Molecular Dynamics Simulations: Final Report

Adrià Meca Montserrat

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1 Molecular Dynamics Simulations code

1.1 Introduction

We consider an isolated system of $N = 125$ particles with density $\rho = 0.7 m/\sigma^3$ 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 $r_{\mathrm{c}} = L/4$ 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:

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

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

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

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

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.
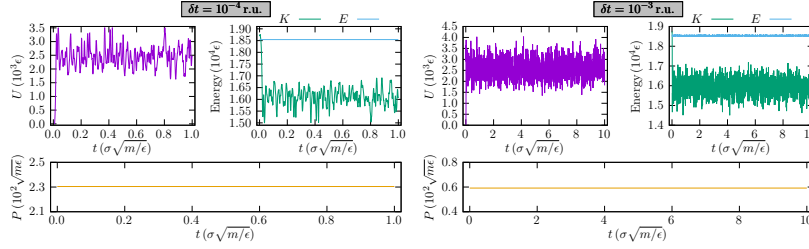

Figure 1: Energies and total momentum calculated with the Velocity Verlet integrator for different time increments δt.

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.
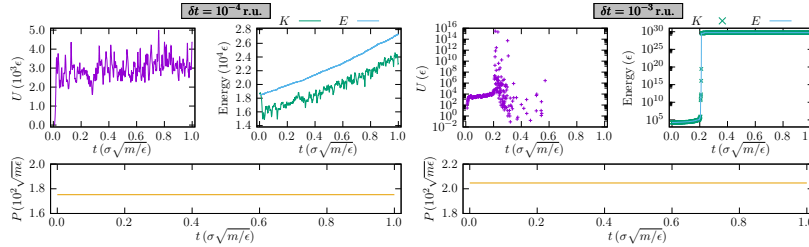

Figure 2: Energies and total momentum calculated with the Euler integrator for different time increments δt.

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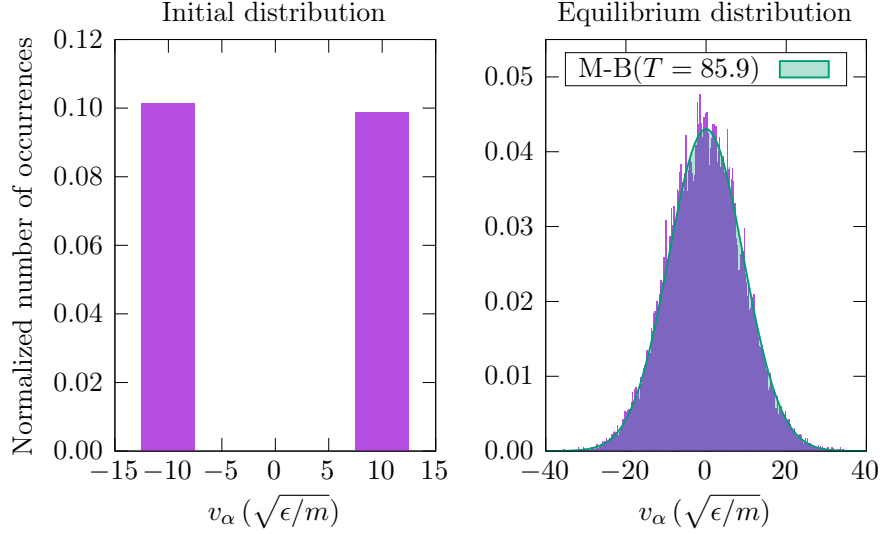
Figure 3: Initial and equilibrium velocity distributions of the particles obtained with the Velocity Verlet integrator for $\delta t = 10^{-4}$.

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 retrive 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

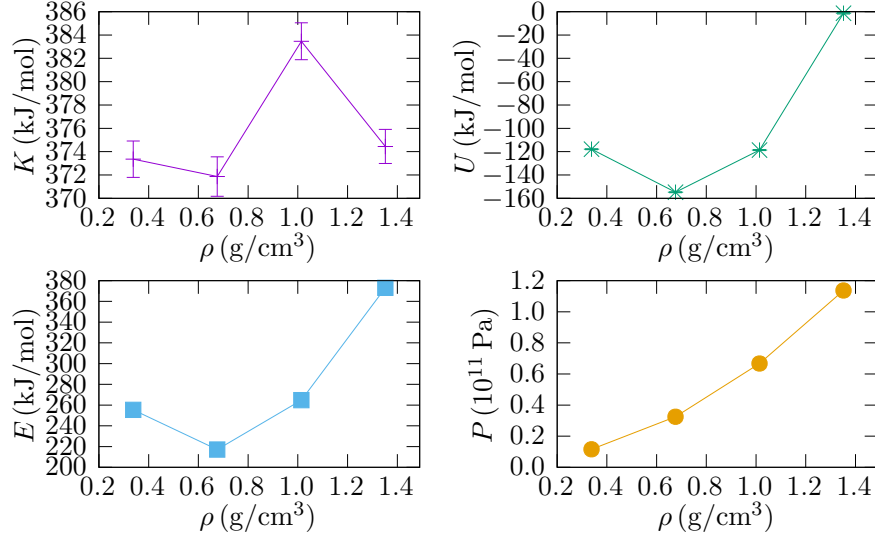frequently and pressure raises.

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 $\rho = 0.6 m/\sigma^3$ and $k_B T = 2\epsilon$; see Figure 5. We repeat the simulation 10 times and we average over the realizations to obtain a more accurate result. Since

$$\text{MSD}(t) = \lim_{t \to \infty} 6Dt,$$

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

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

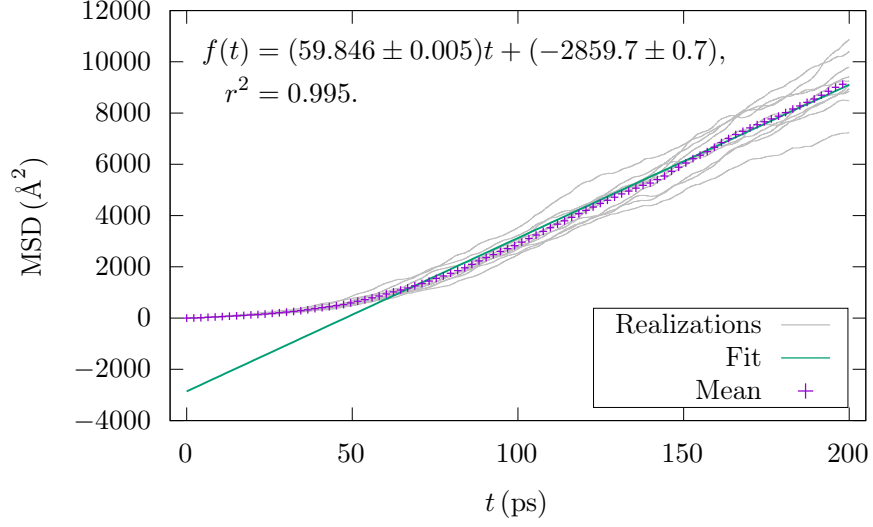where a is the slope of the regression line.

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Figure 5: Mean Square Displacement as a function of time for a system of 125 argon atoms with $\rho = 0.6m/\sigma^3$ and $k_B T = 2\epsilon$.

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

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