

Molecular Dynamics

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1 Methods

Molecular Dynamics simulations consist in numerically integrating the equations of motion of a system, starting from an initial configuration, and measuring time averages of quantities of interest.

1.1 Initial Conditions

Our system consists of N particles in a cubic box $[0, L]^3$, which gives a particle density of $\rho = \frac{N}{L^3}$. The initial positions were chosen at random with uniform probability inside the box.

For initial velocities, we first generate every velocity component randomly with uniform distribution in the interval $[-1, 1]$. We then calculate the total momentum \mathbf{P} , and shift all the velocities equally such that the new total momentum is 0. Then, we rescale every velocity component by the same constant such that the total kinetic energy matches the desired temperature at which we want to perform our simulation:

$$E_{kin} = \sum_{i=1}^N \frac{mv_i^2}{2} = \frac{3Nk_B T}{2}.$$

1.2 Particle Interaction

We consider the Lennard-Jones potential energy between every pair of particles, given by:

$$u(r_{ij}) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] - e_{\text{cut}} & r_{ij} \leq r_{\text{cut}} \\ 0 & r_{ij} > r_{\text{cut}} \end{cases},$$

where

$$e_{\text{cut}} = 4\epsilon \left[\left(\frac{\sigma}{r_{\text{cut}}} \right)^{12} - \left(\frac{\sigma}{r_{\text{cut}}} \right)^6 \right]$$

and r_{cut} is the maximum distance two particles can have from each other to still be affected by each other's potential. In our simulations, we set $r_{\text{cut}} = \frac{L}{3}$.

To obtain the force, we determine the gradient of this potential, which gives:

$$\mathbf{f}_{ij} = -\nabla u = \begin{cases} -48 \frac{\mathbf{r}_{ij}}{r_{ij}^8} \left(\frac{1}{r_{ij}^6} - \frac{1}{2} \right) & r_{ij} \leq r_{\text{cut}} \\ 0 & r_{ij} > r_{\text{cut}} \end{cases},$$

1.3 Integration Scheme

The integration scheme we used in this assignment is the *Velocity Verlet* algorithm, whose recursive process for each particle goes as follows, given it's position $\mathbf{r}(t)$, velocity $\mathbf{v}(t)$ and force acting on it $\mathbf{f}(t)$:

$$\begin{aligned} \mathbf{r}(t + dt) &= \mathbf{r}(t) + \mathbf{v}(t) dt + \frac{\mathbf{f}(t)}{2m} dt^2 \\ \mathbf{v}(t + dt) &= \mathbf{v}(t) + \frac{1}{2m} (\mathbf{f}(t) + \mathbf{f}(t + dt)) \end{aligned}$$

We also apply periodic boundary conditions, not only implicitly in the calculation of the force but also explicitly in the position updates (apply them when a particles falls outside the box), such that all positions are always inside the box.

1.4 NVE and NVT

For the NVE ensemble, we just run the simulation as described above, storing E_{kin} and $E_{potential}$ at every time step. For the NVT ensemble, we define a frequency ν , and at every time step select each particle with probability νdt to ‘undergo a collision with a heat bath at temperature T ’, which in practice means setting its component's values to randomly generated ones according to the Maxwell-Boltzmann distribution:

$$f(v_i) = \sqrt{\frac{m\beta}{2\pi}} e^{-\frac{m\beta}{2} v_i^2},$$

which is a gaussian distribution with mean $\mu = 0$ and standard deviation $\sigma = \frac{1}{\beta m}$.

More specifically, right after we perform the a verlet step, we generate a random number in $[0, 1]$ with uniform probability, and if it less than the Andersen probability νdt we update that particles velocity components, each with a random value according to $f(v_i)$.

