

Monte Carlo Simulations

Random Number Generators

A computer is a precise and deterministic machine, and hence, the output of a computer is predictable and not truly “random”. The word “random” represents the output of a truly random physical process such as the decay of radioactive nuclei. In radioactive decay process, we cannot predict which nucleus is going to decay and when. However, we can say that after time t , how many nuclei would have decayed using probabilistic models. Many books refer to computer generated sequences as “pseudo-random” numbers.

Uniform Deviate

“Uniform deviate” is a random number with a uniform probability distribution.

What does this mean?

1. Random number lies within a specified range, say (0,1)
2. Any number in the range is equally likely to be picked.
3. The basic building block of all “random” number generation is the “uniform deviate”.

Mathematically, for a uniform random number, z , the probability distribution function $u(z)$ is given by

$$u(z) = \begin{cases} \frac{1}{b-a} & \text{for } a \leq z \leq b \\ 0 & \text{otherwise} \end{cases}$$

Linear Congruential Scheme

The most commonly used algorithm for generating uniform deviates is using 1-D map which is called the Linear Congruential Scheme. It is a recursive relation and is given as follows

$$x_n = (ax_{n-1} + c) \bmod m$$

where a , c and m are positive integers; a is called the multiplier, c is the increment and m is the modulus.

Note : $(x \bmod y)$ means the remainder of the division of x by y . For example,

$$1 \bmod 2 = 1$$

$$2 \bmod 2 = 0$$

For the Linear Congruential Scheme, there is a recurrence period, i.e., it will eventually repeat itself. The choice of a , c and m is very important because unless the random number is “random”, i.e., the recurrence period is the maximum possible, the results will not be correct. The value of the random number generated depends on all three parameters. The random number generator thus has to fulfill the requirement that the recurrence period of the sequence be much greater than the number of random numbers needed in a specific calculation. “*Minimal Standard*” generator is the random number generator due to authors Park and Miller and the parameter values are

$$a = 7^5 = 16807$$

$$c = 0$$

$$m = 2^{31} - 1$$

$$x_0 = 12$$

The advantage of this scheme is that it is very fast.

Non-uniform Deviates

Transformation Method

Probability theory says given a probability distribution function $u(z)$, if x is a function of z as in $x(z)$, then, the density function $p(x)$ obeys $|\pi(x)dx| = |u(z)dz|$. Probability remains constant irrespective of variable. So, even if there is a transformation of variables the area under the curve remains constant.

To generate non-uniform deviates x according to $p(x)$, follow the steps given below.

1. Given that $u(z) = \begin{cases} 1 & \text{for } 0 \leq z \leq 1 \\ 0 & \text{otherwise} \end{cases}$, generate z from uniform random number generator.
2. Solve for $x(z)$ by using $\int_0^z u(z) dz = z = \int_0^x \pi(x) dx$. Generating x as per $p(x)$ requires knowledge of $\int_0^x \pi(x) dx$, i.e., this integral should be analytically solvable.

Example

Generate non-uniform deviates x from $\pi(x) = ax$ for x in $(0,1)$ where a is a normalization constant.

$$\int_0^z u(z) dz = \int_0^x \pi(x) dx$$

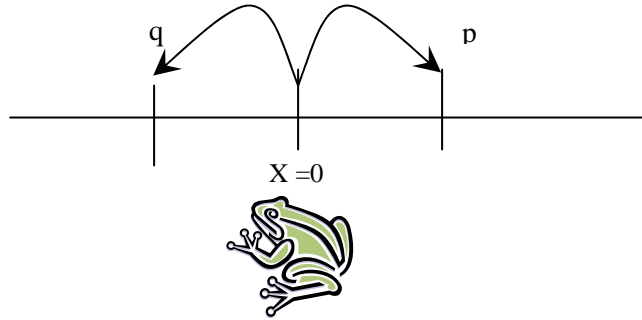
$$\Rightarrow z = \int_0^x ax dx = \frac{1}{2} ax^2$$

$$\Rightarrow x = \left(\frac{2z}{a} \right)^{1/2}$$

Taking the square root of uniform deviate gives a linearly distributed non-uniform deviate.

Random Walk in 1-D

Let us assume the frog in the figure below is our random walker.



Let the frog's initial position is $x = 0$ and every jump has a step-size of length L . The frog jumps forward with a probability p and backward with a probability q . The frog is only allowed to jump along the line and can only take one jump of step-size L after every time interval.

If all N steps taken are in the forward direction, then the total displacement will be $+NL$ and if all N steps are taken in the reverse direction then, then the total displacement will be $-NL$. Hence, the frog can have a range from $-NL$ to $+NL$.

