

Introduce the Noose-Hover thermostat and measure rms-displacement using various thermostats. Discuss advantages and disadvantages of the various thermostats for various thermodynamic measures.

Conclusion

Andersen thermostat correctly samples the canonical phase space, but destroys the trajectory. It should therefore not be used to measure any quantities that depend on the trajectories, i.e., any quantities that are time-dependant. We can still use it to estimate equilibrium values for our bulk material, since that only depends on the possible configurations, and the andersen thermostat correctly samples this phase space. We saw this very clearly in the measurement of the diffusion constant, which was way to low for the Andersen thermostat (by a factor of 4!) since the dynamics are broken by the random collisions.

Thermostats

The objective for a thermostat is to up- or downregulate the temperature of a given MD system. Reasons we might want to use a thermostat include

- Initialize a system at a specfici temperature
- Sample a canonical ensamble (NVT) instead of a micro-cannonical ensamble (NVE)

A thermostat effectively simulates the connection of the system to a heat bath. For a thermostat to be labeled *effective* or *good* it is not only sufficient to get and or keep the system at a given temperature, but it should also

- Preserve real thermodynamics, i.e., it should sample the correct distribution for the canonical ensamble—the Boltzmann distribution.
- Preserve real dynamics, this is a bit harder to define, as it depends on what kind of measurement or result we are interested in. As we will see in this project for example. A bad theromstat might very well keep the system at the right temperature, but due to the nature of the temperature-regulation, the diffusion of the system is disturbed from what it should be in a real physical system.

If a thermostat fails to do this, it might lead to artifacts that are non-physical, i.e., that don't show up in the real world. Or they might give us wrong statistics, meaning our result will not agree with statistics. A good example is the flying ice cube effect, which we will come back to.

There are many possible thermostats that are commonly used, some examples are

- Berendsen thermostat
- Andersen thermostat
- Nöse-Hoover

Thermostats

The most straight-forward and ‘naive’ thermostat is normal velocity scaling. We know that the macroscopic temperature is measured from the kinetic energy

$$\frac{3}{2}Nk_bT = \langle E_k \rangle.$$

If the temperature of our system is above or below our target temperature, that means the average kinetic energy of our particles is too low or too high respectively. We can thus manipulate the temperature of our system by scaling all the velocities in our system to reach the target temperature. If the temperature of our system is given as $T(t)$ and we scale all the velocities in our system by a factor of λ , we get a change in temperature of

$$\Delta T = T(t + \Delta t) - T(t) = (\lambda^2 - 1)T(t).$$

Solving for the scaling factor gives

$$\lambda = \sqrt{T_0/T(t)}.$$

Velocity scaling isn’t very physical, for one it does not allow fluctuations of the temperature, which are normally present in the canonical ensemble.

Berendsen temperature coupling

Instead of scaling the velocity straight to the target temperature, we could do it gradually. This is the basic idea of the Berendsen temperature coupling thermostat. We now let the gradient of the temperature change be proportional to the temperature difference between the system and the reservoir, just like Fourier’s law predicts.

$$\frac{dT}{dt} = \frac{1}{\tau}(T(t) - T_0).$$

the scaling parameter τ defines how strongly coupled the system is to the reservoir. This gives an exponential decay in the temperature difference between the reservoir and system, a timestep will give a temperature change

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

And following the same scaling formula, this gives

$$\frac{\Delta t}{\tau}(T_0 - T(t)) = (\gamma^2 - 1)T(t),$$

solving for γ now results in

$$\gamma = \sqrt{1 + \frac{\Delta t}{\tau} \left(\frac{T_0}{T} - 1 \right)}.$$

The coupling constant τ has to be chosen carefully, in the limit $\tau \rightarrow \infty$ the thermostat is completely inactive, and we have a microcanonical ensemble. If τ is too small however, we approach the simple velocity scaling, meaning the temperature fluctuations are too small ($\tau = \Delta t$ reproduces simple velocity scaling). In our projects we used values of $\tau \approx 20\Delta t$, which agrees with the quoted value of $\tau \approx 0.1$ ps

Use of several thermostats

One may use several thermostats in the same simulations, either for equilibration and sampling phases. Or simultaneously for various substances to avoid the flying ice cube effect.

