Monte Carlo: Simulating liquid Argon

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Introduction

In this report, the behavior of an NVT ensemble when modeled with Metropolis Monte Carlo, composed of Argon atoms, was investigated. Quantities such as: Potential energy, and position was studied. The position of the atoms manifested itself in the form of a radial distribution function $g(r)$, which represented the system's probability of finding an atom at a distance r from another atom. The potential energy of the system was also studied, and the energy of the system was plotted as a function of the number of accepted moves.

Quantities such as the specific heat capacity C_v was computed, and the result was compared to previously obtained results. The simulation implemented periodic boundary conditions, and thus effectively simulated an infinite system, in this case liquid Argon.

Theory & Method

Monte Carlo simulations are a class of algorithms that can be used to sample a molecular system. In contrast to molecular dynamics, Monte Carlo simulations do not require the equations of motion to be solved, and thus are computationally less expensive. This however implies that the Monte-Carlo simulation can not be used to simulate the time evolution of the system but rather the equilibrium state of the system. The energy of the system was modeled with a Lennard-Jones potential,

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right], \tag{1}$$

where r is the relative distance between the atoms, after assuming minimum image convention. The Metropolis Monte Carlo algorithm is structured in the following manner:

1. Pick a random atom
2. Propose a move
3. Calculate the change in energy if this move was supposed to occur
4. Accept or reject the move depending on $\min\left(1, \exp\left[-\beta \Delta E\right]\right)$
5. Update the system (if move was accepted, otherwise keep the system as it was)

This process is repeated for many iterations, such that the system reaches equilibrium. In contrast to molecular dynamics simulations, the Metropolis Monte Carlo algorithm is faster, it runs in $\mathcal{O}(N)$ time, where N is the number of atoms in the system, per iteration[1]. The radial function distribution, (RDF), $g(r)$ is measurement of the probability of finding an atom at a distance r from another atom, and is defined as

$$g(r_i) = \frac{V}{N} \frac{h(r_i)}{4\pi r_i^2 \Delta r}. \tag{2}$$

The specific heat capacity C_v is defined as:

$$C_v = \frac{3k_b}{2} - \frac{N\sigma^2(\mathcal{V})}{k_b T^2}, \tag{3}$$

describes how the energy of the system changes with temperature, and is a measure of the system's ability to store energy.

[1] In the previously implemented Molecular dynamics simulation, the runtime was $\mathcal{O}(N^2)$ per iteration.

Result & Discussion

The Monte Carlo simulation was written in V, a static typed compiler language. The simulation ran for $0.5 \cdot 10^6$ iterations, where the potential energy and the radial function distribution was computed every 1000 iterations. This was done to ensure that the system had reached equilibrium, and that the system was ergodic. The temperature was set to 94.4 K, as this was the temperature at which the system was previously simulated with a Molecular dynamics simulation. The system was constructed in such a way that the acceptance rate was 28.38%. This is close to the target acceptance rate 30%.

The radial function distribution $g(r)$ was computed for each for a subset of iterations, and the average of the radial function was plotted in the figure below, fig 1.

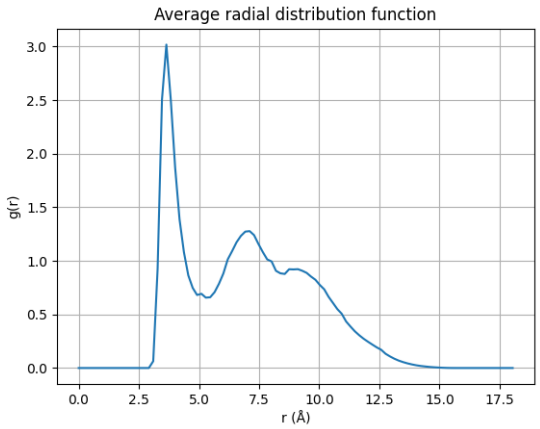

Figure 1: Average radial function $g(r)$

The peaks are located around $r = 3.7$ Å, $r = 7.3$ Å, and $r = 8.7$ Å, which agrees with preciously found results; the previous results were obtained with a Molecular dynamics simulation. Since Monte Carlo simulations are stochastic, the RDF fluctuates around the average value, which is given by the ensemble average, since we enforce ergodicity. Thus, even though this simulation is computed in the NVT ensemble, the RDF still predicts the same equilibrium state as the molecular dynamics simulation, which predicted an NVE ensemble.

