

Introduction to Molecular Dynamics

Numerical Simulation and Scientific Computing II

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Lecture 5



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Prelude: A refresher on Newtonian mechanics

Newtonian mechanics of a single particle

Entity: Structureless, point-like particle with fixed mass m

Goal: Obtain a trajectory $\mathbf{x}(t)$

Inputs: Forces and initial conditions

Newton's 2nd law:

$$m \frac{d^2\mathbf{x}}{dt^2} = \mathbf{f}$$

Some vector quantities:

Force: \mathbf{f}

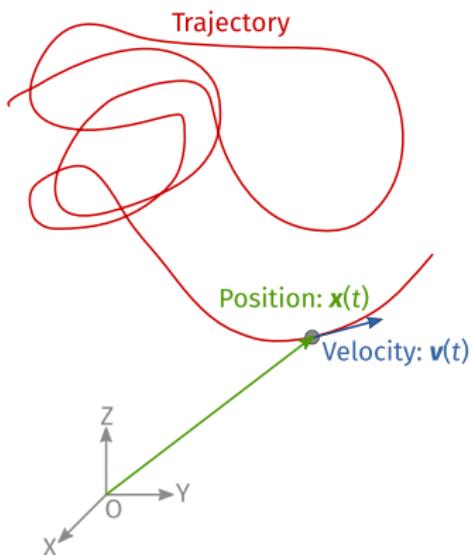
Position: \mathbf{x}

Velocity: $\mathbf{v} = \frac{d\mathbf{x}}{dt}$

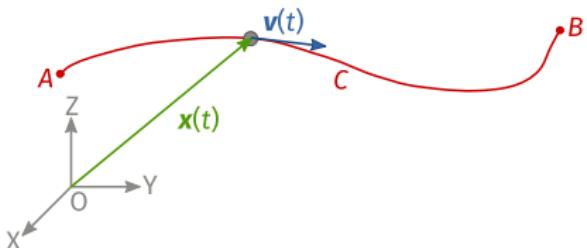
Acceleration: $\mathbf{a} = \frac{d\mathbf{v}}{dt} = \frac{d^2\mathbf{x}}{dt^2}$

Linear momentum: $\mathbf{p} = m\mathbf{v}$

Angular momentum: $\mathbf{l} = \mathbf{x} \times \mathbf{p}$



Work and kinetic energy



The **work** performed by the force \mathbf{f} on the particle as it moves along a trajectory described by the curve C from A to B is defined as the line integral:

$$W_{A \rightarrow B}[C] = \int_C \mathbf{f} \cdot d\mathbf{x}$$

Using the parametrization $\mathbf{x}(t)$ for C :

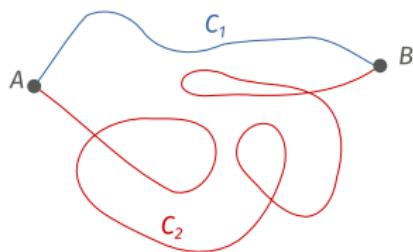
$$W_{A \rightarrow B}[C] = \int_{t_A}^{t_B} \mathbf{f} \cdot \frac{d\mathbf{x}}{dt} dt = m \int_{t_A}^{t_B} \frac{d\mathbf{v}}{dt} \cdot \mathbf{v} dt = \int_{t_A}^{t_B} \frac{d}{dt} \left(\frac{1}{2} m |\mathbf{v}|^2 \right) dt$$

The work is equal to the variation of the **kinetic energy**

$$E_{\text{kin}} = \frac{1}{2} m |\mathbf{v}|^2$$
 along the trajectory.

Conservative force fields and potential energy

- **Force field:** Function $\mathbf{f} : V \subset \mathbb{R}^3 \rightarrow \mathbb{R}^3$ assigning a force to each possible position in a subset V of space.
- \mathbf{f} is **conservative** if V is simply connected and $\oint_C \mathbf{f} \cdot d\mathbf{x} = 0$ for any closed trajectory C in V .



