



TECHNISCHE
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165.144 Simulation of condensed matter

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Summary chapter 2

- Given a potential energy, and some initial configuration, we can compute a trajectory over time using numerical integration

① $\vec{f} = -\nabla E_{\text{pot}}$ and $\vec{f}_i = -\frac{\partial E_{\text{pot}}}{\partial \vec{x}_i}$

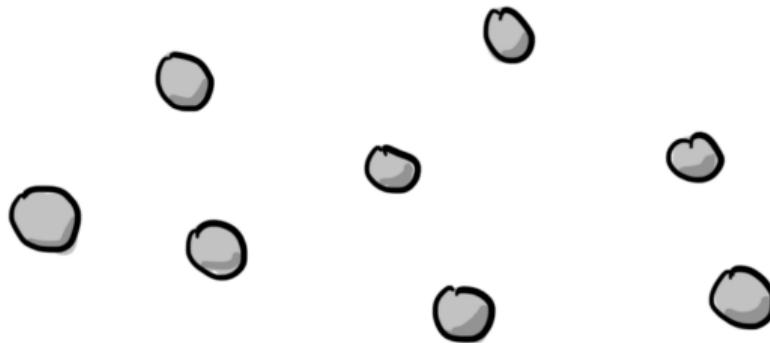
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- Suitable integrators are for example the Leapfrog or Velocity-Verlet algorithm
- Programming a naive, simple MD simulation software is very simple if we disregard all performance considerations



Chapter 3: Simulation of a simple system

Efficiency

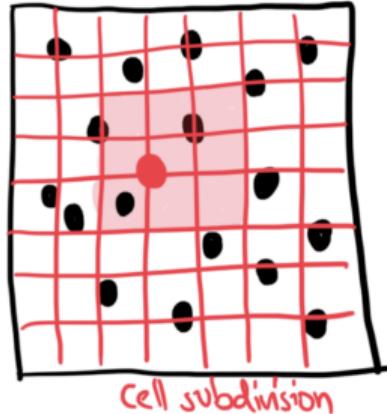
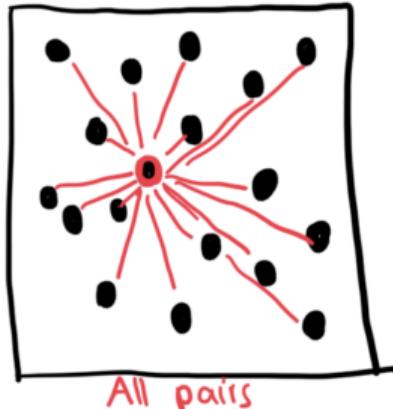
In chapter 2, we looked at the mean kinetic and potential energy per atom, as well as the temperature and pressure of the whole system. However, there are much more interesting quantities to look at...

... but for this we need to compute longer trajectories.

Efficiency

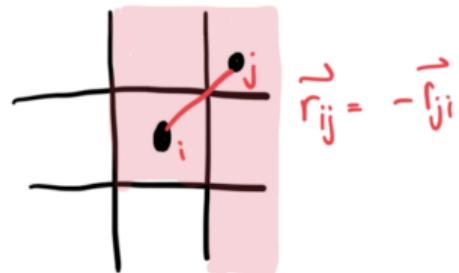
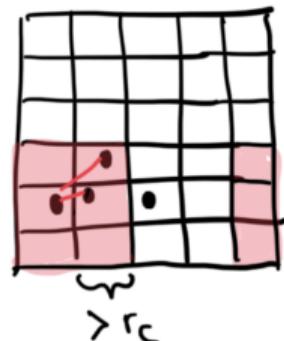
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Our implementation from chapter 2 was very slow even for a small system because the computation of all distances scales with N^2 . Possible methods:



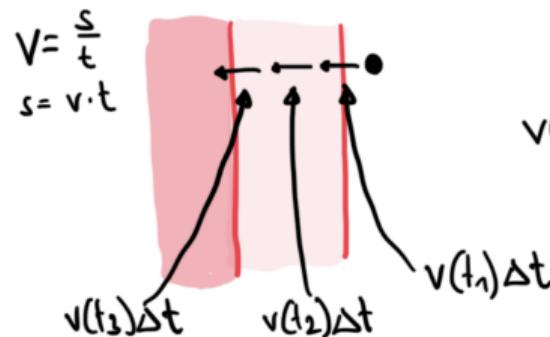
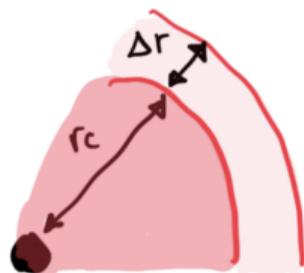
Computing interactions: Cell subdivision