Let N_+ steps be taken in the forward direction and N_- steps in the reverse direction. The probability distribution for the N_+ steps (or N_- steps) is given by the Binomial Distribution Function.

$$\text{Displacement, } x = (N_+ - N_-)L = (2N_+ - N)L$$

$$\text{Average Displacement, } \langle x \rangle = (\langle N_+ \rangle - \langle N_- \rangle)L = (2\langle N_+ \rangle - N)L$$

$$\text{Deviation} = x - \langle x \rangle = 2(N_+ - \langle N_+ \rangle)L$$

$$\text{Mean Square Displacement} = \text{Dispersion} = \langle (x - \langle x \rangle)^2 \rangle = 4(\langle N_+^2 \rangle - \langle N_+ \rangle^2)L^2$$

We know,

$$\langle N_+ \rangle = \sum_{N_+=0}^{+N} N_+ P(N_+) = Np$$

$$\langle N_+^2 \rangle = \sum_{N_+=0}^{+N} N_+^2 P(N_+) = Npq + N^2 p^2$$

$$\sigma_{N_+}^2 = Npq$$

Thus, dispersion is $\sigma_x^2 = 4NpqL^2$ and the mean is $\langle x \rangle = N(p - q)L$.

Algorithm

1. Generate a uniform random number r in the unit interval
2. If $(r \leq p)$ then $x = x + 1$
Else $x = x - 1$

Monte Carlo In The Microcanonical Ensemble

The Demon Algorithm

A crude and obvious method is to fix the number of particles, N , and volume of the system V , while changing the positions and velocities of the individual particles at random and retaining the microstate which has the desired total energy, E . However this method is very inefficient because most trial configurations would not have the desired total energy and would have to be discarded.

A more efficient MC method was developed by Cruetz and co-workers. (Ref. Michel Cruetz, "Microcanonical Monte Carlo Simulation", PRL, 50, pp1411 (1983)). In this method an extra degree of freedom (known as the demon) is added to the original microscopic system of interest. The demon travels around the system transferring energy as the demon attempts to change the dynamical variables of the system. If the desired change lowers the energy of the system, the excess energy is given to the demon. If the desired change raises the energy of the system, the demon gives the required energy to the system, if the demon has sufficient energy. The only constraint is that the demon can not have negative energy, i.e. $E_d \geq 0$

The demon algorithm for a classical system of particles is as follows:

Step1. Choose a particle at random

int $i = (\text{int}) (r * N)$ where r is a uniform deviate between 0 and 1

Step 2. Make a trial change in its position (say)

$\vec{r}_{trial}[i] = \vec{r}_0[i] + (1 - 2r_k)\vec{\delta}_{max}$ where r_k represents uniform deviates between 0 and 1

Step 3. Compute $\Delta E = E_{trial} - E_{old}$ = change in energy of the system due to the trial move.

Step 4. If $(\Delta E \leq 0)$, the system gives $|\Delta E|$ amount of energy to the demon, i.e.

$E_d = E_d - \Delta E$ (ΔE is negative, so, $E_d = E_d + |\Delta E|$), and the trial change is

accepted. $\vec{r}_{new}[i] = \vec{r}_{trial}[i]$ $E_{new} = E_{trial}$

Step 5. If ($\Delta E > 0$) and the demon has sufficient energy for the change i.e. $E_d = E_d - \Delta E$

And the trial configuration is accepted $\vec{r}_{new} = \vec{r}_{trial}$ and $E_{new} = E_{trial}$ otherwise trial configuration is rejected and the configuration remains unchanged.

$\vec{r}_{new} = \vec{r}_{old}$ $E_{new} = E_{old}$

The above steps are repeated until the representative sample of microstates is obtained. After a sufficient number of steps, the demon and the system will have an average energy for each.

Monte Carlo In The Canonical Ensemble

Monte Carlo Integration

Estimation of definite integrals is a problem that seemingly has nothing to do with the problem of randomness. Common numerical methods of determining the value of definite integrals include Trapezoid Rule and Simpson's rule. Numerical methods are used in solving low dimensional integrals. Monte Carlo methods generate a sequence of random numbers to estimate integrals and higher dimensions.

Numerical Integration

Let us consider a 1-D definite integral $I = \int_a^b f(x) dx$

For some choices of the integrand, $f(x)$, integration to determine I can be done analytically, or found in reference books (eg, the standard normal distribution function), or evaluated in the form of a series or numerically.

Geometrical interpretation of the integral I is that I is the area under the curve of $f(x)$ from $x = a$ to $x = b$.

Quadrature Formula (Rectangle Rule)

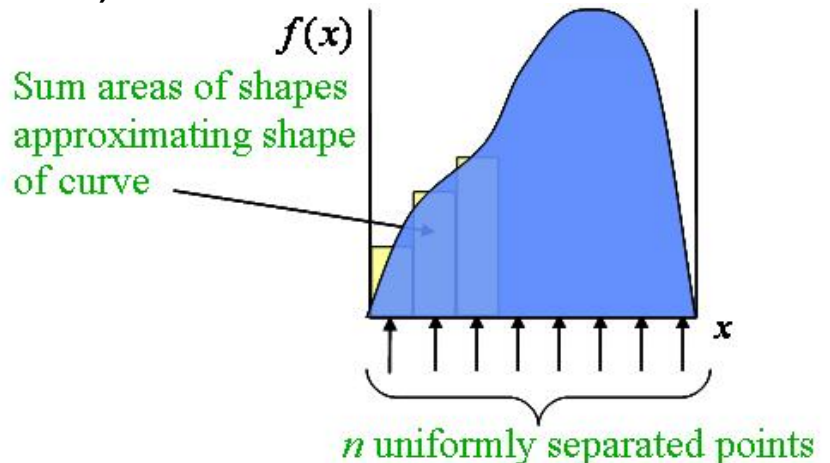
$$I = \int_a^b f(x) dx$$

$$I \sim \sum_{i=1}^n f(x_i) \Delta x_i = F_n$$

$$F_n = \Delta x \sum_{i=1}^n f(x_i)$$

where $\Delta x = \frac{(b-a)}{n}$

$$x_i = x_0 + i\Delta x$$



with $x_0 = a$ and $x_n = b$.

