Scientific Computing II

Molecular Dynamics

Exercise 8: Dimensionless Formulation

We want to simulate Argon using the Lennard Jones model at a mass density $\rho = 1008 kg/m^3$ and temperature $T = 215K$ as well as a time step $\Delta t = 10^{-15}s$. The atomic weight of Argon is 39.9u (i.e. 39.9g correspond to 1 mol). Derive the dimensionless form of the problem using the formulation and formulas from the lecture slides. You may further assume that the Boltzmann constant should be scaled to unity in the dimensionless form, i.e. $k_{B_c} = k_B$.

Solution:
First, we compute the mass of a single Argon atom. Since 1 mol corresponds to $6.022 \cdot 10^{23}$ atoms, we obtain

$$m = \frac{39.9}{6.022 \cdot 10^{23}} g = 6.63 \cdot 10^{-23} g = 6.63 \cdot 10^{-26} kg. \tag{1}$$

From the lecture slides, we know that the Lennard Jones parameters for Argon are given by $\epsilon = 120 k_B$, $\sigma = 0.341nm$. For normalisation, we use $m_c := m$ (characteristic mass), $e_c := \epsilon$ (characteristic energy) and $l_c := \sigma$ (characteristic length) as characteristic quantities and thus obtain that $m^* = 1$, $\epsilon^* = 1$ and $\sigma^* = 1$. Besides, the Boltzmann constant is typically scaled to unity as well which implies that $k_B^* = 1 \Leftrightarrow k_{B_c} = k_B$.
The characteristic time scale is given by

$$t_c = \sigma \sqrt{\frac{m}{\epsilon}} = 2.16 \cdot 10^{-12} s, \tag{2}$$

the characteristic temperature evolves at

$$T_c = \frac{\epsilon}{k_B} = 120K. \tag{3}$$

Besides, the characteristic mass density can be computed to be

$$\rho_c = \frac{m}{\sigma^3} = 1.67 \cdot 10^3 kg/m^3. \tag{4}$$

Next, we can compute the state of our MD system in dimensionless form. Therefore, we need to determine the dimensionless mass density and temperature. The dimensionless mass density is given by
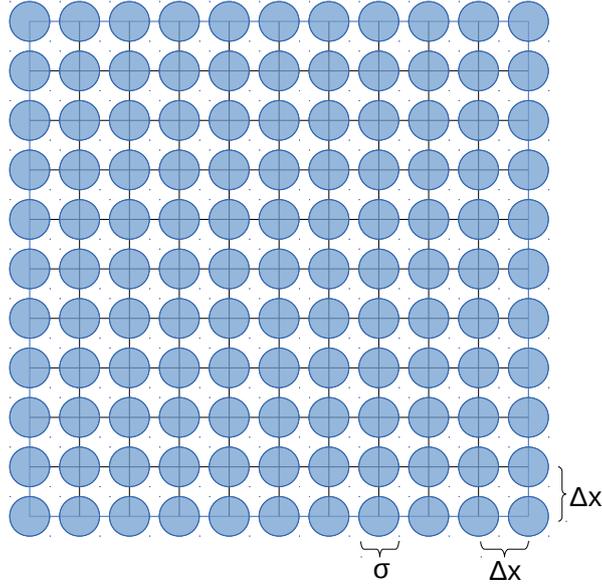
$$\rho^* = \frac{1}{\rho_c} \rho = 0.60. \tag{5}$$

Figure 1: Particles (blue disks) are initialised on a grid with equidistant mesh size Δx in all spatial directions. For sake of simplicity, the two-dimensional case is shown.

Since we scaled the mass of the molecules to unity, the mass and number density are identical in the dimensionless form.

The dimensionless temperature evolves at

$$T^* = \frac{1}{T_c}T = 1.79. \tag{6}$$

For the simulation, we further need to define a dimensionless time step Δt^*. We obtain this time step from

$$\Delta t^* = \frac{1}{t_c}\Delta t = 4.62 \cdot 10^{-4}. \tag{7}$$

Exercise 9: Initial Conditions

Liquids are defined by high number densities $n = N/V$ and high volume fractions $f = \frac{Volume(molecules)}{V}$ where N is the number of molecules, V is the volume which contains the N molecules and $V(molecules)$ corresponds to the effective volume that is occupied by the molecules.