- Divide simulation region into smaller cells with cell edges $> r_c$
- Only atoms in the same or neighboring cells can interact
- Due to symmetry ($r_{ij} = r_{ji}$), we only need to consider half the neighboring cells
 - 3 dimensions: consider 14 neighboring cells
 - 2 dimensions: consider 5 neighboring cells
- Periodic boundary conditions are easy to include into this scheme



Computing interactions: Neighbor-list method

- For each atom, keep a list of neighbors at distances $< r_c + \Delta r$
- Only atoms in the list can interact
- Update list when $\sum_{\text{steps}} \max v_i > \frac{\Delta r}{2\Delta t}$ (which means that in the next timestep, an atom could have travelled all the way from $r > r_c + \Delta r$ to $r < r_c$)
- Δr is chosen to balance memory requirements, number of distances that need to be computed, and how many times the list needs to be refreshed.
- The list refresh can be done with the cell subdivision method



$v(t_1)\Delta t + v(t_2)\Delta t + v(t_3)\Delta t > \Delta r$
→ Particle has moved into inner circle and neighbor list is wrong

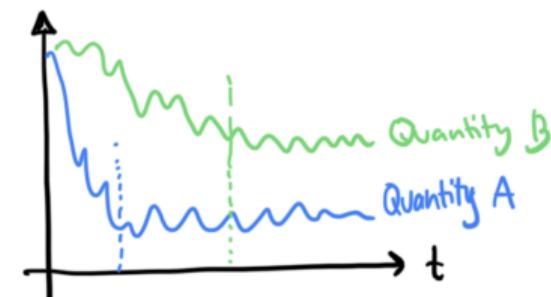
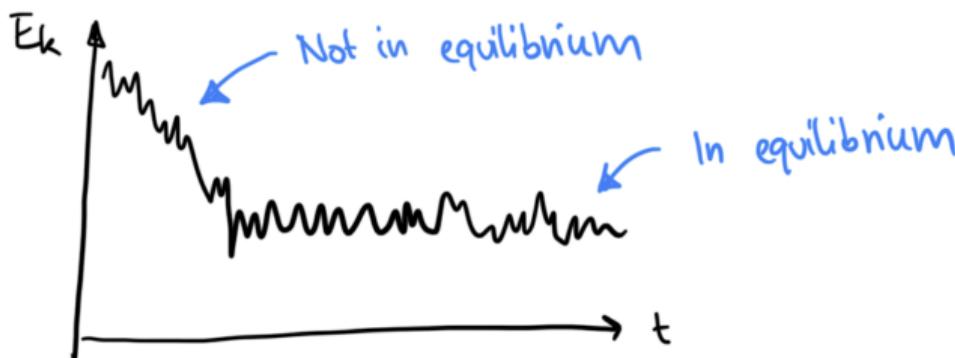
Let's put this to the test!



(Demonstration of all-pairs, cell subdivision and neighbor-list method)

When to start a measurement

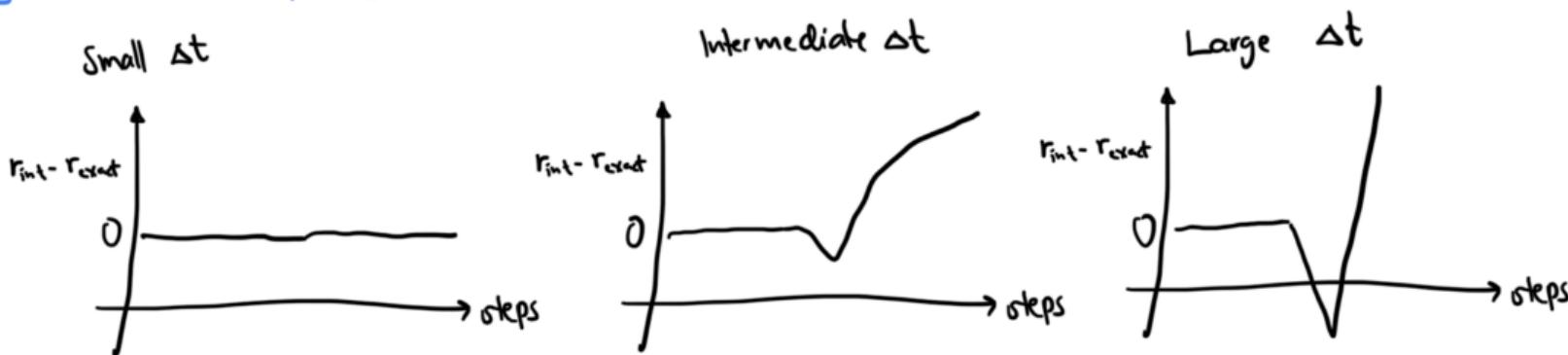
- Properties fluctuate over time, and averaging over a series of timesteps will reduce the fluctuations
- Different quantities relax to their equilibrium averages at different rates
- Only after an equilibrium of the quantities of interest is observed we can start measuring them!
- Equilibration can be accelerated by starting the simulation at a higher temperature and cooling it later (e.g. rescaling the velocities)



