FINAL PROJECT—FYS4460

Introducing the Nosé-Hoover Thermostat in Lennard-Jones Systems

Alexander Fleischer

June 12, 2016

Introduction of the Nosé-Hoover thermostat and measurements of RMS-displacement using various thermostats. Discussion of the various thermostats for for various thermodynamic measures.

1. INTRODUCTION

In this final project, I've extended the studies of the Lennard-Jones system of Argon atoms, that we started in the first project. In particular, I've looked at three different thermostats—the Anderson, Berendsen and Nosé-Hoover thermostats.

Statistical mechanics is all about predicting the thermodynamic properties of a system. These properties could be the equations of state[1], phase transition[2] of the matter and so on. Studying such systems analytically often proves difficult, unless we are looking at idealizes, simple systems[3]. Luckily, we can study the realistic systems through numerical models. Molecular dynamics (MD) is a powerful tool to study the real systems more closely.

In a classical MD simulation we are often interested in studying the *microcanonical ensemble*. The ensemble is all the configurations a system can have under the conditions of constant number of particles N, volume V and total energy E. We therefore often refer to it as the NVE ensemble. A box of volume V with N particles that are unaffected by the surroundings is such an ensemble, and it can obviously have an enormous amount of different sets of states. Over time, we expect that all the particles microstates are equally likely to occur. This is called the *fundamental assumption of statistical mechanics*. If we now take the average of the whole ensemble and all its configurations, we can calculate the thermodynamic properties of the system.

For large and complicated systems, we will have difficulties calculating the ensemble average. Instead we simulate the system and its evolution over time with molecular dynamics methods. The reason for this is that the time-evolution average of our system should give us an estimate of the ensemble average.

---

[1]A thermodynamic equation that relates two or more of the system states, such as temperature, internal energy, pressure and volume.

[2]Going from for example solid to fluid.

[3]Such systems could be the Ising model, ideal paramagnets, Einstein solids etc.

2.   FROM THE MICROCANONICAL TO THE CANONICAL ENSEMBLE

The microcanonical ensemble had a constant energy since we didn't let any energy leave or enter the system. While the energy is constant, there would still be fluctuations in the temperature. By stabilizing the temperature, we go from microcanonical to the *canonical* ensemble. To make the temperature constant, we couple it to a heat bath of some desired temperature. This is called a thermostat.

Obviously energy will travel from or to the heat bath and the total energy is no longer constant—now we have a NVT ensemble.

For a finite system, though we claim to have a NVT ensemble, we will see some temperature fluctuations. We can find averages and variances from the Boltzmann distribution, and the system fluctuates as

$$\frac{\sigma_T}{\langle T \rangle} = \sqrt{\frac{2}{3N}} \tag{2.1}$$

This tells us that the system size determines the size of the fluctuations. As $N \to \infty$, the fluctuations fade away. A consequence is that the energy dies out too, and the microcanonical and canonical ensemble merge together.

To couple the system to the heat bath and creating the canonical ensemble, we will look at three thermostats: the Berendsen, Andersen and Nosé-Hoover thermostats.

A thermostat should satisfy some requirements:

- It should be able to control the temperature of the system such that it is close to the temperature of the heat bath.

- It should not disturb the system dynamics, and it should sample the quantities of the phase space (positions and velocities).

- It should be adjustable.

3.   TEMPERATURE MEASUREMENTS

To measure the temperature of the system in the NVE ensemble, we use the equipartition theorem. The equipartion theorem states that at thermal equilibrium, every quadratic degree of freedom in the Hamiltonian of the system must have an average energy of $1/2 k_b T$. Every atom in the system has three quadratic degrees of freedom in the kinetic energy, and there are N atoms, thus at equilibrium the kinetic energy is

$$\langle E_k \rangle = \frac{3}{2} N k_b T \tag{3.1}$$

This is the ensemble average of the kinetic energy, and as we saw earlier, the time-average for our system should be the same. The estimated temperature is then

$$T = \frac{2}{3} \frac{\langle E_k \rangle}{N k_b} \tag{3.2}$$

4. THE BERENDSEN THERMOSTAT

Many thermostats rescale the velocities of the systems' particles by a factor γ. One of these is the *Berendsen thermostat*. The scaling factor is

$$\gamma = \sqrt{1 + \frac{\Delta t}{\tau}\left(\frac{T_{\text{bath}}}{T} - 1\right)} \tag{4.1}$$

Here τ is called the *relaxation time*: which lets us adjust the (weak) coupling to the heat bath. A greater τ value gives a weaker coupling. This means that the Berendsen thermostat works by dampening the fluctuations of the systems' kinetic energy. The velocity scaling is such that change in temperature is proportional to difference in temperature between the heat bath and the system.

$$\Delta T = \frac{\Delta t}{\tau}(T_0 - T(t)) \tag{4.2}$$

The thermostat is not able to represent a correct canonical ensemble, but for large enough systems, we will achieve approximately correct results. It is often used because it effectively thermalizes the system to the temperature of the heat bath, and can be used to initalize a system before applying the Nosé-Hoover thermostat.

