1 Umbrella sampling

We have already shown how to use several runs at $\beta_1 < \ldots < \beta_R$ to compute averages for any $\beta$ in the interval $[\beta_1, \beta_R]$ and to compute free energy differences. The umbrella sampling (US) method was introduced by Torrie and Valleau in 1977 to perform the same tasks by means of a single simulation. The idea consists in performing MC simulations with a non-Boltzmann-Gibbs distribution function of the form

$$\pi(x) = \frac{1}{Z_\pi} \sum_{i=1}^{R} \alpha_i e^{-\beta_i H(x)},$$

where $i$ runs over the $R$ different temperatures, $\alpha_i$ are positive constants that should be carefully chosen as described below, and $Z_\pi$ is the normalizing factor. Since $\sum_x \pi(x) = 1$, we have

$$Z_\pi = \sum_i \alpha_i Z_i.$$

By sampling the distribution (1) one aims at sampling in a single run the configurations that are typical for all $\beta_i$’s and, as a consequence, all configuration space which is relevant for the computation of $\langle A \rangle_\beta$ with $\beta_1 \leq \beta \leq \beta_R$. In order for the method to work two requirements should be satisfied:

- The temperatures should be finely spaced, so that typical configurations at inverse temperature $\beta_i$ overlap with those at $\beta_{i\pm1}$. If this does not occur, the system is unable to move in configuration space and does not visit the typical configuration domain of all $\beta_i$’s. This condition is the same that occurs in the application of the data reweighting method.

- A second important condition fixes the coefficients $\alpha_i$ or, more precisely, their ratios. We require that the typical configuration domains at each $\beta_i$ have approximately the same probability under $\pi$. For this purpose we require

$$\frac{1}{Z_\pi} \alpha_i Z_i \approx \frac{1}{Z_\pi} \alpha_j Z_j \Rightarrow \frac{\alpha_i}{\alpha_j} \approx \frac{Z_j}{Z_i} = e^{\beta_i F(\beta_i) - \beta_j F(\beta_j)}.$$  

(2)

The algorithm is correct, though not optimal, for any choice of the $\alpha_i$’s, so that it is enough to have a very rough estimate of the free-energy differences to run a US simulation.

Note that we only fix the ratios of the $\alpha_i$’s: this is not a limitation since one can always set, say, $\alpha_1 = 1$, by redefining $Z_\pi$.

Of course, the method is useful only if we are able to obtain canonical estimates at a given $\beta$. Let us define

$$f_\pi(x) = \sum_i \alpha_i e^{-\beta_i H(x)}$$

so that $\pi(x) = f_\pi(x)/Z_\pi$. Then, we have

$$\langle A \rangle_\beta = \frac{\sum_x A(x) e^{-\beta H(x)}}{\sum_x e^{-\beta H(x)}} = \frac{\frac{1}{Z_\pi} \sum_x f_\pi(x) [A(x) e^{-\beta H(x)}/f_\pi(x)]}{\frac{1}{Z_\pi} \sum_x f_\pi(x) [e^{-\beta H(x)}/f_\pi(x)]}$$
We obtain therefore

\[
\langle A \rangle_\beta = \frac{\langle A e^{-\beta H} / f_\pi \rangle_\pi}{\langle e^{-\beta H} / f_\pi \rangle_\pi}.
\] (3)

The umbrella approach is very general and can be applied to any system. In general we consider \(R\) different probability distributions \(\pi_i\) defined on the state space and consider

\[
\pi(x) = \sum_i a_i \pi_i(x)
\]

with \(a_i > 0\) and \(\sum_i a_i = 1\). In the previous example

\[
\pi_i = \frac{1}{Z_i} e^{-\beta_i H} \quad a_i = \frac{Z_i}{Z_\pi} \alpha_i.
\]

The optimality condition (2) translates in

\[
\frac{\alpha_i}{\alpha_j} \approx \frac{Z_j}{Z_i} \Rightarrow \frac{Z_\pi a_i}{Z_i} \frac{Z_j}{Z_\pi a_j} \approx \frac{Z_j}{Z_i} \Rightarrow \frac{a_i}{a_j} \approx 1.
\]

The weights \(a_i\) should be approximately the same to have an optimal distribution.

2 Monte Carlo implementation

The umbrella sampling method can be implemented straightforwardly. Let us consider a system of monoatomic molecules. Suppose that particles are in \(\{\mathbf{r}_1, \ldots, \mathbf{r}_N\}\). A Metropolis update of one particle is performed as in the canonical case. We choose a molecule \(i\) and propose a shift in a cubic box of size \(\Delta^3\). The move is accepted with the Metropolis acceptance probability \(\min(1, R)\), where

\[
R = \frac{\sum_i \alpha_i e^{-\beta_i E_{\text{new}}}}{\sum_i \alpha_i e^{-\beta_i E_{\text{old}}}}
\]

and \(E_{\text{new}}\) and \(E_{\text{old}}\) are the energies of the new and of the old configuration. This means that we accept the move if \(E_{\text{new}} < E_{\text{old}}\) (check that, if this condition holds, \(R > 1\)); otherwise, we accept the move with probability \(R\).