1.5 Autocorrelation and Diffusion

The velocity autocorrelation function for a given time difference Δt is evaluated, for N particles, and a run of length T , is given by:

$$\chi(\Delta t) = \frac{1}{N} \sum_{i=1}^N \frac{1}{T - \Delta t} \sum_{t=1}^{T-\Delta t} \mathbf{v}_i(t) \cdot \mathbf{v}_i(t + \Delta t)$$

With it, the diffusion coefficient D is given by the Green-Kubo relation, where d is the system's dimensionality (3 in our case):

$$D = \frac{1}{d} \int_0^\infty dt \chi(t)$$

2 Results

2.1 NVE ensemble

In our first NVE simulations, we were using $L = 5$ or $L = 10$ and $N = 100$, which created some divergences in E_{kin} and E_{pot} . Of course this was due to the average distance between particles in this configuration being too small, being easy for two particles to be too close (and thus have a huge potential energy) either right at the start of the simulation, when positions are generated randomly, or at any other instant of the simulation. Thus, we thought the most sensible thing to do was to use a higher L and low density, to minimize the possibility of two particles being generated too close to each other at the start. We also used a not very high temperature, such that initial velocities are not too high, which prevents particles from colliding so fast that would make our time step of $dt = 0.001$ too high. Thus, we changed to $L = 25$, which gives density of $\rho = 0.0064$.

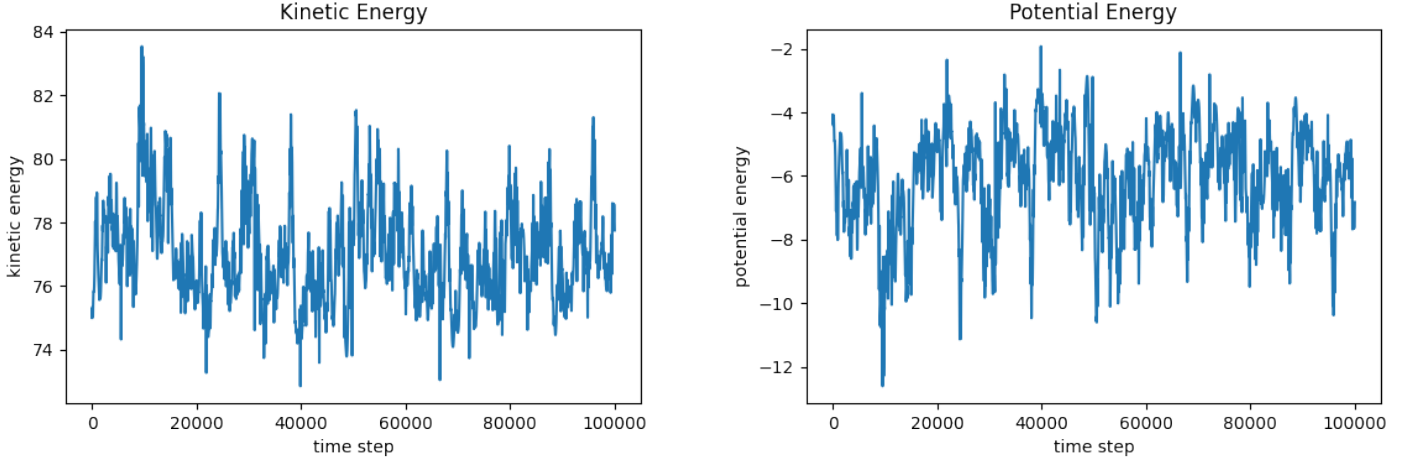


Figure 1: E_{kin} and E_{pot} values for the NVE ensemble, with $N = 100$, $\beta = 2$, $\rho = 0.0064$, $L = 25$

Let's analyze the plots above. Firstly, we have a visual confirmation that the way we initialized the velocities is correct, because the E_{kin} initial value should be $\frac{3}{2} \frac{N}{\beta}$, which is 75 for the values we used for N and β , and that is exactly the starting value that we see in the plot. Secondly, we can see roughly see that E_{kin} and E_{pot} have opposed behaviors, which is to expect from the NVE ensemble, because it's what we'd expect from a constant total energy. This is confirmed by the plot below, where we see that the total energy has a very low fluctuation in percentage around a value which is ≈ 70.93 . We can also see that the values of E_{pot} are negative. For $N = 100$, this implies not all particles are separated from each other by a distance in the 'sweet spot' range where the potential energy has a minimum, but most of them are, which makes sense since the initial velocities are low enough for the particles to converge to those spots instead of heading onto each other quickly and bouncing back outside that range.

