Molecular Dynamics: Lennard Jones Simulations

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Introduction

This report explores the implementation and analysis of a 2D Lennard-Jones molecular dynamics simulation. In this project, we focus on two fundamental ensemble types in molecular mechanics: the microcanonical ensemble (NVE) and the canonical ensemble (NVT).

The microcanonical ensemble (NVE) simulates an isolated system with a constant number of particles (N), volume (V), and total energy (E). The canonical ensemble (NVT), on the other hand, also has a constant number of particles (N) and volume (V), but in this case we keep the temperature (T) constant instead of the energy. This is done, in our case, by using a Berendsen thermostat.

Both types of simulations employ the truncated Lennard-Jones potential, which models both the attractive and repulsive forces between particles.

$$U_{\text{trunc}}(r) = \begin{cases} U(r) - U(r_c), & r \leq r_c \\ 0, & r > r_c \end{cases}, \text{ with } \quad U(r) = 4\left[\left(\frac{1}{r}\right)^{12} - \left(\frac{1}{r}\right)^{6}\right] \tag{1}$$

This potential is a fundamental model in computational physics and is most often used to accurately represents the behavior of noble gases. Furthermore the velocity-Verlet integration scheme is used to solve the equations of motion with the promise of having good computational efficiency and numerical stability.

To improve performance, a cell lists based approach for finding neighboring particles, with the goal of significantly reducing the computational complexity from $O(N^2)$ to $O(N)$. In order to enhance our understand of the system, several key properties of the sytem were analyzed. This includes energy conservation, temperature equilibration, and the radial distribution, providing key insights into the structural organization of particles.

By examining different temperatures and particle counts this project explores how system size and thermal energy affect particle dynamics and structural properties in both NVE and NVT ensembles.

This project was implement using Python, for further information regarding the implementation, consult the README provided in projects root folder.

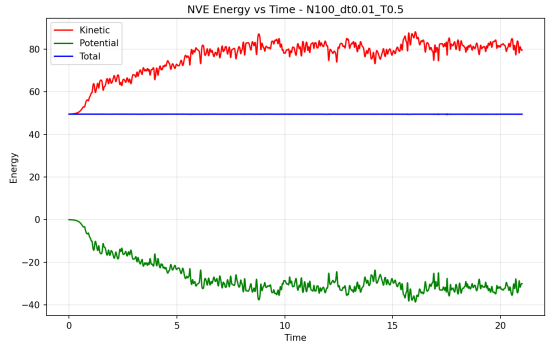
1 Energy-Conserving Dynamics: The NVE Ensemble

For the NVE simulation several different starting configurations were explored. The figure shown in the report were down with 100, 400 and 900 particles and varying timesteps, namely 0.01, 0.02 and 0.005 in order to evaluate the systems energy conservation properties and equilibration.

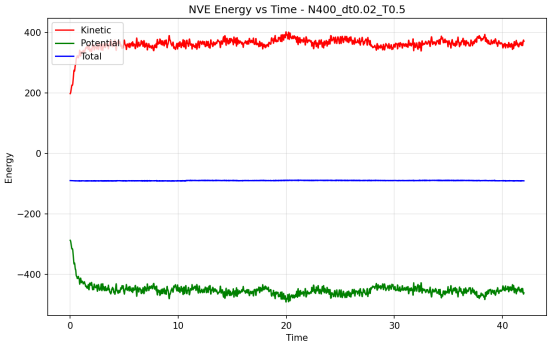
1.1 Energy Conservation

In Figure 1 one can observe the evolution of the kinetic, potential and total energy. All simulations show the expected behavior of constant total energy, while kinetic and potential energies evolve in a complementary pattern, which represent the constant exchange between the two types of energy. Please note that the equilibration period is included in these graphs, which allows us to analyze the time needed for the system to get to a equilibrium state.

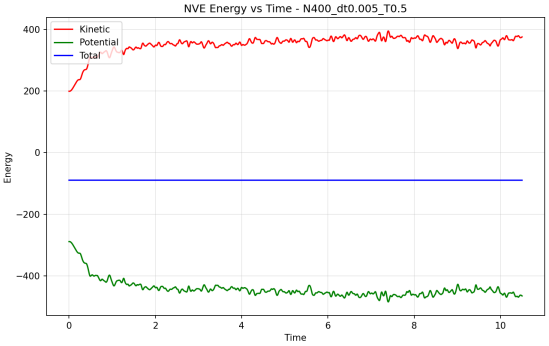
For a system with fewer particle, the graphs are showing that relative fluctuations in both kinetic and potential are larger in comparison to system with more particles. This behavior is expected, then large system usually show a more stable properties, due to the law of large numbers. Furthermore the time required to reach an equilibrium also takes longer in for smaller system in comparison to larger systems.



