M6 Computer Simulation Methods: Problem Sheet for Part II

NST Chemistry Part III — Michaelmas 2021

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1 Monte Carlo Code

1.1 Photon gas (adapted from D. Frenkel Chapter 2.3 and 3.5. excersises)

An electromagnetic field in thermal equilibrium can be described as a phonon gas. From quantum theory of the electromagnetic field, it is found that the total energy of the system (U) can be written as the sum of photon energies:

$$U = \sum_{j=1}^{N} n_j \omega_j \hbar = \sum_{j=1}^{N} n_j \epsilon_j$$

in which ϵ_j is the characteristic energy of a photon with frequency ω_j, $n_j = 0, 1, 2, ..., \infty$ is the so-called occupancy number of mode j, and N is the number of field modes (here we take N to be finite).

(a) Show that the canonical partition function of the system can be written as

$$Q = \prod_{j=1}^{N} \frac{1}{1 - \exp[-\beta\epsilon_j]}$$

Hint: you will have to use the following identity for $|x| < 1$:

$$\sum_{i=0}^{\infty} x^i = \frac{1}{1-x}.$$

For the product of particion functions of two independent systems A and B, we can write

$$Q_A \times Q_B = Q_{AB}$$

when $A \cap B = \oslash$ and $A \cup B = AB$.

(b) Show that the average occupancy number of state j of the photon gas, $< n_j >$, can be calculated analytically, and is equal to

$$< n_j >= \frac{\partial \ln Q}{\partial(-\beta\epsilon_j)} = \frac{1}{\exp[\beta\epsilon_j] - 1}$$

and describe the behavior of $< n_j >$ when $T \to \infty$ and when $T \to 0$.

(c) It is also possible to calculate $< n_j >$ using a Monte Carlo algorithm. For instance, use the following procedure:

i Start with an artitrary value for n_j.

ii Decide at random to perform a trial move to increase or decrease the value of n_j by 1.

iii Accept the trial move with probabiity acc($o \to n$)=min$(1, \exp[-\beta(U(n) - U(o))])$. Note that n_j cannot be negative!

How can this scheme retain detailed balance when $n_j = 0$?
Is the algorithm still correct when trial moves are performed that change n_j with a random integer from the uniform interval $[-5, 5]$?
What happens when only trial moves are performed that change n_j with either -3 or $+3$?

(d) Write a Monte Carlo simulation code in any computer language you know to calculate the average occupancy $< n_j >$ numerically. Include your entire code in your report. **'Algorithm 1'** in the box gives you a guide of what your code should do.

(e) Using your code, plot the average occupation number as a function of $\beta\epsilon \in [0.1, 2]$. Assume that

Algorithm 1: Metropolis algorithm implementation to calculate $< n_j >$

```
1  Program MCPhoton
   Input  : The total number of MC steps to perform TotalMCSteps
   Output: Numerical estimate of n_j, its theoretical value, and the relative error
2  begin
3      currentnj = 1 or currentnj = random                    ▷ Initialize the value of n_j
4      sumnj = 0   ▷ Initialize a variable that will store the sum of n_j during the simulation to compute
         < n_j >
5      for i = 1 to TotalMCSteps do
6          Generate a random number between 0,1
7          Use this random number to randomnly decide to increase or decrease the value of n_j ;
           Hint  : Define a trial value of n_j as either trialnj = currentnj + 1 or
                   trialnj = currentnj − 1
8          Test if trialnj < 0, if it is, force it be 0;
9          Accept the trial move with the probability given in the description above.;
           Hint  : Accepting the trial move means updating the current value of the occupacy number
                   (currentnj) with the proposed trial value (trialnj)
10         Update sumnj, e.g. sumnj = sumnj + currentnj;
11     end
12     Compute the numerical estimate for the average occupancy < n_j > using sumnj
13     Compute the theoretical value given by the equation derived in 1(b)
14     Compute the relative error between the numerical estimate and theorical value
15     Return Output
16 end
```

initially $n_j = 1$, and that $\epsilon_j = \epsilon$ and recalculate the plot with the same $\beta\epsilon$ values using the analytical solution. Plot your calculated values versus those from the analytical solution and include in your report.

(f) Modify your code in such a way that the averages are updated only after a trail move is accepted. Why does ignorign rejected moves lead to erroneous results?

(g) At which values of β does the error you obtain when ignoring rejected moves become pronounced and why?

2 Importance Sampling

Evaluate numerically the integral of $f(x) = 3x^2$ in the interval $x \in [0, 1]$ by using:

i the trapezoidal rule

ii Monte Carlo integration with importance sampling and $g(x) = 1$ as weighting function.

iii Monte Carlo integration with importance sampling and $g(x) = 2x$

iv Monte Carlo integration with importance sampling and $g(x) = 4x^3$

(a) Select a sample size (number of points) and perform multiple runs of your program (taking care not to begin all runs with the same random-number seed), taking statistics to compute the variance of the values given by the runs. This can also be done in Excel, if you prefer.

(b) Compare these results an discuss. Can you propose a better weighting function?

(c) Change the size of the sample (e.g. double or half the number of points), and see how the variance scales.

3 Detailed balance

(a) Below is a transition probability matrix for a four-state system:

$$\begin{bmatrix} 0.1 & 0.9 & 0 & 0 \\ 0.5 & 0.5 & 0 & 0 \\ 0 & 0 & 0.3 & 0.7 \\ 0 & 0 & 0.6 & 0.4 \end{bmatrix} \tag{1}$$

A Markov process that attempts to sample according to these transitions probabilities will be flawed. Explain why.

(b) As we discussed in class, it is common practice in Monte Carlo simulations to increment a running sum not after every Monte Carlo step, but instead to do the increment only after a fixed number of steps. This procedure effectively describes a "super-Markov" sequence, in which each subsequent configuratin in the sequence is obtained by an intervening series of simpler Markov steps.

Show that if the transition probabilities for the simpler Markov steps obey detailed balance, then the transition probabilities for this super-Markov sequence also obey detailed balance for the same equilibrium distribution. Hint: the transition probabilities for the multi-step move are given by Π^n, where Π is the transition-probability matrix for the single-step Markov process. You need to show that Π^n obeys detailed balance for the same equilibrium distribution as Π.