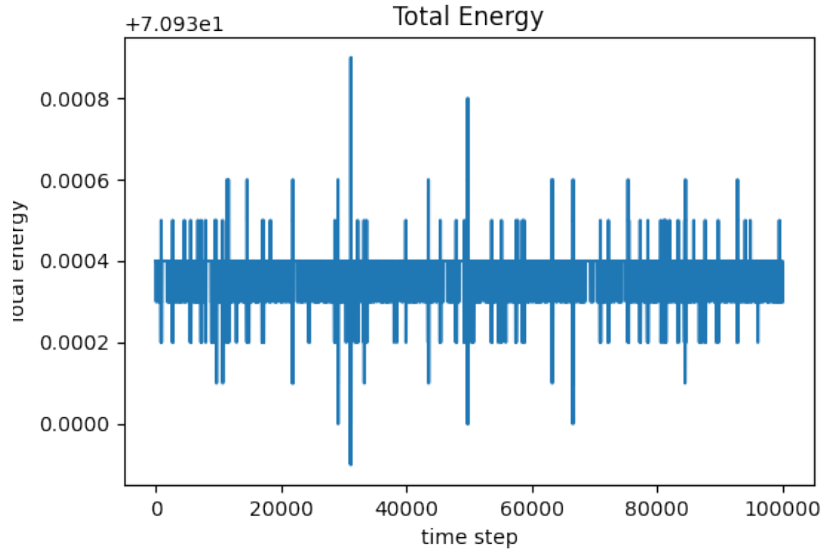


Figure 2: Total Energy values for the NVE ensemble, with $N = 100$, $\beta = 2$, $\rho = 0.0064$, $L = 25$

2.2 NVT ensemble

For the NVT ensemble, we first wanted to check if the thermostat was working correctly, so firstly we generated a lot of samples with the Maxwell Boltzmann distribution we intended to use in the simulations and plotted a normalized histogram of the samples, which came out as desired, represented in the Figure below:

Expected std deviation: 1.41421
Obtained std deviation: 1.4166876778038895

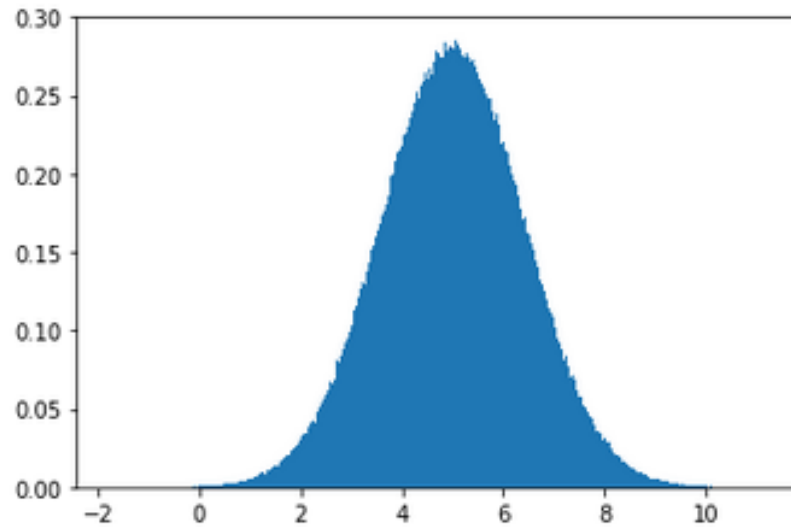


Figure 3: Maxwell-Boltzmann histogram

Secondly, we wanted to make sure that per time step $N \nu dt$ particles were chosen by the thermostat to change their velocity to a Boltzmann one, so we performed a simulation and plotted the average number of particles, which also came out as desired:

