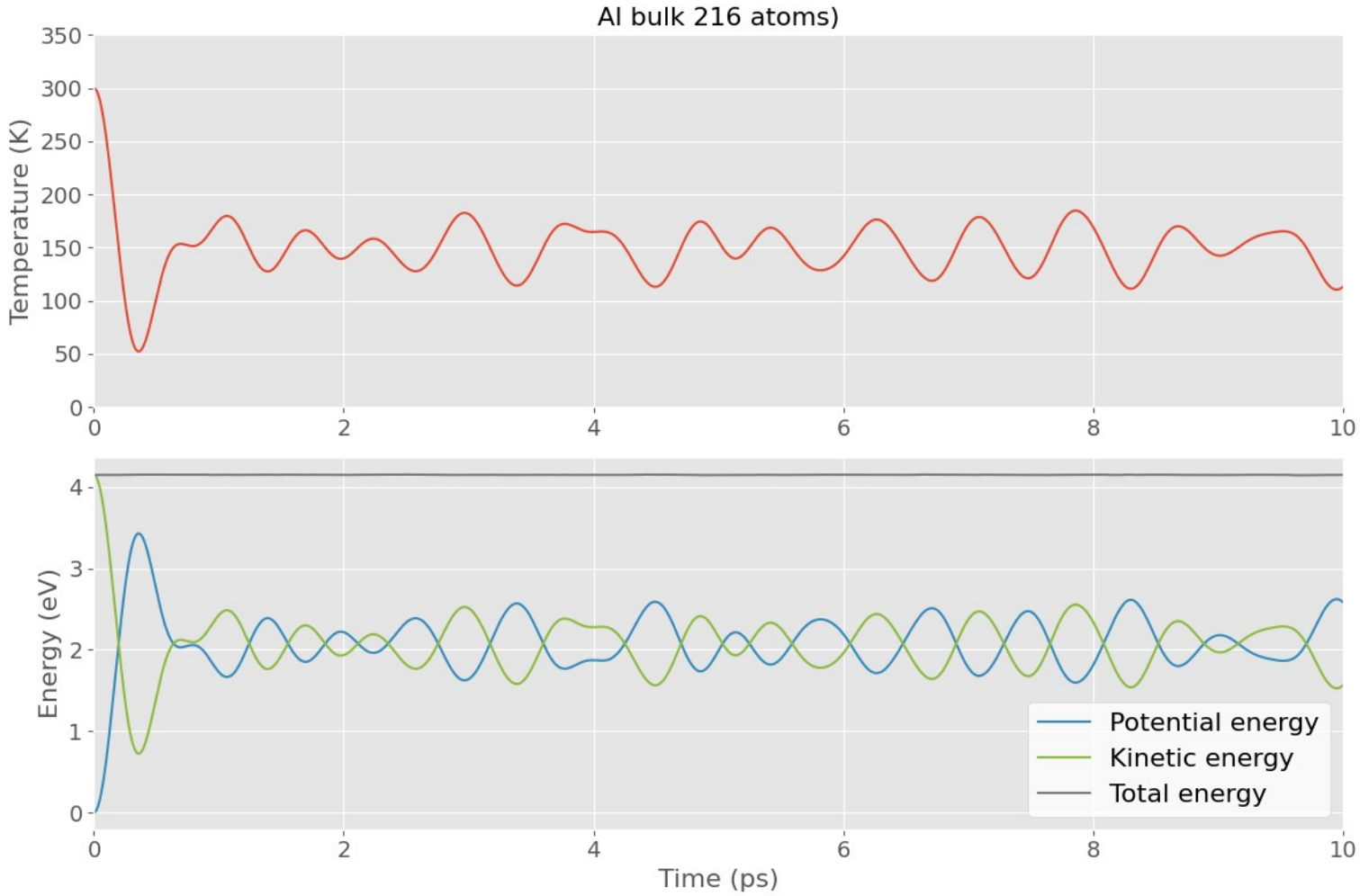
Number of particles, volume, and total energy are constant

Microcanonical ensemble (no external interaction/exchange)

Equipartition of initial energy between kinetic and potential energies

Setting accurately the initial temperature could be difficult using the NVE ensemble

The temperature is not a constant



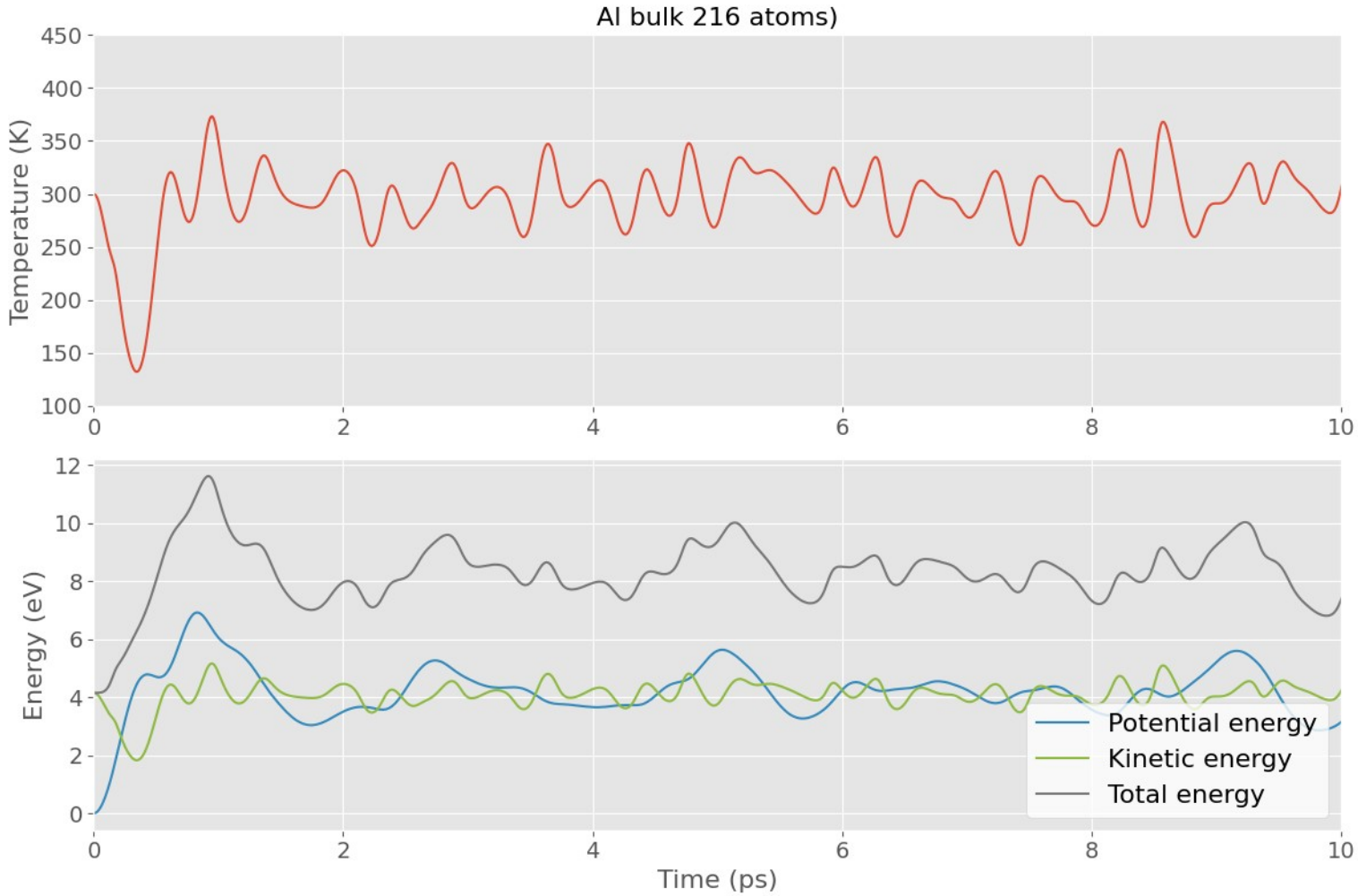
NVT ensemble

Number of particles, volume, and temperature are constant (isothermal-isochoric)

Isothermal-isochoric (canonical) ensemble (external interaction/exchange)

=> The total energy is not a constant

=> The kinetic energy is a constant



NVT can be obtained using a ‘thermostat’

NVT ensemble

Many thermostats have been proposed in the literature:

- Simple rescaling: velocities are rescaled to the target temperature at regular intervals
- Andersen: Velocities randomized (Gaussian distribution) at regular intervals
- Nose-Hoover: each particle is coupled with an external ‘bath’ Classic !
- Berendsen: ‘Stochastic’ rescaling (‘flying ice cube’ issue)
- Bussi-Donadio-Parrinello: Corrected Berendsen (yields the expected canonical distribution)
- Langevin: Competition between friction and a stochastic noise

In all cases, a thermostat parameter (‘strength’ or time) must be set. An optimal value should be determined (to void over-damping and under-damping phenomena).

=> Read the literature and the documentation of codes for good guesses !

NPT runs

Number of particles, pressure (stress tensor), and temperature are constant

Isothermal-isobaric ensemble (external interaction/exchange)

=> The total energy is not a constant

=> The kinetic energy is a constant

A barostat is used in addition to a thermostat:

- Berendsen
- Parrinello-Rahman

Useful for studying thermal expansion, phase transitions, melting points, density of fluids, and more generally, the properties of solids and fluids under pressure (and stresses for solids)

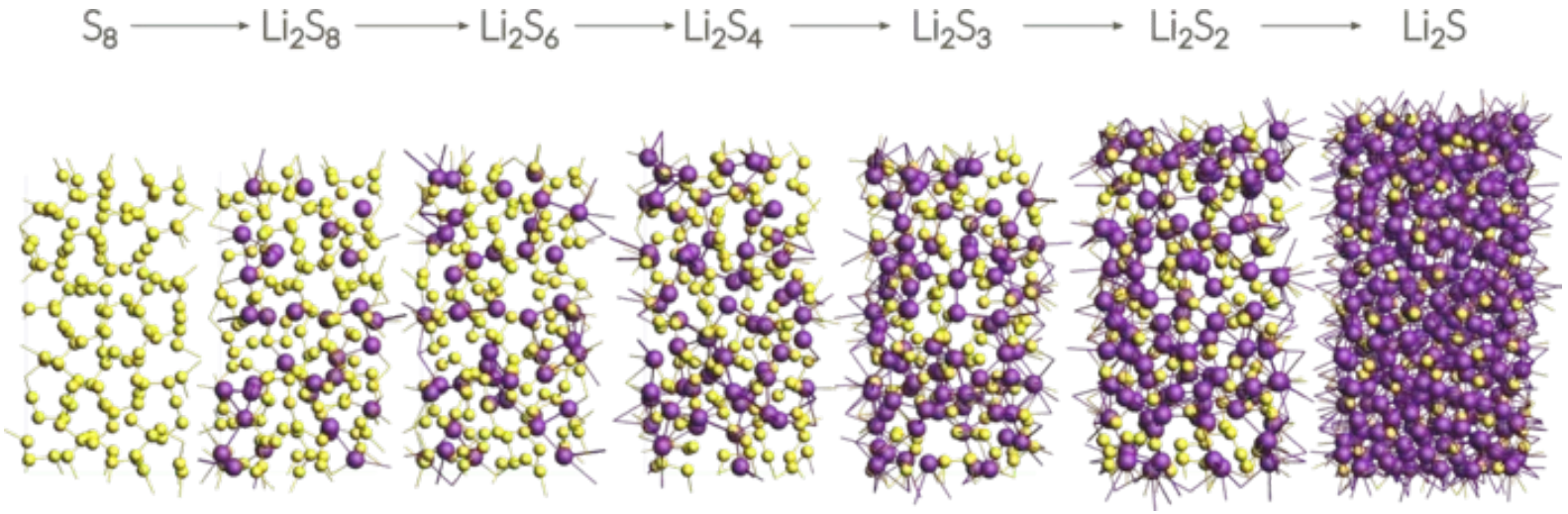
μVT runs

Chemical potentials, volume, and temperature are constant

Grand canonical ensemble

=> The total energy is not a constant

=> The kinetic energy is a constant



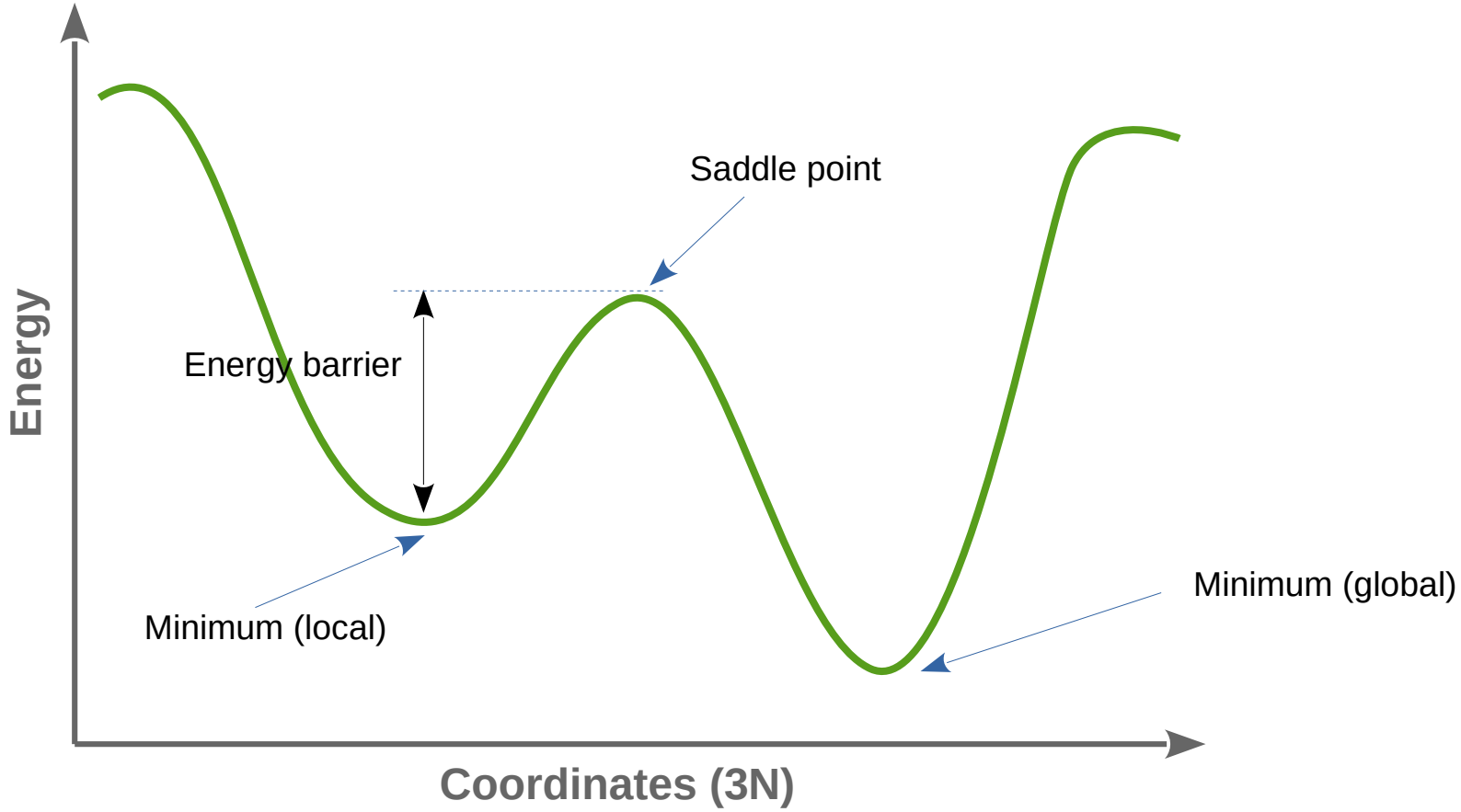
M.M. Islam et al, Phys. Chem. Chem. Phys. (2015)

