

# Metropolis and Wang-Landau Algorithms

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**Abstract.** Metropolis algorithm has been extensively employed for simulating a canonical ensemble and estimating macroscopic properties of a closed system at any desired temperature. A mechanical property, like energy can be calculated by averaging over a large number of micro states of the stationary Markov chain generated by the Metropolis algorithm. However thermal properties like entropy, and free energies are not easily accessible. A method called *umbrella sampling* was proposed some forty years ago for this purpose. Ever since, umbrella sampling has undergone several metamorphoses and we have now multi canonical Monte Carlo, entropic sampling, flat histogram methods, Wang-Landau algorithm *etc.* In these talks I shall tell you of Metropolis algorithm for estimating mechanical properties and of Wang-Landau algorithm for estimating both mechanical and thermal properties of an equilibrium system. I shall make these lectures as pedagogical and self-contained as possible.

## Some Preliminaries

Statistical mechanics helps us go from the micro world of atoms and molecules obeying laws of classical and quantum mechanics to the macro world of thermodynamics describing matter in bulk. In a single stroke, Ludwig Eduard Boltzmann (1844 - 1906) connected physics at the length scales of atoms and molecules to phenomena on length scales of solids, liquids, gases, polymers, magnets, *etc.* The micro-macro synthesis proceeds, very generally, along the following lines.

First, we identify a random variable that corresponds to a thermodynamic property. The average of the random variable over a suitable and well defined statistical ensemble<sup>1</sup> gives

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<sup>1</sup> *e.g.* Gibbs' ensembles : micro canonical for an isolated system; canonical for a closed system; and grand canonical for an open system.

The notion of an ensemble came from James Clerk Maxwell (1831-1879). A **Maxwell's ensemble** is a set, whose elements are drawn from the micro states of the system under considerations. A micro state occurs in the ensemble several times. Number of times it occurs divided by the size of the ensemble equal its probability. Thus, an ensemble contains, not only information about the micro states of the system, but also about their probabilities.

Imagine now, a collection of a large number of identical mental copies of the macroscopic system under consideration. They constitute a **Gibbs' ensemble**. Each member of the Gibbs' ensemble shall be in some micro state of the other. Different members can be in different micro states; But all of them have the same macroscopic properties. This is what we mean when we say they are identical mental copies of the system. When the number of elements in the Gibbs' ensemble is large then the number of systems in a given micro state divided by the size of the ensemble will give the probability of the micro state.

Given the micro states and their probabilities, we can construct an ensemble. This is what we do in Monte Carlo. Given an ensemble, we can calculate the probabilities of the micro states of the macroscopic system to which the ensembles belongs. This is what we do when we derive Boltzmann weight for the micro states employing

the value of the thermodynamic property. As an example, consider internal energy<sup>2</sup> of a thermodynamic system. This property is usually denoted by the symbol  $U$ . Corresponding to this property, we have, in statistical mechanics, energy  $E$  - the kinetic energy and the interaction energy of the atoms and molecules of the macroscopic object. A numerical value for  $E$  can be assigned to each micro state<sup>3</sup> of the macroscopic system. The value of  $E$  will fluctuate when the equilibrium system goes from one micro state to another. These fluctuations are an integral part of an equilibrium description. The average of  $E$  gives the internal energy :  $\langle E \rangle = U$ , and the fluctuations are proportional to the heat capacity<sup>4</sup> :  $\langle E^2 \rangle - \langle E \rangle^2 \propto C_V$ . The symbol  $\langle (\bullet) \rangle$  denotes averaging of the property  $(\bullet)$  over the chosen ensemble.

## Energy

The computation of average energy is now straight forward : Generate a canonical ensemble employing, for example, Monte Carlo method based on Metropolis algorithm; a simple arithmetic average of  $E$  over a Monte Carlo sample of reasonably large size, gives the required answer. The statistical error associated with the finite-sample average can also be calculated from the data obtained in the simulation. Such a neat computational scheme is possible because a numerical value for energy can be assigned to each micro state of the macroscopic system.

## Entropy

How does one calculate entropy ?

We can not assign a numerical value for entropy to any single micro state. Entropy is a property that belongs collectively to all the micro states. While energy is a *private* property (of

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*the method of most probable distribution* where we construct a Canonical ensemble. See any standard text book on statistical mechanics *e.g.* the book written by Pathria [1].

<sup>2</sup> **Internal Energy and the First Law of Thermodynamics** : In thermodynamics, internal energy is defined completely in terms of work done in adiabatic processes : Select a reference point  $O$  in the thermodynamic phase plane. Define a function  $U$  as follows. Assign an arbitrary value to  $U(O)$ . Consider a point  $A$ . Measure or calculate work done in an adiabatic process that takes the system from  $O$  to  $A$ . Then define :  $U(A) = U(O) + W_{O \rightarrow A}^A$ . The superscript  $A$  tells that the process considered is adiabatic. Employ the convention : *work done on the system is positive and work done by the system is negative*. By considering adiabatic processes we can define  $U$  at all points on the phase plane. If there exists a point, say  $B$ , which is not accessible adiabatically from  $O$  then consider an adiabatic process that takes the system from  $B$  to  $O$  for purpose of defining  $U$  :  $U(B) = U(O) - W_{B \rightarrow O}^A$ . Then consider an arbitrary process from  $C$  to  $D$ . Let  $W$  be the work done and  $\Delta U = U(D) - U(C)$ . Then,  $\Delta Q = \Delta U - W$  is called heat and this is a statement of the first law of thermodynamics. Heat is the difference between actual work and adiabatic work. Thus the first law of thermodynamics establishes the mechanical equivalence of heat. As an off-shoot of the first law of thermodynamics we get to define a thermodynamic property called the internal energy, denoted by the symbol  $U$ .