In order to provide initial conditions to a Molecular Dynamics simulation, a common approach consists in mapping the molecules onto a Cartesian grid, cf. Fig. 1. The mesh size Δx is chosen such that the total number of molecules $N := N_x \times Ny \times N_z$ and the (three-dimensional) volume under consideration V yield the required number density n. However, due to the strong repulsive forces in a (Lennard Jones) fluid, the mesh size should typically not be chosen smaller than the interaction depth σ.

What is the maximum volume fraction $f := \frac{Volume(spheres)}{V}$ that can be achieved by this method? $V(spheres)$ shall correspond to the volume that is occupied by spherical Lennard Jones particles with diameter σ. How can we extend the method to even higher volume fractions?

Solution:
We can easily estimate the density by only considering the volume that is filled by particles inside a single grid cell. In the 3D case, we have 8 sectors inside a cell occupied by $1/8 V_s$ where $V_s = \frac{1}{6}\pi\sigma^3$. We thus obtain a max. volume fraction

$$f = \frac{8 \cdot \frac{1}{8}V_s}{\Delta x^3} = \frac{V_s}{\Delta x^3} \overset{\Delta x = \sigma}{=} \frac{1}{6}\pi \approx 0.52. \tag{8}$$

If we require higher volume fractions, one possiblity is shown on the lecture slides (slide 29): the spherical molecules are packed such that on each plane of a respective grid cell, one sphere is located in the middle and is surrounded by four spheres on the corners. Considering the overall volume of the grid cell from slide 29, we see that we obtain the densest packing for a mesh size $\Delta x = \sqrt{2}\sigma$ (use Pythagoras to obtain $\Delta x^2 + \Delta x^2 = (2\sigma)^2$). The red volumes amount to $8 \cdot \frac{1}{8}V_s$, the green volumes to $6 \cdot \frac{1}{2}V_s$. We thus obtain a volume fraction

$$f = \frac{V_s + 3V_s}{2\sqrt{2}\sigma^3} = \frac{\frac{4}{6}\pi\sigma^3}{2\sqrt{2}\sigma^3} = \frac{\pi}{3\sqrt{2}} \approx 0.74. \tag{9}$$

Exercise 10: Thermostat

Let $\bar{v} = \frac{1}{N}\sum_{i=1}^{N} v_i$ denote the average flow velocity in a Molecular Dynamics simulation and

$$T = \frac{m}{dNk_B}\sum_{i=1}^{N}(v_i - \bar{v})^2 \tag{10}$$

a measure for the temperature fluctuations. All molecules are of same material and a mass m. Show that the thermostat

$$v_i^{new} := \bar{v} + \sqrt{\frac{T^{new}}{T}}(v_i - \bar{v}) \tag{11}$$

yields a temperature T^{new} and leaves the average flow velocity unchanged, i.e. $\bar{v}^{new} = \frac{1}{N}\sum_{i=1}^{N} v_i^{new} = \bar{v}$.

Solution:
First, we compute the average velocity for the new velocities v_i^{new}:

$$\frac{1}{N}\sum_{i=1}^{N} v_i^{new} = \frac{1}{N}\sum_{i=1}^{N}\bar{v} + \sqrt{\frac{T^{new}}{T}}(v_i - \bar{v}) = \frac{1}{N}\left(N\bar{v} + \sqrt{\frac{T^{new}}{T}}(N\bar{v} - N\bar{v})\right) = \bar{v} \tag{12}$$

The average velocity thus remains unchanged.
We further compute:

$$\frac{m}{dNk_B} \sum_{i=1}^{N} (v_i^{new} - \bar{v})^2 = \frac{m}{dNk_B} \sum_{i=1}^{N} \left(\sqrt{\frac{T^{new}}{T}} (v_i - \bar{v}) \right)^2 = \frac{T^{new}}{T} \underbrace{\frac{m}{dNk_B} \sum_{i=1}^{N} (v_i - \bar{v})^2}_{=T} = T^{new}.$$

(13)

Programming Exercise 8: Two-Particle System

In the following, we want to consider the motion of a molecule A in proximity of another molecule B which is fixed in space. The interaction of the two molecules is modelled by the 12-6 Lennard Jones potential. The Lennard Jones parameters ϵ, σ and the mass of each molecule m are scaled to unity, $\epsilon = \sigma = m = 1$. Molecule B is fixed at $(0.0, 0.0)$ of our domain throughout the following experiments.

