Molecular Dynamics in the Canonical Ensemble

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In this report we produce a molecular dynamics simulation of a particle in a potential well in the canonical ensemble, investigating the relationship between the ensemble average of energy and the temperature.

1 Simulation

Our particle sits in the potential well given by the function:

$$U(x) = x^8 \tag{1}$$

This function acts similarly to an infinite potential well at low energies - as it provides an abrubt 'barrier' of extremely high energy - while being differentiable at all points, allowing us to apply Verlet integration for the motion. This potential is shown below:

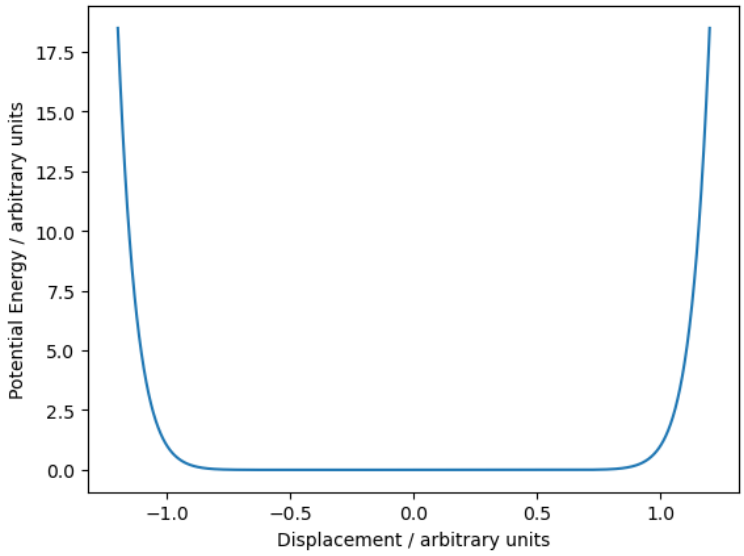

Figure 1: The potential energy function for our system, given by $U(x) = x^8$

To ensure the temperature of our system is kept constant, we apply a Langevin thermostat to the system, ensuring the states we reach are part of the same canonical ensemble.

We can check if our simulation performs correctly by ensuring it conserves energy; the sum of the mechanical energy and the energy added or removed by the thermostat should add to a conserved quantity, which is demonstrated in figure 2.

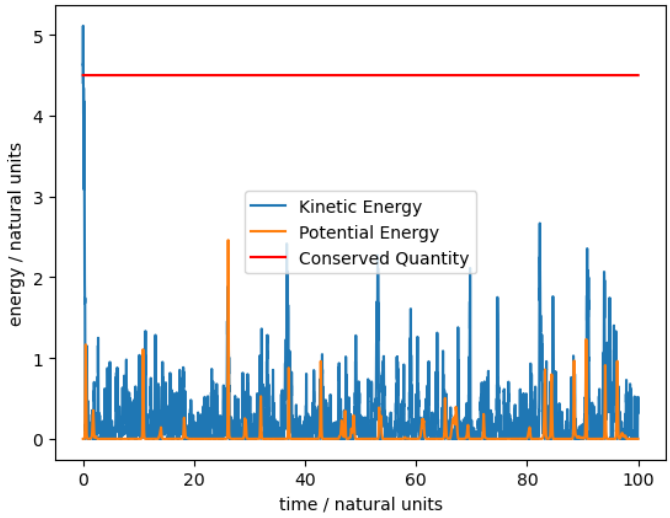

Figure 2: The total energy of our system, including the mechanical energy of the particle and the conserved quantity, which is the sum of the mechanical energy and the energy transfer to and from the heat bath. The simulation was run at a temperature of 0.5 arbitrary units.

2 Ensemble Averaging

To estimate an ensemble average energy for a given temperature we use block averaging and report the error of our simulation. We must first ensure that our particle is at a stable equilibrium to prevent the results being skewed by an initial settling period. We can see the position of the particle throughout the simulation in figure 3, wihch shows us that the particle oscillates around the point $x = 0$ from the start of the simulation.

