

# Molecular Dynamics Simulations: Final Report

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## 1 Molecular Dynamics Simulations code

### 1.1 Introduction

We consider an isolated system of  $N = 125$  particles with density  $\rho = 0.7m/\sigma^3$  trapped in a region with PBC. Initially, the particles are located at the vertices of a simple cubic lattice with a bimodal velocity distribution, with which the kinetic energy  $K$  is compatible with  $k_B T = 100\epsilon$ . Then, we let the system evolve through the action of an integrator (*Velocity Verlet* or *Euler*) for  $10^4$  time steps, and we analyze its thermodynamic properties.

The Lennard-Jones potential describes the interactions between particles:

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

Here, it is written in reduced units since it is more natural to do simulations with dimensionless quantities. We introduce a *cutoff* parameter  $r_c = L/4$  that establishes a distance above which interactions are ignored. This reduces the computational cost, but produces discontinuities in the potential that we must fix with truncation:

$$u_{LJ}(r) = \begin{cases} u_{LJ}(r) - u_{LJ}(r_c) & r \leq r_c, \\ 0 & r > r_c. \end{cases}$$

The Velocity Verlet integrator uses velocities to take the system to the next dynamic step:

$$\begin{aligned} r_i(t + \Delta t) &= r_i(t) + v_i(t)\Delta t + \frac{f_i(t)}{2m_i}\Delta t^2, \\ v_i(t + \Delta t) &= v_i(t) + \frac{f_i(t) + f_i(t + \Delta t)}{2m_i}\Delta t. \end{aligned}$$

It is a fast and convenient algorithm to use when the system interacts with a thermal bath. On the other hand, the Euler integrator uses both distances and

velocities to update the state of the system:

$$r_i(t + \Delta t) = r_i(t) + v_i(t)\Delta t + \frac{f_i(t)}{2m_i}\Delta t^2 + \mathcal{O}(\Delta t^3),$$

$$v_i(t + \Delta t) = v_i(t) + \frac{f_i(t)}{m_i}\Delta t + \mathcal{O}(\Delta t^2).$$

Its disadvantages are the energy drift and the lack of symmetry under time reversal. In both equations,  $f_i$  is the force associated with the Lennard-Jones potential.

## 1.2 Results

Figure 1 shows the results obtained with the Velocity Verlet integrator. For  $\delta t = 10^{-3}$ ,  $K$  and  $U$  fluctuate more intensely. However, in both cases the total energy and momentum are conserved.

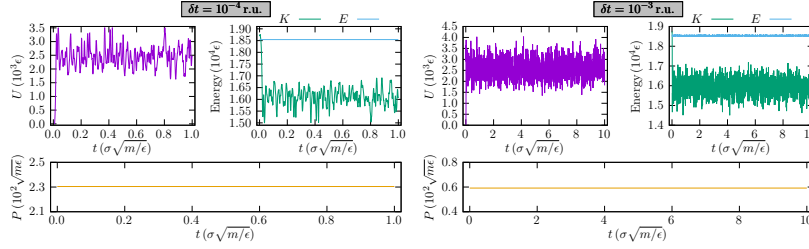


Figure 1: Energies and total momentum calculated with the Velocity Verlet integrator for different time increments  $\delta t$ .

On the other hand, Figure 2 shows the results obtained with the Euler integrator. For  $\delta t = 10^{-4}$ , the energies are reasonable even though the total energy is not preserved. For  $\delta t = 10^{-3}$ , however, the energies blow up which is a manifestation of the integrator's flaws. In both cases, the total momentum is a conserved quantity.

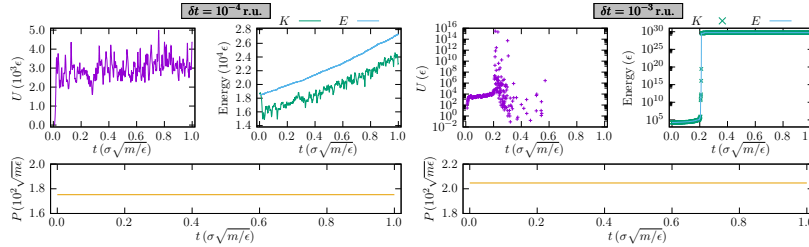


Figure 2: Energies and total momentum calculated with the Euler integrator for different time increments  $\delta t$ .