(a) Write a function `computeForce(xA,xB)` in Matlab which computes the force acting on molecule A due to molecule B. The arguments `xA` and `xB` correspond to the current positions of both molecules.
Write another function `timestep(xA,vA,FA,dt)` which computes the new position and velocity of molecule A. The time stepping should first compute the new velocity v^{new} using the explicit Euler method, $v^{new} = v_A + dt \cdot F_A$, and subsequently determine the new position x^{new} by the Heun-method, $x^{new} = x_A + \frac{dt}{2}(v_A + v^{new})$.

(b) Simulate the movement of molecule A for the following initial conditions using a time step $\Delta t = 0.0001$:

    a) $x_A = (-2, 0)$, $v_A = (0, 0)$, 200 000 time steps

    b) $x_A = (-2, 1)$, $v_A = (1, 0)$, 20 000 time steps

Measure the trajectory of molecule A.

(c) The total energy of the molecular system $E = E_{kin} + U$ is formed by the kinetic energy E_{kin} and the potential energy U of the system and is generally conserved in Molecular Dynamics simulations. Measure the kinetic, potential and total energy for the different cases in (b) by implementing a function `computeEnergy(xA,xB,vA,vB)`. Is the energy conserved over time?

(d) Re-run the simulations of (b) neglecting attractive forces in the Lennard Jones model. For this purpose, remove the power-6 term. Compare the arising trajectory of molecule A with the trajectories from (b).
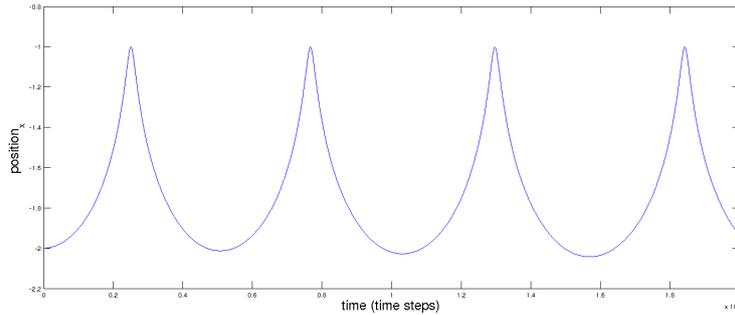
Solution:

(a) See computeForce.m, timestep.m.

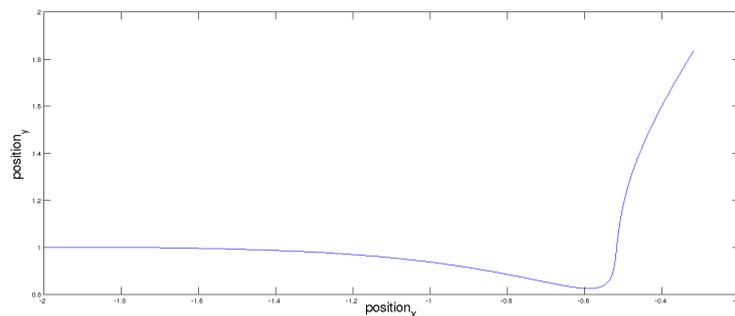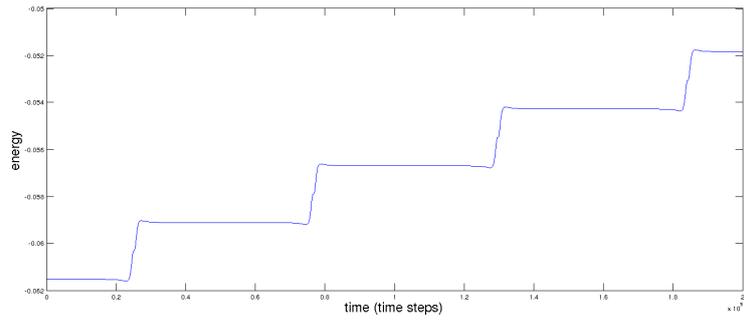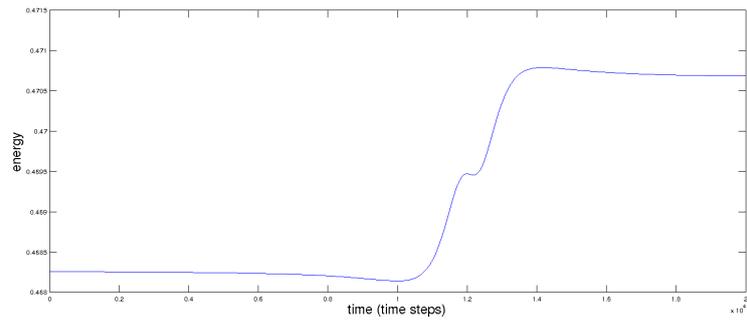Figure 2: position(x-component) plotted over time for the configuration 1.