Obtained by combining MD and Monte Carlo simulations

Useful for studying adsorption equilibrium (at surfaces, in pores, in defects, or in pristine materials), which is useful in thematics like growth, hydrogen storage, lithiation (the example above), etc...

Associated techniques for configuration space exploration

Potential Energy Surface (PES)

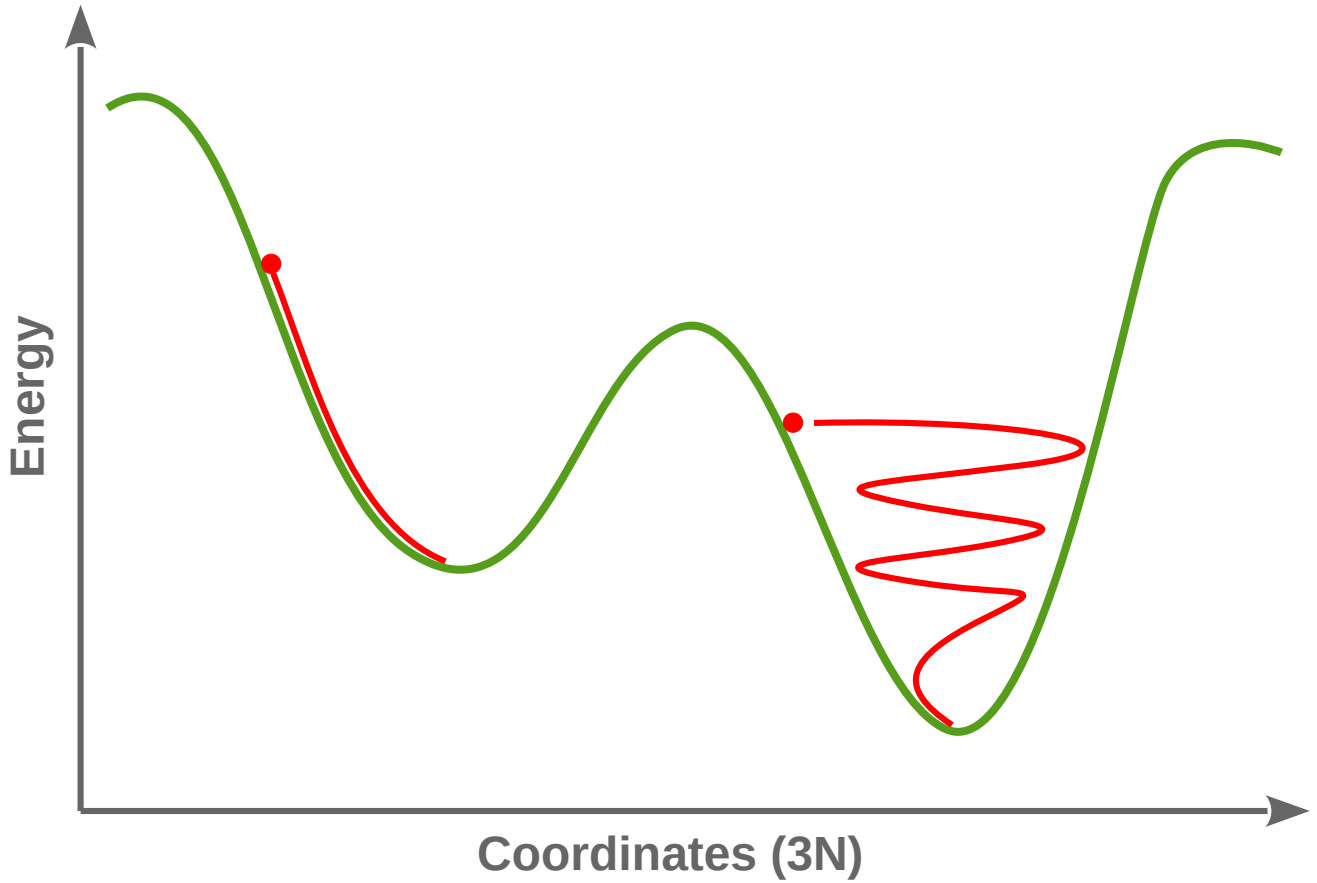


Important objectives:

- Find the lowest energy configuration (0K)
- Find stationary states at finite temperature (equilibrium)
- Evolution of the system under an external force/constraint (out of equilibrium)

Energy minima determination

$T = 0K \quad \mathbf{F} \rightarrow 0 \quad E \rightarrow E_{min}$



‘Static’ techniques

- Conjugate gradient
- Newton-Raphson
- Broyden-Fletcher-Goldfarb-Shanno (BFGS)

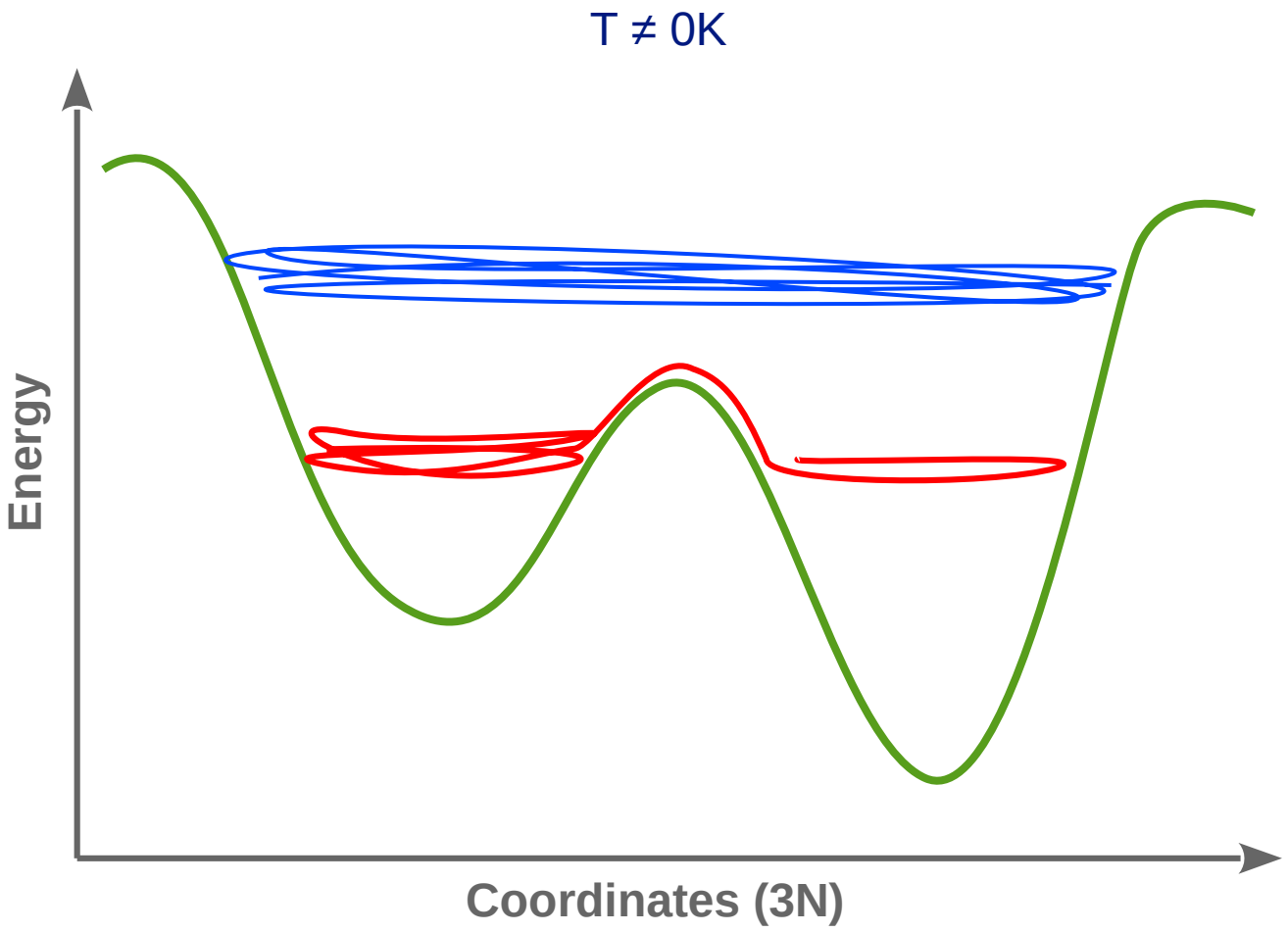
‘Dynamic’ techniques

- Quickmin
- FIRE

Global optimization

See for instance *D.J. Wales, Energy landscapes, Cambridge (2003)*

MD determination of activation energies



MD + Arrhenius plots

$$k = \frac{1}{\tau} = A \exp\left(\frac{-E_a}{k_B T}\right)$$

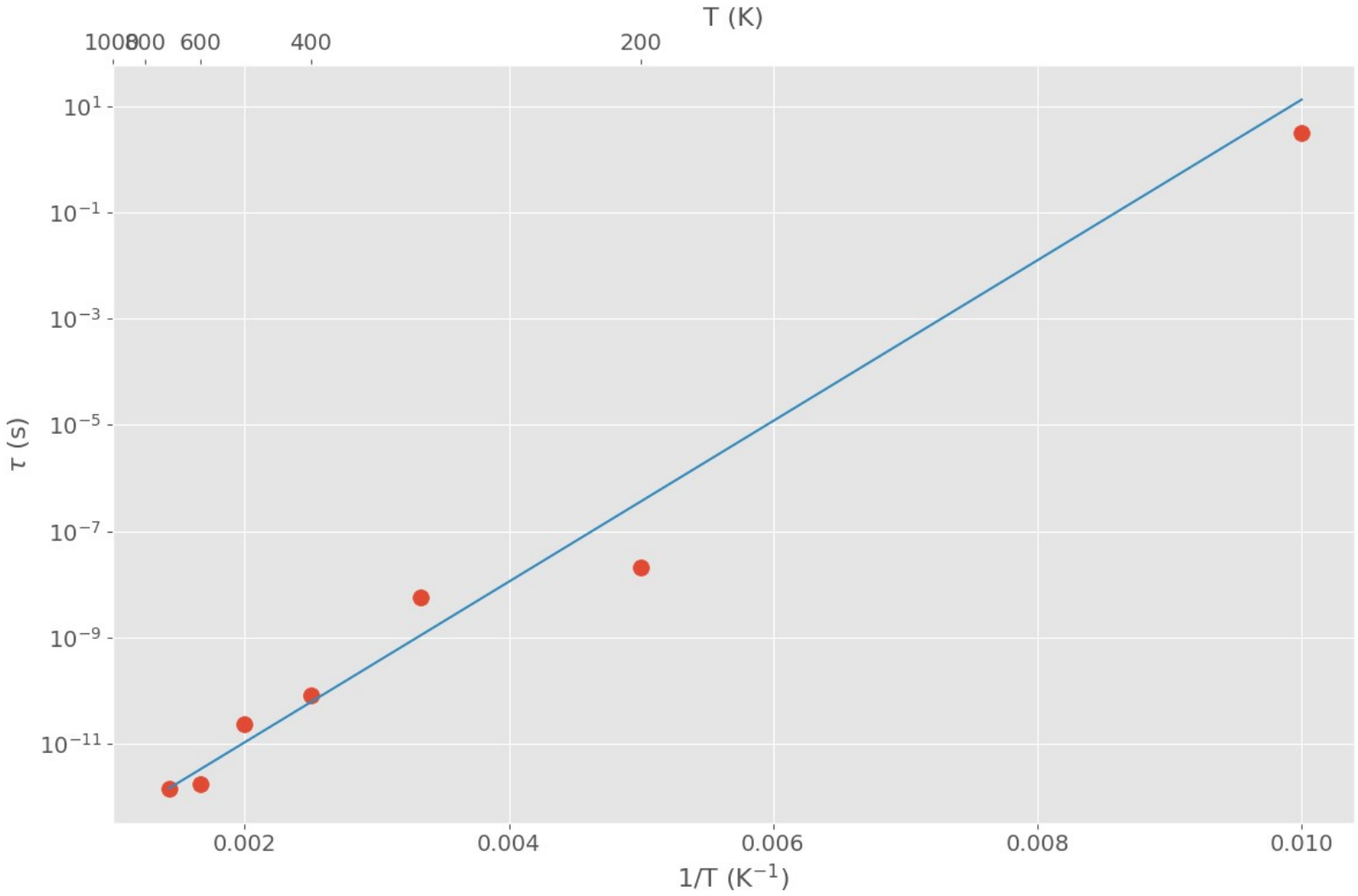
$$\ln\left(\frac{1}{\tau}\right) = \left(\frac{-E_a}{k_B}\right)\left(\frac{1}{T}\right) + \ln A$$

