Exercise 1. Simulating interacting molecules in a box

Goal: This week we are going to learn how interacting molecules can be simulated using constraint forces.

Consider a system of N diatomic molecules (in a box of length L with periodic boundary conditions) that interact with each other. For simplicity we assume that all atoms are identical. Atoms of different molecules interact via the Lennard-Jones potential

$$V(r) = 4\left[\left(\frac{1}{r}\right)^{12} - \left(\frac{1}{r}\right)^{6}\right]$$

with each other. To ensure that the two particles in a molecule keep their distance r we have to add the constraint forces

$$\boldsymbol{g}_1 = \lambda \boldsymbol{r}$$
$$\boldsymbol{g}_2 = -\lambda \boldsymbol{r}$$

to the equation(s) of motion.

Task 1: *Derive an analytical expression for the Lagrange multiplier λ.*

Task 2: *Simulate the system using the Verlet scheme as described in the lecture notes.*

Hint: The distance between the two atoms in a molecule should be small enough such that other molecules do not cross their bond.

Hint: It might be easier to consider the 2D case and check if the behaviour of the molecules is correct before you go to the 3D case.

Task 3 (OPTIONAL): *Extend your program to simulate three-component molecules.*

Solution. Simulating polyatomic molecules constrains the movement of the single particles since they are bound together. These additional constraints can be implemented using Lagrange multipliers. Here, we assume diatomic molecules. The equation of motion for a single atom in the molecule can be stated as

$$\ddot{\boldsymbol{x}}_{ij} = \boldsymbol{f}_{ij} + \boldsymbol{g}_{ij}$$

where $\boldsymbol{f}$ results from the Lennard-Jones potential and $\boldsymbol{g}$ is a constraint force. Let r and d be the actual and the desired distance between the atoms of every molecule, respectively. This allows us to write the constraint as

$$\chi_i = r_i^2 - d^2 = 0$$

such that the constraint forces are

$$\boldsymbol{g}_{ij} = \frac{1}{2}\lambda \nabla_{\boldsymbol{x}_j} \chi_i.$$

To obtain the Lagrange multiplier λ the Verlet algorithm is executed in two steps. In the first step the positions of the particles are updated without considering the constraint forces at all

$$\tilde{\boldsymbol{x}}_{ij}(t + \Delta t) = 2\boldsymbol{x}_{ij}(t) - \boldsymbol{x}_{ij}(t - \Delta t) + \Delta t^2 \boldsymbol{f}_{ij}.$$

In the second step the new particle positions are corrected by only using the constraint forces

$$\boldsymbol{x}_{ij}(t + \Delta t) = \tilde{\boldsymbol{x}}_{ij}(t + \Delta t) + \Delta t^2 \boldsymbol{g}_{ij}.$$

This allows to obtain λ from

$$|\boldsymbol{x}_{i1}(t+\Delta t) - \boldsymbol{x}_{i2}(t+\Delta t)|^2 = d^2$$

which is a quadratic equation in λ and finally yields

$$\lambda_{i,\pm} = \frac{1}{2\Delta t^2 r_i^2}\left(-\langle r_i, \tilde{r}_i\rangle \pm \sqrt{\langle r_i, \tilde{r}_i\rangle^2 - r_i^2(\tilde{r}_i^2 - d^2)}\right)$$

where we take the solution with minimal absolute value.

An example simulation can be found in the file `MD.avi`. A screenshot is shown in Fig. 1.

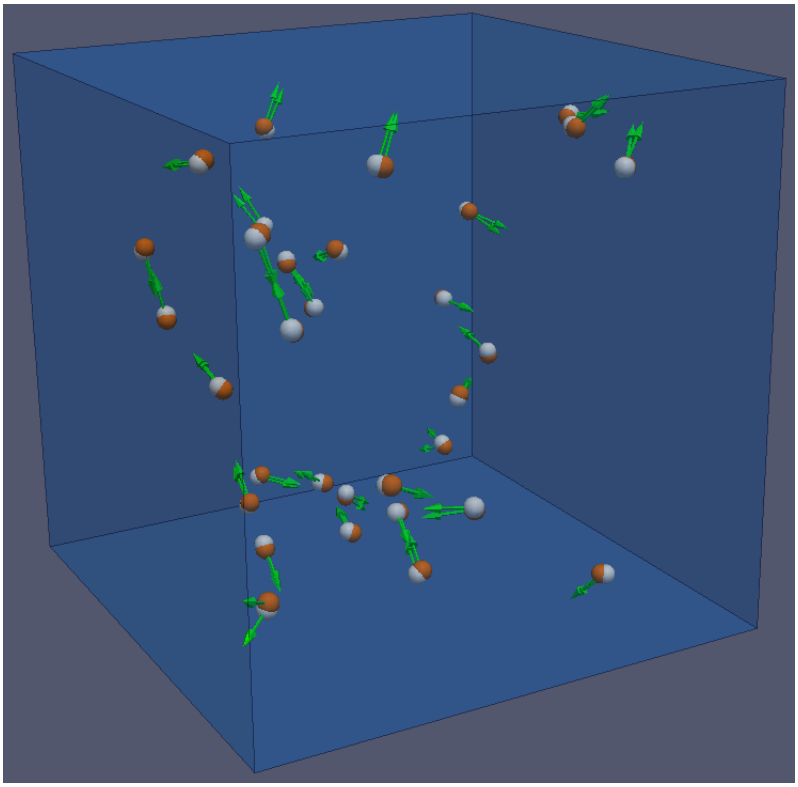

Figure 1: Screenshot of a constraint MD simulation of $N = 30$ molecules in a box of size 10^3 with $dt = 10^{-3}$.