Microcanonical Ensemble

The microcanonical ensemble has constant energy, but the temperature will fluctuate. We start our program with the atoms in a perfect FCC lattice, and stochastic starting velocities drawn from some form of given distribution (Maxwell, Boltzmann, uniform, etc). The system obviously does not start in thermal equilibrium, and so needs time to equilibrate before we can do statistical sampling.

Statistical sampling

The fundamental quantities in our simulation are the position and velocities of all the particles. From these we can easily find the kinetic energies of all the particles and the potential energy of all pair of atoms.

To find the temperature and pressure of the system however, requires us to invoke various statistical mechanics theorems, like the equipartition theorem and the virial theorem.

The equipartition theorem states that any quadratic degree of freedom in a system carries on average an energy of $\frac{1}{2}k_bT$ when the system is in thermal equilibrium. If we sum over all the quadratic degrees of freedom in our system, and there are three for every particle, we then get the total thermal energy

$$\frac{3}{2}Nk_bT,$$

and this total thermal energy must be equal to the kinetic energy of the system, so we have

$$\frac{3}{2}Nk_bT = \langle E_k \rangle.$$

The virial theorem states

$$P = \rho k_bT - \frac{1}{3} \left\langle \sum_{i < j} \vec{F}_{ij} \cdot \vec{r}_{ij} \right\rangle.$$

Where $\rho = N/V$ is the particle density. Using the virial theorem, we can find the average pressure of the system from the positions of the atoms solely (the forces are given as functions of the positions).

Units

We will measure distance in units of σ , so

$$\bar{r} = \frac{r}{\sigma}.$$

We measure energy in units of ϵ , so we have

$$\bar{U} = \frac{U}{\epsilon}.$$

The force is given as the derivative of the potential

$$F = -\frac{dU}{dr},$$

substituting \bar{U} and \bar{r} gives

$$F = \left(\frac{\epsilon}{\sigma}\right) \left(-\frac{d\bar{U}}{d\bar{r}}\right) = \left(\frac{\epsilon}{\sigma}\right) \bar{F},$$

so we see that

$$\bar{F} = \left(\frac{\sigma}{\epsilon}\right) F.$$

We want Newton's 2. law to simplify to

$$\bar{a} = \bar{F},$$

let us see what this means. From the definition of acceleration we get

$$a = \frac{d^2 r}{dt^2} = \frac{\sigma}{t_0^2} \frac{d^2 \bar{r}}{d\bar{t}^2} = \frac{\sigma}{t_0^2} \bar{a}.$$

So we have

$$a = \frac{F}{m} \quad \Rightarrow \quad \frac{\sigma}{t_0^2} \bar{a} = \left(\frac{\epsilon}{\sigma}\right) \frac{\bar{F}}{m} \quad \Rightarrow \quad \frac{\sigma}{t_0^2} = \left(\frac{\epsilon}{m\sigma}\right).$$

Solving for t gives

$$t_0 = \sigma \sqrt{\frac{m}{\epsilon}}.$$

Which will be our unit of time.

This means we find the kinetic energy from

$$K = \frac{1}{2}mv^2 = \frac{1}{2}\frac{\sigma}{mt_0^2}\bar{v}^2 = \frac{1}{2}\epsilon\bar{v}^2 \quad \Rightarrow \quad \bar{K} = \frac{1}{2}\bar{V}^2.$$

And we can find the temperature from for example

$$\frac{1}{2}mv_{\text{rms}}^2 = \frac{3}{2}k_b T \quad \Rightarrow \quad \frac{1}{2}\bar{v}_{\text{rms}} = \frac{3}{2}\frac{k_b}{\epsilon}T \quad \Rightarrow \quad \frac{1}{2}\bar{v}_{\text{rms}} = \frac{3}{2}\bar{T},$$

giving us

$$\bar{T} = \frac{k_b}{\epsilon}T.$$