Histograms and densities of states

For the sake of concreteness let us consider the simulation of an Ising model (ferromagnetic)

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} \sigma_i \sigma_j \quad ; \quad J > 0$$

where the sum extends over nearest neighbours. The order parameter of the ferromagnetic transition is the spontaneous magnetization. The MC simulation is done in the canonical ensemble and visits all energies according to the Boltzmann weight $e^{-\beta E}$

partition function : $Z(T) = \sum_{\{\sigma\}} e^{-\beta \mathcal{H}(\{\sigma\})}$

$$= \sum_{E,M} g(E,M)\, e^{-\beta E}$$

where $g(E,M)$ is the density of states for fixed E and M.
The physical meaning of the density of states gets clearer when we just look at $g(E) \equiv$ number of states with energy E.

Boltzmann: $S(E) = k_B \ln g(E)$ (microcanonical entropy)

The entropy is not a quantity easily obtained from Monte Carlo simulations because this would basically mean that one can calculate the partition function. With this also free energies are hard to get. We will discuss specialized MC algorithms aiming at getting $S(E, \ldots)$ and free energies.

Suppose we are performing a simulation at temperature T_0.
Probability to find state (E,M): $P_{T_0}(E,M) = \frac{1}{Z(T_0)}\, g(E,M)\, e^{-\beta_0 E}$

Wenn wir in der Simulation N Messungen von Paaren (E, M) durchführen sollten wir ein Histogramm erhalten damit Einträgen.

$$H(E, M) \approx N \; P_{T_0}(E, M)$$
$$\approx N \frac{1}{Z(T_0)} g(E, M) \, e^{-\beta_0 E}$$

We can thus obtain an estimate for the density of states from the measured histogram

$$g(E, M) \approx Z(T_0) \frac{H(E, M)}{N} e^{\beta_0 E}$$

From this we can obtain an estimate for the probability distribution at a different (near by) temperature

$$P_T(E, M) \approx \frac{Z(T_0)}{Z(T)} \frac{H(E, M)}{N} e^{(\beta_0 - \beta) E}$$

We finally require $P_T(E, M)$ to be normalized and thus determine the unknown ratio of partition functions

$$\frac{Z(T)}{Z(T_0)} = \sum_{E, M} \frac{H(E, M)}{N} e^{(\beta_0 - \beta) E}$$

$$\Rightarrow \quad \boxed{P_T(E, M) = \frac{H(E, M) \, e^{\Delta\beta E}}{\sum_{E, M} H(E, M) \, e^{\Delta\beta E}}}$$

Histogram Reweighting

Remarks: - useful for exact location of a peak in a response function

- reweighting only possible to nearby values of control parameter (here T)
- problem gets worse with increasing system size

$\rightarrow$ Fig 7.1 from Landau / Binder

Critical point of the 3-d Ising system was determined to be

$$K_c = \frac{1}{k_B T_c} = 0.221\,654\,6(10)$$

Rosengreen conjecture [A. Rosengreen, J. Phys. A 19, 1709 (1986)]

$$\tanh K_c = (\sqrt{5} - 2)\cos\left(\frac{\pi}{8}\right) = 0.221\,658\,63$$

Multiple histogram method

- possibility of interpolation between simulated values of the control parameter
- improved extrapolation capability (though still to be handled with care)

We had: $p_T(E,M) = \frac{Z(T_0)}{Z(T)} \frac{H(E,M)}{N} e^{(\beta_0-\beta)E}$

Let us now assume that we want to predict $p_{T_0}(E,M)$ from simulations performed at temperatures T_i with histograms H_i containing N_i total measurements.

1 histogram:

$$p_0(E,M) = \frac{Z_i}{Z_0}\frac{H_i}{N_i} e^{(\beta_i-\beta_0)E} = \frac{Z_i}{Z_0}\frac{H_i}{N_i} e^{\Delta\beta_i E}$$

multiple histograms:

$$p_0(E,M) = \sum_{i=1}^{n} W_i(E,M)\frac{Z_i}{Z_0}\frac{H_i}{N_i} e^{\Delta\beta_i E}$$

where the weights are normalized: $\sum_{i=1}^{n} W_i(E,M) \equiv 1$

Our histogram errors will be influenced by the autocorrelation times of the simulated control parameters. Besides that we assume a Poisson statistics over different runs with fixed length N_i (we will consider the number of independent measurements N_i/τ_i instead)

