The Harmonic Oscillator

Gareth Tribello[1]
[1]School of Mathematics and Physics

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Abstract

The heat capacity for a 1D classical harmonic oscillator as a function of temperature is estimated by performing constant temperature molecular dynamics. The values that we obtain from simulation are shown to be consistent with the values that the analytic expression for this quantity provide.

1 Introduction

Statistical mechanics describes how the properties of materials can be calculated by determining high-dimensional integrals. Analytic expressions for these integrals can be determined for systems of non-interacting particles and for some systems where the interactions between particles are relatively simple. However, for the majority of Hamiltonians, particularly those that provide accurate descriptions of real physical systems, it is not possible to arrive at an analytic expression for the ensemble average. For these systems, the only way to make progress is to perform an approximate calculation of the ensemble averages using a Monte Carlo method.

In this report, we will investigate how well molecular dynamics (MD) - one of these Monte Carlo methods - performs. We will use MD to calculate the average energy and the heat capacity of a one-dimensional, harmonic oscillator as a function of temperature. For a system this simple it is possible to calculate the partition function and ensemble averages analytically. We will thus show that the predictions of the analytic model are within the statistical errors of the estimates of these quantities that one obtains from MD.

The remainder of this report is laid out as follows. Some details on the system that we have studied are provided in section 2. This section also includes information on the bench marking we did to ensure that the averages that we extract from MD are converged. In section 3 we then report the heat capacity as a function of temperature and show that the results from our simulations match those that would be expected for a harmonic oscillator. We have calculated these heat capacities using two different approaches. The report finishes with a short conclusion in section 4

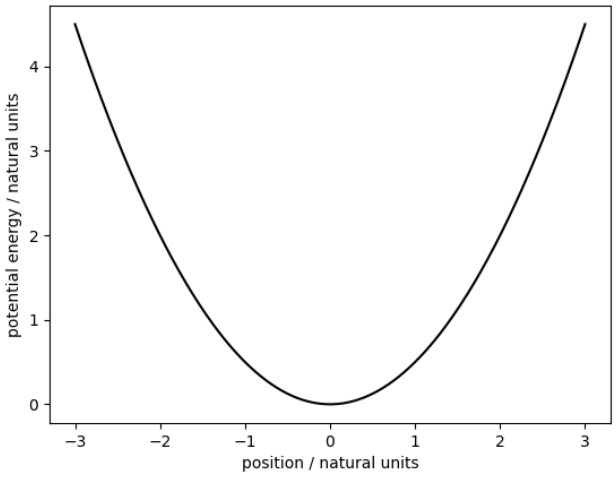

Fig. 1. The potential that the particle sits on in this work.

2 Methods

In this report, we have studied a classical particle with one position, x and one momentum coordinate, p. The particle sits on the following harmonic potential:

$$V(x) = \frac{1}{2}kx^2$$

Figure 1 shows a plot of this function. Furthermore, to simplify matters in what follows we will work in a system of natural units so both k and the mass of the particle will be set equal to 1.

Ensemble averages will be calculated from constant temperature molecular dynamics simulations. We will integrate Newton's equations of motion using the velocity Verlet algorithm with a timestep of 0.01 natural units in these simulations. Temperature will be kept fixed using a Langevin themostat with a friction of 1.0 natural units. Figure 2 shows how the kinetic and potential change over the course of 20000 step simulation that was run using these parameters at a temperature of 0.1 natural units.

The black line in figure 2 shows the conserved quantity for this simulation. This quantity does not change over the course of the simulation so we can conclude that the timestep is appropriately small.

If our thermostat is operating correctly the kinetic energy should fluctuate around a value of $\frac{1}{2}T$, where T is the temperature. You can see that the blue line in figure 2 fluctuates around 0.05 as it should. The average temperature in our simulation is 0.0458.

Figure 3 shows how the position coordinate of the particle changes over the course of the simulation. You can see that the particle takes some time to move away from the initial position and to the equilibrium position at $x = 0$. However, once this equilibration phase is completed the system simply fluctuates around the minimum in the potential. To ensure that

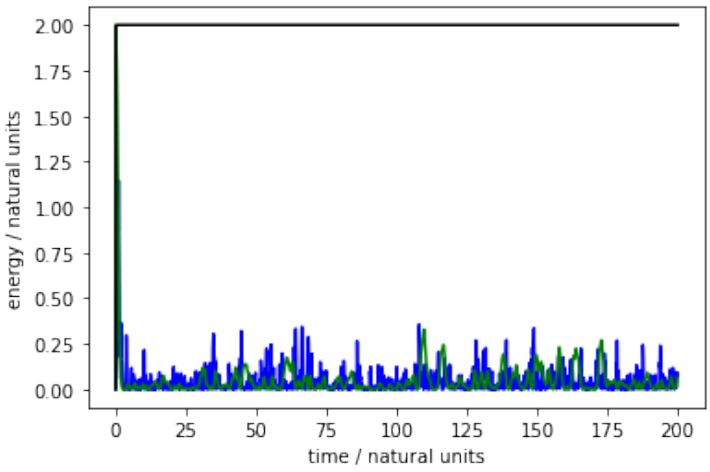

Fig. 2. The kinetic (blue) and potential (green) energies over the course of a 20000 step MD simulation. The most important line in this figure is the black line, which shows the conserved quantity. You can see that this quantity does not change over the course of the simulation, which tells us that the timestep has been set appropriately.

