Exercise 1. Canonical Molecular Dynamics

Goal: So far, we considered microcanonical MD simulations where the total energy of the system is conserved. In this week's exercise we will simulate a system in contact with a thermal reservoir at fixed temperature T. There are several techniques to do this (see lecture notes). We will use the Nosé-Hoover thermostat which is the best in the sense that it reproduces the correct energy distribution corresponding to a canonical system.

The final equations of motion for our system are given by

$$m_i \ddot{\boldsymbol{r}}_i = \boldsymbol{f}_i - m_i \xi \boldsymbol{v}_i$$

$$\dot{\xi} = \frac{1}{Q}\left(\sum_i m_i \boldsymbol{v}_i^2 - (3N+1)k_B T\right)$$

where $3N+1$ is the number of degrees of freedom, T the desired temperature of the system and Q the coupling strength to the heat bath. The friction coefficient ξ is defined as

$$\xi = \frac{\dot{s}}{s}$$

where s is the additional degree of freedom introduced by the heat bath. Note that s itself does not appear in the simulation.

Task 1: *Extend your already existing MD code (exercise sheet 07) to simulate a canonical system with a given temperature.*

Task 2: *Observe the behavior of the instantaneous temperature $\mathcal{T}$ over time.*

Hint: Start with an initial configuration with instantaneous temperature $\mathcal{T}_0$, set the desired temperature T to a different value and observe the behavior of $\mathcal{T}$ over time.

Task 3: *When the system reaches thermal equilibrium, calculate the total energy of the system and plot the distribution. Can you observe the correct distribution?*

Task 4: *Repeat task 2 for different values of Q. What do you notice?*

Solution. We simulated a system of $N = 64$ particles in a box with side length $L = 5$. The final temperature was set to $T = 1$. Starting at $\mathcal{T}_0 = 0$ the system needs some time to equilibrate. This equilibration phase is manifested by large (larger than in equilibrium) fluctuations in the temperature. After the equilibration the instantaneous temperature $\mathcal{T}$ fluctuates with approximately constant amplitude about the desired temperature T. This is shown in Fig. .

The parameter Q describes the coupling to the heat bath. For smaller Q the system converges faster to the equilibium but the amplitudes of the temperature fluctuations around the desired temperature T are larger. For large Q the convergence to the equilibrium is slow but the fluctuations are much smaller. The limit $Q \to \infty$ corresponds to the limit of microcanonical MD.

The distribution of energies is shown in Fig. . We observe that the system energies are sharply peaked around $E \approx -75$. This is what we expect for a canonical system to happen. The relative width of the peak in a canonical ensemble is given by

$$\bar{\Delta E} = \frac{\sqrt{\langle H^2\rangle - \langle H\rangle^2}}{\langle H\rangle} \sim \frac{1}{\sqrt{N}}$$

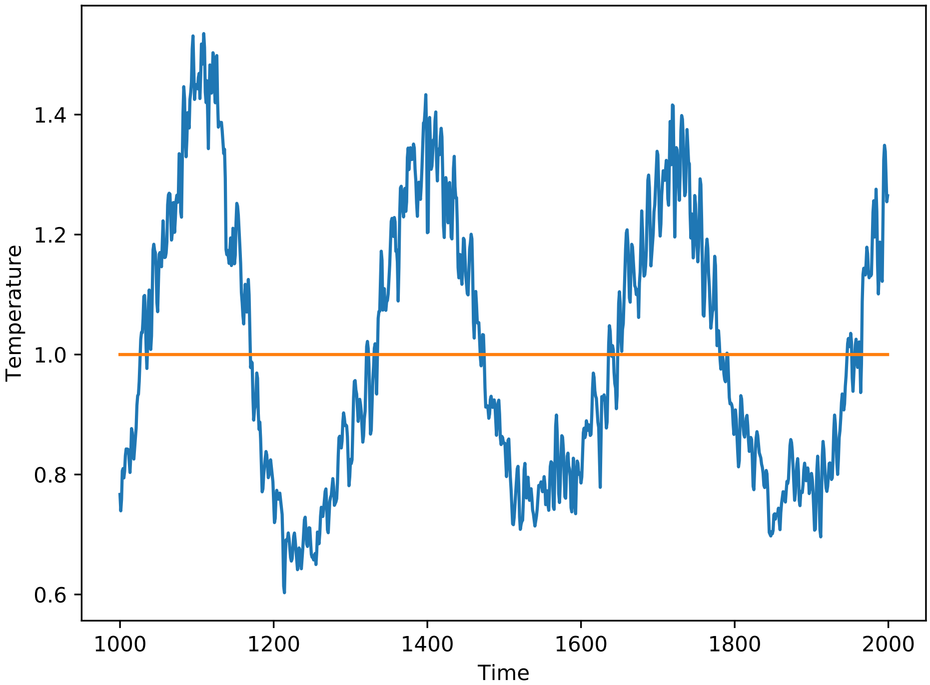

Figure 1: Temperature fluctuations for $Q = 250$.

where H is the Hamiltonian of the system. This means that most systems are expected to have the energy $\langle H \rangle$. For $N \to \infty$, we expect the width of the peak to vanish completely. The tail on the right hand side can be neglected as it belongs to the equilibration phase.

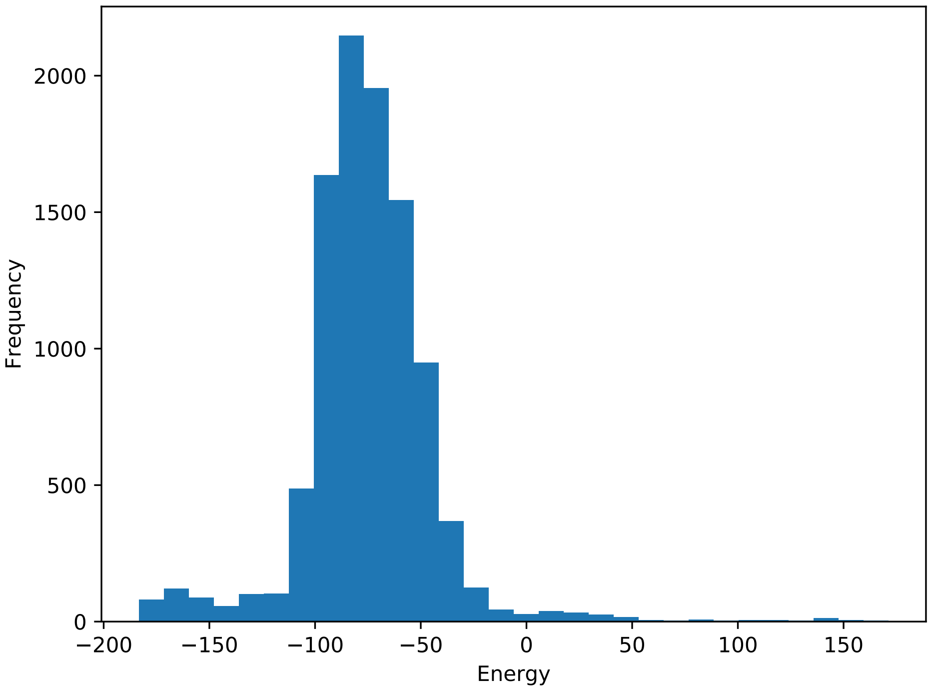

Figure 2: Energy distribution for $Q = 250$.