Thus, we can write,

$$I \sim F_n = \frac{b-a}{n} \sum_{i=1}^n f(x_i)$$

Monte Carlo (MC) Integration

MC Integration is a stochastic approach to evaluate I . It uses the same quadrature formula as in numerical integration but uses a different selection of points.

$$I = \int_a^b f(x) dx$$

$$I \sim \sum_{i=1}^n f(x_i) \Delta x_i = F_n = (b-a) \langle f(x) \rangle$$

where

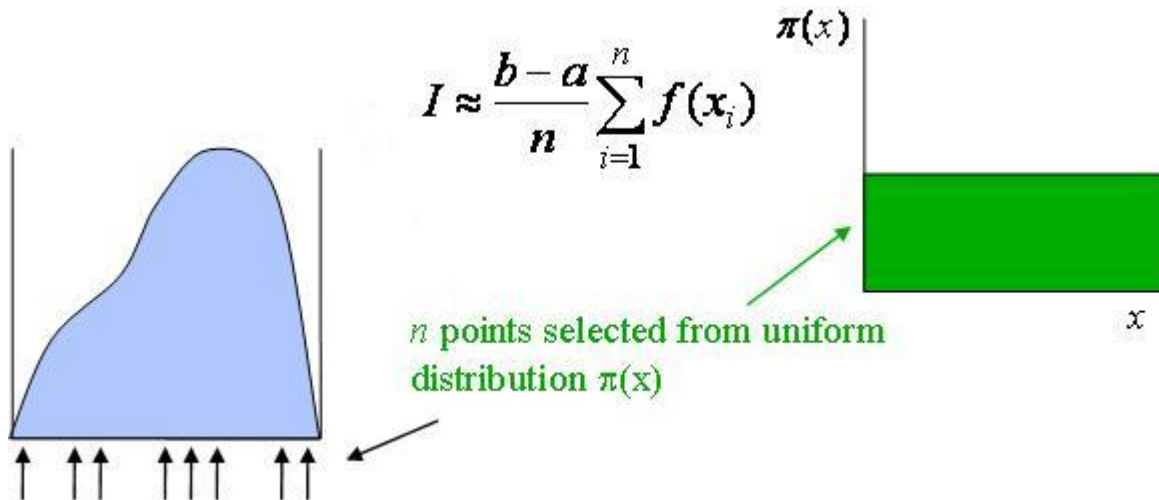
$$\langle f(x) \rangle = \frac{1}{n} \sum_{i=1}^n f(x_i)$$

The n points are selected according to the uniform distribution $u(x)$ such that

$$u(x) = \begin{cases} 1 & \text{for } 0 \leq x \leq 1 \\ 0 & \text{otherwise} \end{cases}$$

Here, x_i is the random number and n is the total number of trials.

The method described above is the “uniform sampling” MC method.



Acceptance/Rejection or Hit/Miss MC

Example: Suppose there is a pond of irregular shape inside a field of known area A . How to estimate the area of the pond, A_p ?

A MC method would be to throw stones such that the stones land at random within the boundary of the field and count the number of splashes, n_s . The splash occurs when a stone lands in the pond. The total number of stones is n_{total} .

$$A_p = \frac{n_s}{n_{total}} A$$

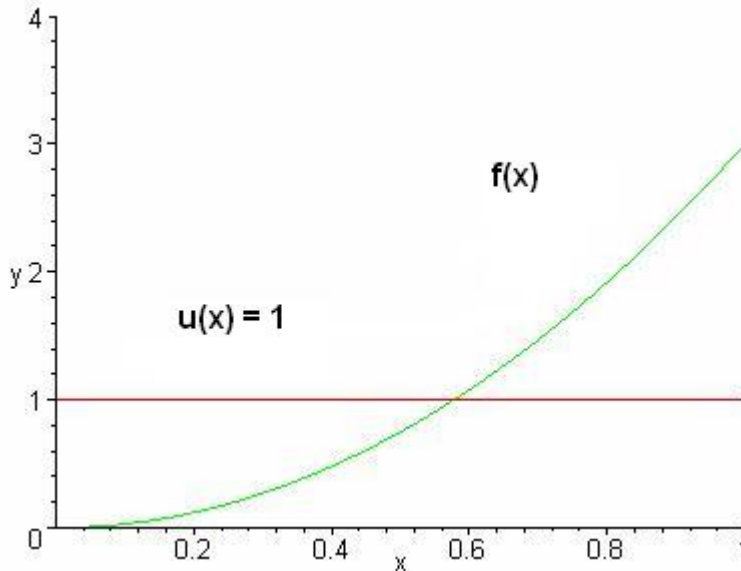
Importance Sampling

To calculate the integral, I , or in effect the area under the curve, more efficiently and obtain accurate results quickly, importance sampling is used. What this technique does is to put more points in regions where the integral receives its greatest contributions.

