10. Molecular Dynamics Simulations

Molecular dynamics simulations

- a technique for computing equilibrium and transport properties of a classical many-body system
- very similar to real experiments in many aspects
- involves preparing a system (a sample), equilibrating it (wait), and computing observables (measurement).
- common mistakes are very similar to those made in real experiments, such as: the system is not prepared correctly, the measurement is too short, or we are not measuring the right thing.

Outline

Receipe for molecular dynamics simulations

- common workflow of a molecular dynamics simulation:
  1. initialize the system including the positions and velocities of the particles
  2. run the simulation by integrating the equations of motion
  3. compute the observables of interest
- all three steps are crucial for a successful simulation
- the second step is often the most time-consuming part of a simulation

Initialization

- assign the initial positions and velocities for all particles
- initial positions should be compatible with the structure that we want to simulate
- should not have particles overlapping with each other, which is often achieved by initially placing the particles on a cubic lattice
- for molecules such as proteins with known structures, we could use the known structure as the initial configuration

Initialization

- initial velocities need to be compatible with the temperature of the system
- from statistical mechanics, we know that the average kinetic energy per degree of freedom is given by

$$\left\langle \frac{1}{2} m v_\alpha^2 \right\rangle = \frac{1}{2} k_B T$$

- more specifically, the velocity components of a particle follow the Boltzmann distribution

$$p(v_\alpha) = \frac{1}{\sqrt{2\pi k_B T/m}} e^{-m v_\alpha^2 / 2 k_B T}$$

- we can assign the initial velocities by sampling from the Boltzmann distribution
- what is the average speed of a water molecule at room temperature?

Outline

The equation of motion

- the equation of motion is given by Newton's second law

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = -\nabla_i U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$$

- an equivalent form is the Hamiltonian equations of motion

$$\frac{d\mathbf{q}_i}{dt} = \frac{\partial H}{\partial \mathbf{p}_i}, \quad \frac{d\mathbf{p}_i}{dt} = -\frac{\partial H}{\partial \mathbf{q}_i}$$

where $\mathbf{q}_i = \mathbf{r}_i$, $\mathbf{p}_i = m_i \mathbf{v}_i$, and

$$\begin{aligned} H(\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_N, \mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N) &= K(\mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N) + U(\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_N) \\ &= \sum_i \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_N) \end{aligned}$$

The Hamiltonian equations of motion

- Hamiltonian equations

$$\frac{d\mathbf{q}_i}{dt} = \frac{\partial H}{\partial \mathbf{p}_i} = \frac{\mathbf{p}_i}{m_i}$$
$$\frac{d\mathbf{p}_i}{dt} = -\frac{\partial H}{\partial \mathbf{q}_i} = -\nabla_i U(\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_N)$$

- in vector form, we have

$$\frac{d}{dt}\begin{pmatrix}\mathbf{q}\\ \mathbf{p}\end{pmatrix} = \begin{pmatrix}0 & \mathbf{I}\\ -\mathbf{I} & 0\end{pmatrix}\begin{pmatrix}\frac{\partial H}{\partial \mathbf{q}}\\ \frac{\partial H}{\partial \mathbf{p}}\end{pmatrix}$$

- a set of first-order differential equations and equivalent to Newton's second law
- provides a more useful framework for understanding the dynamics of a system

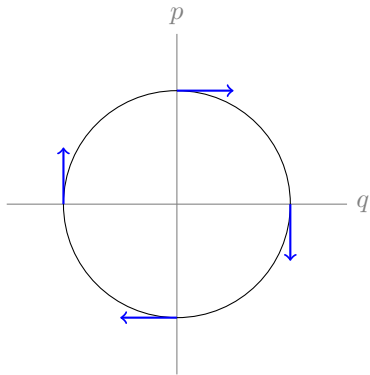
Integrating the Hamiltonian equations of motion

- a solution of the Hamiltonian equations of motion is a trajectory in the phase space of $(\mathbf{q}, \mathbf{p})$
- example: a harmonic oscillator

$$H(q,p) = \frac{p^2}{2m} + \frac{1}{2}kq^2$$

when m $= 1$ and k $= 1$

$$\frac{dq}{dt} = \frac{\partial H}{\partial p} = p$$
$$\frac{dp}{dt} = -\frac{\partial H}{\partial q} = -q$$



Integrating the Hamiltonian equations of motion

- most Hamiltonian systems are not solvable analytically
- need numerical methods to integrate the Hamiltonian equations of motion
- the naive method is the Euler method, which is not a good choice
- a much better method is the leap-frog Verlet method

The Euler method

- naive Euler method

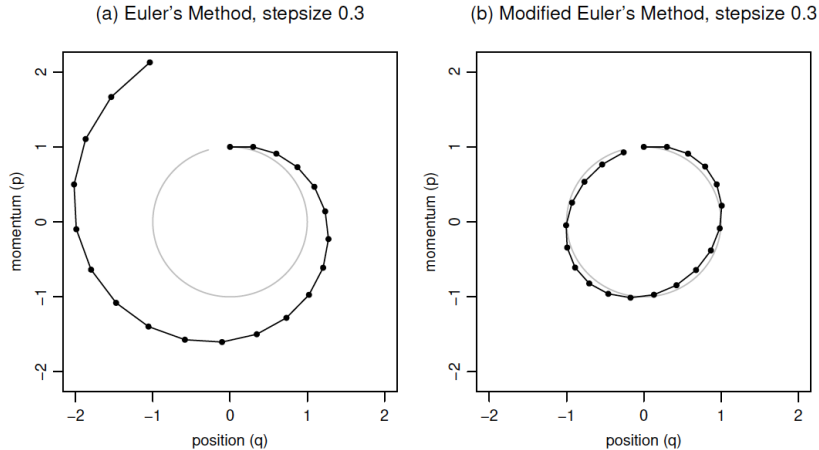
$$p(t+\epsilon) = p(t) + \epsilon \frac{dp}{dt} = p(t) - \epsilon \frac{\partial U}{\partial q}(q(t))$$
$$q(t+\epsilon) = q(t) + \epsilon \frac{dq}{dt} = q(t) + \epsilon \frac{p(t)}{m}$$

- modified Euler method

$$p(t+\epsilon) = p(t) - \epsilon \frac{\partial U}{\partial q}(q(t))$$
$$q(t+\epsilon) = q(t) + \epsilon \frac{p(t+\epsilon)}{m}$$

The Euler method

- numerical trajectory for the 1-d harmonic oscillator



The leap-frog Verlet method

- integration scheme

$$p(t+\epsilon/2) = p(t-\epsilon/2) - 2\frac{\partial U}{\partial q}(q(t))$$
$$q(t+\epsilon) = q(t) + \epsilon\frac{p(t+\epsilon/2)}{m}$$

- is called the leap-frog method because the position and momentum are updated in a staggered fashion
- is a symplectic integrator which preserves the phase space volume
- has better energy conservation properties than the Euler method

The leap-frog Verlet method

- numerical trajectory for the 1-d harmonic oscillator