<sup>3</sup> For example three positions  $(q_1, q_2, q_3)$  and three momenta  $(p_1, p_2, p_3)$  are required to specify a single point particle. For  $N$  particles, we need a string of  $6N$  numbers and this string denotes a micro state of the macroscopic system of  $N$  particles.

$$E = \frac{1}{2m} \sum_{i=1}^{3N} p_i^2 + V(q_1, q_2, \dots, q_{3N}).$$

The energy consists of the kinetic energy and potential energy. Note that energy is defined for each micro state. For a macroscopic system of say  $N$  Ising spins, we have  $2^N$  micro states since each Ising spin can be in either "up" ( $S_i = +1$ ) state or "down" ( $S_i = -1$ ) state.

$$E = -J \sum_{\langle i,j \rangle} S_i S_j,$$

where  $S_i$  is the spin at lattice site  $i$  and  $J > 0$  measures the strength of spin-spin interaction. Spins on nearest neighbour lattice sites interact. The sum runs over all pairs of nearest neighbour spins

<sup>4</sup> called fluctuation dissipation theorem relating equilibrium fluctuations to response of the system to small perturbation.

each micro state) entropy is a *social* or a *pubic* property, see below.

Let  $\Omega = \{\mathcal{X}_\nu : \nu = 1, 2, \dots, \widehat{\Omega}\}$  denote the set of micro states of an equilibrium system; the micro states are discrete, distinct and finite in number.  $\{p(\mathcal{X}_\nu) : \nu = 1, 2, \dots, \widehat{\Omega}\}$  are their probabilities. We use ‘ script  $\mathcal{X}$  ’ to denote micro states of the system and ‘ roman  $X$  ’ to denote micro states of an ensemble or of a Monte Carlo sample or of a Markov chain. The Boltzmann-Gibbs-Shannon entropy is given by

$$S = -k_B \sum_{\nu=1}^{\widehat{\Omega}} p(\mathcal{X}_\nu) \ln p(\mathcal{X}_\nu).$$

In the above,  $k_B$  is the Boltzmann constant<sup>5</sup>.

### Entropy of an Isolated System

For an isolated system the micro states are equally probable<sup>6</sup>. We have,

$$p(\mathcal{X}_\nu) = \frac{1}{\widehat{\Omega}(E, V, N)} \forall \nu.$$

$\widehat{\Omega}(E, V, N)$  is the number of micro states of the isolated system of  $N$  particles, confined to a volume  $V$ , and with a fixed total energy of  $E$ . For an isolated system the expression for entropy simplifies to  $S(E, V, N) = k_B \ln \widehat{\Omega}(E, V, N)$ .

### Entropy of a Closed System

For a closed system at temperature<sup>7</sup>  $T = 1/[k_B\beta]$ , we have

$$p(\mathcal{X}_\nu) = \frac{1}{Q} \exp[-\beta E(\mathcal{X}_\nu)], \text{ where } Q = \sum_{\nu=1}^{\widehat{\Omega}} \exp[-\beta E(\mathcal{X}_\nu)],$$

is called the canonical partition function.

### Entropy of an Open System

For an open system we have

$$p(\mathcal{X}_\nu) = \frac{1}{Q} \exp[-\beta\{E(\mathcal{X}_\nu) - \mu N(\mathcal{X}_\nu)\}], \text{ where } Q(T, V, \mu) = \sum_{\nu=1}^{\widehat{\Omega}} \exp[-\beta\{E(\mathcal{X}_\nu) - \mu N(\mathcal{X}_\nu)\}],$$

is the grand canonical partition function. In the above,  $\mu$  is the chemical potential<sup>8</sup> of the system, and  $N(\mathcal{X}_\nu)$  is the number of particles in the system when it is in micro state  $\mathcal{X}_\nu$ .

Our aim is to simulate physical processes occurring in an equilibrium system and assemble a large number of micro states consistent with the given probabilities. To this end, we start with an arbitrary initial micro state  $X_0(\in \Omega)$ ; then, employing Metropolis rejection algorithm [2] we generate a Markov chain<sup>9</sup>,

$$X_0(\in \Omega) \rightarrow X_1(\in \Omega) \rightarrow X_2(\in \Omega) \rightarrow \dots \rightarrow X_i(\in \Omega) \rightarrow X_{i+1}(\in \Omega) \rightarrow \dots$$

<sup>5</sup>  $k_B = 1.38064852 \times 10^{-23}$  joules/kelvin is called the Boltzmann constant. It helps us convert energy measured in units of kelvin to energy in units of joule.

<sup>6</sup> we call it *ergodicity*; it is an hypothesis; the entire edifice of statistical mechanics is built on this hypothesis.

<sup>7</sup> In thermodynamics, temperature is defined as  $T = (\partial U / \partial S)_{V, N}$ .

<sup>8</sup> the chemical potential gives the change in energy upon addition of a single particle keeping the entropy and volume of the system at a constant value. words  $\mu = (\partial U / \partial N)_{S, V}$ .

<sup>9</sup> **Markov Chain** : Consider a sequence of micro states visited by the system at discrete times starting from

### Metropolis Rejection Algorithm

Let us say we have simulated the Markov chain upto  $X_i \in \Omega$  starting from  $X_0 \in \Omega$ . Thus the current micro state is  $X_i$ . Let  $p_i = p(X_i)$  denote its probability. We make a small random change in the current micro state and construct a trial micro state<sup>10</sup>  $X_t \in \Omega$ . Let  $p_t = p(X_t)$  denote its probability. Calculate  $p = \text{minimum}(1, p_t/p_i)$ . Then, the next micro state in the Markov chain is given by,

$$X_{i+1} = \begin{cases} X_t & \text{with probability } p \\ X_i & \text{with probability } 1 - p \end{cases}$$

The implementation of the above goes as follows :

- Generate a random number<sup>11</sup> uniformly distributed between zero and unity. Denote it by the symbol  $\xi$ .

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$X_0$  at time 0. Let us denote the sequence by  $X_0 \rightarrow X_1 \rightarrow \dots \rightarrow X_{n-1} \rightarrow X_n$ , where the subscript denote the discrete time index. Our interest is to calculate the joint probability of the sequence. From Bayes' theorem we have,

$$P(X_n, X_{n-1}, \dots, X_1, X_0) = P(X_n | X_{n-1}, X_{n-2}, \dots, X_1, X_0) \times P(X_{n-1}, X_{n-2}, \dots, X_1, X_0).$$

If  $P(X_n | X_{n-1}, X_{n-2}, \dots, X_1, X_0) = P(X_n | X_{n-1})$ , then  $X_0 \rightarrow X_1 \rightarrow \dots \rightarrow X_{n-1} \rightarrow X_n$  is a Markov chain : The future depends only on the present and not on the past. Thus, once the present is specified, the future is independent of the past.