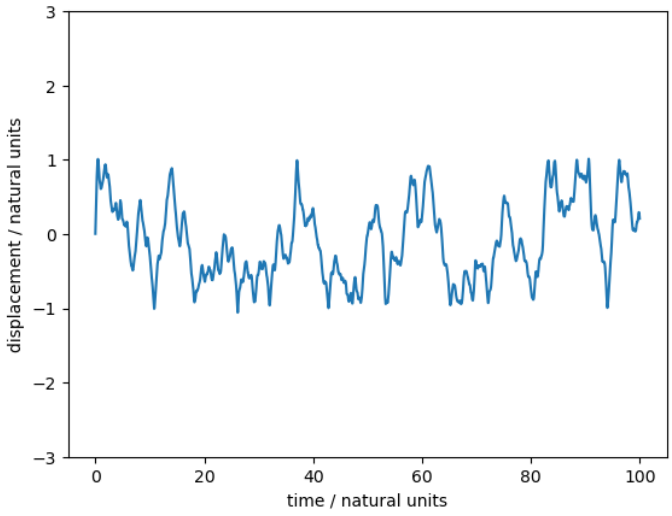

Figure 3: The displacement of our particle over time - computed as 100 000 simulation steps. The particle oscillates, with some degree of random fluctuation, around 0 displacement.

When taking block-averages to calculate ensemble averages and errors, we must ensure we do not under-report the error with blocksizes which are too small. In figure 4 we compare the errors for a range of block sizes and see that at a block size of 100 or lower, the error is underestimated by our method. We then use a block size of 200 in any further calculations.

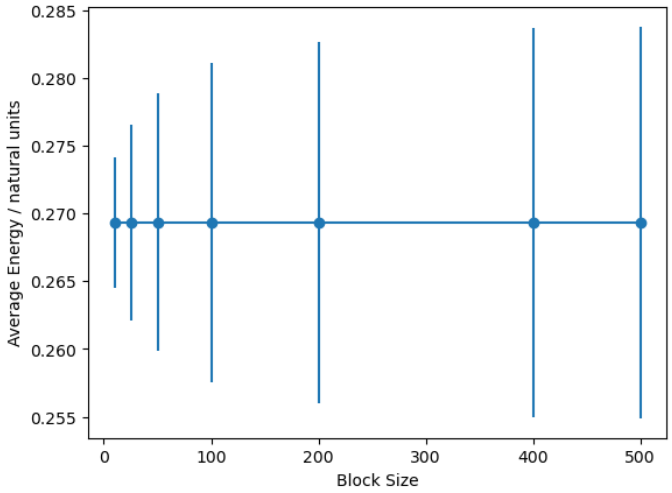

Figure 4: The average energy for a particle in a polynomial potential well, averaged using a molecular dynamics simulation with an error calculated using block averaging with a range of block sizes. We can see that the error is underpredicted for small block sizes, with the true result being reached from a block size of 200.

3 Results

We can now apply our simulation several times for a range of temperatures and record the averages for each. The reult of this is shown in figure 5.

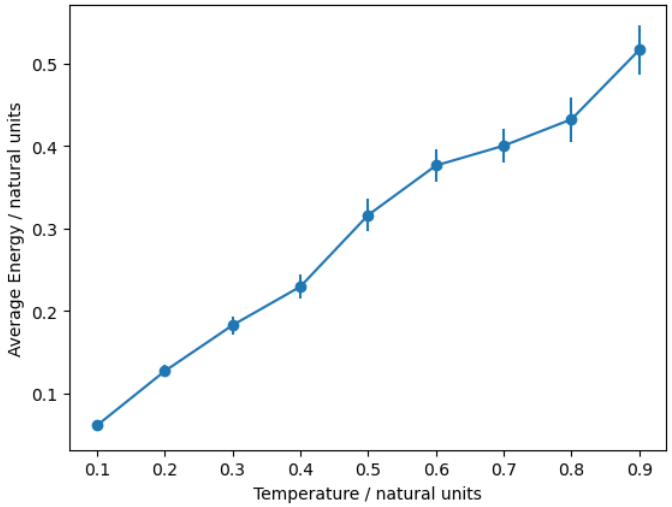

Figure 5: The average energy for a particle in a polynomial potential well as a function of temperature. The result was produced using a molecular dynamics simulation with a Langevin thermostat. The error is shown on the graph.

The relationship shown is approximately linear, with the deviation due to the implementation of the molecular dynamics simulation, which relies on finite approximation and random sampling.