Finally, Figure 3 shows the initial and equilibrium velocity distributions of the particles obtained with the Velocity Verlet integrator for  $\delta t = 10^{-4}$ . The

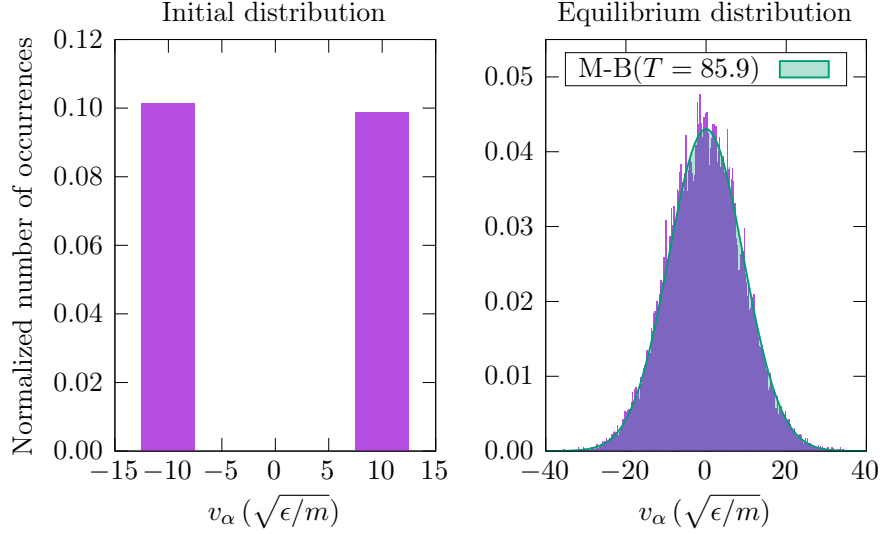


Figure 3: Initial and equilibrium velocity distributions of the particles obtained with the Velocity Verlet integrator for  $\delta t = 10^{-4}$ .

system leaves the initial bimodal distribution as it evolves and cools down, eventually reaching a Maxwell-Boltzmann equilibrium distribution

$$f(v_\alpha) = \frac{1}{\sqrt{2\pi T}} \exp\left(-\frac{v_\alpha^2}{2T}\right).$$

## 2 Properties of a Lennard-Jones liquid

### 2.1 Introduction

We consider a system of  $N = 125$  argon atoms trapped in a region with PBC. Initially, the atoms are at rest at the vertices of a simple cubic lattice. After melting the crystalline structure, we put the system in contact with a thermal bath at  $k_B T = 2\epsilon$  using an Andersen thermostat, and let it evolve with the Velocity Verlet integrator for  $10^6$  time steps. The objective is to obtain the thermodynamic properties of the system.

As in the previous section, the atoms interact through the Lennard-Jones potential and the simulation is carried out with reduced units. Once finished, we retrieve the physical units multiplying the different quantities by an appropriate combination of parameters (Table 1).

### 2.2 Results

Figure 4 shows the energies and pressure of the system for several density values. As density increases, the space available for the atoms shrinks, they collide more

frequently and pressure raises.