Time-step revisited

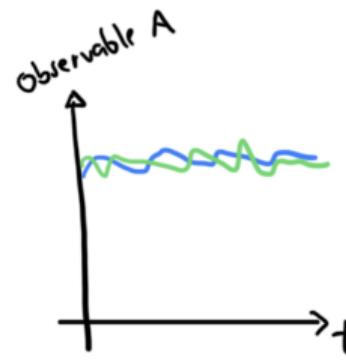
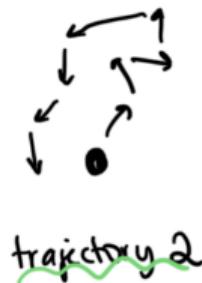
A (much) too large time step can cause our simulation to blow up. However, there are also more subtle effects before that happens: The numerical accuracy of the numerical integration differs between different methods, and depends on Δt .

- Inaccuracies cause a drift in the total energies!
- For a given potential and system: Make a few short test runs and monitor the energy!



Reproducibility

- We can never re-create the EXACT same trajectory (extreme sensibility toward initial conditions, rounding method, exact sequence of machine instructions)
- It is irrelevant since no meaningful physical quantity depends on just a single trajectory realization!
- Extreme sensitivity is the microscopic basis for molecular chaos playing an important role in statistical mechanics
- Equations of motions are time reversible, but in fact this is unobservable in most practical situations



Let's put this to the test!



(Demonstration of energy drift depending on Δt for the soft-sphere potential, as well as different trajectories obtained with different initial conditions)

Properties of a system

Static properties describe measurements of thermodynamic properties, spatial structure and organization

- Potential/kinetic energy, heat capacity, pressure, temperature
- Radial distribution functions
- Number of neighbors
- Order

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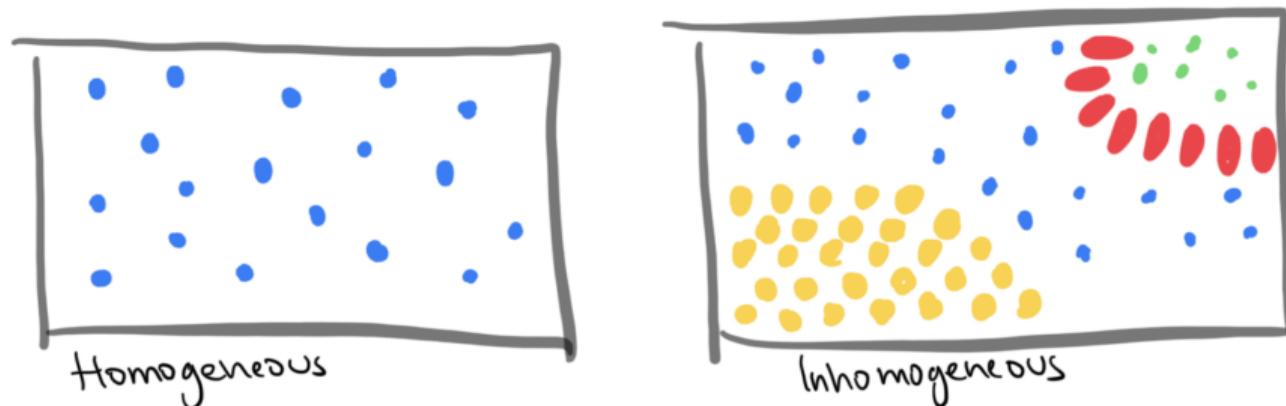
Dynamic properties describe the movements of atoms

- Diffusion coefficients
- Conductivity
- Time-dependent spectroscopy
- Viscosity

Static properties

Can be computed directly from trajectories:

- Straightforward: Homogeneous, stationary (equilibrated) systems, where we can average over time and space
- Inhomogeneous systems: Localized measurements instead of global averages
- Nonstationary over time: No long-term time averaging



Radial distribution function (pair correlation function) $g(r)$

$g(r)$ describes the spherically averaged local organization around any given atom

$$g(r) = \frac{\bar{n}(r)}{\rho V_{\text{shell}}}$$

with $\bar{n}(r)$ the mean number of particles between distance r and $r + \Delta r$, and ρ the number density N/V

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It can be derived from a histogram h_n of discretized pair separations, where $\bar{n}(r_n) = h_n * 2/N$, which is the number of atom pairs (i,j) for which $n\Delta r \leq r_{ij} < (n + 1)\Delta r$

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For small Δr :

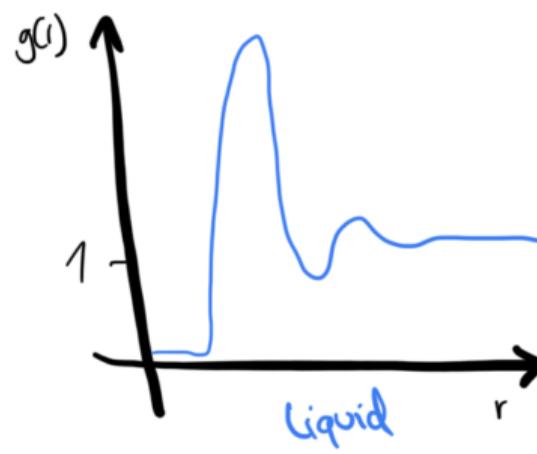
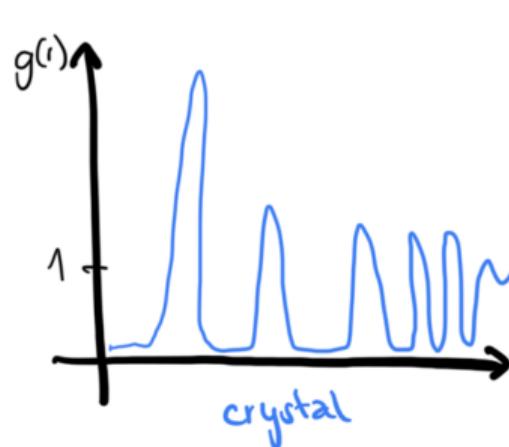
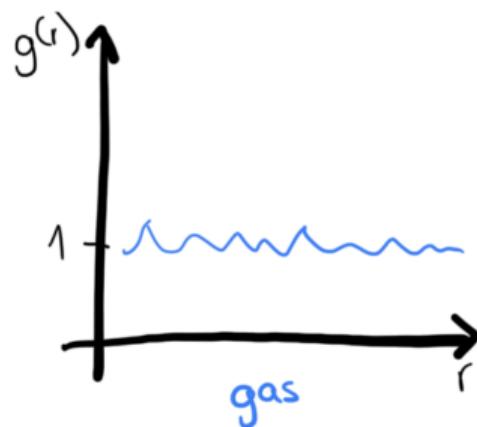
- 3 dimensions: $g(r) \simeq \frac{\bar{n}(r)}{4\pi r^2 \Delta r \rho}$ with $V_{\text{shell}} = \frac{4\pi}{3}(r + \Delta r)^3 - \frac{4\pi}{3}r^3 \simeq 4\pi r^2 \Delta r$
- 2 dimensions: $g(r) \simeq \frac{\bar{n}(r)}{2\pi r \Delta r \rho}$ with $V_{\text{shell}} = \pi(r + \Delta r)^2 - \pi r^2 \simeq 2\pi r \Delta r$

Radial distribution function (pair correlation function) $g(r)$

Characteristics:

- $\rho g(r)d\vec{r}$ is proportional to the probability of finding an atom in the volume element $d\vec{r}$ at a distance r from a given atom
- $\rho V_{\text{shell}} \cdot g(r)$ is the mean number of atoms in a shell of radius r and thickness Δr surrounding the atom.