- For any conservative force field,
$$\oint_{C_1 \cup C_2} \mathbf{f} \cdot d\mathbf{x} = 0 = W_{A \rightarrow B}[C_2] + W_{B \rightarrow A}[C_1]$$
- Therefore, $W_{A \rightarrow B}[C]$ is the same for any trajectory C joining A and B

If we choose a point P as the **origin of energies**,

$$E_{\text{pot}}(\mathbf{x}) = -W_{P \rightarrow \mathbf{x}}$$

is a function of \mathbf{x} called the **potential energy**.

Extracting (conservative) forces from the potential energy

Let us consider one of the directional derivatives of $E_{\text{pot}}(\mathbf{x})$ at \mathbf{x}_0 :

$$\left(\frac{\partial E_{\text{pot}}}{\partial y} \right)_{\mathbf{x}_0} = \lim_{\Delta y \rightarrow 0} \frac{-W_{P \rightarrow \mathbf{x}_0 + \hat{\mathbf{y}}\Delta y} + W_{P \rightarrow \mathbf{x}_0}}{\Delta y} = \lim_{\Delta y \rightarrow 0} -\frac{W_{\mathbf{x}_0 \rightarrow \mathbf{x}_0 + \hat{\mathbf{y}}\Delta y}}{\Delta y}$$

Work is independent from the path \Rightarrow we choose a straight segment in a natural parametrization: $\mathbf{x}(s) = \mathbf{x}_0 + \hat{\mathbf{y}}s, s \in [0, \Delta y]$

$$\left(\frac{\partial E_{\text{pot}}}{\partial y} \right)_{\mathbf{x}_0} = \lim_{\Delta y \rightarrow 0} -\frac{1}{\Delta y} \int_0^{\Delta y} \mathbf{f} \cdot \hat{\mathbf{y}} \, ds = -f_y$$

Valid for all coordinates \Rightarrow The force at a point is equal the gradient of the potential energy at that point with its sign reversed

$$\boxed{\mathbf{f} = -\nabla E_{\text{pot}}}$$

The conservation of mechanical energy

Two expressions for the work performed between A and B :

- $W_{A \rightarrow B} = \Delta_{A \rightarrow B} E_{\text{kin}}$

- $W_{A \rightarrow B} = -\Delta_{A \rightarrow B} E_{\text{pot}}$ (conservative forces only!)

$$\Rightarrow \Delta_{A \rightarrow B}(E_{\text{kin}} + E_{\text{pot}}) = 0.$$

The total **mechanical energy**

$$E = E_{\text{kin}} + E_{\text{pot}}$$

is conserved.

Conservation of linear and angular momentum

Conservation of linear momentum: when $\mathbf{f} = 0$, then

$$\frac{d\mathbf{p}}{dt} = 0 \implies \mathbf{p} \text{ is conserved}$$

Conservation of angular momentum: when the torque $\mathbf{x} \times \mathbf{f}$ is zero, then

$$\frac{d\mathbf{l}}{dt} = 0 \implies \mathbf{l} \text{ is conserved}$$

Important example: conservative central forces, where $E_{\text{pot}}(\mathbf{x})$ only depends on $|\mathbf{x}| \implies \mathbf{f} = -\nabla E_{\text{pot}}$ is parallel to \mathbf{x} .

Newtonian mechanics of a system of M point particles

Same quantities, defined particle by particle

- Masses $\{m_L\}_{L=1}^M$
- Positions $\{\boldsymbol{x}_L\}_{L=1}^M$
- Velocities $\{\boldsymbol{v}_L\}_{L=1}^M$, with $\boldsymbol{v}_L = \frac{d\boldsymbol{x}_L}{dt}$
- Accelerations, forces, linear momenta, angular momenta, etc.

Newton's 2nd law:

$$m_L \frac{d^2 \boldsymbol{x}_L}{dt^2} = \boldsymbol{f}_L, \quad L \in \{1 \dots M\}$$

Mechanical energy for M particles

Work: $W_{A \rightarrow B}[C] = \int_C \mathbf{f} \cdot d^{3M}\mathbf{l}$, where \mathbf{f} includes the $3M$ components of the forces on all particles.