Under Markovian condition, the expression for the joint probability of the chain of micro states, simplifies to

$$\begin{aligned} P(X_n, X_{n-1}, \dots, X_1, X_0) &= P(X_n | X_{n-1}) \times P(X_{n-1}, X_{n-2}, \dots, X_1, X_0), \\ &= P(X_n | X_{n-1}) \times P(X_{n-1} | X_{n-2}) \times P(X_{n-2}, X_{n-3}, \dots, X_1, X_0), \\ &= \dots\dots\dots, \\ &= P(X_n | X_{n-1}) \times P(X_{n-1} | X_{n-2}) \times \dots \times P(X_1 | X_0) \times P(X_0). \end{aligned}$$

Since we are interested in equilibrium properties we consider a sequence of states visited by an equilibrium system : The conditional probability,  $P(X_n | X_{n-1})$  is independent of the time index. In other words

$$P(X_n = \mathcal{X}_\mu | X_{n-1} = \mathcal{X}_\nu) = W_{\mu,\nu},$$

and this quantity is independent of time. We call it time homogeneous Markov chain. Once we know the transition probability matrix  $W$  and initial probabilities of all the micro states, we can calculate the probability of any given Markov Chain. The transition probability matrix  $W$  is a square matrix of size  $\hat{\Omega}$ . We have

$$0 \leq W_{\mu,\nu} \leq 1 \quad \forall \quad \mu, \nu \quad \text{and} \quad \sum_{\mu=1}^{\hat{\Omega}} W_{\mu,\nu} = 1 \quad \forall \quad \nu.$$

$W$  is called Markov matrix or stochastic matrix. Its elements are all between zero and unity; The elements of each column add to unity. Besides, if the elements of each row also add to unity, then we have a doubly stochastic matrix.

<sup>10</sup> For example if we are simulating an Ising spin system, select randomly an Ising spin from the current spin configuration (micro state) and flip it to construct a trial spin configuration. If we are simulating a collection of particles, then select a particle randomly and change its there position coordinates and three momentum coordinates by small random amounts to construct a trial micro state.

<sup>11</sup> employ the random number generator available in your computer. The (pseudo) random numbers are real numbers independently and uniformly distributed between zero and one. Random number generation and testing are non-trivial tasks and they constitute highly specialized areas of research. Most Monte Carlo practitioners are not aware of the subtleties and difficulties associated with random number generation employing deterministic algorithms and testing of the generated random numbers for randomness. We take the available random generator and use it as a black box.

- If  $\xi \leq p$ , then accept the trial state and advance the Markov chain to  $X_{i+1} = X_t$ .
- If not, reject the trial state and advance the Markov chain to  $X_{i+1} = X_j$ .
- Repeat the process on  $X_{i+1}$  to get  $X_{i+2}$ ; and so on.

Generate a long Markov chain. The asymptotic part of the chain shall contain micro states belonging to the ensemble characterized by the probabilities  $\{p(X_\nu) : \nu = 1, 2, \dots\}$ .

### Important Properties of Metropolis Algorithm

- Metropolis algorithm demands only a knowledge of the ratio of probabilities of two micro states belonging to  $\Omega$ . We should know this ratio for all possible pairs of micro states of  $\Omega$ . This implies that we need to know  $\{p(\mathcal{X}_\nu) : \nu = 1, 2, \dots, \widehat{\Omega}\}$  only up to a normalization constant. It is precisely because of this reason we are able to simulate a closed system, since we need to know only the Boltzmann weight  $\exp[-\beta E(\mathcal{X})]$  of each micro state; we need not have any knowledge what so ever of the canonical partition function.
- Metropolis algorithm obeys balance condition<sup>12</sup>. The balance condition tells that the Markov chain shall converge, definitely, to an invariant probability distribution.
- Metropolis algorithm obeys a stricter condition called detailed balance<sup>13</sup>. The consequences of this are two fold.
  - (i) Detailed balance ensures the Markov chain converges to an equilibrium ensemble consistent with the given probability weights of the micro states : Boltzmann weights for canonical ensemble; and Gibbs weights for grand canonical ensemble; *etc.* We can choose the nature of the equilibrium state.

<sup>12</sup> We consider time homogeneous Markov chain, see footnote (9). Let  $P(\mathcal{X}_j, n)$  be the probability for the system to be in micro state  $\mathcal{X}_j$  at discrete time  $n$ . Let  $W_{i,j}$  denote the probability for transition from micro state  $\mathcal{X}_j$  to micro state  $\mathcal{X}_i$  in one time step. We have  $W_{i,j} = P(\mathcal{X}_i | \mathcal{X}_j)$ , the conditional probability that the system is in micro state  $\mathcal{X}_i$  at any instant of time given it was in micro state  $\mathcal{X}_j$  at the previous instant of time. The probabilities obey the equation given below.

$$P(\mathcal{X}_i; n+1) = \sum_{j: j \neq i} P(\mathcal{X}_j, n) W_{i,j} + P(\mathcal{X}_i, n) W_{i,i}$$

We have  $\sum_i W_{i,j} = 1 \forall j$ . Therefore,  $W_{i,i} = 1 - \sum_{j: j \neq i} W_{j,i}$ . We can write the above equation as

$$\begin{aligned} P(\mathcal{X}_i; n+1) &= \sum_{j \neq i} P(\mathcal{X}_j, n) W_{i,j} + P(\mathcal{X}_i, n) \left(1 - \sum_{j: j \neq i} W_{j,i}\right) \\ &= P(\mathcal{X}_i, n) + \sum_{j \neq i} [P(\mathcal{X}_j, n) W_{i,j} - P(\mathcal{X}_i, n) W_{j,i}] \end{aligned}$$

**Balance Condition :** When the system equilibrates we have  $P(\mathcal{X}_i, n+1) = P(\mathcal{X}_i, n) = p(\mathcal{X}_i) \forall i$ . Therefore we have

$$\sum_j [p(\mathcal{X}_j) \times W_{i,j} - p(\mathcal{X}_i) \times W_{j,i}] = 0.$$

This is called the balance condition which ensures that the Markov chain eventually equilibrates.