Typical behavior:



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- functions that depend on the pair separation (potential energy, pressure) can be expressed in terms of integrals involving $g(r)$. E.g. with the pair potential $u(r)$:

$$E_{\text{pot}} = 2\pi N \rho \int_0^\infty r^2 u(r) g(r) dr$$

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- $g(r)$ is related to the experimentally measurable structure factor $S(\vec{k})$ (\vec{k} is the scattering vector) by Fourier transformation

$$S(\vec{k}) = 1 + \rho \int g(\vec{r}) e^{-i \vec{k} \cdot \vec{r}} d\vec{r}$$

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- $g(r)$ can even be measured experimentally using microscopy for large particles

Radial distribution function (pair correlation function) $g(r)$

Error estimates: $g(r)$ can be used to estimate errors in thermodynamic properties due to the energy cutoff. For example, for the mean potential energy:

$$\Delta E_{\text{pot}} = 2\pi\rho \int_{r_c}^{\infty} r^2 u(r) g(r) dr$$

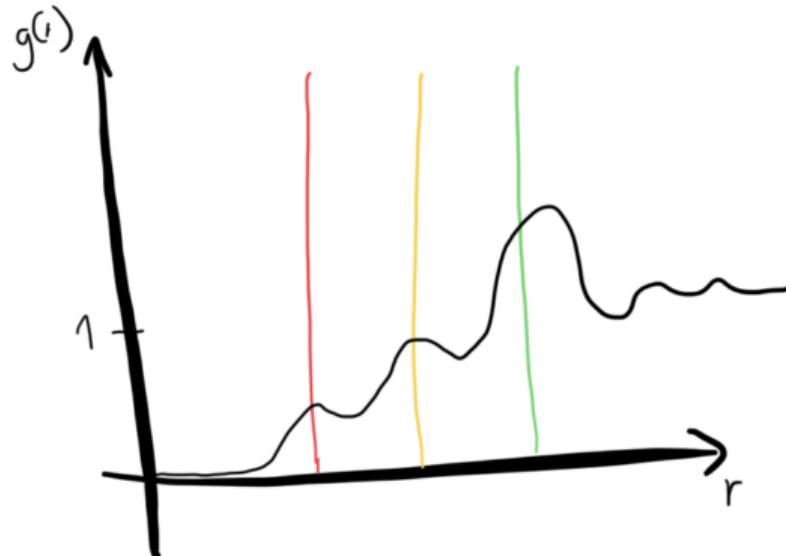
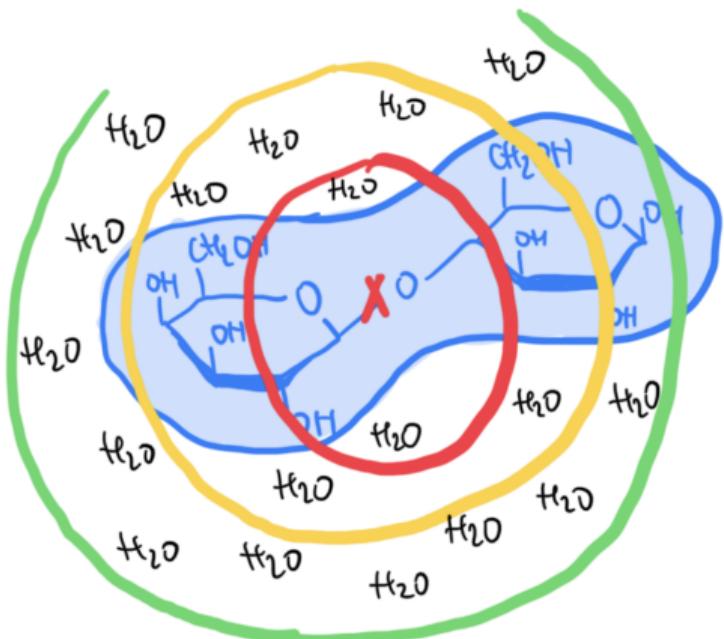
Since $g(r) \simeq 1$ for large r , the calculation can be simplified. For the LJ potential, it can even be evaluated analytically:

$$\Delta E_{\text{pot}} = 8\pi\rho \left(\frac{1}{9r_c^9} - \frac{1}{3r_c^3} \right)$$

Similarly, we can compute the error in the pressure.