Let us consider the definite integral $I = \int_a^b f(x) dx = \int_0^1 3x^2 dx$

In this choice of $f(x)$, most of the contribution to the integral I is from the region near $x = 1$. In MC integration, the quadrature points are chosen not at equal spacing as is done in numerical integration, but according to a density distribution function, $\pi(x)$.

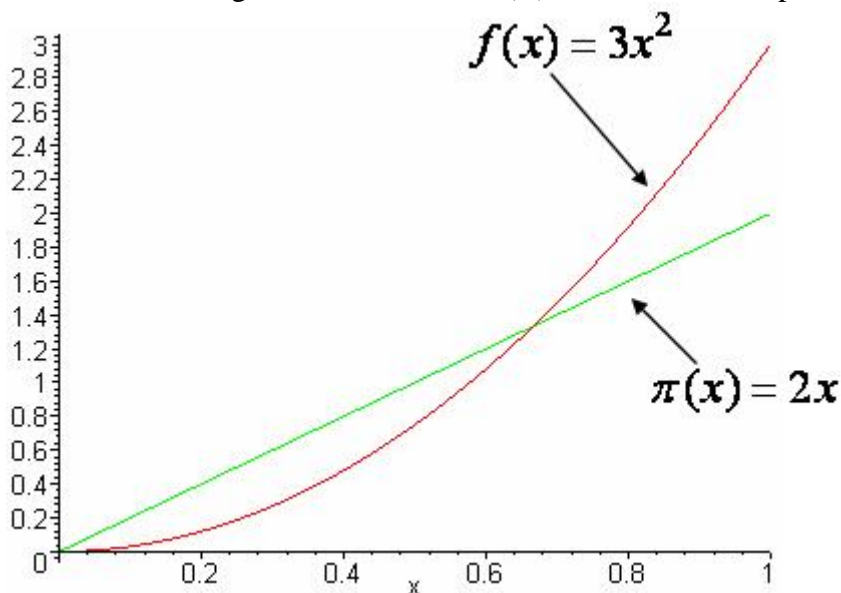
The function, $\pi(x)$, can be chosen to be the uniform distribution. In which case, with reference to figure, there are points chosen which are wasted.



To improve the efficiency, let us choose the points as per a linear distribution such as $\pi(x) = 2x$. This will however introduce a bias. How to remove this bias? For the importance sampled integral, $F_n = \sum_{i=1}^n f(x_i) \Delta x_i$, consider the unevenly spaced abscissa such that the spacing between the points is taken as the reciprocal of local number of points per unit length, i.e.

$$\Delta x_i = \left(\frac{b-a}{n} \right) \frac{1}{\pi(x_i)} = \left(\frac{1}{n} \right) \frac{1}{(2x_i)}$$

This ensures that greater the value of $\pi(x_i)$, more number of points and smaller spacing



So, the importance sampled quadrature integral can be written as

$$I = \int_a^b f(x) dx = \int_0^1 3x^2 dx$$

$$\Rightarrow I = \int_0^1 \frac{f(x)}{\pi(x)} \pi(x) dx \sim \frac{1}{n} \sum_{i=1}^n \frac{f(x_i)}{\pi(x_i)} = \left\langle \frac{f(x)}{\pi(x)} \right\rangle_{\pi(x)}$$

To generate, non uniform deviates as per $\pi(x) = 2x$, use the transformation method.

In the canonical ensemble, the importance sampling algorithm used is called the Metropolis algorithm which is a Markov Process. Let us learn about Markov processes in the next section.

Markov Processes

Stochastic process is a movement through a series of well-defined states in a way that involves some element of randomness. “Stochastic” is a synonym for statistic. Statistics cannot predict which event will occur next, but can predict the average number of times an event can occur.

Markov process is a stochastic process that has no memory of its history. The selection of the next state does not depend on any prior states. The process is fully defined by a set of transition probabilities which are collected in a transition probability matrix, $\Pi = \{\pi_{ij}\}$.

Example:

Consider a hydrocarbon which can exist in three states, viz., trans (state 1), gauche+ (state 2) and gauche- (state 3). The transition probability matrix for this system can be written as follows:-

$$\Pi \equiv \begin{pmatrix} \pi_{11} & \pi_{12} & \pi_{13} \\ \pi_{21} & \pi_{22} & \pi_{23} \\ \pi_{31} & \pi_{32} & \pi_{33} \end{pmatrix}$$

*If in state 1, will stay in state 1
with probability π_{11}*

*If in state 2, will move to state 3
with probability π_{23}*

Requirements of a transition probability matrix

1. All probabilities are non-negative and no greater than unity. $0 \leq \pi_{ij} \leq 1$.
2. Sum of each row is unity. $\sum_j \pi_{ij} = 1$
3. Probability of staying in present state may be non-zero. $\pi_{ii} \geq 0$. This is in contrast to random walk.