Perform several (many) MD runs at different temperatures and record the waiting time before the target transition

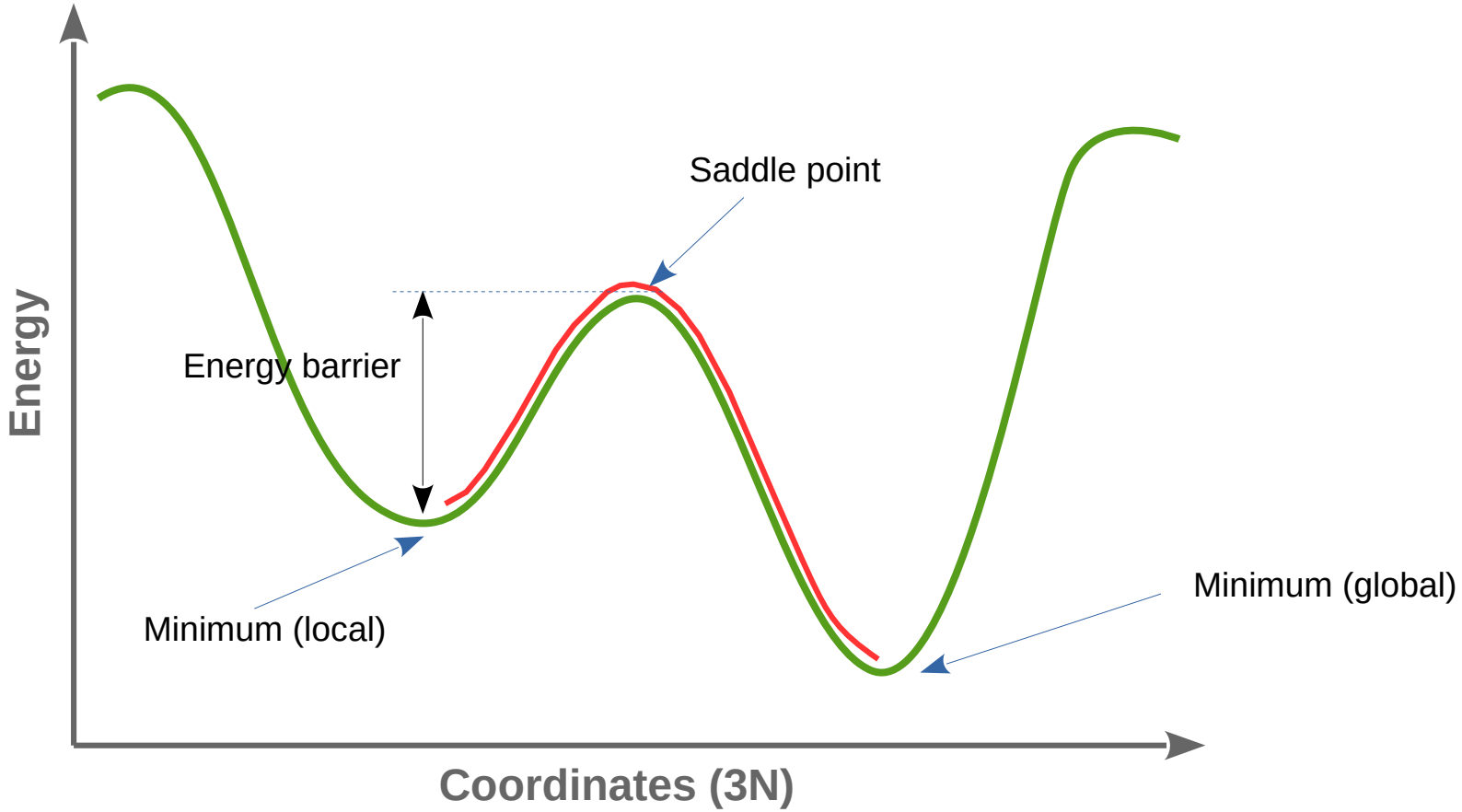
MD determination of activation energies

E_a = 0.3 eV
$A = 10^{13}$ s^{-1}

- General technique
- Many runs required
- Limited to low energies
- Issue if competing mechanism
- Limited temperature range for some materials



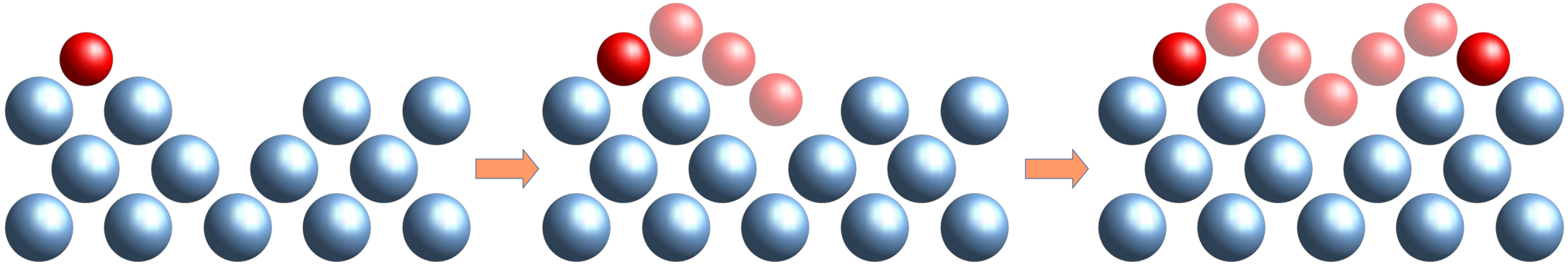
Static determination of activation energies



- Static calculation (no temperature): use of constraints
- Several methods proposed: DRAG, NEB, String, ...
- These methods assume that ending trajectory points are known (at least approximately)
- An initial guess is needed

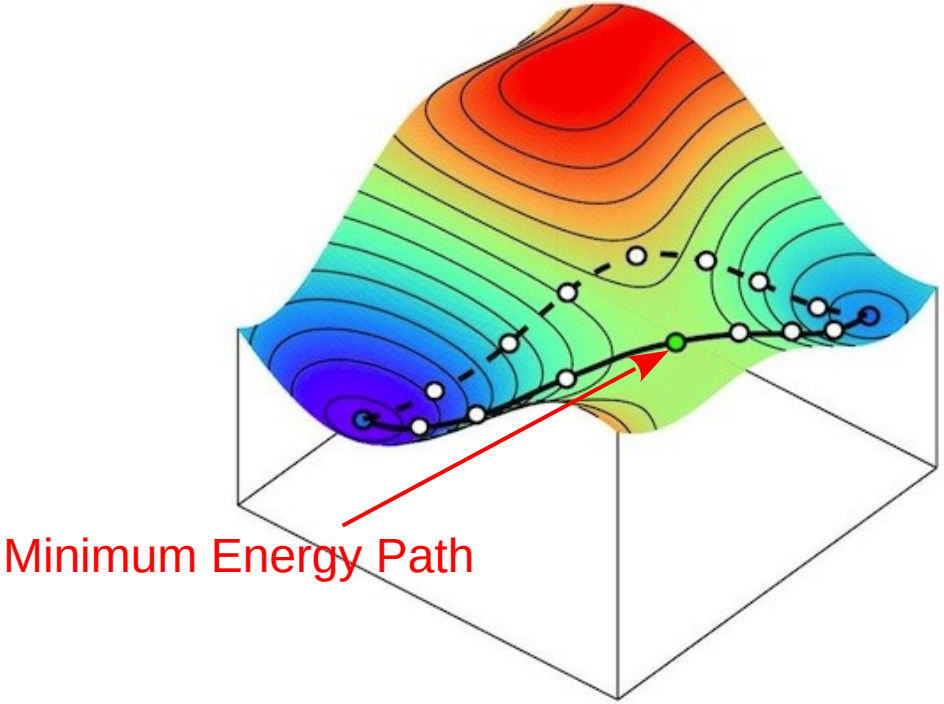
H. Jónsson,Classical and Quantum Dynamics in Condensed Phase Simulations, World Scientific (1998)

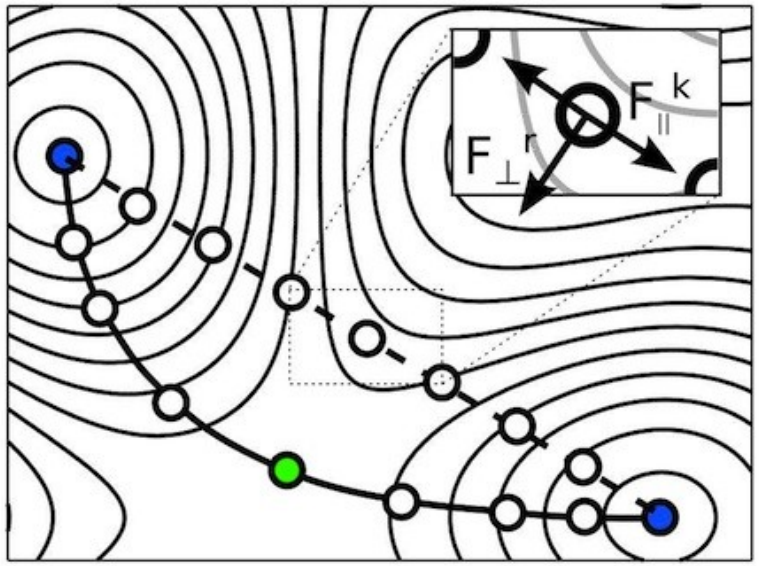
The DRAG method



- Very simple and intuitive
- Several calculations are run, usually sequentially. In those, one coordinate of one atom is constant and set to an increasing value, while all other coordinates are optimized. The chosen atom and coordinates value define the ‘core path’ of the mechanism.
- Efficient, but succeed only when the transition mechanism is ‘simple’, and easy to guess.

The Nudged Elastic Band (NEB) method

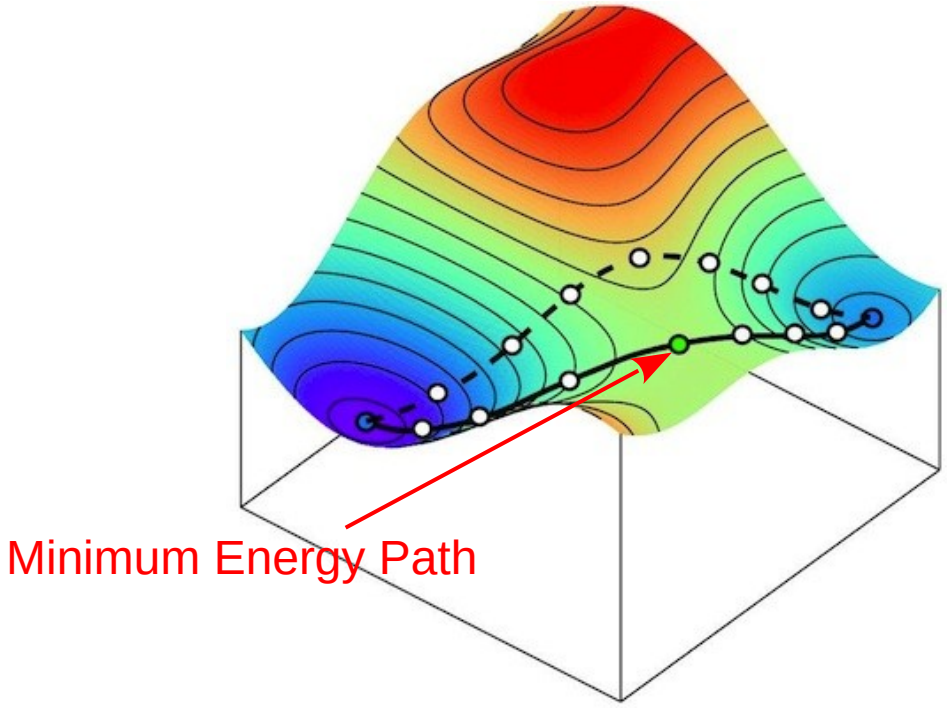


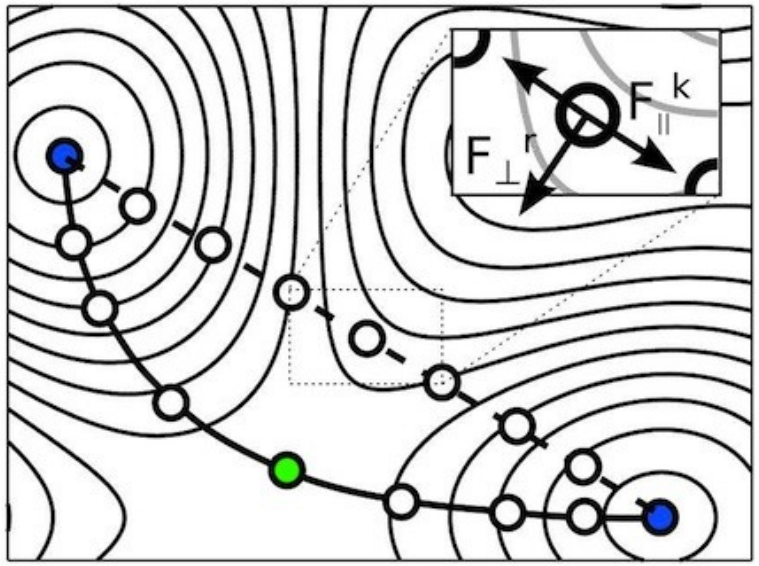


- The first-proposed chain-like method
- Several initial configurations are built, usually as a linear interpolation between starting and ending structures
- Each configuration is then relaxed at 0K, usually simultaneously
- Each configuration is bonded to neighbor configurations with springs, forming a string of configurations in configuration space

