

# Monte Carlo Methods Lecture 17: Histogram Methods

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# Histogram Methods I



- The Monte-Carlo Methods very elegantly side steps the need to compute the partition function.
- Remember, that we only need the ratios of probabilities and hence the normalization, which involves the partition function, cancels out.
- There are, however, situations where we would like to compute for example the free-energy or a free-energy difference directly.
- One could of course do a thermodynamic integration using the appropriate variables that one has previously computed using the Monte-Carlo method.
- We can also make use of all the samples that we have generated during the course of a simulation and analyze and use them in more detail.

Histogram Methods II



- We first look at how we can compute the difference in free-energy [1, 2].
- Let  $\mathcal{H}$  be the Hamiltonian of our system and let  $T_1$  and  $T_2$  be two temperatures.
- We would like to compute the free-energy difference

$$\Delta F = F_1 - F_2 = -kT \ln \frac{Z_1}{Z_2}$$
(1)

For the ratio between the two partition functions we obtain

$$\frac{Z_1}{Z_2} = \frac{1}{Z_2} \int e^{-\mathcal{H}/kT_1} dx \tag{2}$$

$$= \frac{1}{Z_2} \int e^{-\mathcal{H}/kT_2} e^{\mathcal{H}/kT_2 - \mathcal{H}/kT_1} dx$$
 (3)

$$= \langle e^{\mathcal{H}/kT_2 - \mathcal{H}/kT_1} \rangle_2 \tag{4}$$

Thus, we can compute the free-energy difference by computing the expectation value of a new observable  $O = e^{\mathcal{H}/kT_2 - \mathcal{H}/kT_1}$  with respect to the Hamiltonian at temperature  $T_2$ .



There is a catch however. Consider the probability to generate a configuration with energy difference E using  $\mathcal{H}$  at temperature  $T_2$ 

$$p(E) = \frac{1}{Z_2} \int e^{-\mathcal{H}/kT_2} \delta(\mathcal{H}/kT_1 - \mathcal{H}/kT_2 - E) dx$$
(5)

Then the expectation value is given by

$$\langle e^{\mathcal{H}/kT_2 - \mathcal{H}/kT_1} \rangle_2 = \int p(E)e^{-E/kT_2}dE$$
 (6)

- This highlights the problem that we have with computing the free-energy by evaluation a new observable with respect to some Hamiltonian.
- For large systems the function p(E) is very sharply peaked around some value  $\langle E \rangle$ . In general the average is not small.
- The resulting function from the product of p(E) with  $e^{-E/kT_2}$  is again a peaked function but with a shifted average value.
- The success of the above approach thus hinges on the closeness of the two average values and the overlap between the peaked functions.
- Remember the Monte-Carlo method predominately samples the main contributions, i.e. close to the average value if the distribution is sharply peaked.

# Histogram Methods IV



- If the resulting function of the product is shifted too much to small *E* values then the sampling of the overlap region is limited and we get a poor estimate for the free-energy difference.
- We can conclude that we would like to have not so sharply peaked distributions and that the difference that we want to compute should not be too large.
- Now we know how to broaden the distribution: We need to simulate small systems!

Histogram Methods V



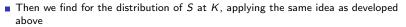
- The above method also shows the direction that we may want to go in using more of the data that we generate during simulation runs.
- The above method suggests that it is possible to extrapolate to values of an observable other than we have computed as long as there is a sufficient overlap between the distributions of the observable.
- This idea has been put forward many times with varying success [3-6, 6-10].
- Let K be a dimensionless parameter (for the Ising model that could be K = J/kT). Further we assume that we can write

$$\beta \mathcal{H} = KS \tag{7}$$

where S is an Operator (if the Hamiltonian represents the Ising model that S would be  $\sum_{\langle i,j \rangle} s_i s_j$ ).

- While we proceed computing new states using the Monte-Carlo method or the Molecular Dynamics method, we keep on generating values for the observable S.
- For each of the generated values we keep a record in a histogram reflecting the distribution of the observable.
- Let  $H(S, K_0, N)$  be the histogram that we have computed using the dimensionless value  $K_0$ . N is the number of configurations that we assembled in the histogram.

Histogram Methods VI



$$P_{K}(S) = \frac{H(S, K_{0}, N)e^{(K-K_{0})S}}{\sum_{\{S\}} H(S, K_{0}, N)e^{K-K_{0}}S}$$
(8)

for the probability to find a value S under the constraint K. We can thus generate an estimate for an observable A that depends on S and K using

$$\langle A(S) \rangle_{\mathcal{K}} = \sum_{\{S\}} A(S) P_{\mathcal{K}}(S)$$
 (9)



# Bibliography I



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