<sup>13</sup> **Detailed Balance :** Look at the balance condition given toward the end of footnote 12 as a sum over  $j$  for each  $i$ . We can make a stricter demand that each term in the sum be zero. Then we get the detailed balance condition :

$$p(\mathcal{X}_j) \times W_{i,j} = p(\mathcal{X}_i) \times W_{j,i} \quad \forall i, j = 1, 2, \dots, \widehat{\Omega}.$$

It is quite easy to show that the Metropolis rejection algorithm obeys detailed balance condition. I leave this as an exercise for you.

- (ii) Detailed balance ensures that the Markov chain is reversible; hence it is most suited for describing an equilibrium system<sup>14</sup>; for, no matter what kind of observations you make on an equilibrium system, you can not tell which way time moves. Equilibrium is a time-reversal invariant state. Detailed balance captures this subtle property.

### Estimation of Averages and Statistical Errors

Generate a Markov chain until it equilibrates<sup>15</sup>. Continue the Markov chain and collect a reasonably large number of micro states  $\{X_i : i = 1, 2, \dots, M\}$  from the equilibrated Markov chain. Let  $O$  be a property of interest and  $O(X)$  its value when the system is in micro state  $X$ . Then the Monte Carlo estimate of the property  $O$  is given by<sup>16</sup>,

$$\bar{O}_M = \frac{1}{M} \sum_{i=1}^M O(X_i); \quad \text{Limit}_{M \rightarrow \infty} \bar{O}_M = \langle O \rangle.$$

A little thought will tell you that the quantity  $\bar{O}_M$  is a random variable. It will fluctuate from one realization of a Monte Carlo sample to another.

What is the nature of these fluctuations ?

The Central limit theorem<sup>17</sup> (CLT) tells that the quantity  $\bar{O}_M$  is a Gaussian random variable when  $M$  is large. The average of the Gaussian is  $\langle O \rangle$  and its variance is  $\sigma^2/M$ , where

<sup>14</sup> By observing an equilibrium system we can not tell which direction time flows. Both directions are equally probable and equally unverifiable. Consider a Markov chain of micro states visited by an equilibrium system :  $X_0 \rightarrow X_1 \rightarrow \dots \rightarrow X_n \rightarrow X_{n+1} \rightarrow \dots \rightarrow X_M$ . The transition probabilities are given by  $W_{i,j} = P(X_n = \mathcal{X}_i | X_{n-1} = \mathcal{X}_j)$

At discrete time  $M$  let us reverse the Markov chain and get  $X_M \rightarrow X_{M-1} \rightarrow \dots \rightarrow X_{n+1} \rightarrow X_n \rightarrow \dots \rightarrow X_1 \rightarrow X_0$ . A little thought will tell you the above is also a Markov chain : for, the future depends only on the present and not on the past for a Markov chain, Hence once the present is specified the future is independent of the past. Past is independent of the future which renders the time reversed chain, Markovian. Let us denote the transition probability matrix of the time reversed chain by the symbol  $W^R$ . We have

$$\begin{aligned} W_{i,j}^R = P(X_n = \mathcal{X}_i | X_{n+1} = \mathcal{X}_j) &= \frac{P(X_n = \mathcal{X}_i, X_{n+1} = \mathcal{X}_j)}{p(\mathcal{X}_j)} = \frac{P(X_{n+1} = \mathcal{X}_j | X_n = \mathcal{X}_i) p(\mathcal{X}_i)}{p(\mathcal{X}_j)} \\ &= \frac{W_{j,i} p(\mathcal{X}_i)}{p(\mathcal{X}_j)} \end{aligned}$$

The condition for reversibility is  $W_{i,j}^R = W_{i,j}$  : The transition probability matrix should be the same for both Markov chains - the time forward and the time reversed. Hence on the left hand side of the above equation replace  $W_{i,j}^R$  by  $W_{i,j}$  and reorganize. Then the condition for reversibility reads as,

$$W_{i,j} p(\mathcal{X}_j) = W_{j,i} p(\mathcal{X}_i).$$

We recognize this as detailed balance, see footnote (13). Thus a Markov chain of micro states of an equilibrium system obeys detailed balance condition and hence is reversible;

<sup>15</sup> calculate the moving average of energy. When it stabilizes to a constant value but for some small statistical fluctuations, we can say the system has equilibrated.

<sup>16</sup> We reserve the symbol  $\langle O \rangle$  to denote the unknown exact value of the canonical ensemble average of the property  $O$  formally given by

$$\langle O \rangle = \frac{1}{Q} \sum_{\nu=1}^{\hat{\Omega}} O(\mathcal{X}_\nu) \exp[-\beta E(\mathcal{X}_\nu)]; \quad Q = \sum_{\nu=1}^{\hat{\Omega}} \exp[-\beta E(\mathcal{X}_\nu)].$$

<sup>17</sup> **Central Limit Theorem:** Let  $X_1, X_2, \dots, X_M$  be identically distributed independent random variables with finite mean,  $\mu$  and finite variance,  $\sigma^2$ . Let  $Y = (X_1 + X_2 + \dots + X_M)/M$ . The central limit theorem (CLT) says that  $Y$  is a Gaussian with mean  $\mu$  and variance  $\sigma^2/M$  when  $M \rightarrow \infty$ . CLT is a glorious culmination of a series of studies starting with the Chebyshev inequality, see *e.g.* [3, 4] : A single number randomly sampled from a distribution, with finite mean  $\mu$ , and finite variance,  $\sigma^2$  can fall outside the interval  $\mu \pm k\sigma$  with a probability not

$\sigma^2 = \langle O^2 \rangle - \langle O \rangle^2$ . A possible statement of the statistical error associated with the Monte Carlo estimate  $\bar{O}_M$  is obtained from the following considerations.