- Kinetic energy: $E_{\text{kin}} = \sum_{L=1}^M \frac{1}{2} m_L |\mathbf{v}_L|^2$
- Potential energy (only for conservative forces!): $E_{\text{pot}} = -W_{P \rightarrow \mathbf{x}}$, where \mathbf{x} contains all positions \Rightarrow not a sum over particles

If a potential energy can be defined, $\mathbf{f}_L = -\nabla_{\mathbf{x}_L} E_{\text{pot}}$ for each particle.

Conservation laws for M particles

Conservation of energy: For conservative forces, the total mechanical energy $E_{\text{kin}} + E_{\text{pot}}$ is conserved.

Conservation of linear momentum: if the net force on the system $\sum_L \mathbf{f}_L$ is zero, the total linear momentum $\sum_L \mathbf{p}_L$ is conserved.

Conservation of angular momentum: if the net torque $\sum_L \mathbf{x}_L \times \mathbf{f}_L$ is zero, the total angular momentum $\sum_L \mathbf{x}_L \times \mathbf{p}_L$ is conserved.

In more advanced formulations of mechanics, these conservation laws emerge directly from the fundamental symmetries of free space: translation symmetry (\mathbf{p}), rotation symmetry (\mathbf{l}) and time translation invariance (E).

For a more in-depth refresher

- H. Goldstein, C. P. Poole & J. L. Safko, *Classical Mechanics*, 3rd edition, Wesley (2002). ISBN: 0201657023
- T. T. Thornton & J. B. Marion, *Classical Dynamics of Systems and Particles*, 5th edition, Brooks/Cole (2004). ISBN: 0534408966

Introduction

Molecular dynamics (MD)

Narrow definition:

- Family of atomistic simulation methods
- State of “atoms” described by:
 1. Positions $\{\boldsymbol{x}_L\}_{L=1}^M$
 2. Velocities $\{\boldsymbol{v}_L = \frac{d\boldsymbol{x}_L}{dt}\}_{L=1}^M$
 3. Internal variables (e.g. electric dipole moment)
- Numerical integration of Newton’s equations of motion for conservative forces:
$$m_L \frac{d^2 \boldsymbol{x}_L}{dt^2} = -\nabla_{\boldsymbol{x}_L} E_{\text{pot}} \Leftrightarrow m_L \frac{d^2 x_L^{(\alpha)}}{dt^2} = -\frac{\partial E_{\text{pot}}}{\partial x_L^{(\alpha)}} \text{ where } \alpha \in \{x, y, z\}$$
- Result: trajectories in phase space $\{\boldsymbol{x}_L(t), \boldsymbol{v}_L(t)\}_{L=1}^M$

Wait a minute...

Isn't classical mechanics **wrong**?

- Wronger than some things, less wrong than others [I. Asimov, *The Relativity of Wrong*, Doubleday (1988). ISBN: 0385244738]
- Better question: Can it be applied here?

The challenges:

- Relativistic effects:**
- Weak as long as $|v_L| \ll c$ and no intense gravitational fields involved
 - (Mostly) not very relevant for our simulations

- Quantum mechanics:**
- Fundamental physics of electrons
 - Totally necessary at the atomistic level
 - Effects survive in the macroscale: indistinguishability, quantization...
 - Underpins all of materials science

Is MD even worth discussing?

The ~~\$\\$~~ honest answer

A proper quantum-mechanical treatment of large system is unfeasible.
Even for a stationary solution:

"Quantum-chemical" (wave-function-based) methods:

- Exponential barrier (curse of dimensionality)
- \lesssim Hundreds of electrons

Density functional theory:

- Overcomes the exponential barrier
- Still \lesssim thousands of atoms

Time-dependent quantum methods are even more constrained

\Rightarrow Until conceptual and algorithmic revolutions,
MD is here to stay.

Some support from quantum mechanics

Born-Oppenheimer approximation:

- The dynamics of electrons and nuclei can be decoupled (conditions apply)
- Fix the nuclei, solve for the electrons, get effective potential energy

Ehrenfest theorem:

$$\frac{d\langle \mathbf{p}_L \rangle}{dt} = -\nabla_{\mathbf{x}_L} E_0$$

⇒ Newton's 2nd law holds in an average sense and a potential energy for the atomic nuclei can be defined.

