Exercise 07

Free Energy Pertubation

Deadline: Please hand in your protocol as a single pdf file to **saleksic@zedat.fu-berlin.de** by **Thursday, 30th June, 10.15 a.m.**. Protocol should contain Python code, plots, and comments.

7.1 Free energy perturbation (50 P)

Consider four states - A, B, C, and D - which have the following harmonic potential energy functions

$$\begin{aligned} V_A(x) &= 2 \cdot (x+2)^2 - 2 \\ V_B(x) &= 1.2 \cdot x^2 \\ V_C(x) &= 5 \cdot (x-1.5)^2 - 2 \\ V_D(x) &= 0.5 \cdot (x-3)^2 + 1 \end{aligned} \tag{1}$$

Assume that

$$\beta = \frac{1}{k_B T} = 1\,. \tag{2}$$

(a) Plot the Boltzmann distributions of these four states into a single graph. (10 P)

(b) Calculate all possible free energy differences between these four states using the free energy perturbation formula (15 P)

$$\Delta A_{AB} = A_B - A_A = -k_B T \ln \left\langle \exp\left(\frac{V_A(x) - V_B(x)}{k_B T} \right) \right\rangle_A \,. \tag{3}$$

(c) Verify that the the free energy differences are consistent with the fact that the free energy is a state function. (10 P)

(d) Order the states according to their free energies. Can you understand the ordering by considering the potential energy functions? (15 P)

7.2 Markov chain Monte Carlo sampling (50 P)

Next you will generate trajectories which samples the Boltzmann distributions of the four states using the Markov chain Monte Carlo algorithm. Each new configuration (i.e. value of x in this exercise) is generated by a two-step procedure

1. A trial configuration x_{trial} is generated by drawing from a normal distribution which is centered at the current configuration x_t

$$x_{\text{trial}} \sim \mathcal{N}(x_t, \sigma^2) \tag{4}$$

2. The trial configuration is accepted or rejected by drawing a number k from a uniform distribution in $[0, 1[$ and comparing k to an acceptance criterion

$$p_{\text{acc}} = \exp(-\beta \Delta V) \tag{5}$$

with

$$\Delta V = V(x_{\text{trial}}) - V(x_t)\,. \tag{6}$$

If the trial configuration is accepted, it is added to the trajectory ($x_{i+1} = x_{\text{trial}}$), otherwise the current configuration is added to the trajectory ($x_{i+1} = x_i$).

Markov chain Monte Carlo algorithm

Data : potential energy function: V[x], initial position x[0], thermodynamic beta: beta=2/sigma^2, width of Gaussian distribution for trial moves number of sampling steps: N

Result : Full trajectory [1:N]

```
x[0] = initialPosition;
for t = 0 to t = NT − 1 do
    xTrial = RandomGaussianNumber[x[t], sigma];
    deltaV = V[xTrial] - V[x[0]] ;
    k = RandomNumber[0,1];
    if k<exp[-beta * deltaV] then
        x[t+1] = xTrial;
    else
        x[t+1] = x[t]
    end
end
```

Algorithmus 1 : Markov chain Monte Carlo algorithm to sample the Boltzmann distribution associated to a potential energy function $V(x)$.

(a) Analyze the algorithm and explain, with which probability a trial move is accepted if its energy is

- higher than
- equal to
- lower than

the energy of the current state. (10 P)

(b) Implement the algorithm and simulate trajectories in all four potentials. (30 P)

(c) Plot the distribution of x-values in your trajectories and compare them to the exact Boltzmann distribution from problem 7.1. (10 P)