Monte Carlo Methods
Lecture 17: Histogram Methods

Dieter W. Heermann

Heidelberg University

January 2, 2020

UNIVERSITÄT HEIDELBERG
ZUKUNFT SEIT 1386

- 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.

UNIVERSITÄT HEIDELBERG ZUKUNFT SEIT 1386

- 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

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

- For the ratio between the two partition functions we obtain

$$\begin{aligned} \frac{Z_1}{Z_2} &= \frac{1}{Z_2} \int e^{-\mathcal{H}/kT_1} dx & (2) \\ &= \frac{1}{Z_2} \int e^{-\mathcal{H}/kT_2} e^{\mathcal{H}/kT_2 - \mathcal{H}/kT_1} dx & (3) \\ &= < e^{\mathcal{H}/kT_2 - \mathcal{H}/kT_1} >_2 & (4) \end{aligned}$$

- 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.

Histogram Methods III

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

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

Then the expectation value is given by

$$< e^{\mathcal{H}/kT_2 - \mathcal{H}/kT_1} >_2 \quad = \int p(E) e^{-E/kT_2} dE \tag{6}$$

- 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 $< E >$. 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.

- 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 $\sum_{<i,j>} s_i s_j$).
- 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

- Then we find for the distribution of S at K, applying the same idea as developed above

$$P_K(S) = \frac{H(S, K_0, N)e^{(K-K_0)S}}{\sum_{\{S\}} H(S, K_0, N)e^{K-K_0 S}} \tag{8}$$

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

$$< A(S) >_K = \sum_{\{S\}} A(S) P_K(S) \qquad . \tag{9}$$

Bibliography I

UNIVERSITÄT HEIDELBERG
ZUKUNFT SEIT 1386

[1] C. H. Bennett. J. Comput. Phys. , 22:245, 1976.

[2] D. Frenkel and Academic Press New York B. Smit, *Understanding Molecular Simulation: From Algorithms to Application*. 1996. 1996.

[3] G. M. Torrie and 187 J. P. Valleau, *J. Comput. Phys.* **23**. 1977. 1977.

[4] A. M. Ferrenberg and 2635 R. H. Swendsen, *Phys. Rev. Lett.* **61**. 1988. 1988.

[5] K. K. Mon A. M. Ferrenberg in *Computer Simulation Studies in Condensed Matter Physics III*, eds. D. P. Landau and Heidelberg) H.-B. Schüttler (Springer-Verlag. 1991. 1991.

[6] A. M. Ferrenberg and 5081 D. P. Landau, *Phys. Rev. B* **44**. 1991. 1991.

[7] B. Berg and T. Neuhaus. *Phys. Lett. B*, 267:249, 1991.

[8] B. Berg and T. Neuhaus. *Phys. Rev. Lett.*, 69(9), 1992.

[9] B. A. Berg. *J. Stat. Phys.*, 82:343, 1996.

[10] B. A. Berg, U .Hansmann, and T. Neuhaus. *Phys. Rev. B*, 47:497, 1993.

Index I