H. Jónsson,Classical and Quantum Dynamics in Condensed Phase Simulations, World Scientific (1998)

The Nudged Elastic Band (NEB) method

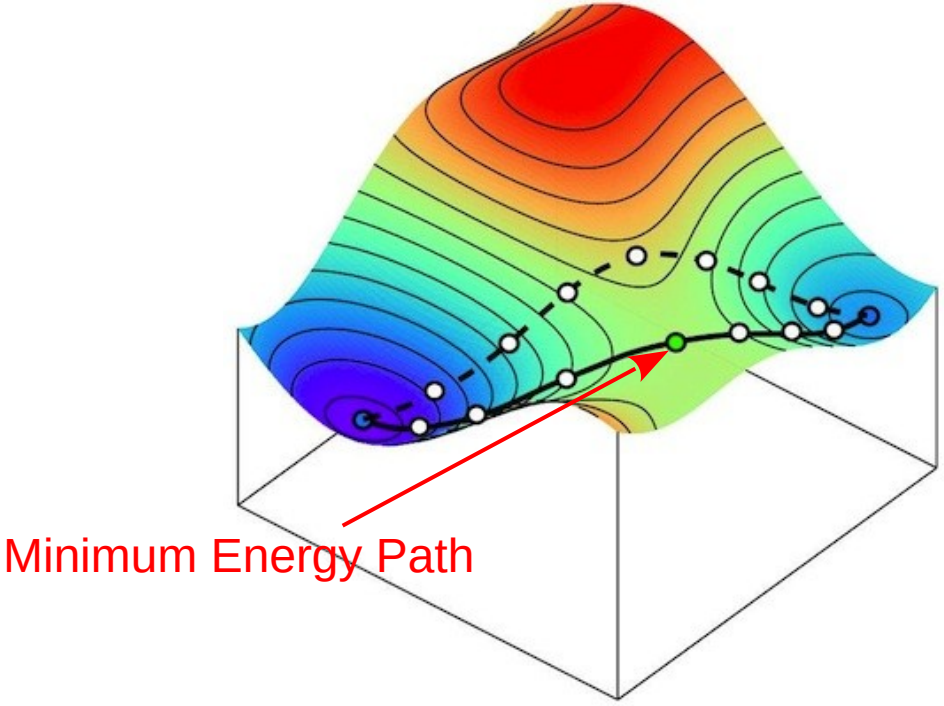


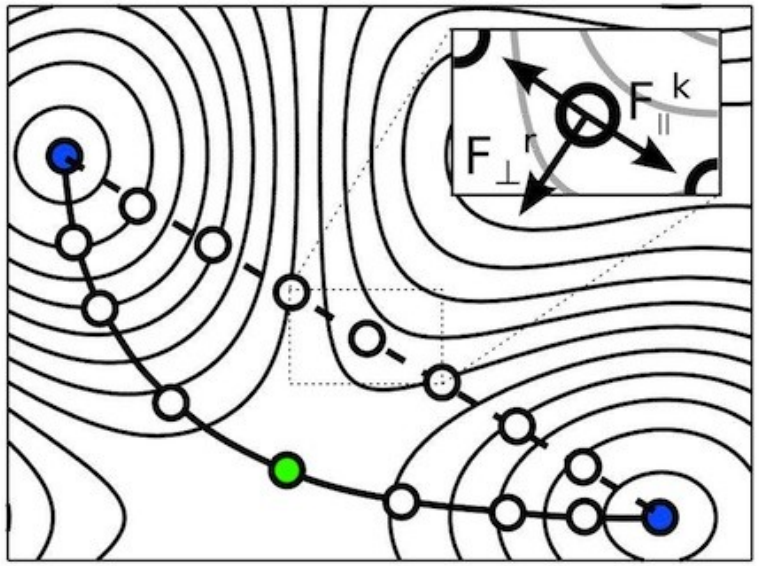


- The relaxation is done using only ‘spring’ forces, parallel to the string of configurations, and the true forces, perpendicular to the string
- The relaxation brings the chain of state close to the minimum energy path between ending points

H. Jónsson,Classical and Quantum Dynamics in Condensed Phase Simulations, World Scientific (1998)

The Nudged Elastic Band (NEB) method

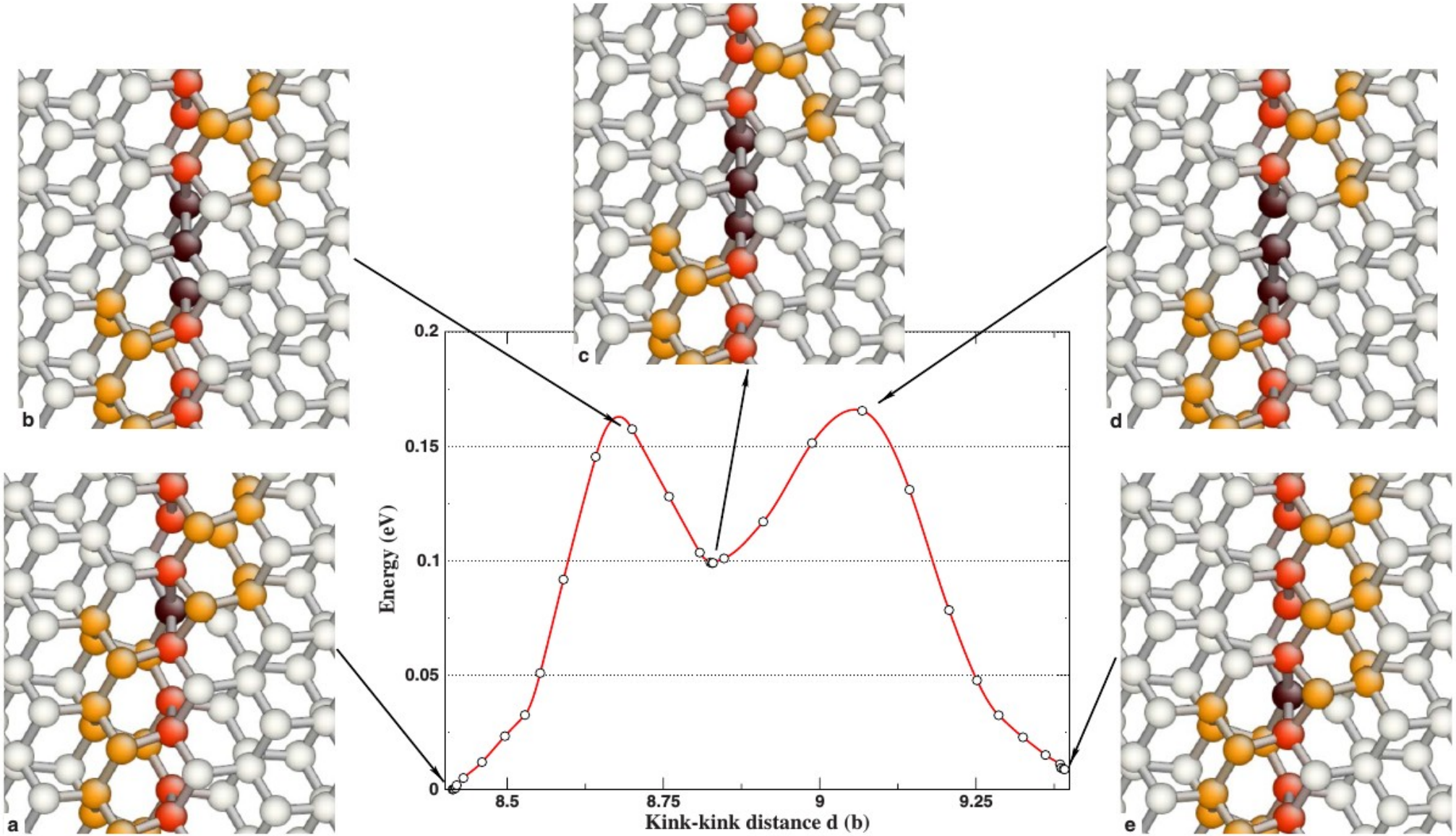




- Very robust approach, easy to increase accuracy (more replicas), and easy to implement in codes (available in many). Several refinements (climbing images,free-end...)
- The joint relaxation of many replicas can be difficult (bad scaling), and the spring constants between replicas should be carefully chosen.
- NEB is like a conjugate gradient method for minimum energy path. The relaxation brings the chain of state close to the minimum energy path between ending points. The initial guess is critical

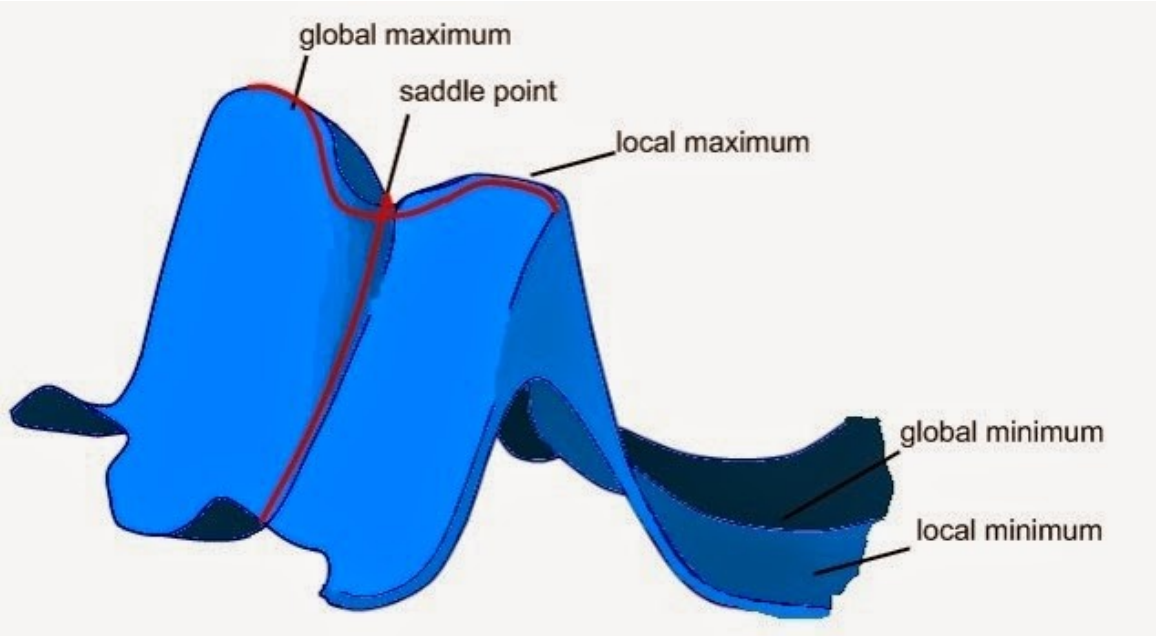
H. Jónsson,Classical and Quantum Dynamics in Condensed Phase Simulations, World Scientific (1998)

NEB: an example



Dimer, ART

- When the ending state and the mechanism are not known
  → Dimer (Jónsson), ARTn (Mousseau)
- Starting from the minimum energy configuration, an exit direction is randomly chosen
- The configuration ‘climbs’ towards the nearest saddle point. Once it is reached, a simple relaxation is done allowing to reach the minimum in the next basin.



- It is possible to perform a dynamic evolution (coupled with KMC for instance)
- More or less efficient depending on the potential energy surface (Slide prepared BEFORE the talk of Antoine Jay)
- Complicated (or counter-intuitive) mechanisms can be found with these techniques

Scales and data issues

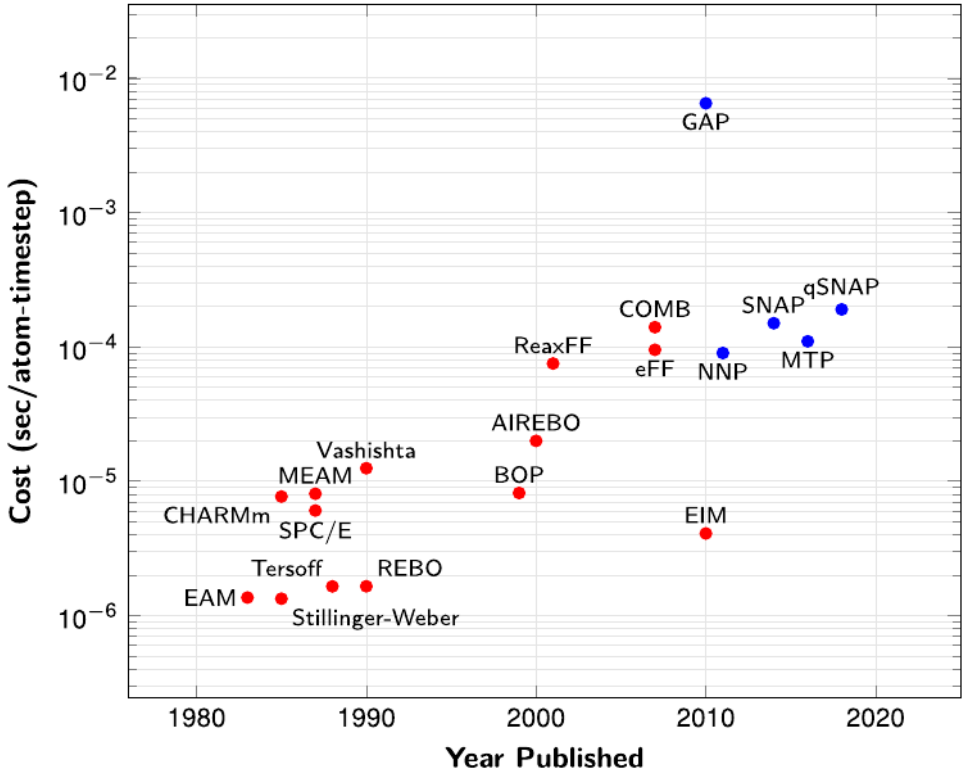
Computational cost of the simulation

The computational cost of MD is essentially due to the calculation of the interaction between particles/atoms

- Depends on the complexity of the interatomic potentials
  LAMMPS: optimized routines for certain classes of potentials, GPU-based calculations

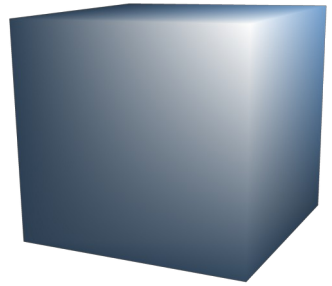
- Depends on the number of interactions to be calculated
  For short-range potentials, the use of a cutoff allows to restrict the calculation between nearest neighbors. A O(N) scaling is obtained.
  For long-range potentials (i.e. Coulombic potentials), all interactions need to be calculated, and the cost increases (and the scaling worsens)

- Charge equilibration if variable charge model (oxides). Requires an additional iterations cycle



A. P. Thomson et al. Comput. Phys. Com. (2022)

Space scale



Simulation with N atoms → dimensions ~ $\sqrt[3]{N}$ for a 3D system

Let us consider a 3D volume of about $(50\ nm)^3$, i.e. 6-9 10^6 atomes.