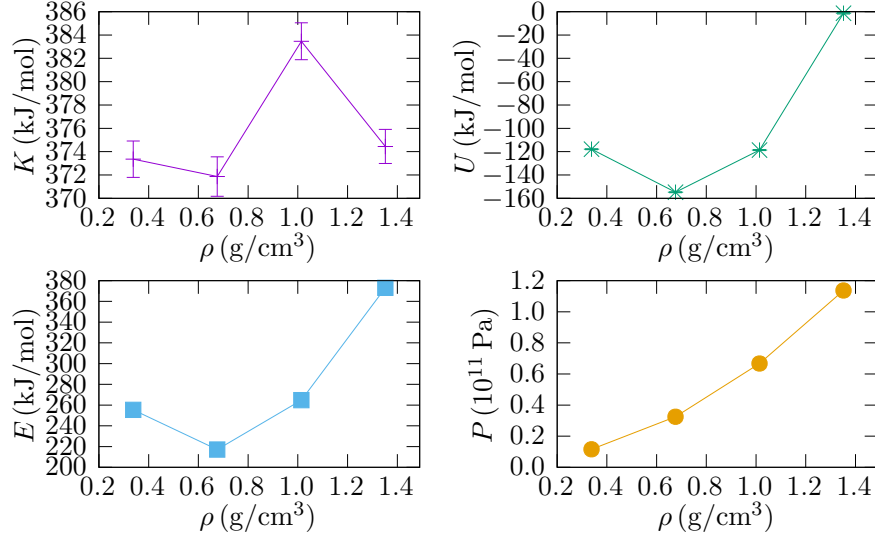


Figure 4: Equilibrium values of the averages of the energies and pressure of the system evaluated with the Velocity Verlet integrator. The error bars come from the block average method.

We also study the time evolution of the Mean Square Displacement (MSD) of argon atoms for  $\rho = 0.6m/\sigma^3$  and  $k_B T = 2\epsilon$  without PBC; see Figure 5. We repeat the simulation 10 times and we average over the realizations to obtain a more accurate result. Since

$$\text{MSD}(t) = 6Dt \quad (t \rightarrow \infty),$$

we can calculate the diffusion coefficient  $D$  with a linear regression:

$$D = \frac{a}{6} = 9.9743 \pm 0.0008 \text{ \AA}^2/\text{ps},$$

where  $a$  is the slope of the regression line.

## References

- [1] C. Calero, *Slides on Molecular Dynamics Simulations*, UB-UPC, 2021.
- [2] I have created a GitHub repository that contains the codes I have used to obtain the results.

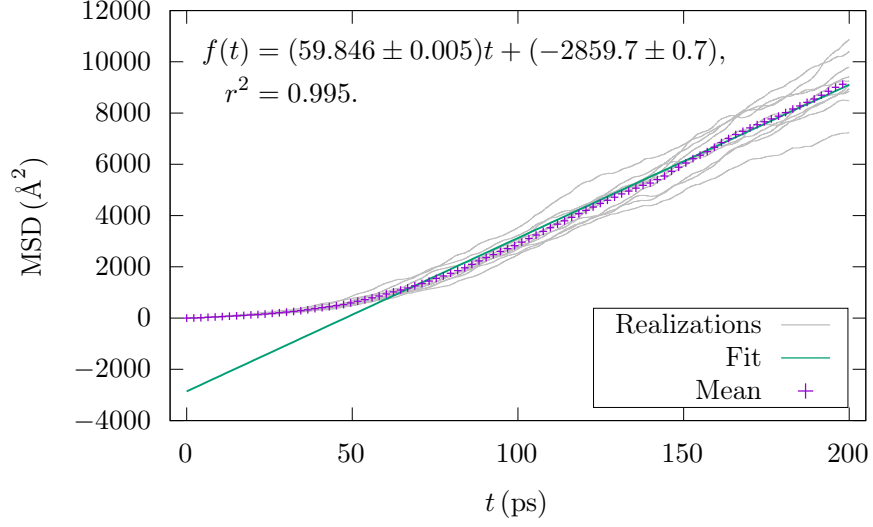


Figure 5: Mean Square Displacement as a function of time for a system of 125 argon atoms with  $\rho = 0.6m/\sigma^3$  and  $k_B T = 2\epsilon$  without PBC.

Table 1: Combinations of parameters required to retrieve the physical units of different quantities of interest.

| Physical quantity | Unit                       |
|-------------------|----------------------------|
| Length            | $\sigma$                   |
| Energy            | $\epsilon$                 |
| Mass              | $m$                        |
| Time              | $\sigma(m/\epsilon)^{1/2}$ |
| Velocity          | $(\epsilon/m)^{1/2}$       |
| Force             | $\epsilon/\sigma$          |
| Pressure          | $\epsilon/\sigma^3$        |
| Temperature       | $\epsilon/k_B$             |