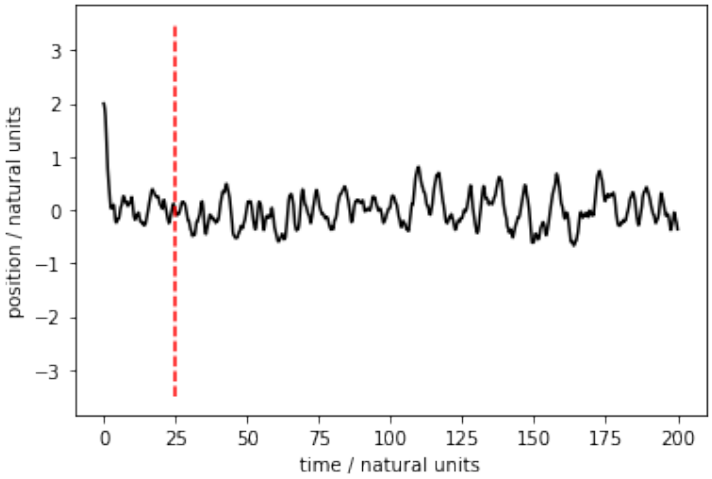

Fig. 3. The position the particle takes during 20000 step MD simulation. You can see that after a short equilibration, the particle fluctuates around the minimum at $x = 0$ during the simulation. The red dashed line shows how we divide our trajectories into an equilibration phase and a production part. The system is assumed to be equilibrating during the first 25 time units of of the simulation. Everything to the left of the right line is thus discarded and is not used when we calculate averages.

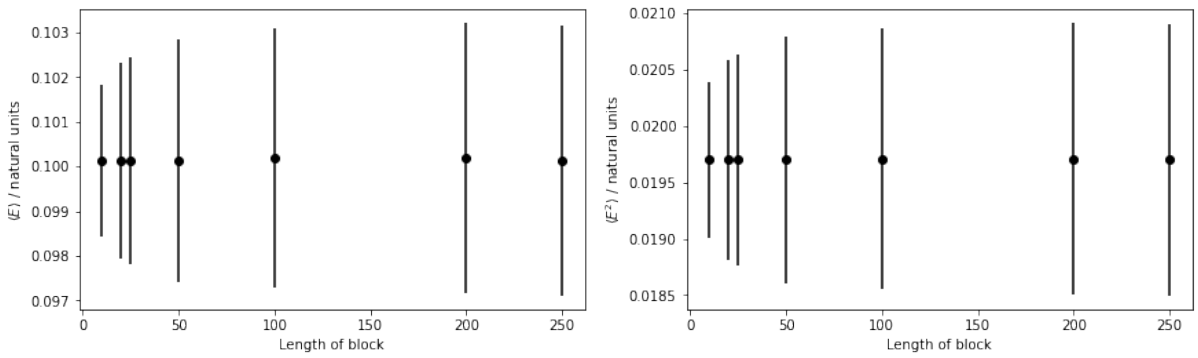

Fig. 4. The dependence of the estimates of $\langle E \rangle$ (left) and $\langle E^2 \rangle$ (right) on the sizes of the blocks that they were computed from. The averages (black dots) do not depend on the size of the blocks. However, you can see that when the blocks are small the error on the average (length of lines) is underestimated.

this part of the simulation where the system is equilibrating does not corrupt our averages we discard the statistics that are collected during the first 25 time units of all our simulations in what follows.

To calculate the heat capacities in section 3 we need to determine the average energy, $\langle E \rangle$, and $\langle E^2 \rangle$. As MD will give us an approximate average, we also need suitable estimates for the errors on these quantities. These errors for a 95% confidence limit are determined by block averaging. Figure 4 shows how the estimates of the errors depends on the lengths of the blocks that we use. This figure was generated by running a 1000000 step MD simulation in which statistics were collected every 10 steps.

Figure 4 shows that the error on the ensemble averages is underestimated when blocks with less than 50 statistics are used. We thus use blocks with a length of 100 to calculate all averages in what follows.

3 Results

Figure 5 shows how the average energy of the harmonic oscillator changes with temperature. The black dots in this figure are ensemble averages that were calculated from 1000000 step MD simulations at each of the temperatures. Averages were extracted from these simulations in the manner described in section 2.