For a ten times larger simulations (in terms of atoms number), the system dimension are increased by only $\sqrt[3]{10}$~2.15, leading to dimensions ~ $(100\ nm)^3$, but a simulation 10 times longer (for O(N) potentials)

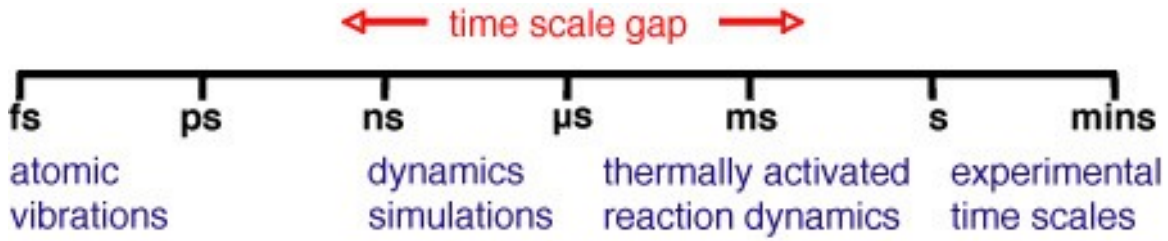
Very large simulations are restricted to short times (and vice versa)

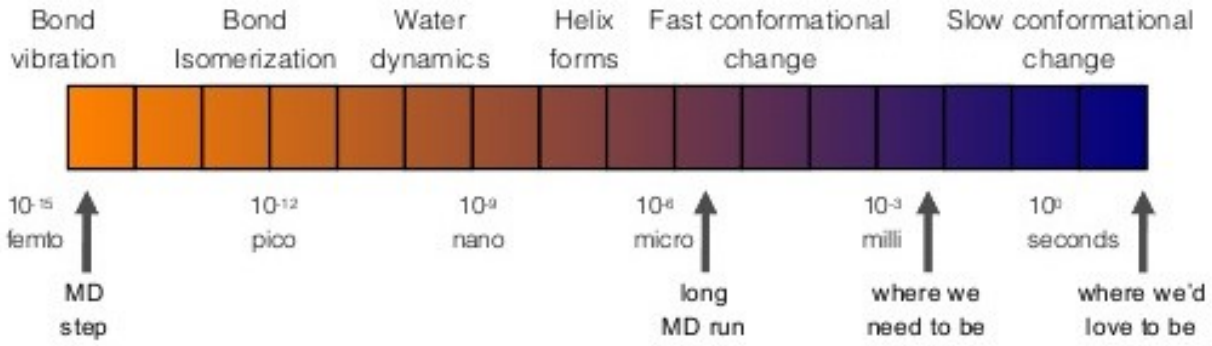
The upper threshold of MD simulations are usually restricted to several tens of nanometers (up to hundred nanometers)

Mesoscopic or macroscopic scales are out of reach

Time scale

Usual values for timestep are ~1 fs
→ one needs 10^6 iterations for a MD simulation duration of 1 ns





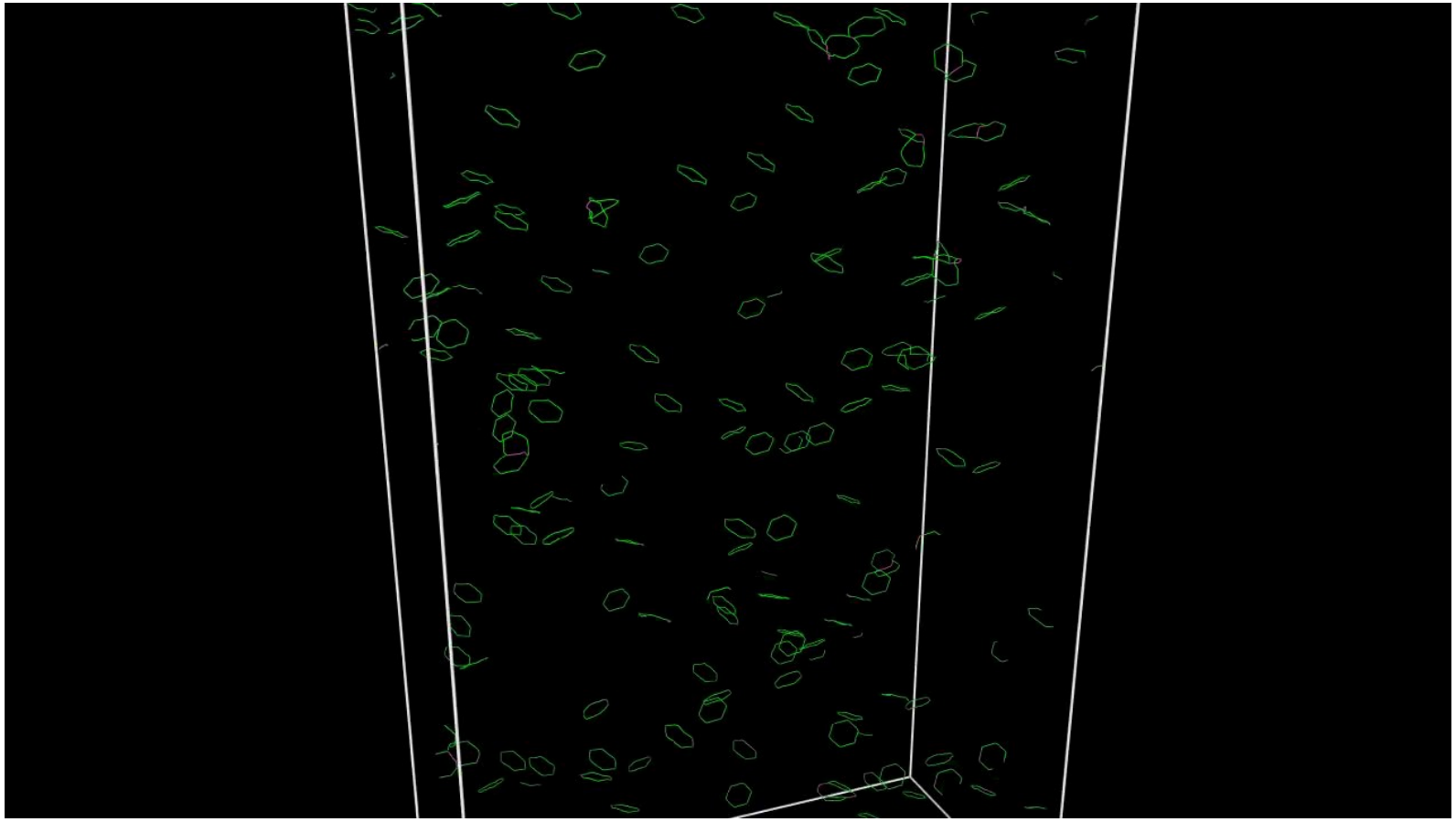
MD suited to model many physical phenomena, but their characteristic timescale is often 10^{-6}s - 1s.

In materials science, the MD time is often at best 1 ns (depending on potential), i.e. a gap of 10^3 - 10^9 !!!

It is hardly possible to model the dynamical evolution of a system over macroscopic times using MD simulations

An example of a large scale simulation

Plastic deformation of Ta
268 millions of atoms
~ 85 x 169 x 338 nm^3
EAM potential



A. Zepeda-Ruiz et al., Nature 550, 7677 (2017)

The data issue

An MD simulation……generates about 1 exabyte (=10^{18} bytes) of digital data in just one day on the full Sequoia supercomputer, an amount comparable to Google's estimated worldwide storage capacity.

V.V. Bulatov et al., Nature 2017

Example: MD simulation with 10^7 atoms, and total time of 1ns, i.e. 10^6 iterations
One image of the system (position, force, velocity, id, type) ~ 800 Mo
Saving one image for each iteration then amounts to ~ 800 To (which frequency to save images ?)

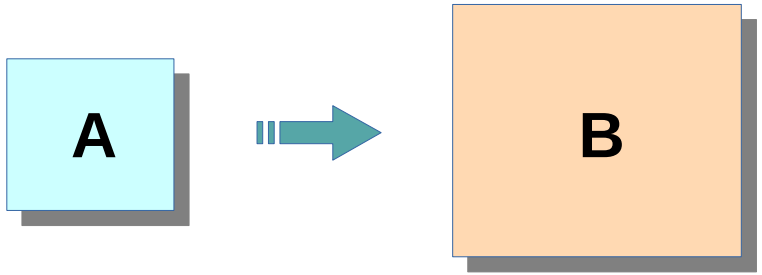
Treatment of this huge amount of data requires to make post-treatments which becomes more and more longer (and sometimes even longer than the simulation itself), and to develop specific tools to extract the meaningful information.

It is then possible to simulate larger systems, over longer times, but the price to pay is also to manage an increasing amount of data to store and analyze.

Overcoming space and time scale issues

Sequential coupling (time or space)

‘Feed’ the high scale technique (less accurate/reliable) by the low scale one (more accurate/reliable)



- Accurate calculation of a set of fundamental properties using DFT, then generation of an interatomic potential using this specific database
- MD calculation of dislocation core properties (stability, mobility, interaction mechanisms) → Discrete Dislocation Dynamics calculations → Constitutive equations in FE codes
- MD/DFT calculations of atomistic mechanisms and associated activation energies → Kinetic Monte Carlo simulations

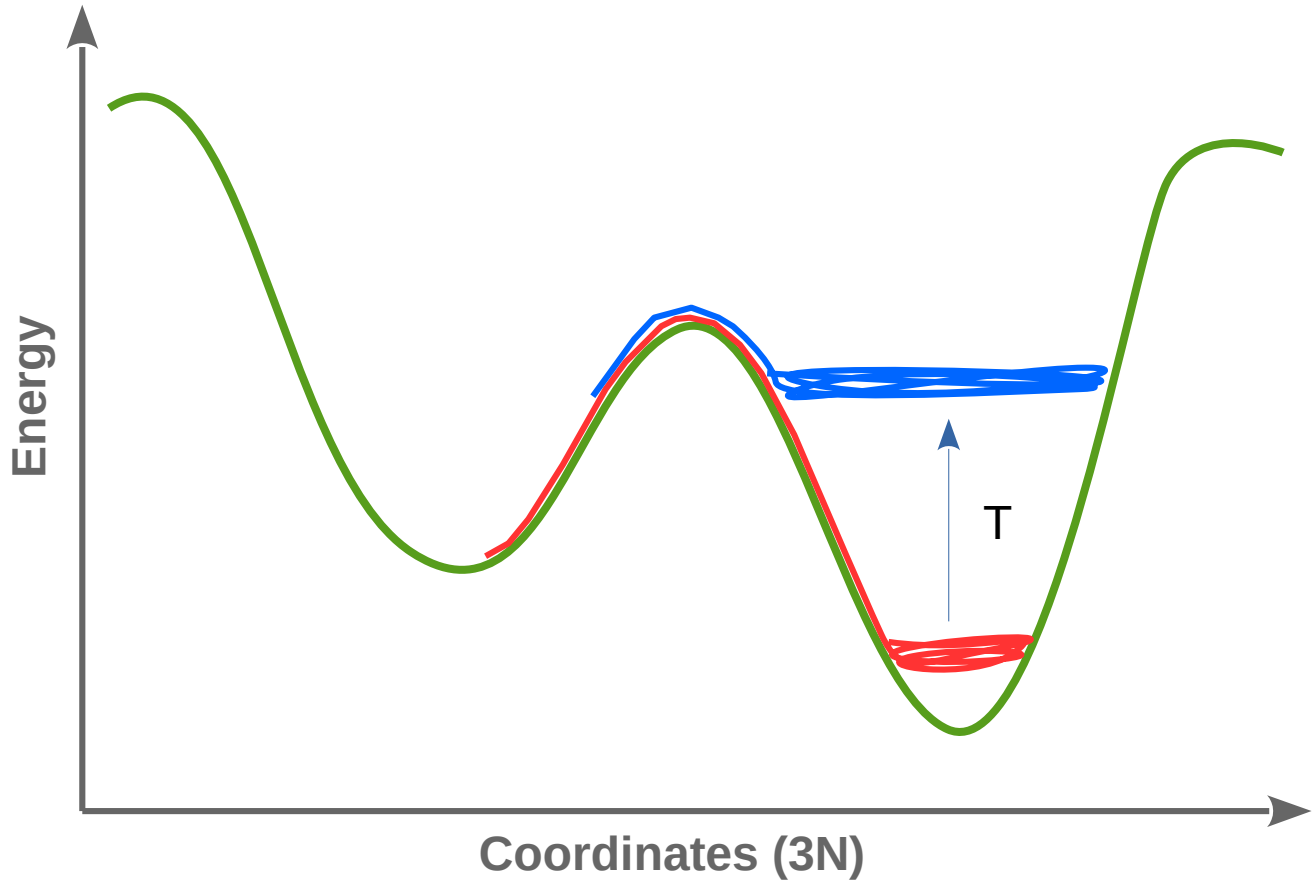
Accelerated MD techniques

- With available computational resources, one can investigate an enormous amount of possible systems (with molecular dynamics). The true issue is the time scale.
- Several approaches allowing for extending simulation time have been developed
  - Temperature Accelerated Dynamics
  - Parallel Replica Dynamics
  - Hyperdynamics
  - Metadynamics
  - Adaptative Biasing Force
  - Steered Molecular Dynamics
  - Targetted Molecular Dynamics
  - Basin hopping