$$\delta^2 \overline{H_i(E,M)} = \overline{H_i(E,M)}$$

Let us now calculate the variance for our estimate of $p_0(E,M)$:

$$\overline{p_0^2(E,M)} = \sum_{i,j} \frac{w_i w_j}{N_i N_j} \frac{z_i z_j}{z_0^2} \underbrace{\overline{H_i H_j}}_{2\delta_{ij}(\overline{H_i}^2 + \overline{H_i}) + \overline{H_i}\,\overline{H_j}(1-\delta_{ij})} e^{\Delta\beta_i E} e^{\Delta\beta_j E}$$

$$\overline{p_0^2(E,M)} = 2\sum_i \frac{w_i^2}{N_i^2}\left(\frac{z_i}{z_0}\right)^2 (\overline{H_i}^2 + \overline{H_i}) e^{2\Delta\beta_i E} + \sum_{i,j} \frac{w_i w_j}{N_i N_j} \frac{z_i z_j}{z_0^2} \overline{H_i}\,\overline{H_j} e^{\Delta\beta_i E} e^{\Delta\beta_j E}$$

$$\sum_i \frac{w_i^2}{N_i^2}\left(\frac{z_i}{z_0}\right)^2 \overline{H_i} e^{2\Delta\beta_i E}$$

thus $\overline{p_0(E,M)} = \sum_i \frac{w_i}{N_i} \frac{z_i}{z_0} \overline{H_i} e^{\Delta\beta_i E}$

now we have $\overline{H_i}(E,M) = N_i\, p_i(E,M)$

$$\Rightarrow \overline{p_0(E,M)} = \sum_i w_i \underbrace{\frac{z_i}{z_0} p_i e^{\Delta\beta_i E}}_{p_0} = p_0 \sum_i w_i = p_0$$

When we plug this into the equation for $\overline{p_0^2(E,M)}$

$$\overline{p_0^2(E,M)} = \left(\sum_i \frac{w_i}{N_i} \frac{z_i}{z_0} \overline{H_i} e^{\Delta\beta_i E}\right)^2 + \sum_i \frac{w_i^2}{N_i^2}\left(\frac{z_i}{z_0}\right)^2 \overline{H_i} e^{2\Delta\beta_i E}$$

$$= p_0^2 + p_0 \sum_i \frac{w_i^2}{N_i} \frac{z_i}{z_0} e^{\Delta\beta_i E}$$

$$\Rightarrow \overline{\Delta p^2(E,M)} = p_0 \sum_{i=1}^{n} \frac{w_i^2}{N_i} \frac{z_i}{z_0} e^{\Delta\beta_i E}$$

Minimize this under the constraint $\sum_i w_i = 1$

$$\frac{\delta}{\delta w_k}\left[\overline{\Delta p^2(E,M)} - \alpha \sum_i w_i\right] = 0$$

$$\Leftrightarrow 2 p_0 w_k \frac{z_k}{z_0 N_k} e^{\Delta\beta_k E} - \alpha = 0$$

$$\Rightarrow w_k = \frac{\alpha}{2p_0} \frac{z_0 N_k}{z_k} e^{-\Delta\beta_k E}$$

Normalization $\frac{\alpha}{2\rho_0} = \sum_k \frac{z_0 N_k}{Z_k} e^{-\Delta\beta_k E}$

$$\Rightarrow \quad W_k = \frac{\frac{z_0 N_k}{Z_k} e^{-\Delta\beta_k E}}{\sum_i \frac{z_0 N_i}{Z_i} e^{-\Delta\beta_i E}}$$

And with that we obtain our best estimate for $\rho_0(E, M)$:

$$\boxed{\rho_0(E, M) = \frac{\sum_{i=1}^{M} H_i(E, M)}{\sum_{i=1}^{n} N_i \, z_0/Z_i \, e^{-\Delta\beta_i E}}}$$

This equation, however, still contains the unknown partition functions Z_i

$$Z_i = \sum_{E,M} g(E, M) e^{-\beta_i E} = z_0 \sum_{E,M} \rho_0(E, M) e^{-\Delta\beta_i E}$$

$$\boxed{Z_i = \sum_{E,M} e^{-\Delta\beta_i E} \frac{\sum_{j=1}^{n} H_j(E, M)}{\sum_{j=1}^{n} N_j / Z_j \, e^{-\Delta\beta_j E}}}$$

Implicit relation between the Z_i; we can only determine the ratio between different Z_i, not their absolute value $\Leftrightarrow$ we can only determine free energy differences not absolute free energies.

