Chapter 6 Monte Carlo Method in Statistical Mechanics

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6.1

Suppose we have M sets of data, each of which contains N data points. Let σ be the standard deviation of one set, which should also be the same with the set of all the data points, and σ_M be the standard deviation of the M means. From probability theory we know

$$\sigma_M \approx \frac{\sigma}{\sqrt{N}}. \tag{1}$$

$$\Delta\langle G\rangle_T = \sqrt{\left(\frac{L}{T}\right)^2 \sum_I \left(\langle G\rangle^I - \langle G\rangle_T\right)^2} = \sqrt{\frac{L}{T}\sigma_L^2} \approx \sqrt{\frac{L}{T}\left(\frac{1}{L}\sigma^2\right)} = \frac{\sigma(G)}{\sqrt{T}} \approx \sigma(\langle G\rangle_T). \tag{2}$$

6.2

The 2D Ising model below the critical temperature can be a good example for quasi-ergodic, if one cannot help the trajectory overcome the free energy barrier.

6.3

Following the idea in the text, At equilibrium in the given ensemble

$$P_v \propto \exp(-\beta E_v + \xi M_v), \tag{3}$$

$\dot{p}_v = 0$ and

$$\frac{p_{v'}}{p_v} = \exp(-\beta\Delta E_{vv'} + \xi\Delta M_{vv'}), \tag{4}$$

where

$$\Delta E_{vv'} = E_{v'} - E_v, \qquad \Delta M_{vv'} = M_{v'} - M_v. \tag{5}$$

Thus

$$\frac{w_{vv'}}{w_{v'v}} = \frac{p_{v'}}{p_v} = \exp(-\beta\Delta E_{vv'} + \xi\Delta M_{vv'}). \tag{6}$$

Thus the Metropolis algorithm in the given ensemble is

$$w_{vv'} \propto \begin{cases} 1, & -\beta\Delta E_{vv'} + \xi\Delta M_{vv'} \geqslant 0 \\ \exp(-\beta\Delta E_{vv'} + \xi\Delta M_{vv'}), & -\beta\Delta E_{vv'} + \xi\Delta M_{vv'} < 0. \end{cases} \tag{7}$$

6.4

For such a model, in every unit time, one can randomly choose one spin s_i, and then attempt to change it by adding or subtracting one. If the attempt is not allowed by the boundary $-10 \leqslant s_i \leqslant 10$, then in this step we do nothing; otherwise we generate a random number $a \in [0, 1)$, and calculate the probability $p = \exp(-\beta \Delta E_{vv'})$. If $a < p$ then we change the spin as planned. Otherwise we do nothing in this step (attempt rejected).

This algorithm follows the idea of Metropolis algorithm and satisfies the detailed balance condition.

If the step size $\Delta s_i = s_i(t+1) - s_i(t) > 1$, the average acceptance of the attempted moves may decrease. Here we suppose the step size does not lead to a non-ergodicity. However, the average step size should be the same (if rejected, then count the step size as zero for that step).

6.5

Run the code on computer and observe.

6.6

$$\begin{aligned} Q' =& \sum_v \exp(-\beta' E_v) = \sum_v \exp[-(\beta + \beta' - \beta)E_v] = \sum_v \exp(-\beta E_v) \exp[-(\beta' - \beta)E_v] \\ =& Q \sum_v \exp(-\beta E_v) \exp[-(\beta' - \beta)E_v]/Q \\ =& Q\langle \exp[-(\beta' - \beta)E_v]\rangle \end{aligned} \tag{8}$$

$$A' = -\ln Q' = -\ln Q - \ln\langle \exp[-(\beta' - \beta)E_v]\rangle = A - \ln\langle \exp[-(\beta' - \beta)E_v]\rangle. \tag{9}$$

Thus one can run a Monte Carlo simulation under the temperature β and obtain the free energy A under this temperature, and then calculate the free energy A' under β' by the equation (9).

6.7

Imagine a 20×20 2D system. Suppose $5 \times 5 = 25$ solute molecules are gathered to form a 5×5 block some where in the lattice. Under the microcanonical ensemble the probability of forming this kind of configurations is

$$p = 400 \Big/ \binom{400}{25} \approx 1.185 \times 10^{-37}. \tag{10}$$

6.8

If the windows are too narrow, the acceptance rate can be too high, because it is easier to hit the boundary of the windows.