And probably many others

Temperature accelerated dynamics

- Increase the temperature to get transitions during short time simulations
- ‘Artificial’ enhancement of mechanisms activation
- Not suited for materials with low melting temperature
- Assume that all possible thermally activated mechanisms scale together
- Allow to discover new transition mechanisms

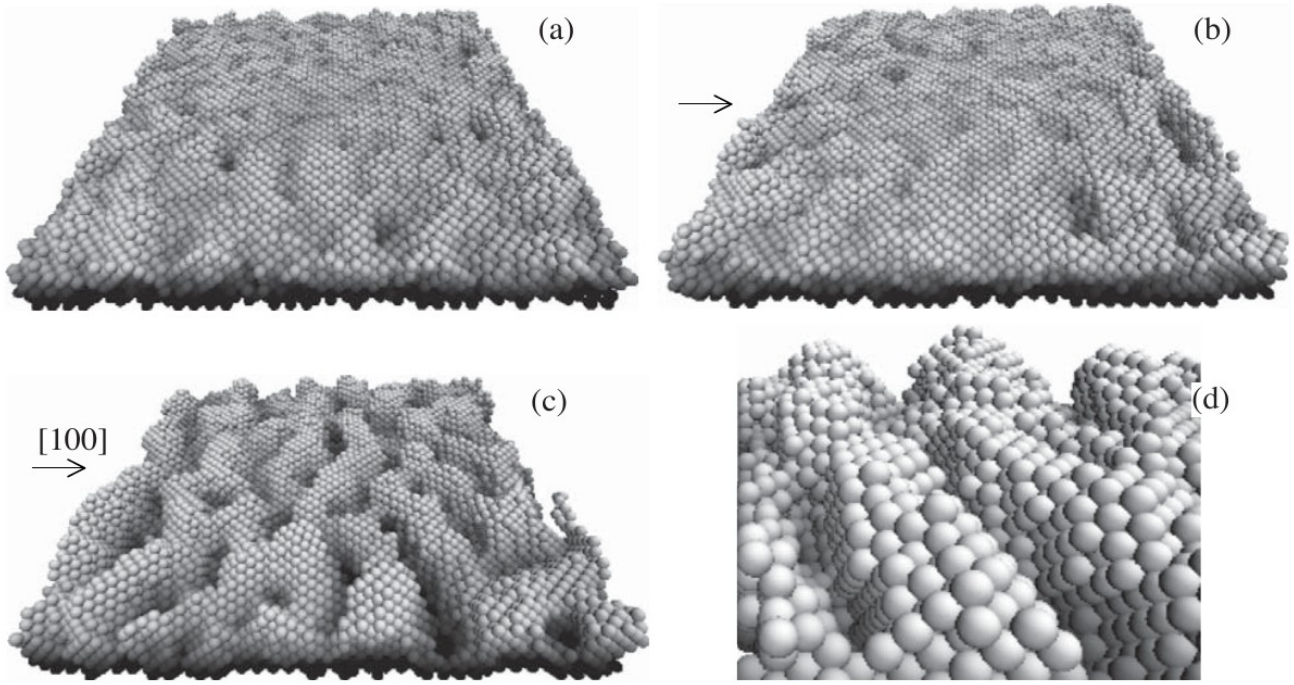


Temperature accelerated dynamics

- Spurious effects of high temperature can be corrected (Voter et al.)
- The idea is to filter events that should not occur at the target temperature

Can be used if

- System with rare events (high energies)
- Transition state theory is valid (not correlated mechanisms)
- Harmonicity
- No influence from pre-exponentional factors



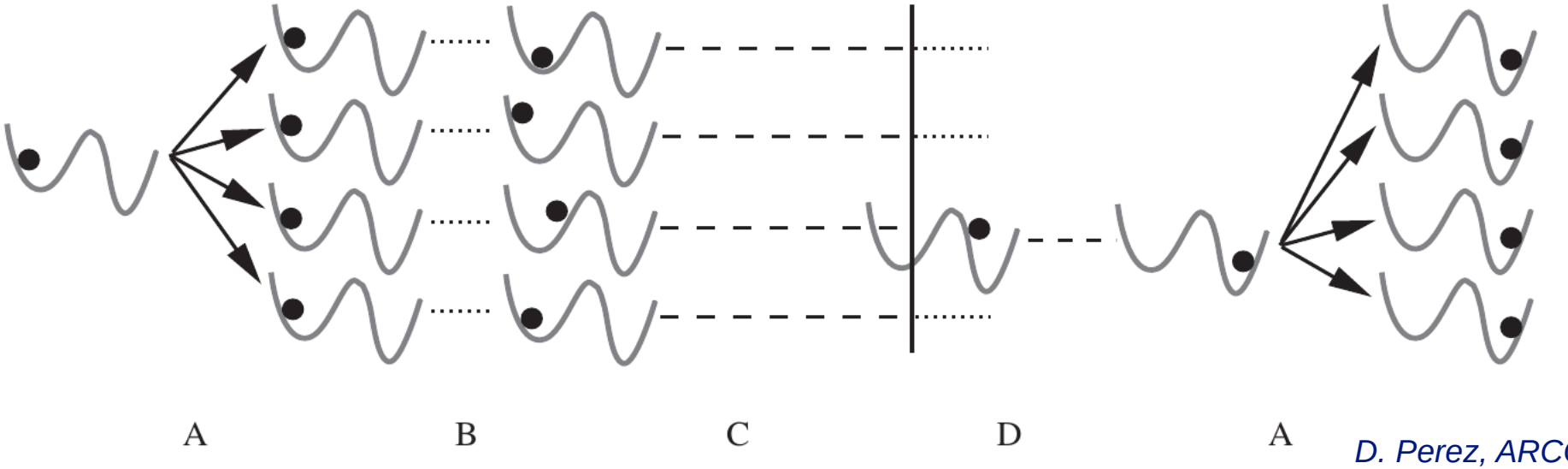
Cu/Cu(001) growth

- Exp: 1 ML/min
- MD: 10^8 ML/s
- TAD: 5×10^3 ML/s

Shim et al, PRL (2008)

Parallel Replica Dynamics

- Use the fact that modern calculators are massively parallel → temporal parallelisation



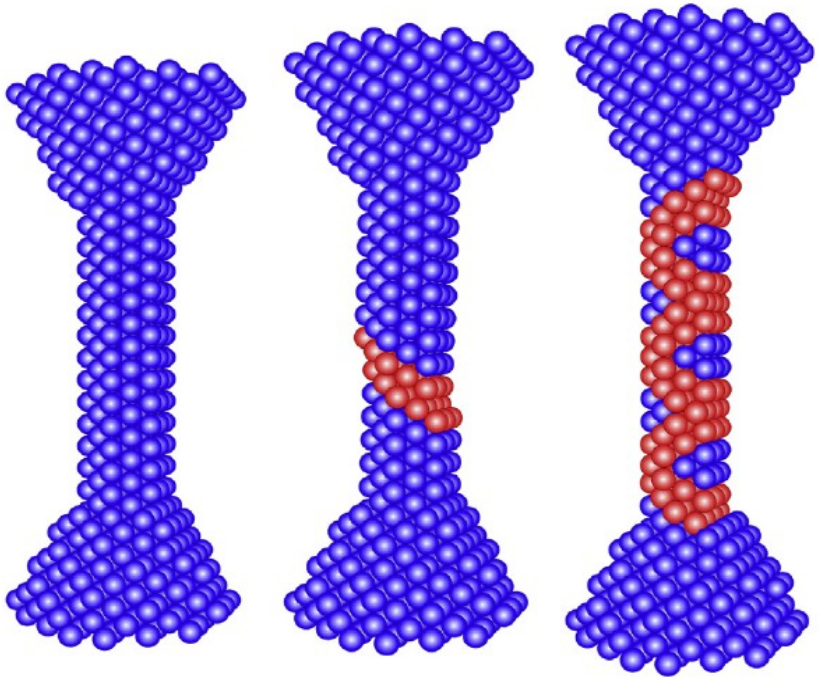
D. Perez, ARCC (2009)

- Very high time boost in many cases (depends on event frequency and CPU numbers)
- Exact dynamics (correlated events are allowed)
- Special coding is necessary to detect events, and a large number of CPU is required

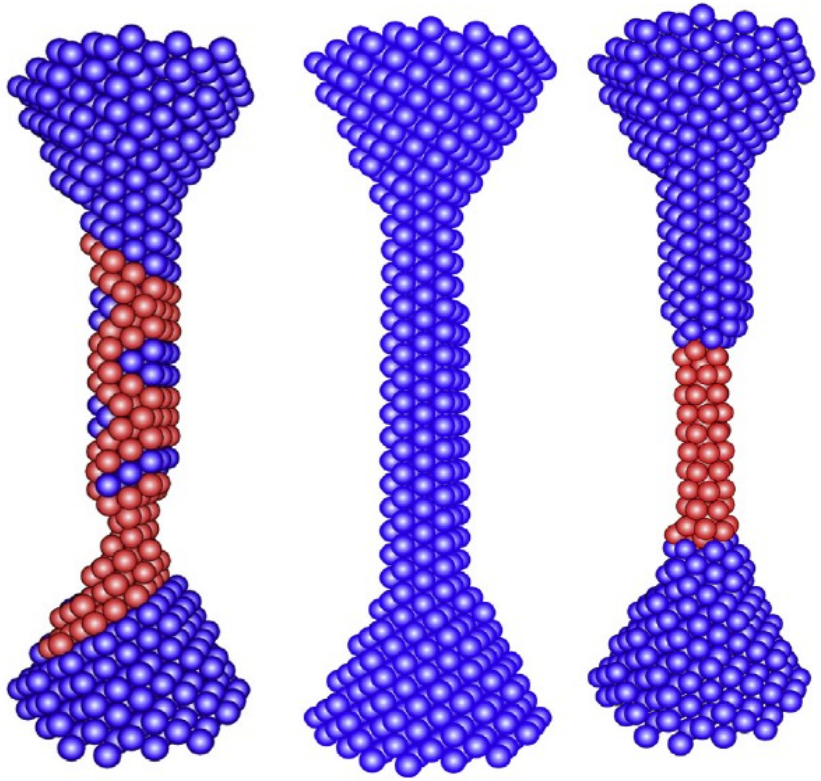
A. Voter, Phys. Rev. B (1998)

Parallel Replica Dynamics

Tensile deformation of thin Ag nanowires



Initial stages: partial dislocations, leaving multiple stacking faults



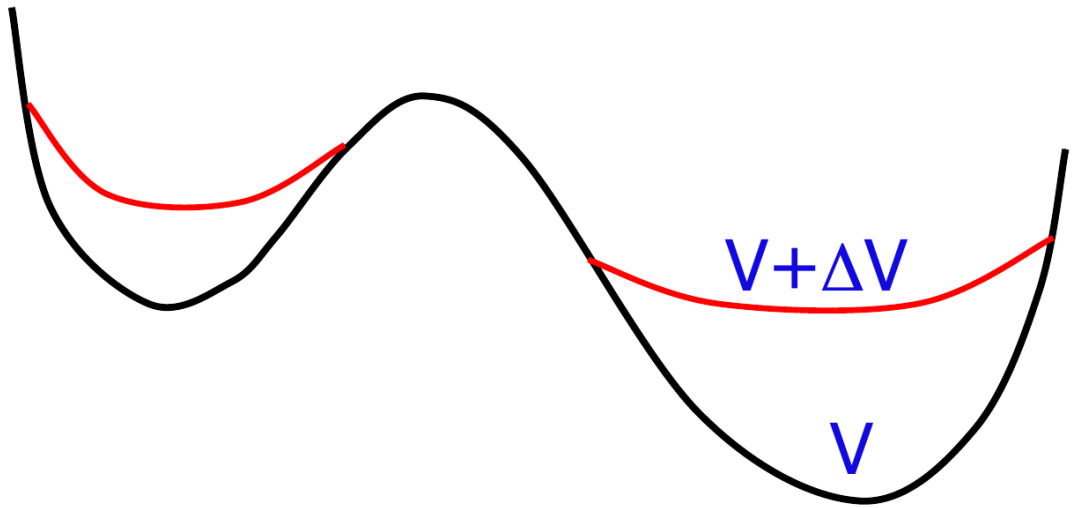
10^8 s^{-1} 10^3 s^{-1}

Necking SF healing Phase change

D. Perez et al, Comp. Mat. Sci. (2015)

Hyperdynamics

- The PES is (cleverly) modified with a bias potential, in order to increase the event rate