Figure 3: y- vs. x-component of the position of molecule *A* (over time) for configuration 2.

(b) See exercise8.m. The trajectory of the first case is shown in Fig. **??**, where the position of molecule *A* (x-component) is plotted over time. Due to the attractive *and* repulsive forces, the molecule is moving towards and away from molecule *B* in an oscillatory manner. Considering the long-time behaviour shows that the current integration scheme is not conservative with this respect since the magnitude of the oscillation increases over time (not visible from the plot). The trajectory of the second scenario is shown in Fig. **??**: the x- and y-component of molecule *A* are plotted. Molecule *A* is first attracted by the molecule *B*. When approaching *B* the repulsive force moves *A* diagonally away from *B* again, due to *A*'s initial velocity.

(c) See computeEnergy.m. The energy for both configurations is shown in Fig. **??**. The energy obviously is not conserved. Two effects need to be considered. First, we keep molecule *B* fixed. This corresponds to an external force that we apply to this molecule: we always choose this force as big as the resulting force from the interaction of molecule *B* with molecule *A*, but with opposite sign. Second, the time integration scheme we apply in this exercise is not energy-conserving. Studies with two moving particles reveal that the second effect has a bigger impact in the two considered configurations.

(d) Removing any attractive forces from the simulation yields a completely different quality of the trajectories. The respective plots are shown in Fig. **??**.

Configuration 1

Configuration 2

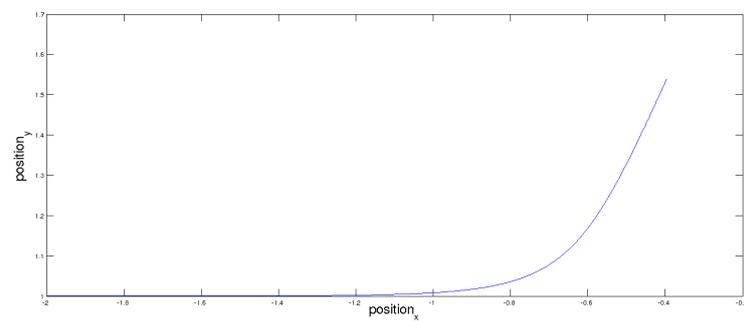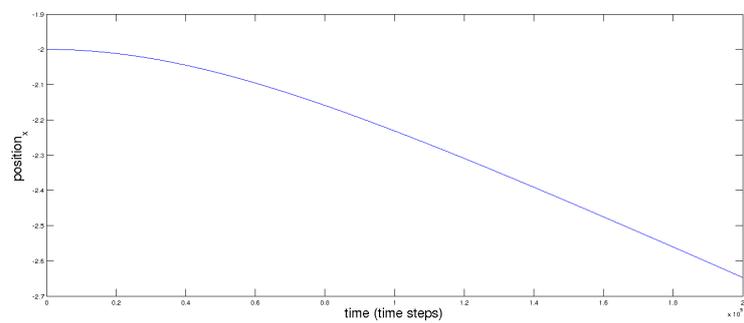Figure 4: Energy plotted over time for both configurations.

Figure 5: position(x-component) plotted over time for the configuration 1 (top) and y- vs. x-component of the position of molecule A (over time) for configuration 2 (bottom).