Take a Gaussian random variable with mean  $\zeta$  and standard deviation  $\Sigma$ . The area under the Gaussian<sup>18</sup> between  $\zeta - \Sigma$  and  $\zeta + \Sigma$  is 0.682695. This means that with 68.27% confidence, you can say that a randomly sampled number from the Gaussian shall lie between  $\zeta - \Sigma$  and  $\zeta + \Sigma$ . The one-sigma confidence interval provides a neat quantification of the statistical error associated with Monte Carlo estimates, see below.

We calculate the second moment,

$$\bar{O}_M^2 = \frac{1}{M} \sum_{i=1}^M O^2(X_i); \quad \text{Limit}_{M \rightarrow \infty} \bar{O}_M^2 = \langle O^2 \rangle.$$

From the calculated values of the first and second moments we estimate the variance as,

$$\sigma_M^2 = \bar{O}_M^2 - (\bar{O}_M)^2. \quad (\sigma^2 = \langle O^2 \rangle - \langle O \rangle^2 = \text{Limit}_{M \rightarrow \infty} \sigma_M^2).$$

We can now calculate the one-sigma confidence interval; we quote the Monte Carlo result as  $\bar{O}_M \pm \sigma_M/\sqrt{M}$ . The above means that with 0.6827 probability we can expect the Monte Carlo estimate  $\bar{O}_M$  to lie in the one sigma interval around  $\langle O \rangle$ ; *i.e.* to lie between  $\langle O \rangle - \sigma_M/\sqrt{M}$  and  $\langle O \rangle + \sigma_M/\sqrt{M}$ .

The statistical error decreases with increase of  $M$ . This is indeed a desirable property. This tells us, atleast in principle, we will get things right if  $M$  is sufficiently large. Usually we would be interested in comparing our Monte Carlo predictions with experiments. Hence we can take the Monte Carlo sample size to be large enough to ensure that the statistical error is less than the experimental error bar.

However, notice the statistical error decreases painfully slowly with the sample size. The decrease is logarithmically slow : to better the results by one extra decimal accuracy we need to increase the sample size a hundred fold. Often this would prove to be an exercise in futility; for, the computing time is linear in  $M$ .

We need variance reduction devices that significantly reduce the fluctuations without affecting the averages. Importance sampling is a variance reduction device. It helps us sample micro states from important regions of the sample space *e.g.* micro states with high Boltzmann weights. Notice a randomly selected micro state would be, most likely, of high energy<sup>19</sup>, hence of low Boltzmann weight; its contribution to the partition sum would be negligible. In fact the Metropolis algorithm is an importance sampling device. I am not going to talk of importance sampling or of other variance reduction techniques; those interested can consult for example [5, 6, 7].

Instead, in what follows, I am going to investigate the nature of the invariant distribution of the Markov chain of micro states whose probabilities are inversely proportional to the density of states : micro states of high entropy region have low probabilities; and those of low entropy region have high probabilities. This kind of prescription does not describe any physical system. Nevertheless constructing a Markov chain with these probabilities for the micro states, has certain advantages and this will become clear in the sequel.

more than  $1/k^2$ . Then came several laws of large numbers and these led eventually to the Central Limit Theorem (CLT), see any standard text book, *e.g.* [3, 4] on probability theory and stochastic processes to know more on these issues.

<sup>18</sup>

$$\frac{1}{\Sigma\sqrt{2\pi}} \int_{\zeta-\Sigma}^{\zeta+\Sigma} dx \exp\left[-\frac{(x-\zeta)^2}{2\Sigma^2}\right] = 0.682695$$

<sup>19</sup> entropy increases with energy.

### Markov Chain with Flat Energy Histogram

Consider a system with micro states  $\Omega = \{\mathcal{X}_\nu : \nu = 1, 2, \dots, M\}$ . Let  $\widehat{\Omega}(E)$  denote its density of states. For purpose of illustration we assume that the density of states is known. Let  $\mathcal{X}_\mu \in \Omega$  and  $E_\mu = E(\mathcal{X}_\mu)$ . We prescribe  $P(\mathcal{X}_\mu) \propto 1/\widehat{\Omega}(E_\mu)$ . Let me emphasize two points, at the risk of being repetitive, before we proceed further :

- We do not know the density of states before hand<sup>20</sup>.
- There is no physical system for which the probability of a micro state is inversely proportional to the density of states <sup>21</sup>.

Nevertheless we shall consider Monte Carlo simulation of such an un-physical system employing Metropolis algorithm and investigate the invariant probability density of the Markov chain it generates.

Let  $X_i$  be the current micro state in the Markov chain and  $E_i = E(X_i)$  its energy. We have  $p_i = p(X_i) \propto 1/\widehat{\Omega}(E_i)$ . Let  $X_t$  be the trial state and  $E_t = E(X_t)$  its energy. We have  $p_t = p(X_t) \propto 1/\widehat{\Omega}(E_t)$ . The probability of acceptance of the trial micro state is then given by

$$p = \text{minimum} \left( 1, \frac{p_t}{p_i} \right) = \text{minimum} \left( 1, \frac{\widehat{\Omega}(E_i)}{\widehat{\Omega}(E_t)} \right)$$

Note that if the trial micro state belongs to a lower entropy region it gets accepted with unit probability; however if it belongs to higher entropy region its acceptance probability is less than unity. Thus the algorithm pushes the Markov chain preferentially toward low entropy region. This preference cancels statistically exactly the natural tendency of randomly sampling of trial micro states from high entropy region. As a result the Markov chain shall have equal number of micro states in equal regions of energy. In other words the energy histogram of the visited micro states shall be flat.