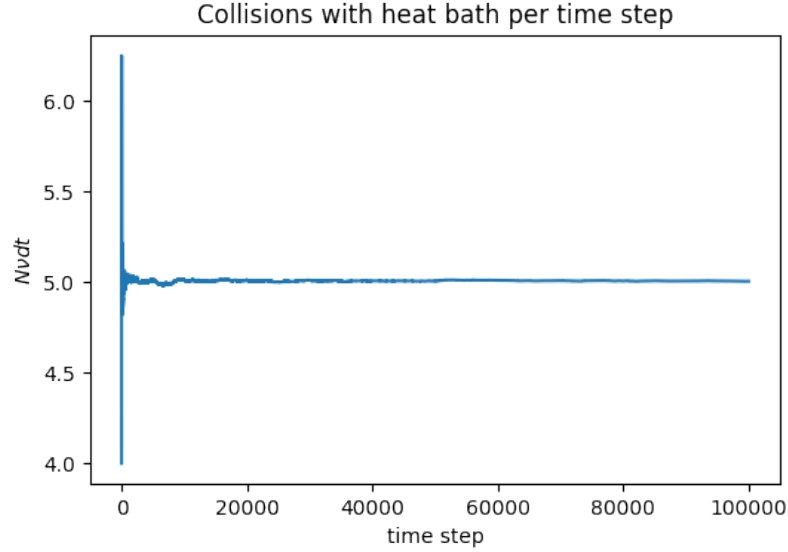


Figure 4: Average number of particles colliding with the heat bath per time step, with $N = 100$, $\nu = 50$, $dt = 0.001$

Running the simulations, we obtained the following curves for E_{kin} and E_{pot} :

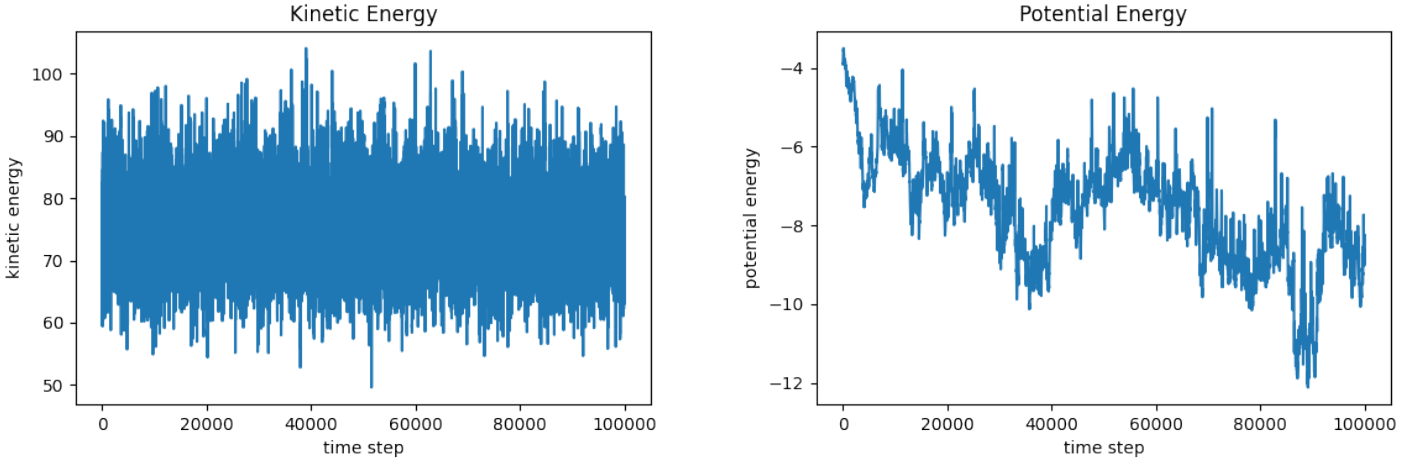


Figure 5: E_{kin} and E_{pot} values for the NVT ensemble, with $N = 100$, $\beta = 2$, $\rho = 0.0064$, $L = 25$, $\nu = 50$

We can observe that E_{kin} oscillates around the value 75, which makes sense since that is the value we determined for the initial E_{kin} , according to $E_{\text{kin}} = \frac{3Nk_B T}{2}$. Because E_{kin} only differs from the temperature T by a factor which is constant along the simulation, we can thus verify with confidence that the thermostat is working, i.e. is keeping the temperature roughly constant around the desired value. With the thermostat on, energy is not conserved, which means there is not direct observation we can make that relates our E_{kin} curve with our E_{pot} curve. Because of this lack of evident correlation, we don't think there is anything important to say about our total energy curve, represented below.