Distribution of State Occupancies

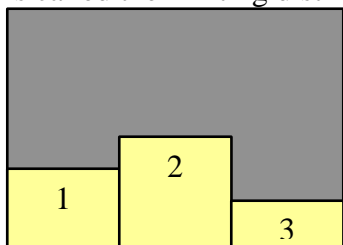
Consider process of repeatedly moving from one state to the next, choosing each subsequent state according to Π

$1 \rightarrow 2 \rightarrow 2 \rightarrow 1 \rightarrow 3 \rightarrow 2 \rightarrow 2 \rightarrow 3 \rightarrow 3 \rightarrow 1 \rightarrow 2 \rightarrow 3 \rightarrow \text{etc.}$

Here, we find,

$$\begin{aligned} n_1 &= 3 & \pi_1 &= 0.33 \\ n_2 &= 5 & \pi_2 &= 0.42 \\ n_3 &= 4 & \pi_3 &= 0.25 \end{aligned}$$

One could construct a histogram to describe the number of times visited in each of the three states during the process. After a long period of sampling, steady state is reached and the histogram does not change with continued sampling. The histogram so obtained is called the limiting distribution of the Markov process.



Limiting distribution

We consider now how the limiting distribution relates to the Π . Consider the product of Π with itself

$$\begin{aligned}\Pi^2 &\equiv \begin{pmatrix} \pi_{11} & \pi_{12} & \pi_{13} \\ \pi_{21} & \pi_{22} & \pi_{23} \\ \pi_{31} & \pi_{32} & \pi_{33} \end{pmatrix} \times \begin{pmatrix} \pi_{11} & \pi_{12} & \pi_{13} \\ \pi_{21} & \pi_{22} & \pi_{23} \\ \pi_{31} & \pi_{32} & \pi_{33} \end{pmatrix} \\ &= \begin{pmatrix} \pi_{11}\pi_{11} + \pi_{12}\pi_{21} + \pi_{13}\pi_{31} & \pi_{11}\pi_{12} + \pi_{12}\pi_{22} + \pi_{13}\pi_{32} & \text{etc.} \\ \pi_{21}\pi_{11} + \pi_{22}\pi_{21} + \pi_{23}\pi_{31} & \pi_{21}\pi_{12} + \pi_{22}\pi_{22} + \pi_{23}\pi_{32} & \text{etc.} \\ \pi_{31}\pi_{11} + \pi_{32}\pi_{21} + \pi_{33}\pi_{31} & \pi_{31}\pi_{12} + \pi_{32}\pi_{22} + \pi_{33}\pi_{32} & \text{etc.} \end{pmatrix}\end{aligned}$$

Look closely at the first (1,1) element. It is the sum of three terms. The first term, $\pi_{11}\pi_{11}$ is the probability of staying in state 1 for two successive steps, given that the system started in state 1. Similarly, the second term in the sum $\pi_{12}\pi_{21}$ the probability that the system moves in successive steps from state 1 to state 2, and then back again. Finally the third term is the probability of moving from 1 to 3 and back to 1. Thus the (1,1) terms in the product matrix contains all ways of going from state 1 back to state 1 in two steps. Likewise, the (1,2) term of the product matrix is the probability that the system moves from state 1 to state 2 in exactly two steps. The same interpretation holds for all the terms in the product matrix. Thus the square of Π is a two-step transition-probability matrix, and in general the multiple product Π^n is the n-step Π

$$\Pi^n \equiv \begin{pmatrix} \pi_{11}^{(n)} & \pi_{12}^{(n)} & \pi_{13}^{(n)} \\ \pi_{21}^{(n)} & \pi_{22}^{(n)} & \pi_{23}^{(n)} \\ \pi_{31}^{(n)} & \pi_{32}^{(n)} & \pi_{33}^{(n)} \end{pmatrix}$$

where each term $\pi_{ij}^{(n)}$ is defined as the probability of going from state i to state j in exactly n Markov steps.

Let us define $\pi_i^{(0)}$ as a unit state vector for simplicity, thus (for a 3-state system)

$$\pi_1^{(0)} = (1 \ 0 \ 0) \quad \pi_2^{(0)} = (0 \ 1 \ 0) \quad \pi_3^{(0)} = (0 \ 0 \ 1)$$

Then $\pi_i^{(n)}$ is a vector describing the probabilities for ending at each state after n Markov steps beginning at state i

$$\pi_1^{(n)} = \pi_1^{(0)} \Pi^n \equiv (1 \ 0 \ 0) \begin{pmatrix} \pi_{11}^{(n)} & \pi_{12}^{(n)} & \pi_{13}^{(n)} \\ \pi_{21}^{(n)} & \pi_{22}^{(n)} & \pi_{23}^{(n)} \\ \pi_{31}^{(n)} & \pi_{32}^{(n)} & \pi_{33}^{(n)} \end{pmatrix} = (\pi_{11}^{(n)} \ \pi_{12}^{(n)} \ \pi_{13}^{(n)})$$