Ab-initio (Born-Oppenheimer) molecular dynamics

Recipe to generate a trajectory:

Initialization

1. Fix a set of positions $\{\mathbf{x}_L\}$ for nuclei

Main loop

1. Obtain the electronic ground state energy $E_0(\{\mathbf{x}_L\})$
2. Use E_0 an effective potential energy for the nuclei
3. Compute its derivatives (forces)
4. Integrate equations of motion
5. Update coordinates and velocities

Extremely useful, but

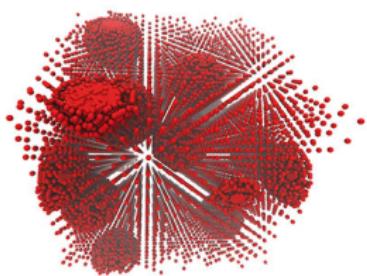
- Limited by the quantum solver step
- Cannot reproduce quantum effects on the nuclei

Classical molecular dynamics

Orientative limits of ab-initio molecular dynamics:

- Hundreds of atoms
- Some picoseconds

Classical molecular dynamics is based on a parametrization of the potential energy, abstracting away the electrons.



Reference: M. Bernreuther *et al.*,
*Innovative HPC Methods and Application
to Highly Scalable Molecular Simulation
(IMEMO)*, Inside 10 (2012) 50:

- Simulation of nucleation
- 4.13×10^{12} particles

Classical MD simulations with $10^5 - 10^6$ particles are within everyone's reach.

The ingredients of MD

The ingredients

At least four elements are necessary for an MD study:

1. A way to construct $E_{\text{pot}}(\boldsymbol{x}_L)$ (a **potential**)
2. An integration scheme
3. Boundary conditions (in a general sense)
4. A method to extract information from the trajectory

Wish list for a numerical integrator

Indispensable compatibility with classical mechanics:

- Time-reversible
- Symplectic (preserves phase-space volumes)
- Energy- and momentum-conserving

Desirable properties:

- Stable (no exponential deviation from actual solution)
- Fast
- No high-order derivatives or additional evaluations
(E_{pot} expensive, > 85% of simulation time)

Good to have:

- Accurate
- Compact in terms of memory

A first attempt

Taylor expansion based on the available information at time t : Is

The Euler integrator

$$\boldsymbol{x}(t + \Delta t) = \boldsymbol{x}(t) + \boldsymbol{v}(t)\Delta t + \frac{1}{2}\boldsymbol{a}(t)(\Delta t)^2$$

$$\boldsymbol{v}(t + \Delta t) = \boldsymbol{v}(t) + \boldsymbol{a}(t)\Delta t$$

See results in [Elliptical orbit.ipynb](#)

The velocity Verlet integrator

With just a small change:

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

See results in [Elliptical_orbit.ipynb](#)

Questionable error analysis

The velocity Verlet algorithm has a more favorable truncation error:

Taylor:

$$\begin{aligned}\mathbf{x}(t + \Delta t) &= \mathbf{x}(t) + \mathbf{v}(t)\Delta t + \frac{1}{2}\mathbf{a}(t)(\Delta t)^2 + \mathcal{O}[(\Delta t)^3] \\ \mathbf{v}(t + \Delta t) &= \mathbf{v}(t) + \mathbf{a}(t)\Delta t + \mathcal{O}[(\Delta t)^2]\end{aligned}$$

Velocity Verlet:

$$\begin{aligned}\mathbf{x}(t + \Delta t) &= \mathbf{x}(t) + \mathbf{v}(t)\Delta t + \frac{1}{2}\mathbf{a}(t)(\Delta t)^2 + \mathcal{O}[(\Delta t)^3] \\ \mathbf{v}(t + \Delta t) &= \mathbf{v}(t) + \frac{\mathbf{a}(t) + \mathbf{a}(t + \Delta t)}{2}\Delta t + \mathcal{O}[(\Delta t)^3]\end{aligned}$$

Proof (I)