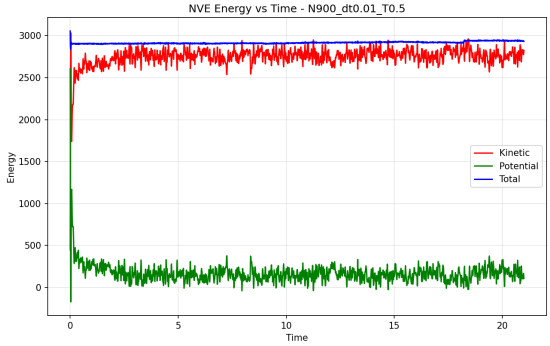
(a) N=100 particles with dt=0.01 and T=0.5



(b) N=400 particles with dt=0.02 and T=0.5



(c) N=400 particles with dt=0.005 and T=0.5



(d) N=900 particles with dt=0.01 and T=0.5

Figure 1: **Energy Conservation in NVE Ensemble** Analysis of total, kinetic, and potential energies over time for different system configurations.

1.2 Time Step Dependence

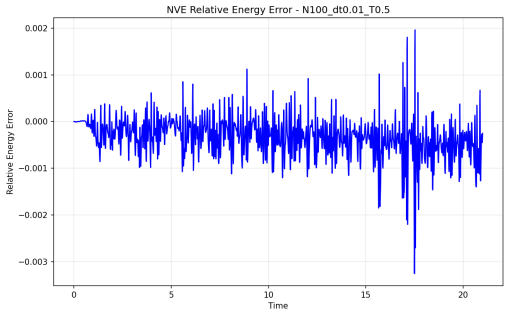
Figure 2 yields a crucial insight into the choice of a proper time step, by looking at the energy conservation error as a function of time. When comparing two simulation with the same size (in our case $N = 400$) and different time steps $dt = 0.02, 0.005$ we can make the following key observations, that the simulation with the large ($dt = 0.02$) step size, shows an significantly larger energy conservation error in comparison to the lower time step of $dt = 0.005$. This confirms the expected error that the velocity-Verlet integration scheme has, where for smaller time steps the scheme is more accurate resulting in a smaller energy conservation error.

1.3 Temperature Evolution

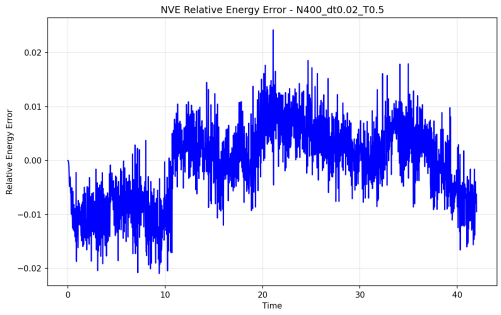
Figure 3 depicts the evolution of temperature over the duration of the simulation including the "warmup" period. We observe in all cases an initial temperature adjustment, followed by fluctuations around a constant temperature. Unlike the NVT ensemble where we have a target temperature, these NVE simulations have an initial temperature and then it evolves freely, based on the system dynamics. This is expected in NVE simulations due to the energy redistribution between kinetic and potential energy until the system reaches a natural equilibrium. We can observe that these fluctuations decrease when the number of particles increases and vice versa. These equilibrium times closely resemble the observed that of the energy evolution seen in Figure 1.

1.4 Momentum Conservation

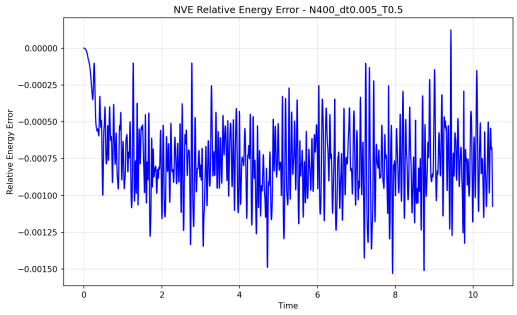
While not explicitly shown in the figures, all the simulation exhibit zero total momentum through out the complete simulation. In the real time visualization of this project, the indicator for total momentum is displayed. This conservation confirmed the proper implementation of the periodic boundary conditions and other physical properties.