Radial distribution function (pair correlation function) $g(r)$

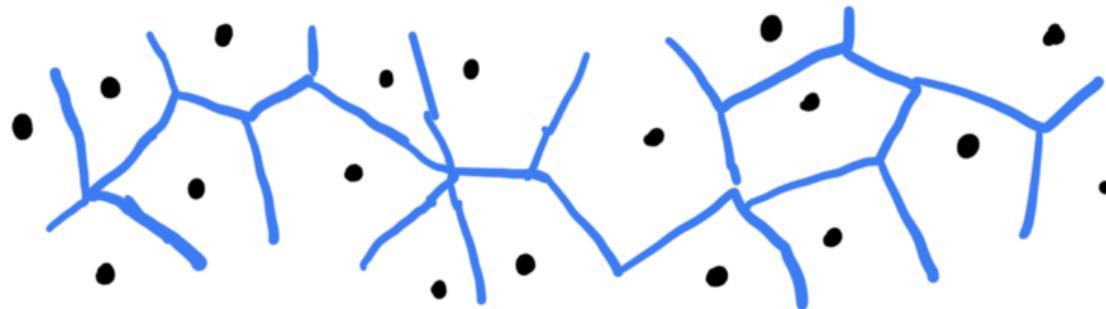
Limitations:



Local order

Local order gives information about e.g. how molecules are organized, how large the exposed surface of a large molecule is, etc.

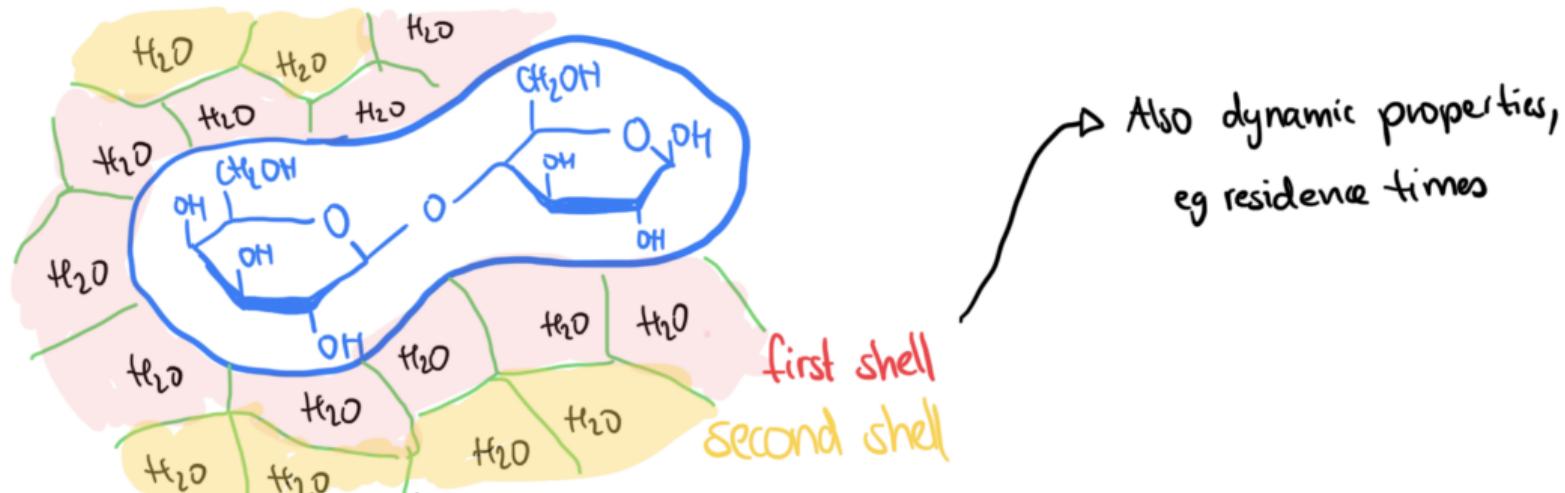
Voronoi subdivision (= tessellation): Construct polyhedra around atoms/molecules such that all points that are closer to a particular atom/molecule than any other belong to its polyhedron. Adjacent atoms/molecules then share a common face of their polyhedra.



Voronoi tessellation

What is it used for?

- Shape of polyhedra and their volume have a physical meaning
- Accurate neighbor counts even for non-spherical molecules
- Computation of solvation shells
- For mixtures: Number of specific species in the x-th solvation shell



Long-range order

$g(r)$ primarily addresses the local structure, and gives only little direct information on long-range (crystalline) order.

The local density at a point \vec{r} can be expressed as a sum over atoms:

$$\rho(\vec{r}) = \sum_j \delta(\vec{r} - \vec{r}_j)$$

Fourier-transforming $\rho(\vec{r})$ gives

$$\rho(\vec{k}) = \frac{1}{N} \sum_j e^{-i \vec{k} \cdot \vec{r}_j}$$

To test for long-range order, we compute $|\rho(\vec{k})|$, and can, for example, follow how a system solidifies.

Static properties



(Demonstration of static properties of different systems)