Exercise 09

Monte Carlo simulation

Deadline: Please hand in your protocol in pdf format by Thursday, the 5th of June 2018, 10 am to jan.joswig@fu-berlin.de. The protocol should contain analytical solutions, short discussions, Python-code and plots.

9.1 Lennard-Jones potential

Consider the Lennard-Jones potential for a Xe−Xe interaction

$$U(r) = \varepsilon \left[\left(\frac{r_\mathrm{m}}{r} \right)^{12} - 2 \left(\frac{r_\mathrm{m}}{r} \right)^{6} \right] \tag{1}$$

with $\varepsilon = 1.77\,\mathrm{kJ\,mol^{-1}}$ and $r_\mathrm{m} = 0.41\,\mathrm{nm}$.

1. Write a Python-script that samples the Boltzmann-distributed inter-atomic distance in the NVT-ensemble using a (Metropolis) Monte Carlo algorithm. Starting from an arbitrary value $r(s = 0)$, you should generate a trajectory of sufficient length according to the following scheme (see also script p. 130):

- Draw a trial value $r'(s + 1)$ as a symmetric displacement of $r(s)$ as:

$$r'(s + 1) = r(s) + (2\xi - 1)\delta \tag{2}$$

  where $\xi \in [0, 1]$ is a uniform random number and δ is the maximum width of the step.
- Evaluate the energy difference $\Delta U = U(r') - U(r)$.
- Draw another uniform random number $\Xi \in [0, 1]$ end check if

$$\Xi < \mathrm{e}^{-\beta \Delta U} \tag{3}$$

  where the Boltzmann-factor $\beta = \frac{1}{k_\mathrm{B}T}$ with k_B denoting the Boltzmann-constant.
- If that's the case, accept the step $r(s + 1) = r'(s + 1)$, and if not, reject it $r(s + 1) = r(s)$.

2. What would be a reasonable value for δ and how does the choice influence the acceptance-ratio of steps?
3. Repeat the simulation at different temperature values (e.g. 5, 40, 80 K), plot the distribution of r (histogram) and compare it to the exact solution.

9.2 2D-potential

Consider the two-dimensional double-well potential

$$U(x, y) = (x^2 - 1)^2 + (x - y) + y^2 \tag{4}$$

and repeat the tasks of exercise 9.1 for this case. Give an expression for the population of the minima as a function of the temperature.