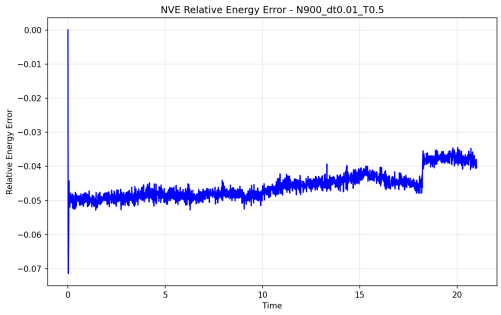
(a) N=100 particles with dt=0.01 and T=0.5



(b) N=400 particles with dt=0.02 and T=0.5

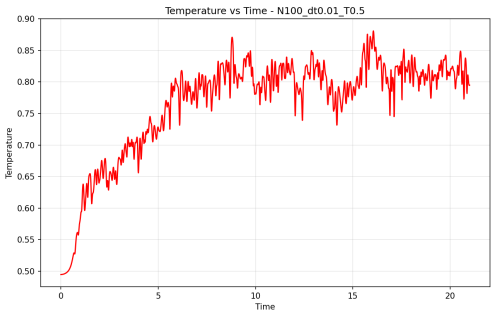


(c) N=400 particles with dt=0.005 and T=0.5

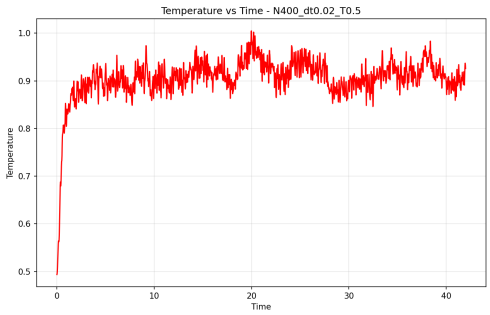


(d) N=900 particles with dt=0.01 and T=0.5

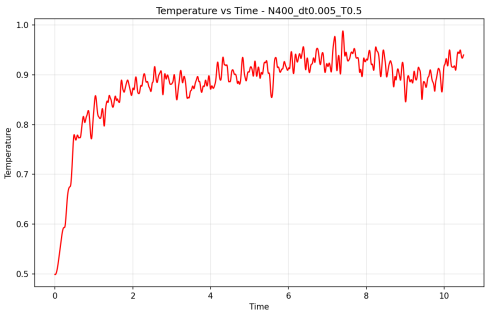
Figure 2: **Energy Conservation Error Analysis in NVE Ensemble** Relative energy conservation error over time for different system configurations.



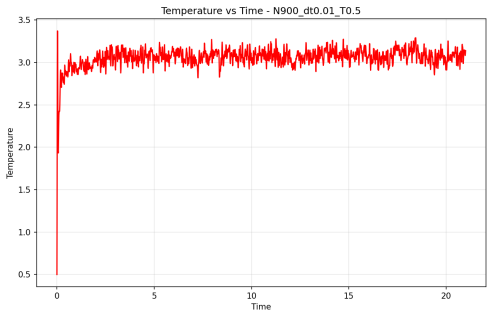
(a) N=100 particles with dt=0.01 and T=0.5



(b) N=400 particles with dt=0.02 and T=0.5



(c) N=400 particles with dt=0.005 and T=0.5



(d) N=900 particles with dt=0.01 and T=0.5

Figure 3: **Temperature Evolution in NVE Ensemble** Analysis of temperature fluctuations over time for different system configurations.

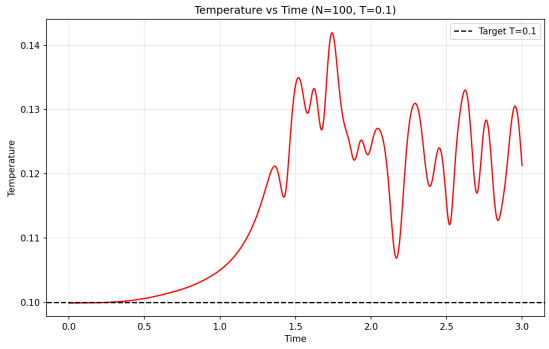
2 Temperature-Regulated Dynamics: The NVT Ensemble

For the NVT simulation we use the Berendsen thermostat with a relaxation time parameter of $\frac{dt}{\tau} = 0.0025$ to maintain constant temperature using various number of particles and target temperatures. In order to analyze the results we use the temperature evolution plots (Figure 4), which show how the system reaches its target temperature. Furthermore we plot the radial distribution function, shown in Figure 5 at the final time step, showing how density varies as a function of distance.