Expansion of \mathbf{v} around $t + \frac{\Delta t}{2}$, evaluated at t and $t + \Delta t$:

$$\begin{aligned}\mathbf{v}(t) &= \mathbf{v}\left(t + \frac{\Delta t}{2}\right) - \mathbf{a}\left(t + \frac{\Delta t}{2}\right) \frac{\Delta t}{2} + \frac{1}{2} \mathbf{j}\left(t + \frac{\Delta t}{2}\right) \left(\frac{\Delta t}{2}\right)^2 + \mathcal{O}[(\Delta t)^3] \\ \mathbf{v}(t + \Delta t) &= \mathbf{v}\left(t + \frac{\Delta t}{2}\right) + \mathbf{a}\left(t + \frac{\Delta t}{2}\right) \frac{\Delta t}{2} + \frac{1}{2} \mathbf{j}\left(t + \frac{\Delta t}{2}\right) \left(\frac{\Delta t}{2}\right)^2 + \mathcal{O}[(\Delta t)^3],\end{aligned}$$

where $\mathbf{j} = \frac{d^3 \mathbf{x}}{dt^3}$ (called "jerk"). Subtracting both:

$$\mathbf{v}(t + \Delta t) = \mathbf{v}(t) + \mathbf{a}\left(t + \frac{\Delta t}{2}\right) \Delta t + \mathcal{O}[(\Delta t)^3]$$

Proof (II)

For the acceleration:

$$\mathbf{a}(t) = \mathbf{a}\left(t + \frac{\Delta t}{2}\right) - \mathbf{j}\left(t + \frac{\Delta t}{2}\right) \frac{\Delta t}{2} + \mathcal{O}[(\Delta t)^2]$$

$$\mathbf{a}(t + \Delta t) = \mathbf{a}\left(t + \frac{\Delta t}{2}\right) + \mathbf{j}\left(t + \frac{\Delta t}{2}\right) \frac{\Delta t}{2} + \mathcal{O}[(\Delta t)^2]$$

Adding both together:

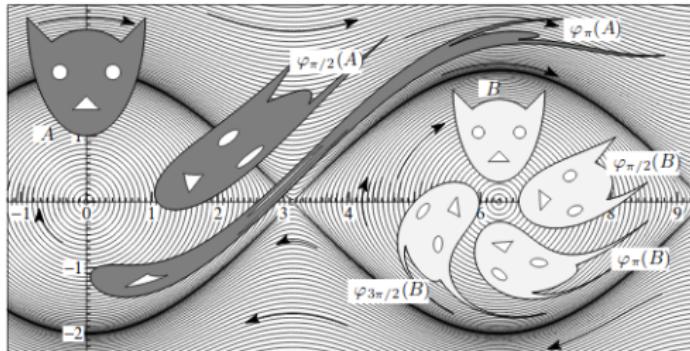
$$\mathbf{a}\left(t + \frac{\Delta t}{2}\right) = \frac{\mathbf{a}(t) + \mathbf{a}(t + \Delta t)}{2} + \mathcal{O}[(\Delta t)^2]$$

Substituting this into the expansion of \mathbf{v} :

$$\mathbf{v}(t + \Delta t) = \mathbf{v}(t) + \frac{\mathbf{a}(t) + \mathbf{a}(t + \Delta t)}{2} \Delta t + \mathcal{O}[(\Delta t)^3]$$

The real reason why velocity Verlet works

- A velocity Verlet step is a **symplectic transformation**.
Generalization of the idea of an area-preserving map in (x, p) space:

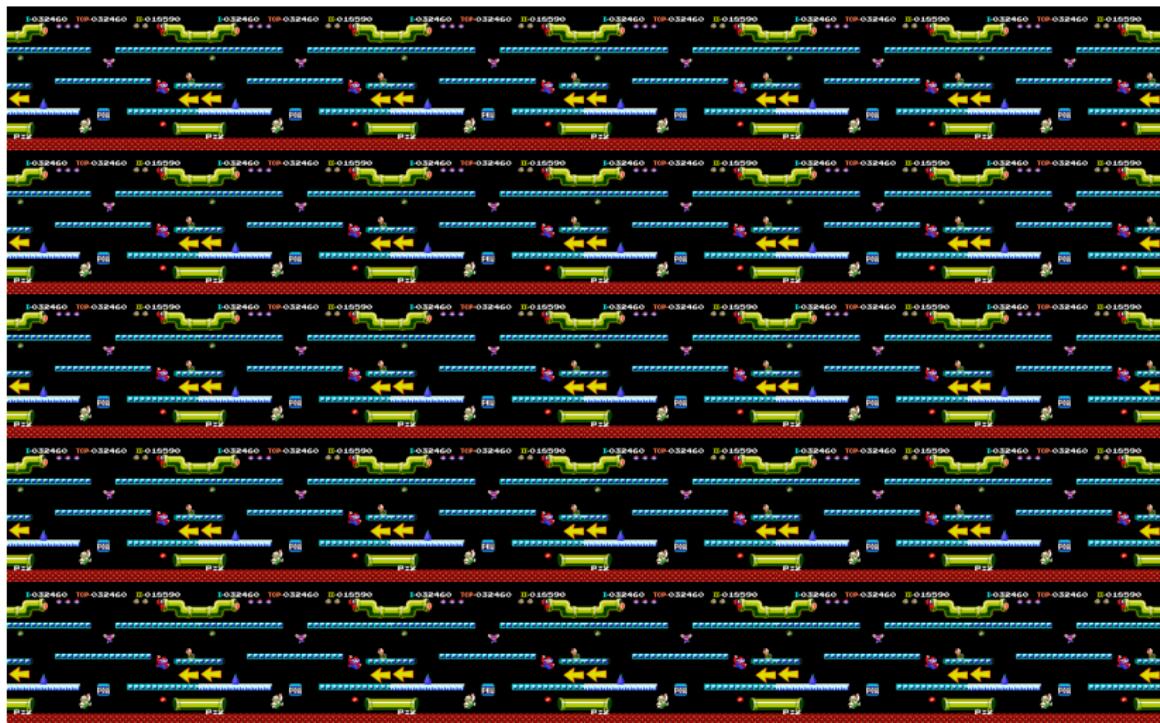


- Systematic study and design: See Vorlesung "Geometric Numerical Integration" an der TU München (2010),
<http://www.unige.ch/~hairer/polycop.html>
- E.g.: symplectic Runge-Kutta

Periodic boundary conditions



Periodic boundary conditions



Periodic boundary conditions



MD is powerful and scalable, but cannot tackle the number of molecules that make up a macroscopic phase. Periodic boundary conditions fold the coordinates into the simulation box, so that there are infinite interacting copies of it.

Periodic boundary conditions, in practice

A particle L in the central copy of the simulation box interacts with **all the images** of each other particle J in all copies of the simulation box.
To implement this:

Long-range potentials:

The sum over images is implemented partly in real space and partly in Fourier space (Ewald-like methods) or using the fast multipole method (FMM). Notable example: electrostatic interactions.

Short-range potentials:

Minimum-image convention – only the image of J closer to L is taken into account. Examples: potentials with cutoffs, quickly decreasing functions.

Most potentials can be split into a long-range and a short-range part.

Implementing the minimum-image convention

Completely general case:

- Simulation box: general space-filling shape
- Related to the **closest vector problem** (class of lattice problem)
- Probably NP-hard, slow, best avoided

Easy, frequent case:

- Simulation box: parallelepiped with sides L_x , L_y and L_z
- Let $\Delta\mathbf{x} = \mathbf{x}_L - \mathbf{x}_J$ be a vector joining L with any arbitrary image of J
- $\Delta\mathbf{x} = (\Delta x, \Delta y, \Delta z)$ is reduced to its value in the minimum image convention simply through:

$$\left. \begin{aligned}\Delta x_{\text{m.i.}} &= \Delta x - L_x \left\lfloor \frac{\Delta x}{L_x} \right\rfloor \\ \Delta y_{\text{m.i.}} &= \Delta y - L_y \left\lfloor \frac{\Delta y}{L_y} \right\rfloor \\ \Delta z_{\text{m.i.}} &= \Delta z - L_z \left\lfloor \frac{\Delta z}{L_z} \right\rfloor\end{aligned} \right\}, \text{ where } \lfloor z \rfloor \equiv \text{round}(z)$$

Boundary conditions: constant T or p

- Newton's equations $\Rightarrow (N, V, E)$ simulation
- Need modifications for (N, V, T) or (N, p, T)
- E.g.: Thermostats must affect the statistical distribution of velocities. Many deterministic and random approaches exist.