D. Perez, ARCC (2009)

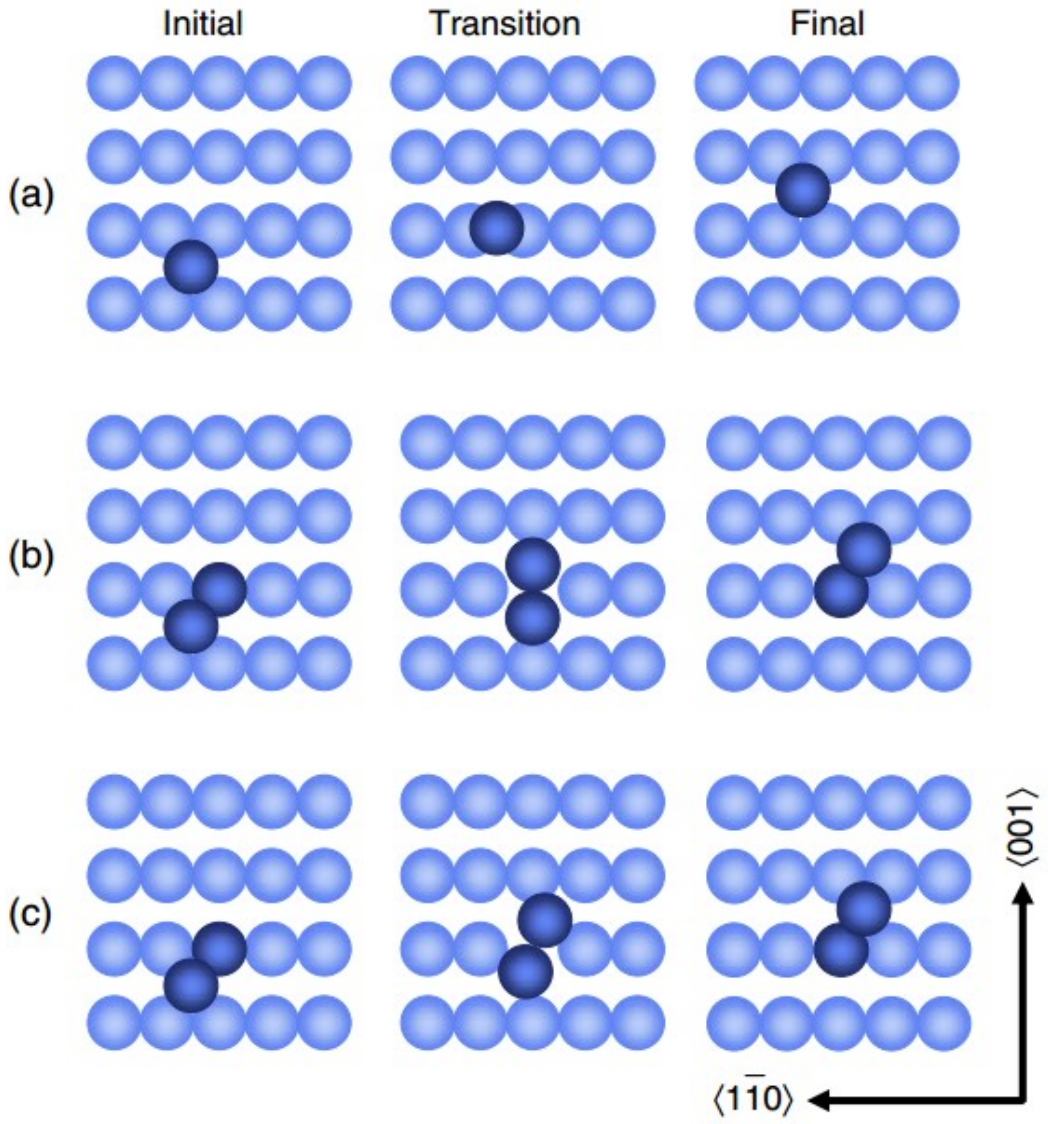
- Assume that transition state theory is valid (no correlated events)
- The main issue here is obviously how to build the bias potential (must vanish at saddle points). This is the objective of intensive investigations
- The simulation time becomes $t_{hyper} = \Delta t_{MD} \exp\left[\Delta V(R(t))/k_B T\right]$

A. Voter, J. Chem. Phys (1997)

Hyperdynamics

Diffusion of small clusters on a surface
(Here Al/Al(001))

Identification of several diffusion
mechanisms in a limited MD time

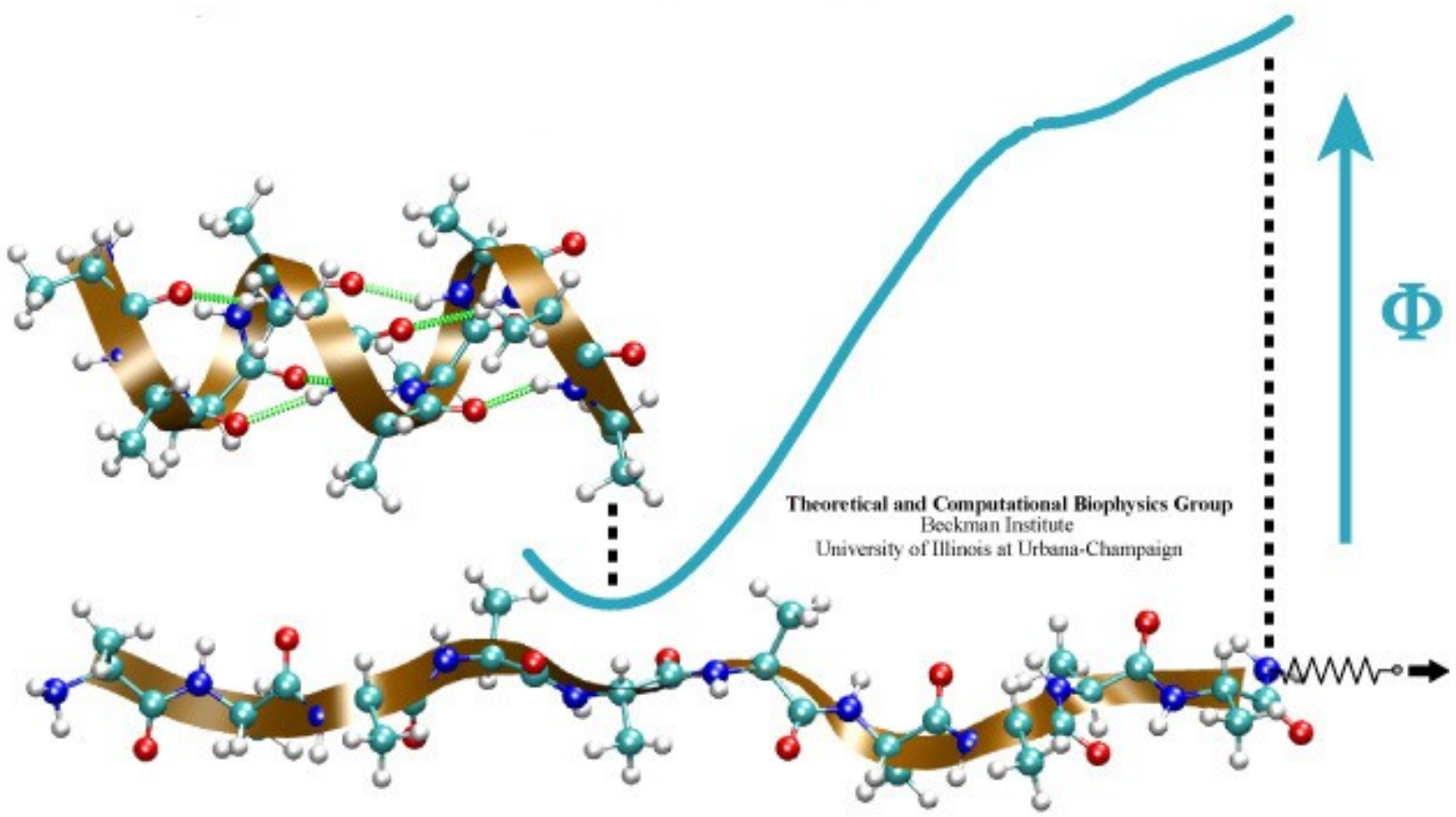


K. Fichthorn, J. Phys. Cond. Mat. (2009)

Steered and targetted molecular dynamics

- The system is forced to evolve towards a target final configuration, using specific constraints (for instance forces or velocities are applied to a group of atoms).

- Allows for searching complex, counter-intuitive, transition paths.
- The dynamic is biased
- Quantities like free energy can be estimated



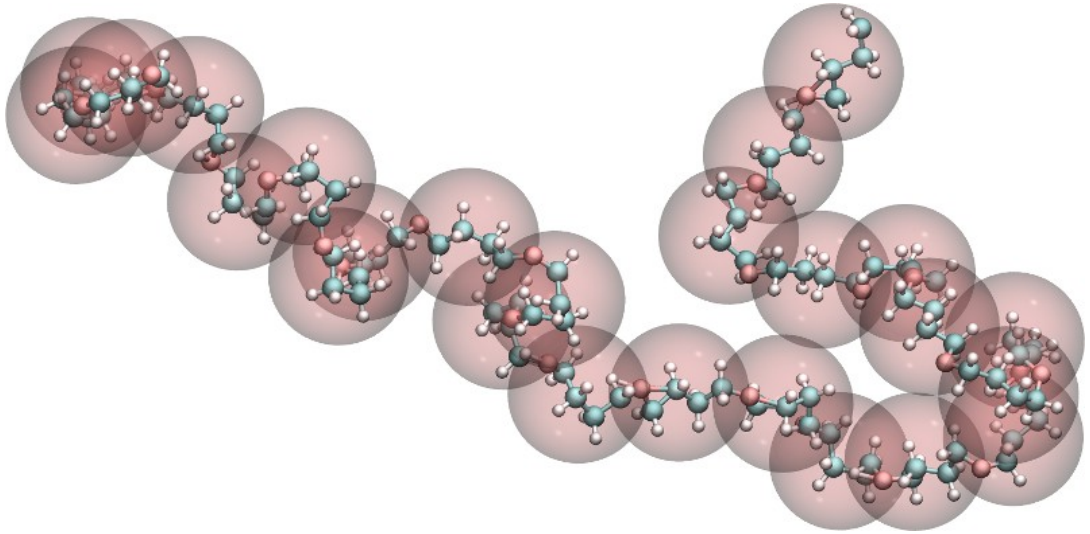
S. Park et al, J. Chem. Phys (2003), J. Chem. Phys. (2004)

Coarse grained Molecular Dynamics

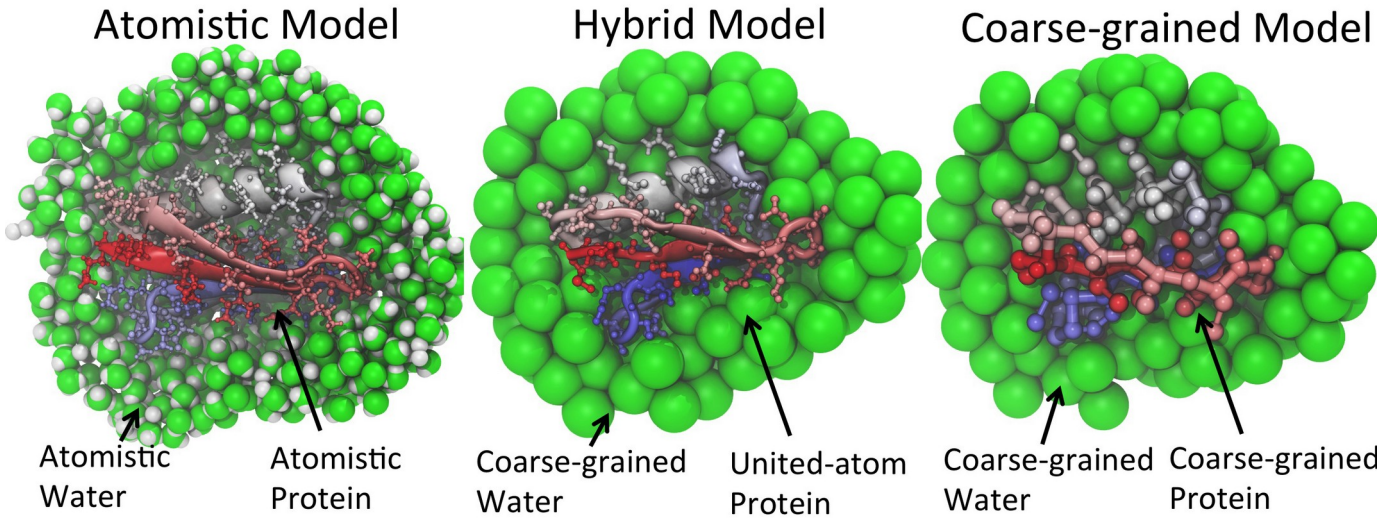
The ‘base unit’ (usually the atom) is replaced by a bigger entity (often a molecule), and a different interaction model

The internal dynamic of the new unit is ignored

Larger spacer and time scale can be reached



http://compmech.lab.asu.edu/research.php



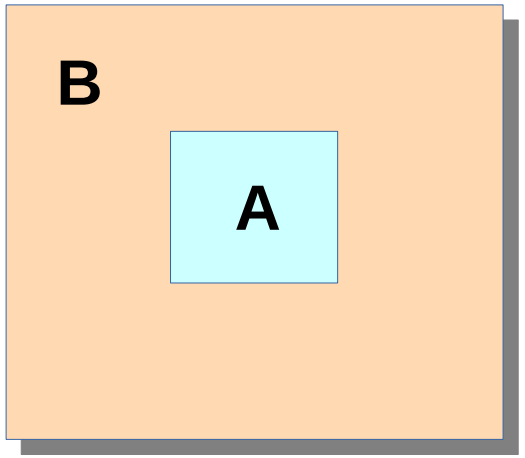
http://www.ks.uiuc.edu/Research/cgfolding/

Analogy with approachs like DDD, finite elements, pseudopotentials

Essentially used in chemistry, biochemistry, soft matter, etc...