The limiting distribution corresponds to $n \rightarrow \infty$, and will be independent of the initial state i if the Π describes an ergodic process.

$$\pi_1^{(\infty)} = \pi_2^{(\infty)} = \pi_3^{(\infty)} \equiv \pi$$

The limiting distribution obeys a stationary property.

$$\pi = \lim_{n \rightarrow \infty} [\pi_i^{(0)} \Pi^n] = \left(\lim_{n \rightarrow \infty} [\pi_i^{(0)} \Pi^{n-1}] \right) \Pi = \pi \Pi$$

Thus,
 $\pi = \pi \Pi$

$$\pi_i = \sum_j \pi_j \pi_{ji}$$

where the sum extends over all states. If the limiting probabilities π_i and the transition probabilities π_{ij} all satisfy the following relation

$$\pi_i \pi_{ij} = \pi_j \pi_{ji}$$

This relation is known as *detailed balance*, or the *principle of microscopic reversibility*. As demonstrated below, it presents a sufficient condition but it is not a necessary condition.

The limiting probabilities π_i and the transition probabilities π_{ij} also satisfy the eigenvector equation as presented before, as is easily shown

$$\begin{aligned} \pi_i &= \sum_j \pi_j \pi_{ji} \\ &= \sum_j \pi_i \pi_{ij} \\ &= \pi_i \sum_j \pi_{ij} = \pi_i \end{aligned}$$

For a given Π , it is not always possible to satisfy detailed balance; e.g. for this Π

$$\Pi = \begin{pmatrix} 0.1 & 0.5 & 0.4 \\ 0.9 & 0.1 & 0.0 \\ 0.3 & 0.3 & 0.4 \end{pmatrix}$$

Here, $\pi_3 \pi_{32} \neq \pi_2 \pi_{23}$

One of the elements (π_{23}) is zero, while its detailed-balance counterpart (π_{32}) is not zero. Detailed balance cannot be satisfied for this pair (unless perhaps π_3 is zero, but this clearly is not the case here since there is a route to state 3 from state 1).

Deriving transition probabilities

The utility of detailed balance is not in determining the limiting distribution from a set of transition probabilities. In fact, we have to answer the question given a desired π , what transition probabilities will yield this as a limiting distribution? Construct transition probabilities to satisfy detailed balance.

Example

For the limiting distribution, $\pi = (0.25 \quad 0.5 \quad 0.25)$, generate Π .

No unique solution, many possible choices.

$$\Pi = \begin{pmatrix} 0.97 & 0.02 & 0.01 \\ 0.01 & 0.98 & 0.01 \\ 0.01 & 0.02 & 0.97 \end{pmatrix}$$

Metropolis Algorithm

This algorithm is useful for computing averages such as $\langle f \rangle = \frac{\int f(x) p(x) dx}{\int p(x) dx}$ where

$p(x)$ is an arbitrary probability distribution function that need not be normalized. We need to know only the limiting distribution and not the transition probabilities.

Let state k be represented by the variable, x_k , and we want to generate x_{k+1} .

Algorithm

Step 1) Choose a trial variable $x_{\text{trial}} = x_k + d_k$ where $d_k = (1-2r_1)*d_{\text{max}}$

Step 2) Calculate $w = p(x_{\text{trial}})/p(x_k)$

Step 3) If ($w > 1$) accept the trial change and $x_{k+1} = x_{\text{trial}}$

else If ($w < 1$) generate random number r_2

if ($r_2 \leq w$) accept the trial change $x_{k+1} = x_{\text{trial}}$

else $x_{k+1} = x_k$

This algorithm was first published in the landmark paper *Journal Of Chemical Physics*, 1953, 21, pp 1087.

Metropolis Algorithm as applied to the Canonical Ensemble

1. Establish an initial microstate. For example, all N atoms are assigned initial positions.
2. Make a random trial change in the microstate.

a. Choose an atom at random: $i = (\text{int})(r_1 * N)$ where r_1 is a uniform deviate between 0 and 1.

b. Make a trial displacement

$$x_{\text{trial}} = x_i + (1 - 2r_2) \delta_{\text{max}}$$

$$y_{\text{trial}} = y_i + (1 - 2r_3) \delta_{\text{max}}$$

$$z_{\text{trial}} = z_i + (1 - 2r_4) \delta_{\text{max}}$$

Apply Periodic Boundary Conditions

3. Compute $\Delta E = E_{\text{trial}} - E_{\text{old}}$ = change in energy of the system due to trial change.

4. If $(\Delta E \leq 0)$ accept the trial microstate as the new microstate and goto step 8.
5. If $(\Delta E > 0)$ compute $w = \exp[-\beta\Delta E]$.
6. Generate uniform deviate r_5 .
7. If $(r_5 \leq w)$ accept trial microstate as the new microstate
Else reject and retain old microstate as the new microstate.
8. Determine the value of desired macroscopic property.
9. Steps 2 to 8 constitute one MC step. Repeat steps 2 to 8 N times (to allow for the possibility for all N atoms to move) for 1 MC cycle.
10. Complete maximum number of MC cycles specified and calculate averages.