A rescaling thermostat

$$\mathbf{v}'_L = \mathbf{v}_{\text{CM}} + \alpha (\mathbf{v}_L - \mathbf{v}_{\text{CM}})$$

$$\alpha = \sqrt{1 \pm \frac{\Delta E}{E_{\text{kin},R}}}$$

$$E_{\text{kin},R} = \frac{1}{2} \sum_L m_L |\mathbf{v}_L|^2 - \frac{1}{2} \sum_L m_L |\mathbf{v}_{\text{CM}}|^2$$

- For systems with surfaces, boundary effects have to be considered
- Equilibrium or non-equilibrium? Imposed gradients

Post-processing: Averages

- For theoretical foundations, see e.g. D. Chandler, *Introduction to Modern Statistical Mechanics*, Oxford (1987). ISBN: 9780195042771.
- Underlying assumption: time averages $\frac{1}{t_{\max}} \int_0^{t_{\max}} \bullet dt$ can approximate statistical averages over the state space of the system $\langle \bullet \rangle$.

Examples:

Geometric/mechanical:

$$\rho(\mathbf{x}) = \lim_{V \rightarrow \{\mathbf{x}\}} \frac{1}{V} \int_V \sum_L \langle \delta(\mathbf{x}' - \mathbf{x}_L) \rangle d^3 \mathbf{x}'$$

Thermodynamical:

$$T = \frac{\langle E_{\text{kin}} \rangle}{\frac{3}{2} M k_B}$$

($k_B = 1.380\,649 \times 10^{-23} \text{ J K}^{-1}$: Boltzmann constant)

Post-processing: Fluctuations (standard deviations)

Connected with "linear response" / second derivatives of the entropy:
specific heats, thermal expansion coefficients, compressibilities...

E.g.: isobaric specific heat

$$c_v = \frac{1}{M} \left(\frac{\partial E}{\partial T} \right)_V = k_B \frac{\langle E_{\text{kin}} \rangle^2}{\sigma_{E_{\text{kin}}}^2}, \text{ where } \sigma_{E_{\text{kin}}}^2 = \langle (E_{\text{kin}} - \langle E_{\text{kin}} \rangle)^2 \rangle$$

Simple calculation strategy: $\sigma_f^2 = \langle f^2 \rangle - \langle f \rangle^2$.

Post-processing: Spatial correlations

Example: pair correlation function between atom types a and b

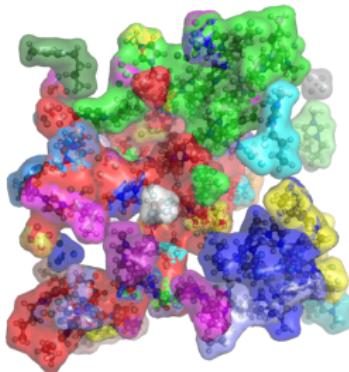
$$g_{ab}(r) = \frac{1}{4\pi r^2} \frac{V}{M_a M_b} \sum_{L=1}^{M_a} \sum_{J=1}^{M_b} \langle \delta(|\mathbf{x}_L - \mathbf{x}_J| - r) \rangle$$

Interpretation: density of particles of type b at a distance r from a particle of type a , relative to a system with completely random positions.

First order of description of the structure of a fluid:

- Peaks at nearest-neighbor distances
- Can be integrated to measure coordination
- Useful for detecting homo-/heterocoordination

Post-processing: Cluster formation



Method:

- Define a notion of connectivity (distances, angles...)
- Build a **graph**

Clusters are extracted as **connected components** (depth-first or breadth-first search). A giant connected component can signal **percolation** (interesting in e.g. ionic systems).