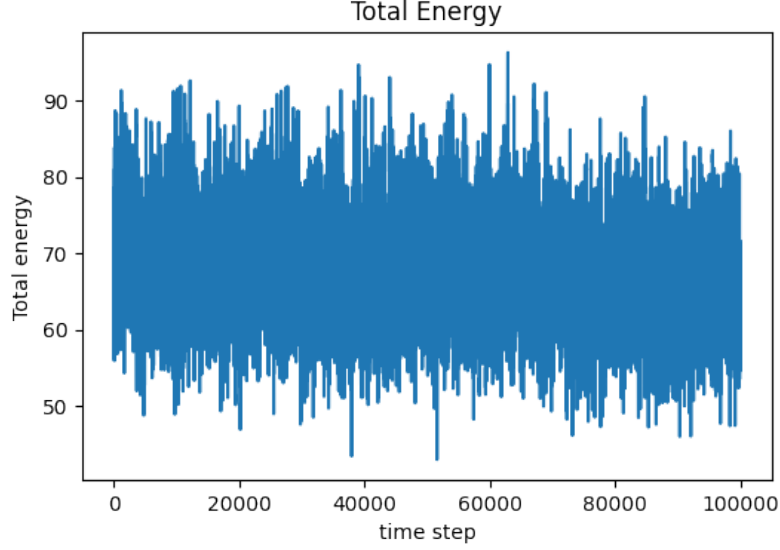


Figure 6: Total Energy values for the NVT ensemble, with $N = 100$, $\beta = 2$, $\rho = 0.0064$, $L = 25$, $\nu = 50$

2.3 Diffusion

2.3.1 NVE

Below we represent the velocity autocorrelation function we obtained for the NVE ensemble simulation to which the plots in the NVE section refer to.

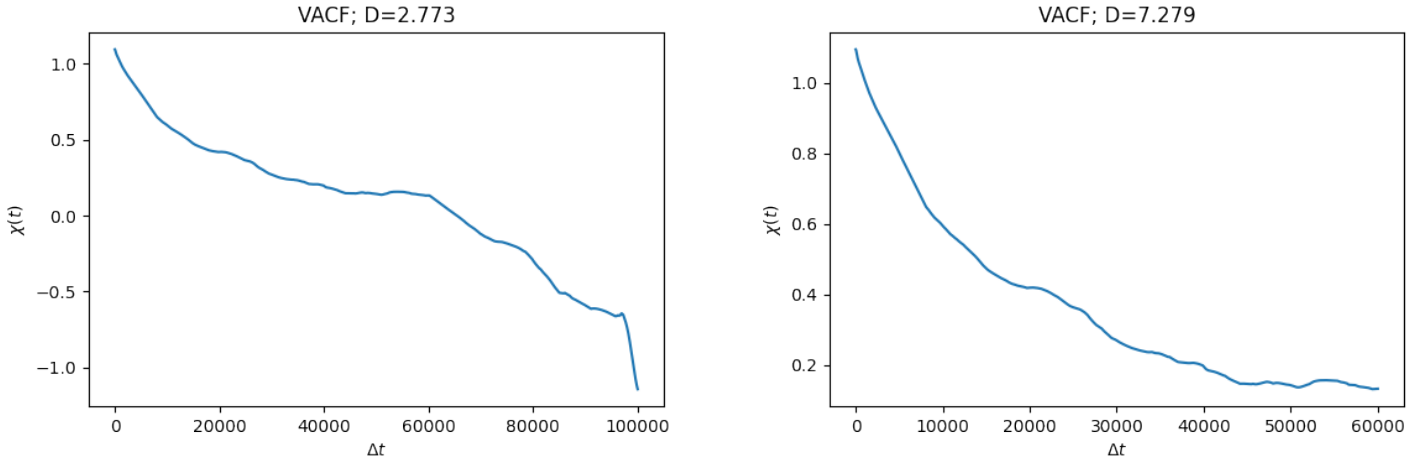


Figure 7: Velocity autocorrelation function for NVE ensemble, with $N = 100$, $\beta = 2$, $\rho = 0.0064$, $L = 25$