Concurrent coupling

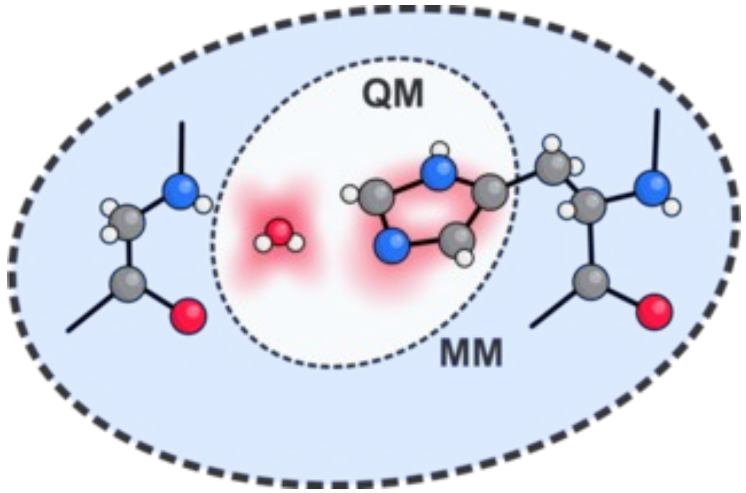
Couple the high scale technique (less accurate/reliable) with the low scale one (more accurate/reliable)



- Spatial extension of the dynamics
- Well suited for some problems (long range interactions, boundary issues, …)
- The coupling is done by alternating between the two methods, or by a concurrent dynamics

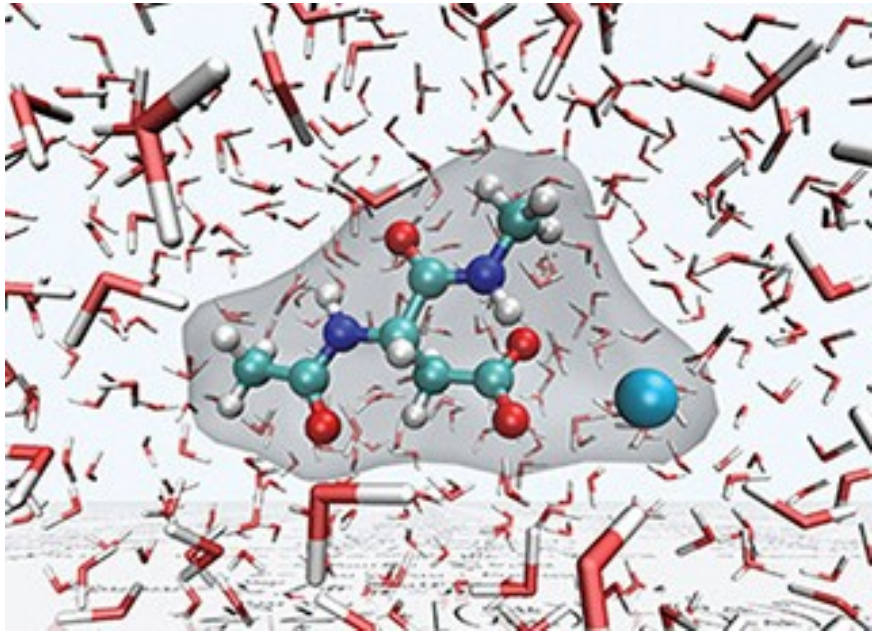
QM/MM

- Historically, QM/MM is the first approach to try spatial division (A. Warshel and M. Levitt, J. Molecular Biology (1976))



‘Active’ region: described by a QM method
‘Surrounding’ region: described by MM method

- Essentially developed and used in chemistry



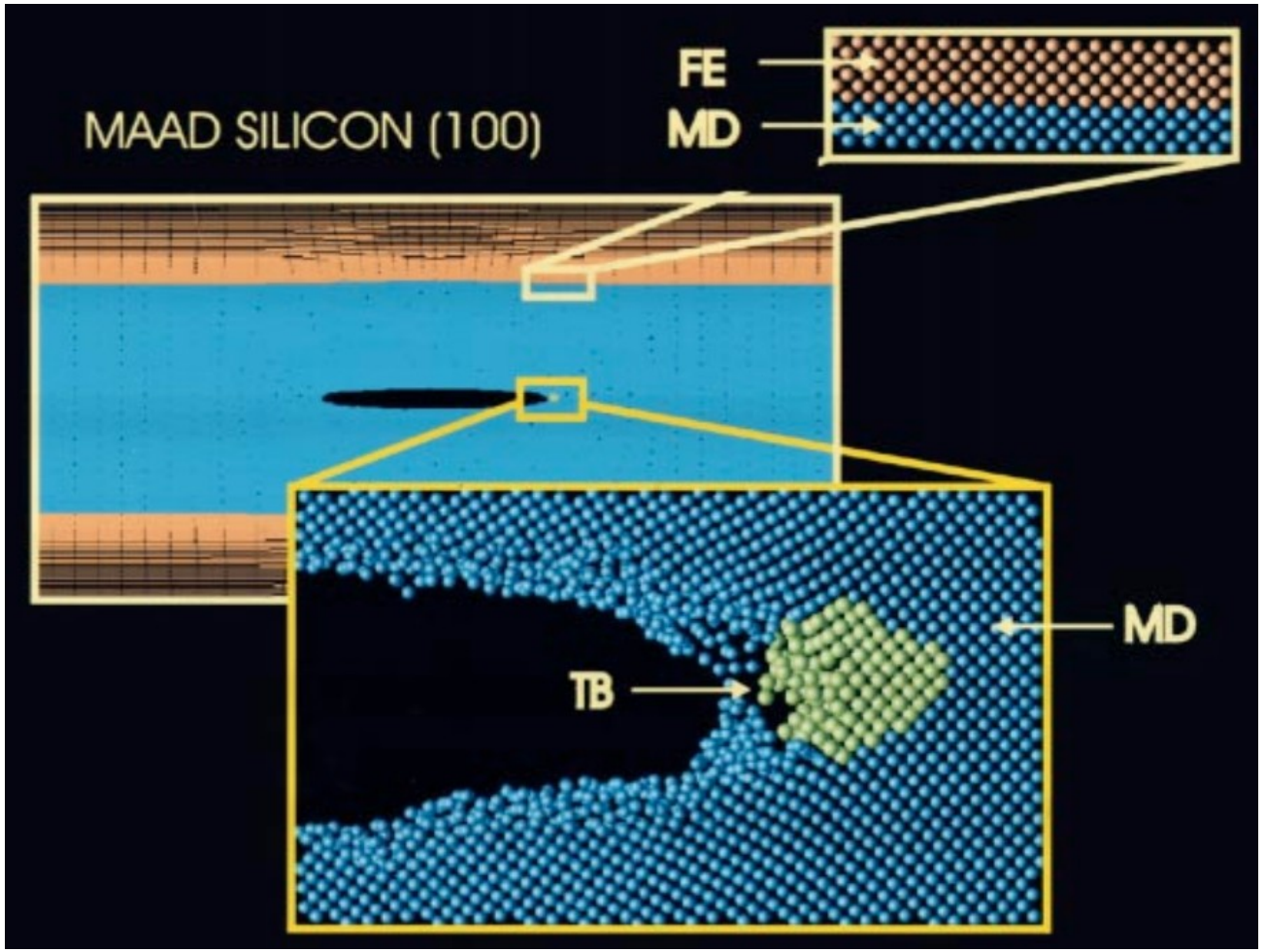
Ca ion interacting with amino-acid in water
Andreas W. Götz et al., J. Comput. Chem. (2013)

Fracture: a multiscale problem

- The inherent multiscale nature of fracture makes it a good problem for MD multiscale techniques

- Macroscopic Atomistic Ab initio Dynamics (MAAD)

- Couple finite elements – potentials – tight-binding

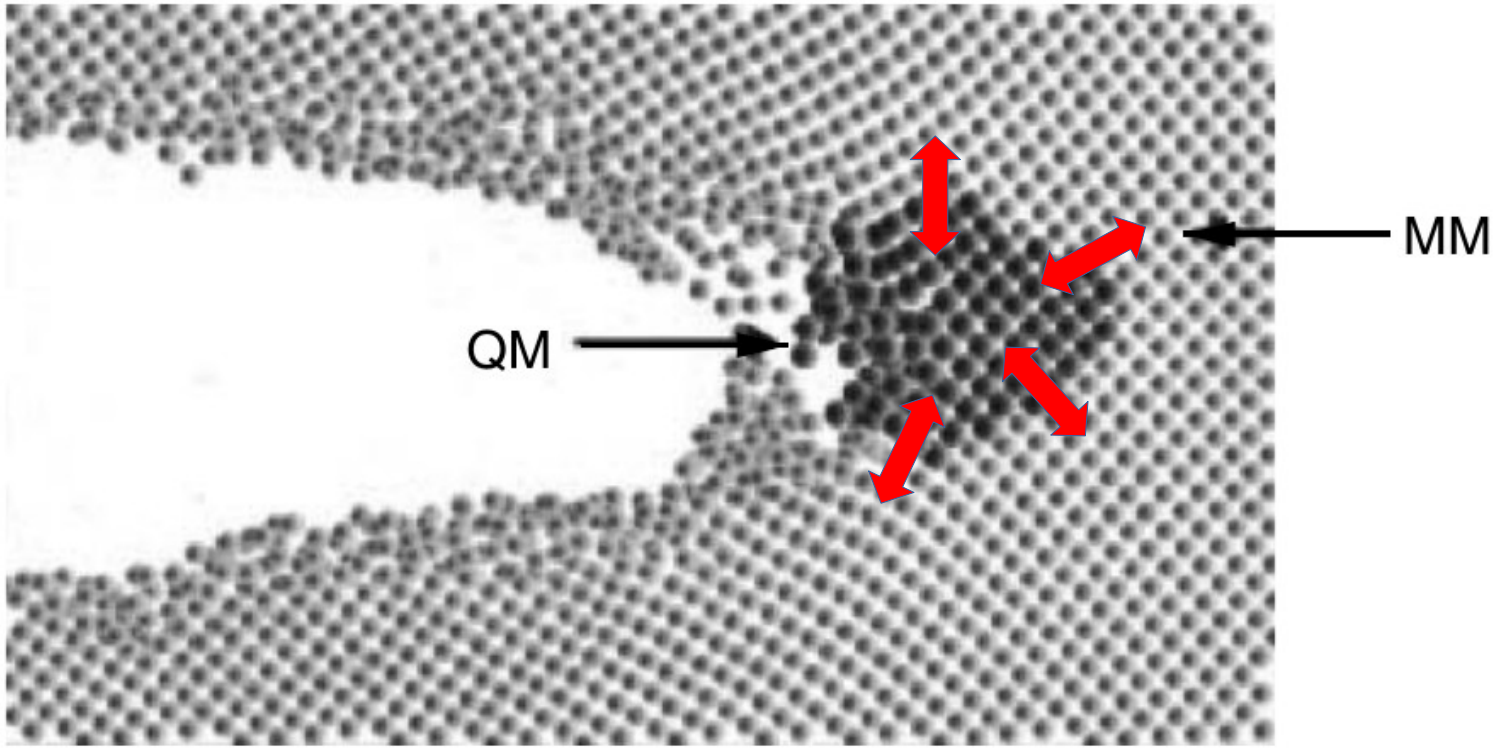


Abraham et al. EuroPhys. Lett. 1998

Fracture: a multiscale problem

- Two regions described by two different formalisms

- It is necessary to find a seamless way to couple the regions, with no artefacts, in order to simulate an homogeneous system.
- Several approaches, which will not be detailled here



N. Bernstein et al. Rep. Prog. Phys. (2009)

Resources

Available MD codes

- Several MD codes, often open source and free to use for academics, CPU/GPU parallelized, with full documentation, can be found on the net

  LAMMPS : Material sciences, https://www.lammps.org

  NAMD : Biochemistry, https://www.ks.uiuc.edu/Research/namd/

  GROMACS : Biochemistry, https://www.gromacs.org

  GULP : Materials science, https://gulp.curtin.edu.au/

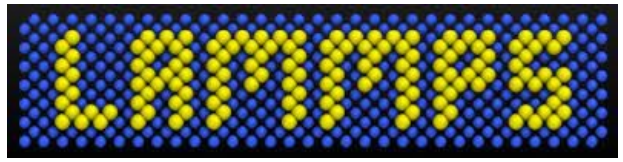
  AMBER : Biochemistry, https://ambermd.org/

  NWCHEM : Biochemistry, https://www.nwchem-sw.org/

  and also Python packages (HOOMD-blue)

- Several Python packages like ASE, mdapy, pysimm, atomman, and codes like Atomsk, can be used for setting up MD input, and analysing the output

LAMMPS



- Open source, parallellized, fast (CPU/GPU)
- Modular, user oriented, usable as a library
- Largely documented, forum for help, tutorials,…
- Focus on materials science
- Includes analysis descriptors and tools
- Options to investigate problems in many domains:
  - Thermal, vibrational, mechanical properties
  - Growth, transport
  - Irradiation, catalysis, phase transition
  - etc….

A. P. Thomson et al. Comput. Phys. Com. (2022)

Books and papers

Computational Physics, J.M. Thijssen, Cambridge University Press 1999

Computer Simulation of liquids, MP Allen and DJ Tildesley, Oxford University Press 1987

Computer Simulation in Materials Science, Interatomic potentials, simulation Techniques and Applications, Ed. M. Meyer and V. Pontikis, NATO ASI series vol 205 Kluwer Academic Publishers 1991

Molecular Dynamics Simulation: Elementary Methods, J.M. Haile, Wiley 1997

Molecular Modelling: Principles and Applications, A.R. Leach, Pearson 2001

Molecular Modeling and Simulation, T. Schlick, Springer, 2002

Understanding Modern Molecular Dynamics, M. E. Tuckerman and G. J. Martyna, J. Phys. Chem. B 2000, 104, 159-178

Dynamique moléculaire appliquée aux matériaux, C. Becquart and M. Perez, Techniques de l'ingénieur, 2010

Thank you for listening