Post-processing: Time autocorrelation functions

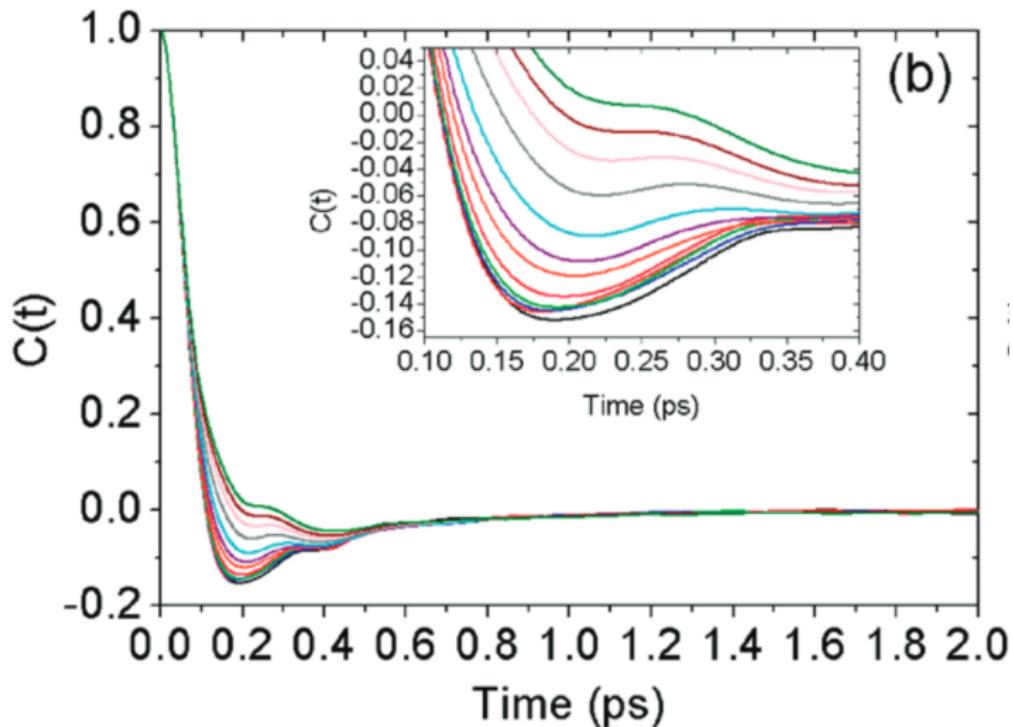
The **Green-Kubo** relations provide formulas for transport coefficients like the thermal conductivity tensor:

$$\kappa^{(\alpha\beta)} = \frac{V}{k_B T^2} \int_0^\infty \langle j_Q^{(\alpha)}(0) j_Q^{(\beta)}(t) \rangle dt, \text{ where } j_Q \text{ is the heat current}$$

Particularly difficult to converge! Two possibilities:

- Direct calculation (discretization and cutoff in the integral)
- Calculation in frequency space (FFT, correlation theorem, filters to minimize aliasing and noise)

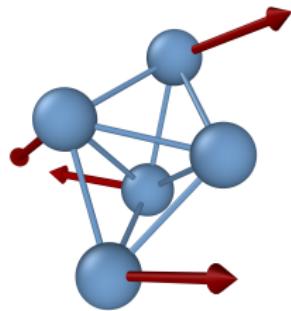
Post-processing: Relaxation times



Connected to confinement, time to first collision...

Post-processing: Normal modes

Low-energy, bounded movements of the system (generalization of molecular vibrations):



Their frequencies create peaks in the **power spectrum** of the velocity time-autocorrelation function.

Post-processing: Infinite diversity

- Free energy profiles
- Cage correlations
- Hydrogen bonds
- Diffusion
- Dielectric response
- Protein folding ...

A survey of available software

Popular MD software

Ab initio:

- Most DFT software, both commercial (e.g. VASP) and free (e.g. Quantum ESPRESSO)
- **CP2K**: <http://www.cp2k.org>

Classical and mixed:

- **LAMMPS**: <http://lammps.sandia.gov>
- OpenMD: <http://www.openmd.org>
- **NAMD**
Scalable Molecular Dynamics:
<http://www.ks.uiuc.edu/Research/namd/>
- **GROMACS**
FAST. FLEXIBLE. FREE.
 : <http://www.gromacs.org>

Steps of a practical MD simulation

At the very least:

1. Particle placement (random algorithms, pre-solvated boxes...)
2. Energy relaxation
3. Stabilization run
4. Production run
5. Post-processing

Possibly: equilibrium and non-equilibrium steps, parameter sweep, "pull" simulation, particle addition and removal, hybrid quantum-mechanical/molecular-mechanics...

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Lecture 5



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