5. THE ANDERSEN THERMOSTAT

Another simple thermostat is the *Andersen thermostat*. It works by simulating collisions between particles in the system and in the heat bath. For every particle in the system we generate a random number uniformly generated between 0 and 1. If the number is less than $\Delta t/\tau$, we let the particle be one of the colliding particle. Thus the particle needs a new velocity, which is generated from a Boltzmann distribution with standard deviation $\sqrt{k_B T_{\text{bath}}/m}$. We can adjust the thermostat by changing τ, which can be considered the *collision time*. The collision time describes the strength of the coupling beween the system and the heat bath.

Assuming ergodicity, the Andersen thermostat gives us a canonical distribution of microstates. The Algorithm is non-deterministic and thus not time-reversible. It should only be used when measuring time-independent properties. Diffusion, which is something we have looked at, should not be calculated if the system has been influenced by the Andersen thermostat.

The thermostat is useful for equilibrating the system, but disturbs the natural vibrations of the crystal structure.

In project 1 we experienced that the Berendsen thermostat gave smaller fluctuations in the system than the Andersen thermostat.

6. THE NOSÉ-HOVER THERMOSTAT

Our goal in this project was to implement a more complicated and better thermostat. This is the Nosé-Hoover thermostat, and we wish to compare it to the two others. The Nosé-Hoover thermostat introduces the heat bath as an additional pair of degrees of freedom to the system—making the heat bath part of our system. It is done by introducing the degrees of freedom in the systems Lagrangian. It is done in such a way that when the total acts like a micro-canonical ensemble, the actual degrees of

freedom samples a canonical ensemble. It relies on that we introduce the virtual mass $Q > 0$ and the virtual velocity $\dot{\tilde{s}}$. The Lagrangian,

$$\mathcal{L} = \sum_i \frac{1}{2} m_i (s\dot{r}_i)^2 - u(r) + \frac{1}{2} Q \dot{s}^2 - g k_b T_0 \ln s \tag{6.1}$$

The first two terms are the kinetic and potential energy of the actual system, while the two last are the kinetic and potential energy of $\tilde{s}$. Here g is $3N + 1$ in the Nosé formalism. This uses $\tilde{s}$ as a time-scaling parameter, and the actual time step is not constant. In the Hoover formalism, $g = 3N$, and there is no time scaling. This means the time-step is constant. Then we can choose a friction parameter $\gamma = \dot{s}/s$. Now we don't have to solve the equations of motion for for the velocity (or momentum), and only include the friction in the equations. In MD units we then have

$$\dot{v} = F - \gamma v, \qquad \dot{r} = v, \qquad \dot{\gamma} = \frac{1}{Q}\left(2K - 3NT_0\right) \tag{6.2}$$

The integration scheme is now

$$v_{i+1/2} = v_i + (F_i - \gamma_i v_i)\frac{\Delta t}{2} \tag{6.3}$$

$$\gamma_{i+1/2} = \gamma_i + \frac{1}{Q}(2K_i - 3NT_0)\frac{\Delta t}{2}. \tag{6.4}$$

$$r_{i+1} = r_i + v_{i+1/2}\Delta t \tag{6.5}$$

$$v_{i+1} = v_{i+1/2} + (F_{i+1} - \gamma_{i+1}v_{i+1/2})\frac{\Delta t}{2} \tag{6.6}$$

$$\gamma_{i+1} = \gamma_{i+1/2} + \frac{1}{Q}(2K_{i+1} - 3NT_0)\frac{\Delta t}{2}. \tag{6.7}$$

The thermostat has now been included in the integration scheme which makes it an implicit scheme—unlike the other thermostats which do not rely on a particular scheme.

7. CONCLUSION

We first looked at two thermostats that are easy to understand and implement.

The Berendsen thermostat is easy to use, but as we saw it does not sample the canonical ensemble correctly. It should therefore only be used for initialization.

The Andersen thermostat on the other hand samples the canonical ensemble. It is also easy to use, but it is a stochastic method and thus not time-reversible or deterministic. The thermostat can give good results, but it also disturbs the dynamics of the system, and messes up the trajectory. It should therefore not be used for measuring time-dependent quantities such as diffusion.

The aim of the project was to study the more complicated Nosé-Hoover thermostat. It is unlike the two others both deterministic and it samples the canonical ensemble. It is harder to implement and understand, and it turns the equations of motion into a (semi-) implicit scheme.