

Two replicas are sampling distributions  $p_1(x)$  and  $p_2(x)$  and are currently at states  $x_1$  and  $x_2$ . The probability for accepting an exchange is then given by

$$p_{\text{acc}}(x_1, x_2 | p_1, p_2) = \min \left\{ 1, \frac{p_1(x_2) p_2(x_1)}{p_1(x_1) p_2(x_2)} \right\}. \quad (1)$$

Assume  $p_1$  and  $p_2$  depend on  $x$  only through a common function  $E(x)$ , the “energy”, that is, we have  $p_i(x) = p_i(E(x))$ .

To calculate the average acceptance rate  $\bar{p}_{\text{acc}}$ , we calculate the expectation value of  $p_{\text{acc}}$  with respect to the joint distribution  $p(x_1, x_2) = p_1(x_1)p_2(x_2)$  and we have

$$\bar{p}_{\text{acc}} = \int \int p_{\text{acc}}(x_1, x_2 | p_1, p_2) p_1(x_1) p_2(x_2) dx_1 dx_2. \quad (2)$$

This is a double integral over two potentially high-dimensional variables. To make progress, we introduce the density of states (DOS)  $g(E)$ , which counts the multiplicity of energies:

$$g(E) = \int dx \delta(E - E(x)) \quad (3)$$

Using the DOS, we can write the expectation value of any function  $f(x)$  which depends on  $x$  only via the energy  $E$  (meaning, again,  $f(x) = f(E(x))$ ), as an integral over  $E$  instead of  $x$ :

$$\int dx f(E(x)) = \int dE g(E) f(E) \quad (4)$$

We further note that often, we only know distributions  $p$  up to a normalization constant  $Z$ , and we have

$$p(x) = \frac{1}{Z} q(x) \quad (5)$$

Using the DOS, above equation and the assumption that  $q(x) = q(E(x))$ , we can now rewrite the expected acceptance rate as an integral over energies:

$$\bar{p}_{\text{acc}} = \frac{1}{Z_1 Z_2} \int \int dx_1 dx_2 \min \left\{ 1, \frac{q_1(E(x_2)) q_2(E(x_1))}{q_1(E(x_1)) q_2(E(x_2))} \right\} q_1(E(x_1)) q_2(E(x_2)) \quad (6)$$

$$= \frac{1}{Z_1 Z_2} \int \int dx_1 dx_2 \min \{ q_1(E(x_1)) q_2(E(x_2)), q_1(E(x_2)) q_2(E(x_1)) \} \quad (7)$$

$$= \frac{1}{Z_1 Z_2} \int \int dE_1 dE_2 g(E_1) g(E_2) \min \{ q_1(E_1) q_2(E_2), q_1(E_2) q_2(E_1) \} \quad (8)$$

Note that the normalization constants  $Z_1, Z_2$  can be written in terms of the energies  $E$ , too:

$$Z_i = \int dx q(E(x)) = \int dE g(E) q(E) \quad (9)$$

Long story short: if we have access to  $g(E)$ , we can estimate the expected acceptance rate by means of simple numeric approximation of one-dimensional and two-dimensional integrals over energies.

We can get a good estimate of  $g(E)$  via multiple histogram reweighting; it is

essentially an estimate of  $g(E)$  at every sampled value and thus the integrals collapse into weighted sums.

More specifically, for the Boltzmann ensemble, we have

$$p_1(x) = \frac{1}{Z(\beta_1)} \exp(-\beta_1 E(x)) \quad (10)$$

$$p_2(x) = \frac{1}{Z(\beta_2)} \exp(-\beta_2 E(x)) \quad (11)$$

Assuming we have an estimate of  $g(E)$  from multiple histogram reweighting, this means we can calculate the expected acceptance rate for any two pairs of inverse temperatures  $\beta_1, \beta_2$ . Say now that  $\beta_0 = 1$  gives us the distribution we actually are interested in and  $\beta_N = \epsilon \approx 0$  is an almost uniform distribution. This suggests an iterative algorithm to get a sequence  $\beta_0 > \beta_1 > \dots > \beta_N$  for which the acceptance rates between simulations at consecutive temperatures  $\beta_i, \beta_{i+1}$  are attain a constant value  $\bar{p}_{\text{acc}}^{\text{target}}$ : we start with  $\beta = 1$  and lower  $\beta$  in increments of  $\Delta\beta$ , until the expected acceptance rate drops below  $\bar{p}_{\text{acc}}^{\text{target}}$ . We then save the  $\beta$  value before the last decrement as  $\beta_1$ . We then calculate acceptance rates between  $\beta_1$  and steadily decreasing  $\beta$  values, until the acceptance reate drops below  $\bar{p}_{\text{acc}}^{\text{target}}$  again and we save the previous  $\beta$  value as  $\beta_2$  and so on and so forth. At one point, we will hit a predefined  $\beta_{\text{min}}$ . We then terminate and have obtained the desired sequence of  $\beta$  values as our optimized schedule.