Set $Z_1 = 1$ arbitrarily and determine all other $(n-1)$ Z_j self consistently from above equations.

Umbrella Sampling

Let us consider now a system of N particles at temperature T in the volume V.

Let us consider two systems with different potential energy U_1 and U_0.

We consider a simulation with potential U_1 and measure the difference ... for a ... $U_1(\vec{r}^N) - U_0(\vec{r}^N)$ ...

The probability for this difference to be equal to ΔU is:

$$p_1(\Delta U) = \frac{1}{Z_1} \int d\vec{r}^N e^{-\beta U_1} \delta(U_1 - U_0 - \Delta U)$$

$$= \frac{Z_0}{Z_1} e^{-\beta \Delta U} \frac{1}{Z_0} \int d\vec{r}^N e^{-\beta U_0} \delta(U_1 - U_0 - \Delta U)$$

$$= \frac{Z_0}{Z_1} e^{-\beta \Delta U} p_0(\Delta U)$$

Remember: $\Delta F = F_1 - F_0 = -k_B T(\ln Z_1 - \ln Z_0) = k_B T \ln \frac{Z_0}{Z_1}$

$$\Rightarrow p_1(\Delta U) = e^{\beta \Delta F} e^{-\beta \Delta U} p_0(\Delta U)$$

Integration over ΔU:

$$1 = e^{\beta \Delta F} \int d\Delta U \, e^{-\beta \Delta U} p_0(\Delta U)$$

$$\Rightarrow e^{-\beta \Delta F} = \langle e^{-\beta \Delta U} \rangle_0$$

The free energy difference between systems 1 and 0 can be obtained by the average of a canonical simulation in the system 0.

Example: Widom insertion method

The chemical potential of a particle is the free energy difference between a system with $N+1$ particles with respect to one with N particles at constant volume and temperature

$$\mu = -k_B T \ln \frac{Z_{N+1}}{Z_N}$$

$$= \mu_{id}(\rho) - k_B T \ln \frac{\int d\vec{r}^{N+1} e^{-\beta U(\vec{r}^{N+1})}}{\int d\vec{r}^{N} e^{-\beta U(\vec{r}^{N})}}$$

Define $\Delta U = U(\vec{r}_{N+1}) - U(\vec{r}_N)$

$$\Rightarrow \mu = \mu_{id}(\rho) - k_B T \ln \underbrace{\int d\vec{r}_{N+1} \langle e^{-\beta \Delta U} \rangle_N}$$

average $e^{-\beta \Delta U}$ over all positions of $\vec{r}_{N+1}$ in the simulation volume and over all possible configurations of the other particles.

Simulation algorithm (Widom's insertion method)

- Simulate a canonical system (N, V, T)
- from time to time select a number of M random positions $\vec{r}_n$ in the box and sum up $e^{-\beta \Delta U(\vec{r}_n)}$
- continue simulation without actually inserting the particle.

Remark: fails at higher densities due to too large probability for an overlap between inserted and simulated particle

Generally the simple estimate works if systems are very similar (see histogram vs. multiple histograms)

Reason: Configurations with high $e^{-\beta U_1}$ have also to be probable in a simulation with U_0, i.e. $e^{-\beta U_0}$ has to be large also.

Idea: Sample not according to U_1 or U_0 but with an umbrella potential $\pi(\vec{r}^N)$

Rewrite
$$\langle e^{-\beta \Delta U} \rangle_0 = \frac{\int d\vec{r}^N \, \pi(\vec{r}^N) \, e^{-\beta \Delta U(\vec{r}^N)} / \pi(\vec{r}^N)}{\int d\vec{r}^N \, \pi(\vec{r}^N) \, e^{-\beta U_0(\vec{r}^N)} / \pi(\vec{r}^N)}$$

$$\equiv \frac{\langle e^{-\beta \Delta U} / \pi \rangle_\pi}{\langle e^{-\beta U_0} / \pi \rangle_\pi}$$