Thus the Markov chain visits all regions of energy with equal ease. It does not see any energy barriers, insurmountable or otherwise, that might be present in the system under investigation. This is a huge advantage because there are indeed energy barriers that emerge at temperatures close to the first order phase transition and which are responsible for super critical slowing of the dynamics. Also glassy systems have free energy profile with numerous ups and downs. Though we get an un-physical ensemble as a result employing inverse of the density of states in a Markov chain Monte Carlo method based on Metropolis rejection, there seem to be certain desirable properties for the ensemble. Of course we do not know yet the density of states. Perhaps it is a good idea to investigate further and invent methods that that help obtain the density of states. May be if we embark on such an enterprise we may have to to forgo the comforts of Markov Chain methodology and of the detailed balance present in the Metropolis rule. But then, we shall get easy access to entropy and other thermal properties, which eluded the Markov chain Monte Carlo practitioners.

What is it that renders calculation of entropy a difficult task ? To answer this question we have to realize that the usefulness of the Monte Carlo methods considered upto now, is tied

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<sup>20</sup> After all, if we know the density of states then we can make an estimate of all the properties of the system employing the well developed machinery of thermodynamics and statistical mechanics. There would arise no compulsive need for a Monte Carlo simulation. We may still decide to carry out Monte Carlo simulation, assemble an 'entropic' ensemble, and extract physical quantities employing un-weighting and re-weighting techniques. I shall tell you of this later in my talk

<sup>21</sup> The set  $\Omega$  shall contain all the micro states of the "un-physical" system. These micro states can be of different energy. Let us group them in terms of their energies. Then we can say all the micro states of a group are equally probable and this probability is given by the inverse of the density of states at that group energy. Each group would then constitute a micro canonical ensemble.



crucially to our ability to assign a numerical value of the property  $O$  to every micro state of the system. Consider estimating a property like entropy. We can not assign a numerical value for entropy to any single micro state of the system. All the micro states collectively own entropy. Hence thermal properties in general and entropy in particular are not easily accessible.

For computing thermal properties we need to go beyond Boltzmann Monte Carlo methods. That non-Boltzmann sampling can provide a legitimate and perhaps superior alternative to Boltzmann methods has been recognized even during the very early days of Monte Carlo practice, see *e.g.* [8] and to these issues we turn our attention, below.

Torrie and Valleau [9] were, perhaps, the first to propose a non-Boltzmann algorithm to calculate the thermal properties. Their method called umbrella sampling has since undergone a series of metamorphoses. We have the multi-canonical Monte Carlo of Berg and Neuhaus [10], entropic sampling of Lee [11] and the algorithm of Wang and Landau [12]. We describe below the Wang-Landau algorithm.

### Wang-Landau Algorithm

Wang and Landau [12] proposed an algorithm to estimate iteratively the density of states of the system. The algorithm is described below.

At the beginning of the simulation, define a function  $g(E)$  and set it to unity for all  $E$ . Define also an histogram  $H(E)$  and set it to zero for all  $E$ . Start with an arbitrary initial micro state  $X_0$ . Let  $E_0 = E(X_0)$  be its energy. Update  $g(E)$  and  $H(E)$  as follows :

$$g(E_0) = g(E_0) \times \alpha; \quad H(E_0) = H(E_0) + 1.$$

Here  $\alpha$  is the Wang-Landau factor and we take  $\alpha = e^1 = 2.7183$  in the first iteration. Generate a chain of micro states

$$X_0 \rightarrow X_1 \rightarrow \dots \rightarrow X_i \rightarrow X_{i+1} \rightarrow \dots$$

as per the algorithm described below.

Let  $X_i$  be the current micro state. Construct a trial micro state  $X_t$ . We need to decide whether to accept the trial state for advancing the chain. We take a decision on the basis of the  $g(E)$  updated at the end of the previous step in which we selected the micro state  $X_i$ . Let  $E_i = E(X_i)$  and  $E_t = E(X_t)$ . We have

$$p_i \propto \frac{1}{g(E_i)} \quad \text{and} \quad p_t \propto \frac{1}{g(E_t)}.$$

Define

$$p = \text{minimum} \left( 1, \frac{p_t}{p_i} \right) = \text{minimum} \left( \frac{g(E_i)}{g(E_t)} \right).$$

The next micro state in the chain is

$$X_{i+1} = \begin{cases} X_t & \text{with probability } p \\ X_i & \text{with probability } 1 - p \end{cases}$$

Once  $X_{i+1}$  is selected, the function  $g(E)$  and the histogram  $H(E)$  are updated. Carry out the simulation of the chain of micro states until the energy histogram becomes flat over, at least, a small range of energy. This constitutes one Wang-Landau iteration.

Note that the density-of-state-function  $g(E)$  is updated at every step and the updated function is employed for decision making, from the very next step. As a result the chain of micro states generated, is not Markovian. The probability of transition between two micro states at any time step in the chain depends on how many times the chain has visited these

two micro states in its past. The transition from present to future depends on the entire past. Hence we shall refer to the sequence of micro states as simply a chain and not prefix it with the adjective "Markov".

At the end of the first Wang-Landau iteration, change  $\alpha$  to  $\sqrt{\alpha}$ . Reset  $H(E)$  to zero for all  $E$ ; but continue with  $g(E)$ . Carry out the second Wang-Landau iteration. The histogram would spread out and would at the same time become flatter over a wider range of energy.

Upon further iterations the value of alpha will move closer and closer to unity. For example, after some twenty five iterations we shall have  $\alpha = 1 + 3 \times 10^{-7}$ . The histogram of energy would become flat at least over the range of energy of interest after a few Wang-Landau iteration runs.

The flatter the histogram, closer would be  $g(E)$  to the true but unknown density of states  $\hat{\Omega}(E)$ . We take  $g(E)$  obtained at the end of the last iteration - the one which generates a reasonably flat energy histogram, as an estimate of  $\hat{\Omega}(E)$ , the true density of states.

We can define a suitable criteria for measuring the flatness of the histogram. For example we can consider the histogram to be flat if the smallest and largest entries do not differ from each other by say more than say ten percent. Depending upon the requirement of accuracy and the availability of computing resources, we can relax or tighten the flatness criterion.

