

Molecular dynamics simulations in the canonical ensemble

In the canonical ensemble, the temperature T is kept constant in the thermodynamic limit. In a finite-sized system, that means that the temperature will fluctuate around T with a well-defined variance. One way to set the temperature in the canonical ensemble is using the Heyes thermostat, which works as follows. During the simulation, we will occasionally attempt to rescale all velocities by a factor z , with $-\ln z$ being evenly distributed in an interval between $-\Delta$ and Δ . After rescaling, the total kinetic energy has increased or decreased by a factor z^2 . The distribution of the total kinetic energy E_k in d dimensions should follow

$$P(E_k) = C \left(\sqrt{E_k} \right)^{d(N-1)} \exp \left(-\frac{E_k}{k_B T} \right).$$

To attain this distribution in the simulation, we accept the rescaling move with a probability

$$p_{acc}(E_k \rightarrow z^2 E_k) = \min \left(1, z^{d(N-1)} \exp \left(-\frac{E_k(z^2 - 1)}{k_B T} \right) \right).$$

1. Thermostat

- (a) Implement the Heyes thermostat for the Lennard-Jones-like simulation system from the 3rd problem sheet. Take care that the algorithm is still time reversible by putting the rescaling between the two half-step updates of the velocity \mathbf{v} in the velocity Verlet algorithm. Pick Δ relatively small, in order to disturb the dynamics as little as possible. It is not necessary (but also not wrong) to apply the thermostat every time step.

- (b) Calculate the kinetic temperature

$$T_k(t) = \sum_{i=1}^N \frac{m_i v_i^2(t)}{k_B N_f},$$

with $N_f = dN - d - 1$ being the number of degrees of freedom. Plot the temperature as a function of time for two different set temperatures T .

2. Phase diagram

Depending on the density and the temperature, the system can be in the solid, liquid, or gas phase. To find in which phase the system is, we calculate the radial distribution function in two dimensions

$$g(r) = \frac{2L^2}{N^2} \sum_i \sum_{j>i} \frac{\delta(r_{ij} - r)}{2\pi r},$$

with L being the box length and r_{ij} the distance between particles i and j . The delta function can be calculated as $\delta(r_{ij} - r) = \varepsilon^{-1}$ if $|r_{ij} - r| < \varepsilon$ and zero otherwise.

- (a) Implement the calculation of $g(r)$ in the simulation, averaging over time. Note that the evaluation can be included in the force calculation to reduce the computational load.

In the solid phase, $g(r)$ shows a long range order of continuous oscillations. In the liquid phase, $g(r)$ exhibits a short range order, oscillating but reducing to $g(r) = 1$ for $r \rightarrow \infty$. In the gas phase $g(r)$ shows at most a single peak.

- (b) Calculate the radial distribution function for a few different values of the packing fraction ϕ and the temperature T . Try to find three combinations of T and ϕ that describe systems in the gas, liquid, and solid phase, respectively. Plot the $g(r)$ and a snapshot of these three simulation systems.

3. Diffusion constant

For long times t , the diffusion constant D can be evaluated from the mean square displacement $\Delta r(t)^2 = \langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle$ as

$$\Delta r(t)^2 = 2dDt.$$

- (a) Estimate the diffusion constant D for a system in the liquid state from the mean square displacement. Make a plot of $\Delta r(t)^2$ as a function of time. What happens for short times?

Alternatively, the diffusion constant can be calculated from the velocity autocorrelation function

$$D = \frac{1}{d} \int_0^\infty dt \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle.$$

- (b) Plot the velocity autocorrelation function. Calculate D from the autocorrelation function and compare it to your result using the mean square displacement. Note that the autocorrelation of a variable $A(t)$ can be calculated using the Fourier transform,

$$\begin{aligned} \tilde{a}(\omega) &= \int_0^\theta dt A(t) \exp(i\omega t) \\ G_A(\omega) &= \lim_{\theta \rightarrow \infty} \frac{1}{2\pi\theta} \langle |\tilde{a}(\omega)|^2 \rangle \\ \langle A(0)A(\tau) \rangle &= \int_{-\infty}^\infty d\omega G_A(\omega) \exp(-i\omega\tau). \end{aligned}$$