Special case: temperature scaling, i.e. $U_1 = \lambda_1 U_0$

Suppose we want to obtain statistics in a temperature interval (T_{min}, T_{max}). An intuitive choice to generate uniform sampling would be:

$$\pi(\vec{r}^N) = \sum_{i=1}^{N} w_i \, e^{-\beta_i U(\vec{r}^N)}$$

with $T_1 = T_{min}$, $T_N \equiv T_{max}$

The weights $w_i(T_i, V)$ should be chosen in a way that each term in π contributes equally to the configuration space integral of π. This is realized by:

$$w_i \sim \exp\{\beta_i F_{ex}(T_i, V)\}$$

only the interaction dependent part.

$$\Rightarrow \quad \Pi(\vec{r}^N) = \sum_i \exp\left\{ \beta_i \left[F_{ex}(T_i, V) - U(\vec{r}^N) \right] \right\}$$

How to obtain the $F_{ex}(T_i, V)$?

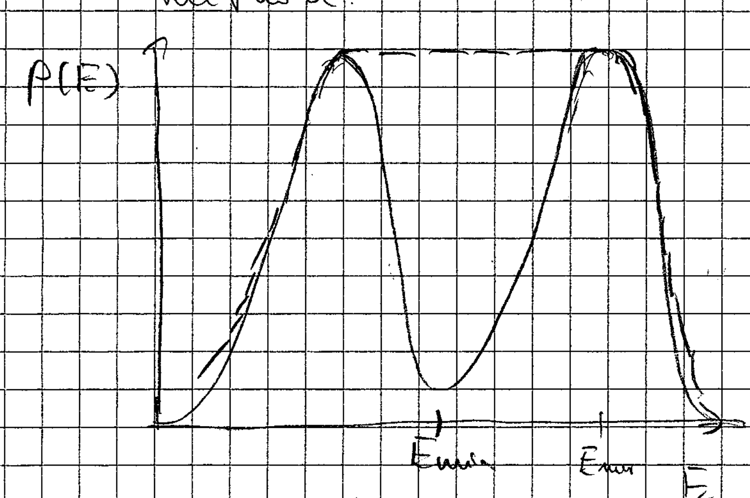
i) Estimate on the basis of approximate equation of state

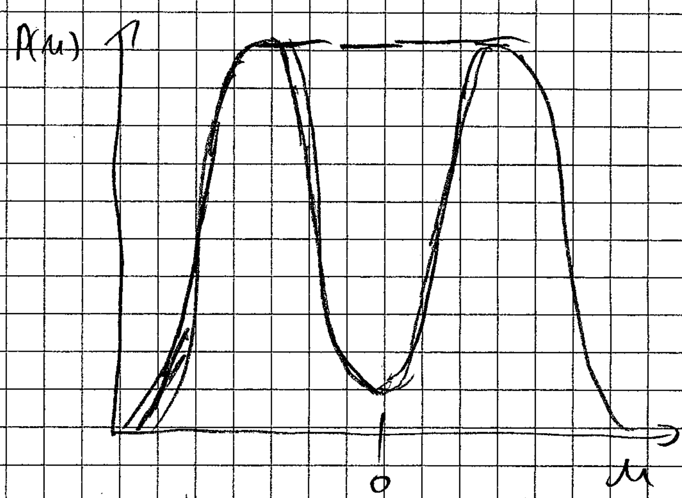
ii) Estimate or refine from simulation. Start from constant 'w' and measure $\langle e^{\beta \delta U} \rangle \approx e^{\beta \Delta F}$ and iterate

iii) with final guess perform measurement simulation

Remark: i) if the $F_{ex}(T_i, V)$ were known exactly all the terms would be equal and the whole energy range $\langle U \rangle (T_{min}) \leq E \leq \langle U \rangle (T_{max})$ would be sampled with equal probability

ii) This is the principle of the multicanonical MC method.





First order phase transitions suffer from exponential slowing down. Prob. Probability to sample state E_m

$P_L(E_{min}) / P_L(E_{max}) \sim e^{-\beta \Delta F} \sim e^{-\beta V \Delta f}$

$\hookrightarrow$ Use modified „umbrella" Hamiltonian to create random walk between the two maxima