There is no hard and fast rule about either the choice of the initial value of the Wang-Landau factor or about how it decreases to unity from one iteration to the next. The choice of  $\alpha = \alpha_0 = e^1$  at the beginning of the first iteration and the square-root rule of decrease, were recommended by Wang and Landau[12]. In principle,  $\alpha_0$  can be any real number greater than unity and it should decrease, preferably monotonically, to unity. Some authors, see *e.g.* [13, 14], have found it advantageous vary  $\alpha$  non-monotonically at least initially. The important point is any choice of variation of  $\alpha$  that flattens the histogram would serve the purpose. In a sense the histogram provides a diagnostic tool with which you can monitor whether you are doing things right or wrong. The flatness of the histogram tells you how close has the density of states converged to its true value.

The Wang-Landau algorithm estimates the density of states only upto a normalization constant. In other words the micro canonical entropy is estimated only upto an additive constant. This is quite adequate since we need to calculate only change in entropy rather than absolute entropy in almost all applications.

In principle we can stop here. Once we know the density of states then we can employ the machinery of thermodynamics and know everything else about the system.

## Entropic Ensemble

Alternately, we can employ the converged density of states in a production run and generate a large ensemble of micro states. The sequence of micro states generated in the production run constitute a legitimate Markov chain, obeying detailed balance. However the invariant probabilities are un-physical : the probability of a micro state  $\mathcal{X}$  is inversely proportional the density of states at  $E = E(\mathcal{X})$ . The Markov chain obeys detailed balance and hence convergence to the desired ensemble, though unphysical, is guaranteed.

Let us call the set of micro states generated in the production run as an an entropic ensemble or Wang-Landau ensemble. By employing un-weighting and re-weighting techniques<sup>22</sup> we can make from the entropic ensemble, statically reliable estimates of physical quantities.

<sup>22</sup> Let me explain un-weighting and re-weighting in a simple manner[5, 6]. Let  $x$  be a random variable and  $f(x)$  its probability density. Let  $h(x)$  be some function of  $x$ . The  $f$ -ensemble average of  $h$  is formally expressed as,

$$\langle h \rangle_f = \int_{-\infty}^{+\infty} dx h(x) f(x),$$

Let  $g(x)$  be a density function. Let us generate an ensemble  $\Omega_g = \{x_i : i = 1, 2, \dots M\}$  by random sampling

In what follows I shall show how to convert the entropic ensemble to a micro canonical ensemble and to a canonical ensemble.

### Entropic Ensemble $\rightarrow$ Micro Canonical Ensemble

Let  $\{X_i : i = 1, 2, \dots, M\}$  denote a set of  $M$  micro states belonging to the entropic ensemble. These micro states have been sampled from a probability distribution

$$p(X_i) \propto 1/g(E(X_i)).$$

Hence we first carry out un-weighting, see footnote (22) :

$$W(X_i) = \frac{1}{1/g(E(X_i))} = g(E(X_i)).$$

Note that the micro states of the entropic ensemble are not necessarily of the same energy. In fact the ensemble contains equal number of micro states in equal regions of energy - in other words the energy-histogram is flat. For a micro canonical ensemble all micro states are of the same energy and are equally probable. Hence the re-weighting factor is  $1 \times \delta(E - E(X_i))$ ; the delta function ensures that we assemble only those micro states with the desired energy. Thus we have

$$W(X_i) = g(E(X_i)) \delta(E - E(X_i)).$$

Let  $O(X_i)$  be the value of a property when the system is in micro state  $X_i$ . The micro canonical ensemble average of  $O$  is given by,

$$\langle O \rangle_{\mu C}(E) = \lim_{M \rightarrow \infty} \frac{\sum_{i=1}^M O(X_i) g(E(X_i)) \delta(E(X_i) - E)}{\sum_{i=1}^M g(E(X_i)) \delta(E(X_i) - E)}$$

In the above we have taken  $E$  as the energy of the isolated system described by the micro canonical ensemble.

Thus weighted averaging over micro states of given energy belonging to the *un-physical* entropic ensemble equals averaging over a *physical* micro canonical ensemble modeling an isolated system.

### Entropic Ensemble $\rightarrow$ Canonical Ensemble

The un-weighting factor remains the same as the one derived for converting entropic ensemble to micro canonical ensemble. The re-weighting factor however is the Boltzmann weight. Thus  $W(X_i) = g(E(X_i)) \times \exp[-\beta E(X_i)]$ . All the micro states of the entropic ensemble contribute to the canonical ensemble average.

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from  $g(x)$ . Our aim is to make an estimate of  $\langle h \rangle_f$  employing the set  $\Omega_g$ . Consider the following.

$$\langle h \rangle_f = \int_{-\infty}^{+\infty} dx h(x) f(x) = \int_{-\infty}^{+\infty} dx h(x) \frac{f(x)}{g(x)} g(x) = \langle h (1/g) f \rangle_g$$

The above is an exact result. The left hand side is an  $f$  ensemble average of  $h$ . The right hand side is a  $g$  ensemble average of  $h$  un-weighted by  $1/g$  and re-weighted by  $f$ . The implementation goes as follows.

$$\langle h \rangle_f = \lim_{M \rightarrow \infty} \frac{1}{M} \sum_{i=1}^M h(x_i) \times \frac{1}{g(x_i)} \times f(x_i); \quad x_i \in \Omega_g.$$

The canonical ensemble average of  $O$  is given by

$$\langle O \rangle_C = \lim_{M \rightarrow \infty} \frac{\sum_{i=1}^M O(X_i) g(E(X_i)) \exp[-\beta E(X_i)]}{\sum_{i=1}^M g(E(X_i)) \exp[-\beta E(X_i)]}$$

Thus the weighted average over the *unphysical* entropic ensemble is equivalent to average over a *physical* canonical ensemble modeling a closed system.

From one single ensemble of micro states we can calculate averages over a large number of distinct canonical ensembles at different temperatures. This is a huge advantage especially for problems in which we need the properties on a fine grid of temperatures in the neighbourhood of a phase transition.

### End Note

I have talked about Metropolis algorithm to sample micro states from a given ensemble, physical or otherwise. If sampling is done from a physical ensemble we call it Boltzmann Monte Carlo. Boltzmann sampling has been eminently successful for estimating mechanical properties like energy. The reason is simple. A value for a mechanical property can be assigned to each micro state.