We can calculate the partition function, Z, for the harmonic oscillator that we have investigated in our MD simulations by computing the following definite integral:

$$Z = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\beta(x^2+p^2)/2} \mathrm{d}x \mathrm{d}p$$

When this integral is inserted into Sympy we find that:

$$Z = \frac{2\pi}{\beta}$$

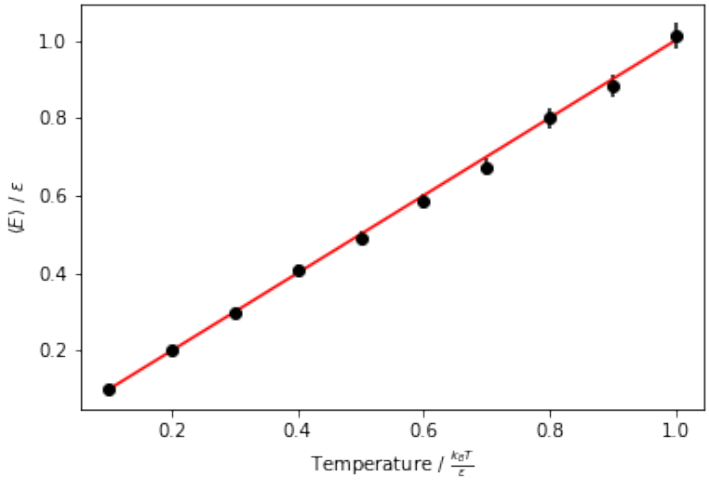

Fig. 5. The average energy of a harmonic oscillator as a function of temperature. The black dots are estimates of this ensemble average that were obtained from MD simulations. A 95 % confidence limit is shows on these estimates. The red line is the analytic expression for the average energy of a harmonic oscillator.

as long as we make the assumption that $\beta > 0$, which is reasonable as $\beta = \frac{1}{k_B T}$. We can determine the ensemble average of the energy by recalling that:

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}$$

Hence, for a harmonic oscillator:

$$\langle E \rangle = \frac{1}{\beta} = k_B T$$

In this work we are using a system of natural units so $k_B = 1$. The red line in figure 5 is the line $y = x$. This line, therefore, indicates the analytic expression above for the average energy of our Harmonic oscillator. You can see that this line is within the error bars on our MD simulations. What we get from simulation is thus consistent with what we obtain the theory above.

The constant volume heat capacity for a material is defined as:

$$C_v = \left(\frac{\partial \langle E \rangle}{\partial T} \right)$$

For the harmonic oscillator that we have studied in this work the heat capacity is thus $k_B = 1$.

We can estimate the heat capacity for our harmonic oscillator from the average energies in figure 5 by taking finite differences. The heat capacities, as well as errors that indicate a 95% confidence limit on our estimates, that we obtain using this approach are shown in black in figure 6.

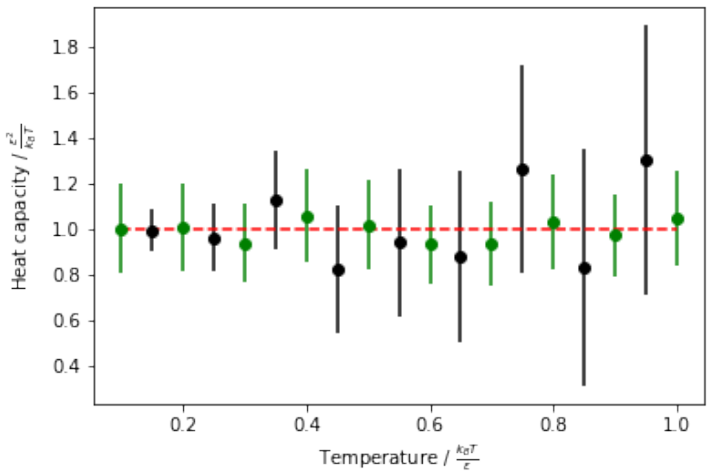

Fig. 6. The heat capacity as a function of temperature for a 1D harmonic oscillator. The black dots show the estimates for the heat capacity that were obtained by finite differences. The green points show the estimates that were obtained from the fluctuations in the energy. The red dashed line shows the analytic expression for the heat capacity of a harmonic oscillator as a function of temperature.

We can also estimate the heat capacity in an MD simulation using:

$$C_v = \frac{1}{k_B T^2} \left(\langle E^2 \rangle - \langle E \rangle^2 \right)$$

The estimates that we get for the heat capacity using this formula are shown in green in figure 6. You can see that the errors on these estimates are smaller than the errors on the estimates that we get using finite differences. However, for both methods the errors on our estimates for the heat capacity are larger than the differences between the difference between the estimate and the true heat capacity.

4 Conclusions

We have shown that we can use MD simulation to determine how the heat capacity for a one-dimensional, classical harmonic oscillator depends on temperature. The results that we obtain using this approximate methods are consistent with the analytic results for this system that can be easily derived. We can thus have some confidence in using MD simulation to determine heat capacities for systems where there is no suitable analytic expression for this quantity.

The analytic and numerical approaches that we have used for investigating the behaviour of the harmonic oscillator are only really appropriate when the temperature is large. When the temperature is low this approach is not appropriate because it assumes that particles are classical. At low temperatures, the particles true quantum nature begins to affect their properties and needs to be considered using techniques such as path integral simulations.