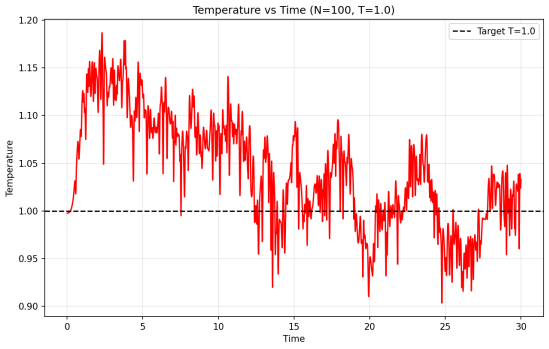
2.1 Temperature Regulation

In Figure 4 the plot show the application of the Berendsen thermostat across different configurations, the following observation can be made for each individual plot:

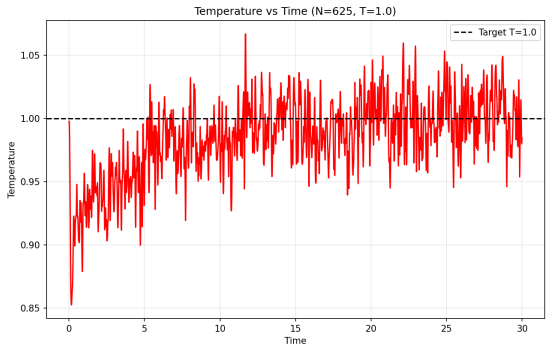
- For $N = 100$ and $T = 0.1$ in Subfigure 4a we observe that the thermostat fails to precisely maintain the target temperature, instead having an equilibrium at roughly 0.12 with very large oscillations. This shows that the Berendsen thermostat struggles to control the temperature in small systems at low temperatures. This could suggest to adjust the relaxation parameter, so the thermostat can more effectively handle the temperature.
- For $N = 100$ and $T = 1.0$ in Subfigure 4b the system shows initially temperature higher than the target temperature and then afterwards it approaches the target temperature and starts oscillating around it. These oscillations are rather high indicating the challenge of precise temperature control in small systems.
- For $N = 625$ and $T = 1.0$ in Subfigure 4c similar to the previous case we can observe a similar pattern of initial equilibration phase and then an oscillation around the target temperature, but in this case the system has reduced fluctuations amplitudes. This indicates that an increasing number of particles improves the temperature stability.
- For $N = 900$ and $T = 1.0$ in Subfigure 4d we can observe that the system starts at a significantly higher temperature than the target temperature and then gradually decreases until it reaches the target temperature. In comparison to the other cases this cooling process is rather smooth, which highlights the stability of system with a higher number of particles.



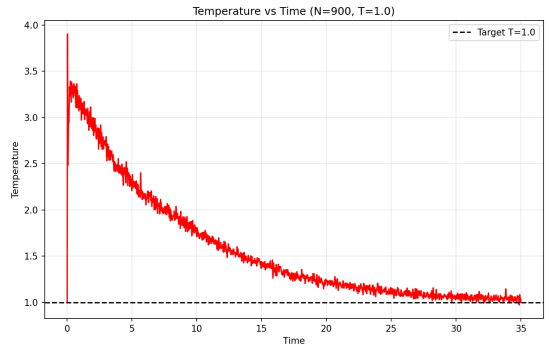
(a) N=100 particles with T=0.1



(b) N=100 particles with T=1.0



(c) N=625 particles with T=1.0



(d) N=900 particles with T=1.0

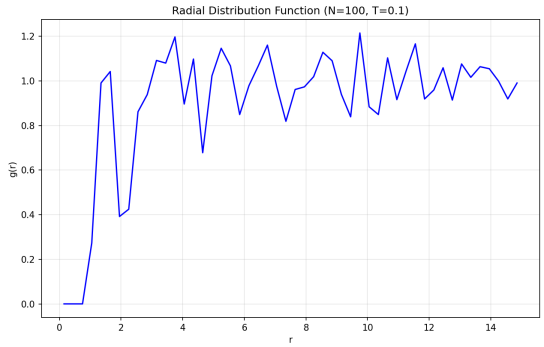
Figure 4: **Temperature Regulation in NVT Ensemble** Temperature evolution for different system configurations using the Berendsen thermostat.