However Boltzmann sampling is quite clumsy when it comes to estimating thermal properties like entropy and free energies. The clumsiness owes its origin to the fact that a numerical value for entropy can not be assigned to any single micro state. All the micro states, collectively, own entropy. Entropy is a property of an ensemble and not of any single micro state. This problem about estimating entropy was recognized even in the early days of Monte Carlo practice by Torrie and Valleau[9]; they invented umbrella sampling which addresses these issues. Umbrella sampling has since inspired and given rise to a whole lot of non-Boltzmann methods; the latest to arrive is the method of Wang and Landau[12]. I have told you of the basic idea behind Wang-Landau algorithm and described how to implement it on a practical problem.

The take-home-message is that non-Boltzmann Monte Carlo methods are as good as Boltzmann methods, if not more, for calculating mechanical properties. Besides, they provide reliable estimates of thermal properties, not easily accessible to Boltzmann Monte Carlo methods.

I must quickly add that all is not cozy about Wang-Landau algorithm. There are issues and there are difficulties. A typical Monte Carlo aficionado, see *e.g.* [15], does not feel comfortable since the algorithm does not obey detailed balance; in fact, the chain generated is not Markovian. What guarantees convergence of  $g(E)$  to  $\hat{\Omega}(E)$  ?

Also the algorithm performs poorly on systems with continuous degrees of freedom. There is a slowing down of dynamics but now due to entropy barriers. These and related problems have attracted the attention of several authors, see *e.g.* [13, 14, 16, 17, 18] and remedies have been suggested. But in my opinion no satisfactory solution has yet emerged. All the remedies suggested seem ad-hoc.

There are also issues about error - both systematic and statistical - associated with the computed density of states. How does one translate the non-flatness of the energy histogram to error bars in the estimated density of states ? After all, the pride of a Monte Carlo practitioner lies often in his ability to compute not only averages, but also associated statistical errors. But then we do not know how to calculate Monte Carlo error bars in a Wang-Landau simulation.

I hope these and other issues would get resolved satisfactorily soon and non Boltzmann Monte Carlo methods would emerge as standard tools in the arsenal of a Monte Carlo practitioner. With this optimistic note, let me end these talks. In case you have some more queries, and you want to discuss further on issues raised in this talk, do not hesitate to get in touch with me at k.p.n.murthy@gmail.com (.)

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## References

- [1] R K Pathria, *Statistical Mechanics*, Second Edition, Butterworth - Heinemann (1996).
- [2] N.Metropolis, A.W.Rosenbluth, M.N.Rosenbluth, A.H.Teller, and E.Teller, *Equation of State Calculations by Fast Computing Machines*, Journal of Chemical Physics **21** 1087 (1953); see also G.Bhanot, *The Metropolis Algorithm*, Reports of Progress in Physics **51**, 429 (1988).
- [3] W.Feller, *An Introduction to Probability Theory and Applications I and II*, John Wiley (1968)
- [4] A.Papoulis, *Probability Theory, Random Variables, and Stochastic Processes* McGraw Hill (1965)
- [5] K.P.N.Murthy, *Monte Carlo Methods in Statistical Physics*, Universities Press (2004)
- [6] K.P.N.Murthy, *Monte Carlo : Basics*, Report ISRP - TD-3, Indian Society for Radiation Physics, Kalpakkam Chapter (2000); see arXiv:cond-mat/014215v1, 12 Apr. 2001.
- [7] E.J.McGrath, and D.C.Irving, *Techniques for Efficient Monte Carlo Simulation* Volume III : Variance Reduction, Report SAI - 72 - 590 - LJ , Office of the Naval Research, Department of the Navy, Arlington, Virginia 22217 USA (March 1973)
- [8] L.D.Fosdick, *Monte Carlo Computation on the Ising Lattice* in Methods of Computational Physics, Vol. 1, Editor B Adler, p.245 (1963).
- [9] G.M.Torrie, and J.P.Valleau, *Non-physical sampling distributions in Monte Carlo free-energy estimation: Umbrella sampling*, Journal of Computational Physics **23** 187 (1977).
- [10] B.A.Berg, and T.Neuhaus, *Multi canonical ensemble: A new approach to simulate first-order phase transitions*, Physical Review Letters **68**, 9 (1992).
- [11] J.Lee, *New Monte Carlo algorithm: Entropic sampling*, Physical Review Letters **71**, 211 (1993); *Erratum*, **71**, 2353 (1993)
- [12] F.Wang, and D.P.Landau, *Efficient, Multiple-Range Random Walk Algorithm to Calculate the Density of States*, Physical Review Letters **86**, 2050 (2001).
- [13] D.Jayasri, V.S.S.Sastry, and K.P.N. Murthy, *Wang-Landau Monte Carlo simulation of isotropic-nematic transition in liquid crystals*, Physical Review E **72**, 36702 (2005).
- [14] P.Poulin, F.Calvo, R.Antoine, M.Broyer, and, P.Dugord, *Performances of Wang-Landau algorithms for continuous systems*, Physical Review E **73**, 56704 (2006).
- [15] W.Janke, *Monte Carlo Simulations in Statistical Physics From Basic Principles to Advanced Applications*, in: Order, Disorder and Criticality: Advanced Problems of Phase Transition Theory, Vol. 3 (edited by Y. Holovatch), World Scientific (2012)pp. 93-166.
- [16] B.J.Schulz, K.Binder, M.Müller, and D.P.Landau, *Avoiding Boundary Effects in Wang-Landau Sampling* Physical Review E **67**, 67102 (2003).
- [17] C.Zou, and R.N.Bhatt, *Understanding and Improving the Wang-Landau Algorithm*, Physical Review E **72**, 25701(R) (2005).
- [18] A. Tröster, and C. Dellago, *Wang-Landau Sampling with Self Adaptive Range*, Physical Review E **71**, 66705 (2005),

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<sup>23</sup> Board of Research for Nuclear Sciences, Department of Atomic Energy.