Note that after relaxation or equilibration cycles all sums of macroscopic properties are reset to zero so that averages are determined only over production cycles.

In the above algorithm, if $E_{\text{trial}} < E_i$, then $\Delta E \leq 0.0$, so that the system moves to a lower energy state. However, even some higher energy states are accepted i.e. when $\Delta E > 0$ as this enables an atom trapped in the local minimum to jump out and move to the global minimum. Say, an atom is in the local minimum and wants to move out to a state j such that $E_j > E_{\text{localmin}}$ then the $\Delta E_{\text{localmin}} = E_j - E_{\text{localmin}}$. Now an atom in the global minimum wanting to move to state j will require $\Delta E_{\text{globalmin}} = E_j - E_{\text{globalmin}}$. Since, $E_{\text{localmin}} > E_{\text{globalmin}}$, $\Delta E_{\text{localmin}} < \Delta E_{\text{globalmin}}$ and $w_{\text{localmin}} > w_{\text{globalmin}}$. This means that it will be easier to generate a random number r between 0 and w_{localmin} as compared to 0 and $w_{\text{globalmin}}$. And, the atom is more likely to remain in the global minimum as compared to the local minimum.

Metropolis Algorithm In Other Ensembles

Metropolis algorithm in the Isothermal Isobaric Ensemble is as follows:

1. Initialize the position of all N atoms in an initial volume. There should be no overlap in positions.
2. Choose a trial move at random. The two possible moves are atom displacement trials and volume change trials. Both trials have to be completed for one MC cycle. The frequency ratio of atom displacement trials : volume change trials = N: 1
3. Atom displacement trials are as seen in the Canonical ensemble.
4. Volume change trial is given below:
 - a. Change the volume of the simulation cell at random, i.e.,

$$\ln V_{\text{trial}} = \ln V_i + d \ln V = \ln V_i + (1 - 2r) \delta_{\text{max}}$$
 - b. Calculate $L_{\text{trial}} = V_{\text{trial}}^{1/3}$
 - c. Scale positions of all N atoms. $x_{\text{trial}} = \frac{x_{\text{old}}}{L_{\text{old}}} * L_{\text{trial}}$

- d. Determine w as $w = e^{-\beta P(V_{trial} - V_{old})} e^{+N \ln \left(\frac{V_{trial}}{V_{old}} \right)} e^{-\beta(U_{trial} - U_{old})}$
- e. Generate a uniform deviate, $r' \in (0,1)$
- f. If $(r' < w)$ accept the trial change
 $V_{new} = V_{trial}$ and for all N atoms $x_{new} = x_{trial}$
 Else reject the trial change
 $V_{new} = V_{old}$ and for all N atoms $x_{new} = x_{old}$
5. Step 4 constitutes one MC cycle, thus, for a trial volume change 1 MC step = 1 MC cycle as all N atoms are scaled to new positions.
6. Steps 2 to 4 are repeated until maximum number of MC cycles is reached.

CASE STUDY

The Ising Spin Model

The Ising model is a simple, interacting spin model that can be conveniently used to study the paramagnetism to ferromagnetism transition. This model was proposed by Lenz and investigated by his graduate student, Ising, to study the phase transition from a paramagnet to a ferromagnet.

Definition Of A Paramagnet

A substance that can be magnetized by an external magnetic field and disappears as the field disappears is said to be a paramagnet.

Definition Of A Ferromagnet

A ferromagnet on the other hand is a substance in which the domains are aligned by an external magnetic field (eg. from another permanent magnet) so that it becomes a permanent magnet.

At temperatures lower than the **Curie temperature**, the system behaves as a ferromagnet and for temperatures above the Curie temperature (T_C), the system behaves as a paramagnet.

Ising (in 1925) computed the thermodynamic properties of the model and discovered that the model does not have a phase transition in 1-D. However, for higher dimensions (2-D and 3-D), others showed that the model does exhibit a phase transition.

In the Ising model, a fixed lattice is constructed and spins are placed at each lattice points.

The assumptions of the Ising model are as follows:-

1. Each lattice site may have only one of two discrete spin values associated with it, where +1 is for an “up” spin and -1 is for a “down” spin.
2. Only the nearest neighbour spins interact
3. The kinetic energy of the particles themselves is neglected.

Therefore, in the Ising model, for a lattice containing N sites each with spin s_i , a particular configuration or microstate of the lattice is specified by the set of variables $\{s_1, s_2, s_3, \dots, s_i, \dots, s_N\}$ for all the lattice sites. The macroscopic properties of the system are determined by the nature of the accessible microstates. Thus, if s_i represents the value of spin on site i , then the net scaled magnetic moment or magnetization, M , is given

$M = \sum_{i=1}^N s_i$. Therefore, the state of the system is specified when the values of all the spin are given.