2.2 Radial Distribution Analysis

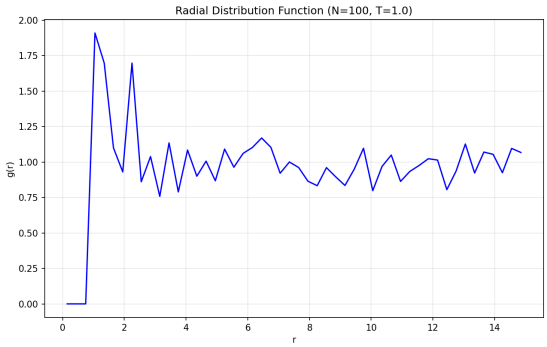
Figure 5 shows the radial distribution function, after equilibration for each of the system configurations. This reveals crucial insight into of the organization of the particles and even allows us to identify the physical state of the matter.

- For $N = 100$ and $T = 0.1$ in Subfigure 5a the RDF shows strong oscillations with distinct peaks extending to large distances. This indicates a solid crystalline structure, where the particles maintain a shell like structure of neighbors at specific distances. Due to the low temperature the movement of the particle is severely impaired, resulting in an order structure with long range correlation.
- For $N = 100$ and $T = 1.0$ in Subfigure 5b the RDF presents a clear pronounced peak around 1.1, afterwards we can observe less defined peaks. This would indicate either a low-density liquid or possibly a dense gas.
- For $N = 625$ and $T = 1.0$ in Subfigure 5c the RDF again shows a clear peak, followed by a smooth approach towards unity at larger distances. This is characteristic behavior for a liquid phase with moderate density.
- For $N = 900$ and $T = 1.0$ in Subfigure 5d the RDF exhibits a well defined structure with multiple distinguishable peaks even for large distances. The higher number of particles leads to a high compressed liquid or a dense amorphous state. The system shows enhanced structural organization, due to its high density, placing it closer to liquid-solid phase.

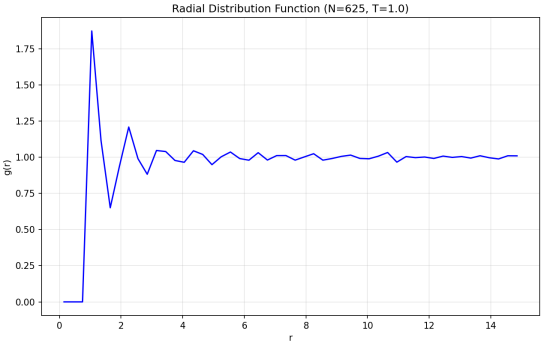
Another important observation is the across all the RDFs the first peak occurs around $r = 1.1$, which corresponds closely to the expected minimum of the Lennard-Jones Potential, giving further insurance to the validity of the simulations.



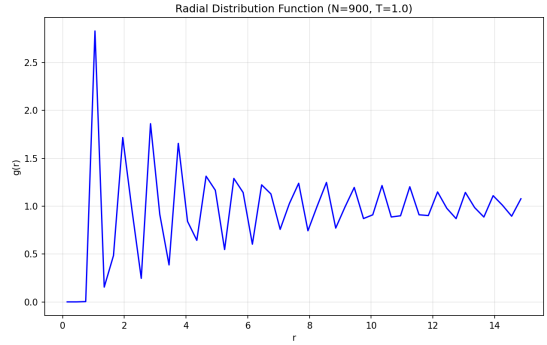
(a) N=100 particles with T=0.1



(b) N=100 particles with T=1.0



(c) N=625 particles with T=1.0



(d) N=900 particles with T=1.0

Figure 5: **Radial Distribution Functions in NVT Ensemble** Radial distribution functions for different system configurations

Conclusion

This study showed that the Lennard-Jones systems in NVE and NVT ensemble revealed multiple key findings. The NVE simulations with energy conservation was strongly depending on the step size with smaller steps yielding a better conservation. Furthermore the systems with a larger number of particles show greater stability and faster equilibration.

In NVT simulation, the Berendsen thermostat effectively regulated the temperature with different degrees of precision depending on the system configuration. The phase showed different behaviour depending on the number of particles and target temperature. Furthermore the RDF provided a very valuable insight to determine these states, with the peaks serving as sort of fingerprint to identify the state.