Simulating interacting diatomic molecules in a box

Goal: Learn simulating interacting molecules using constraint forces.

Consider a system of N diatomic molecules in a 3-dimensional square box of side-length L with periodic boundary conditions. We will assume the pairwise intermolecular interactions are described by the Lennard-Jones potential

$$V(r) = 4\left(r^{-12} - r^{-6}\right), \tag{1}$$

where r is the separation between two particles.

The intramolecular interactions that hold the molecules together are modelled by a constraint that pairs of atoms in a molecule have a fixed distance r. This can be ensured by adding the constraint forces

$$\begin{aligned} \vec{g}_1 &= \lambda r, \\ \vec{g}_2 &= -\lambda r, \end{aligned} \tag{2}$$

to the equations 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.*

Keep in mind the following points:

- *The distance between the two atoms in a molecule should be small enough such that other molecules do not travel across their bond.*
- *It might be easier to test your implementation in the 2-dimensional case before going to the 3-d case.*

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

Solution. We use constraint forces, denoted by $\vec{g}$, to model the intramolecular interactions that ensure that molecules stay together rigidly. Specifically we take diatomic molecules of identical particles and we set their mass to $m = 1$:

$$\ddot{\vec{a}} = \vec{f}_{\mathrm{LJ}} + \vec{g}, \tag{S.1}$$

where $-\vec{f}_{\mathrm{LJ}}$ is the gradient of the Lennard-Jones potential V_{LJ}, modelling the interactions *between* the molecules.

Let d be the distance to be fixed between the molecules and r be the actual distance. To derive the constraint force, we express the deviation from the rigidity constraint as

$$\chi_{\mathrm{intra}} = r^2 - d^2 = 0. \tag{S.2}$$

Note that this corresponds to replacing the Hamiltonian for the system with $H = T + U$, where T is the kinetic energy and

$$U = V_{\mathrm{LJ}} + \lambda \chi_{\mathrm{intra}} \tag{S.3}$$

is the generalised potential energy which leads to the Newton's equations S.1 through $\ddot{\vec{a}}_i = -\nabla_{\vec{x}_i} U$. In particular, the constraint forces are given by

$$\vec{g}_i = \frac{1}{2}\lambda \nabla_{\vec{x}_i} \chi. \tag{S.4}$$

We can read-off from this a nice interpretation: the constraint force is a simple harmonic oscillator with a time dependent spring constant given by the Lagrange multiplier λ.

To satisfy the constraint, the spring constant must be adapted during the course of the simulation. More concretely, we carry out the time evolution in two separate steps for intermolecular and intramolecular interactions. In the first step, we use the Verlet algorithm to reach a fictitious intermediate position $\tilde{\vec{x}}$:

$$\tilde{\vec{x}}_{\mu i}(t + \Delta t) = 2\vec{x}_{\mu i}(t) - \vec{x}_{\mu i}(t - \Delta t) + \Delta t^2 \vec{f}^{\mathrm{LJ}}_{\mu i}(t), \tag{S.5}$$

where we denote the index of the molecule by $\mu = 1, \cdots, N$ and the index of the atom in the molecule by $i = 1, 2$. In the second step, we correct this by incorporating the constraint forces via:

$$\vec{x}_{1i}(t + \Delta t) = \tilde{\vec{x}}_{1i}(t + \Delta t) + \Delta t^2 \vec{g}_{i,12}(t), \tag{S.6}$$

where $\vec{g}_{i,12} = \lambda_i(t)(\vec{x}_{1i} - \vec{x}_{2i})$ and we adapt the spring constant $\lambda(t)$ by solving the quadratic constraint equation

$$|\vec{x}_{1i}(t + \Delta t) - \vec{x}_{2i}(t + \Delta t)|^2 = d^2 \tag{S.7}$$

at each time step. Explicit solution therof yields

$$\lambda_i^{\pm}(t) = \frac{1}{2\Delta t^2 d^2} \left\{ -\vec{r}_i(t) \cdot \tilde{\vec{r}}_i(t) \pm \sqrt{\left[\vec{r}_i(t) \cdot \tilde{\vec{r}}_i(t)\right]^2 - d^2 \left[\tilde{r}_i(t)^2 - d^2\right]} \right\}, \tag{S.8}$$

where $\vec{r}_i = \pm\left[\vec{x}_{1i}(t) - \vec{x}_{2i}(t)\right]$ and $\tilde{\vec{r}}_i(t) = \pm\left[\tilde{\vec{x}}_{1i}(t) - \tilde{\vec{x}}_{2i}(t)\right]$ and it can be seen that the roots are the same for both $\vec{g}_{i,12}$ and $\vec{g}_{i,21}$. We take the solution with that is closer to zero since taking the larger root leads to the unphysical situation where the distance constraint is ensured by exchanging the positions of the particles. Observe that the spring constant can take either sign, correspondingly compensating for both $r < d$ and $r > d$ cases.