The potential energy of the system, modeled by a Lennard-Jones potential (eq (1)), was used to model the energy of the system. If the energy decreased, the move was accepted, and if the energy increased, the move was accepted with a probability $\exp[-\beta \Delta E]$. Here ΔE is the difference in energy between the potential new configuration and the old configuration, and $\beta = \frac{1}{k_b T}$. The average energy of the system is computed in accordance to:

$$\langle \mathcal{V} \rangle = \frac{1}{n} \sum_{i=1}^{n} \mathcal{V}_i,$$

where n is the number of data points. This was computed to be: $\langle \mathcal{V} \rangle = -14.79$ eV, which is in agreement with the previously obtained results. The energy of the system was plotted as a function of the number of accepted moves, and the result is shown in fig 2.

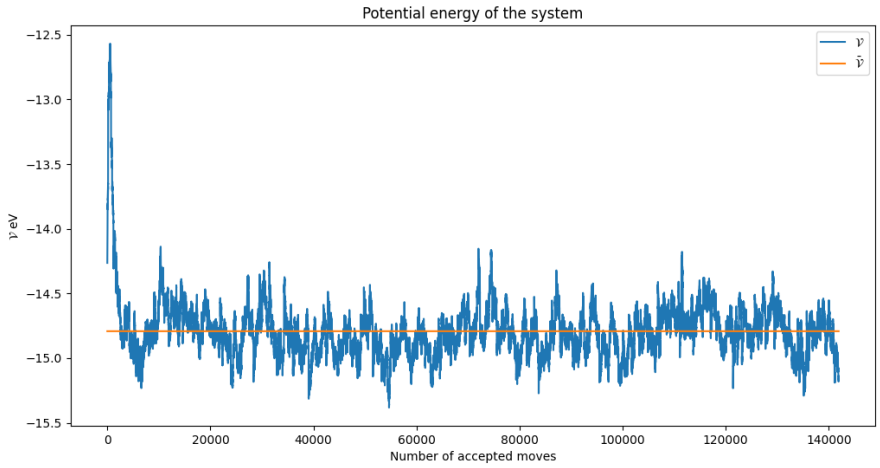

Figure 2: Energy of the system as a function of accepted moves

As the number of accepted moves increases, the potential energy quickly equilibrates, and fluctuates around the average value. To ensure that the system had equilibrated, the block-average method was implemented. This is shown in the figure below:

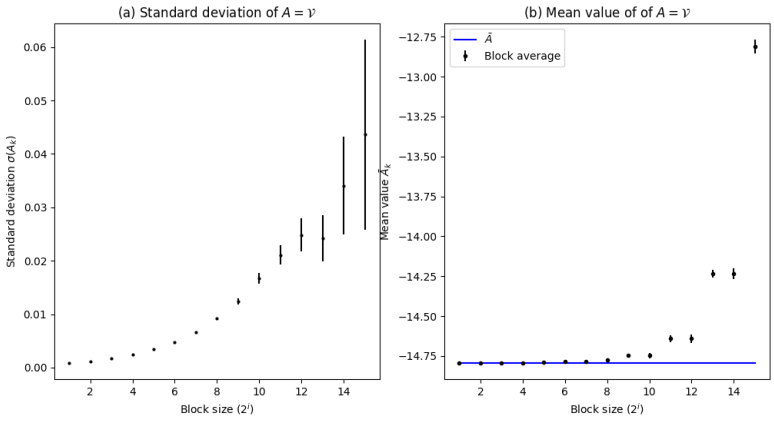

Figure 3: Block average of the potential energy

There is a plateau around $2^{12} = 4096$ block-transforms. This indicates that the system has equilibrated, and that the potential energy indeed fluctuates around the true average of the ensemble. The standard deviation of the potential energy is thus computed to be $\sigma(\mathcal{V}) = 0.22$ eV. The standard deviation of $\sigma(\bar{\mathcal{V}}) = 0.02$ eV, which is signifcantly smaller.

The specific heat-capacity is computed in accordance to eq (3), and was found to be:

Conclusion

In this report, the behavior of an NVT ensemble when modeled with Metropolis Monte Carlo, composed of Argon atoms, was investigated. The radial distribution function $g(r)$ was computed, and the potential energy of the system was studied. Both of these quantities were in agreement with previously obtained results, which were obtained with a Molecular dynamics simulation. As the number of accepted moves increases, the potential energy quickly equilibrates, and fluctuates around the average value, similar to the previous simulation. This is expected in the simulated ensemble.