An important feature of the correlation function is that when two consecutive system configurations are highly correlated, as we had in the Ising single flip procedure, and as we have here, because the verlet procedure is completely deterministic and two consecutive system configurations are very similar. In those cases, as it is mentioned in the Ising notes, an autocorrelation function goes approximately as $e^{-t/\tau}$, and we think the first part of our plot, roughly until $t = 60000$, highly resembles that

curve, as we can see in the left curve. We find it a bit odd that that first part is compatible with what we expected, by the previous argument, and then the autocorrelation shows negative values.

Firstly, we can argue that as Δt approaches the total simulation time T , the sum used to determine the correlation function starts having less and less terms (e.g. for $\Delta t = T$, only value per particle is used), and thus the values around that final range start having less and less statistical significance. However, we also think it could be related to the average time a particle needs for it to have enough close encounters with other particles such that it reverts the direction of it's velocity vector, which would produce negative terms in the correlation calculation.

As far as the diffusion constant goes, the full run gives us $D \approx 2.773$, and the 'statistically relevant' part gives us $D \approx 7.279$.

2.3.2 NVT

Below we represent the velocity autocorrelation function we obtained for the NVT ensemble simulation to which the plots in the NVT section refer to.

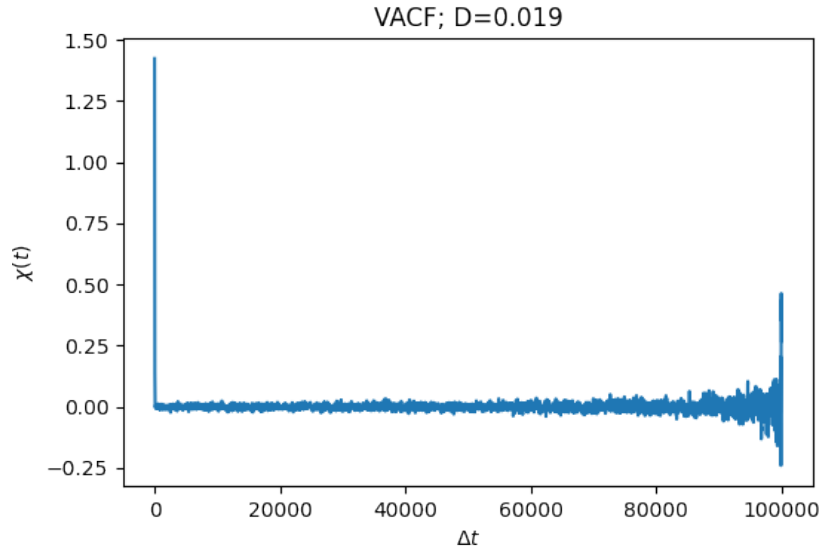


Figure 8: Velocity autocorrelation function for the NVT ensemble, with $N = 100$, $\beta = 2$, $\rho = 0.0064$, $L = 25$, $\nu = 50$

When the Andersen thermostat is switched on, when a certain particle is chosen to undergo a collision with the heat bath, it's velocity becomes completely uncorrelated with it's previous velocities, as its component values are changed to randomly generated ones. In our simulation, approximately 5 out of the 100 particles undergo this collision per time step, so in average 20 time steps are needed for every particle's velocity to have completely lost correlation with it's previous velocities, which is very little in the scale of the entire simulation. In the plot, we can see that the autocorrelation drops from 1.5 to 0 almost abruptly, and from there it's stays pretty much constant, which is completely compatible with the previous argument. Another important thing we can observe is that the autocorrelation starts to 'falsely' enlarge as Δt approaches T , which just comes in handy to support the argument of lack of statistical significance we gave before, for the NVE ensemble.