It is necessary to know the dependence of the total energy on the configuration of the spins. The total energy E of the Ising model is given by

$$E = -J \sum_{i=1}^N \sum_{j=NN(i)}^{No \text{ repeats}} s_i s_j - H \sum_{i=1}^N s_i$$

where H is the magnetic field strength from the uniform external magnetic field; the summation refers to the sum over all different nearest neighbour pairs with no repeats;

J is the exchange constant, a measure of the strength of interaction between neighbouring spins.

1-D Ising model

The 1-D case does not show phase transition from para- to ferro- magnet. However, the 1-D model is analytically solvable and can be used to validate the code.

PBC: For a 1-D lattice, application of PBC results in the lattice becoming a ring and spins at sites 1 and N interact with one another and have the same number of interactions as do other spins,. If we do not apply PBC, the sites 1 and N have only 1 nearest neighbour unlike sites 2 to $N-1$, which have two each. PBCs wrap the system back on itself, so that end spins are neighbours.

For thermodynamic property calculations, the 1-D Ising model with no spin interactions is known as the ideal Ising model with $J = 0$. The energy expression thus reduces to

$$E = -H \sum_{i=1}^N s_i$$

First, let us find the expression for the canonical partition function for this model.

N = total number of spins in the system

$$\text{For } N = 2, \quad Q = \left(e^{-\beta H} + e^{+\beta H} \right)^2$$

$$\text{For } N = 3, \quad Q = \left(e^{-\beta H} + e^{+\beta H} \right)^3$$

Similarly, for any given N , $Q = \left(e^{-\beta H} + e^{+\beta H} \right)^N = \left(2 \cosh(\beta H) \right)^N$

Implementation of Metropolis algorithm for Ising model

Step 1: Establish an initial microstate which is a random configuration of spins.

Step 2: Make a random trial change in the microstate. Choose a spin at random and flip the spin.

Step 3: Compute the change in energy of the system due to trial change.

Step 4: If the energy change is negative or zero, then accept the trial change and the new microstate is the trial microstate and goto step 7.

Step 5: If the energy change is positive, compute the Boltzmann's weighting factor, w .

Step 6: Generate a uniform deviate r between (0,1) and if ($r \leq w$), then accept the trial change otherwise retain the previous microstate as the new microstate.

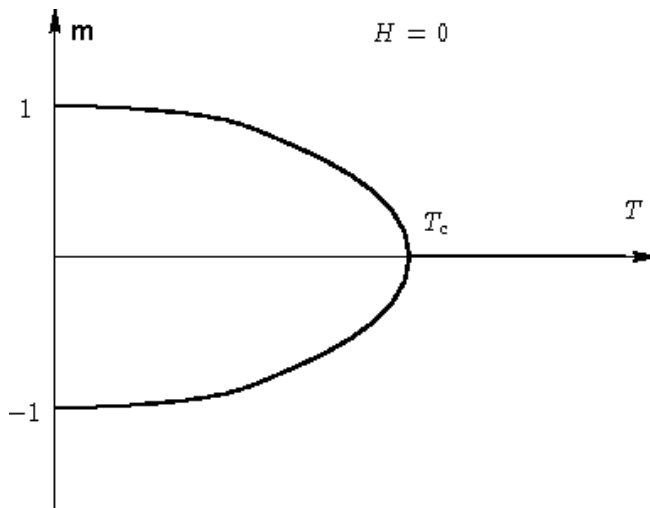
Step 7: Determine the value for E and M (or any other property to be measured).

Step 8: Repeat steps 2 through 7 for the required number of times, N_{trials} (sample adequate microstates).

Step 9: Compute averages over the N_{trials} .

Physics:

The flipping of single spins can be thought as a reasonable approximation to the real dynamics of an anisotropic magnet whose spins are coupled to the vibrations of the lattice. The coupling leads to random spin flips. It is expected that 1 Monte Carlo step per spin is proportional to the average time between single spin flips observed in the laboratory. The application of the Metropolis algorithm to the Ising model is known as “single spin flip dynamics”.



A non-zero m means a net number of spins are aligned in a particular direction and hence $|M|/N = m$ is termed the “order parameter” of the system. Near the Curie temperature, we can characterize the behaviour of m by the power law. Near Curie temperature, T_c , we can write $m(T) \sim (T_c - T)^{\beta_c}$ where β_c is a critical exponent with values of 0.125 for 2-D Ising model and 0.32 for 3-D Ising model. As properties at and around the critical point are difficult to measure experimentally, this power law behaviour is important.

For vapour –liquid equilibria (VLE), analogous results have been observed with the density difference as the order parameter. The equation is as follows:

$$\rho_L - \rho_v = B(T - T_c)^{\beta_c}$$

Here, B is the proportionality constant and the critical exponent is the same as that for the Ising model.

In a simulation, we often locate phase transition by computing the thermodynamic properties of the individual phases, then finding the coexistence point where temperature, pressure and chemical potential of all species in all the bulk phases are equal. For, VLE the most common simulation method in use is the Gibbs' Ensemble Monte Carlo (GEMC) method