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01 – 11

Monte Carlo as a Tool to Solve Problems in Theoretical Science

Dr. Dev Raj Mishra
Department of Physics,
R.H.Government Post Graduate College, Kashipur, U.S.Nagar,
Uttarakhand -244713 INDIA.
e-mail: *dr_devraj_mishra@yahoo.co.in*

Abstract — The pedagogical introduction about the the Monte Carlo technique is presented. Metropolis, Wolff and Heat bath algorithsarebreifly discussed. The method to simulate coupled chemical reactions by applying Gillespie algorithm in Simulation of the Lotka-Volterra model is also discussed.

Keywords-Simulation,*Monte Carlo, Metropolis, Gillespie,*

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I. INTRODUCTION

Metropolis and Ulam[1] suggested a method to solve certain type of problems using a statistical approach. They called this statistical method as Monte Carlo method. Statisticalsamplingis in the use even before the invention of computers.French mathematicianComte de Buffon (1707-1788) evaluated the value of π using random throws of needle of length$l$on a plane marked with some parallel long lines separated by a distance t (see Fig. 1). Let x is the position of the center of the needle $0 \le x \le l$ and θ the angle formed by theneedle with the axis perpendicular to the lines $(-\pi/2 \le \theta \le \pi/2)$, the probability that the needle crosses the lines is given as

$$P = \frac{2}{t\pi}\int_0^{\frac{l}{2}} dx \int_{-\arccos\left(\frac{2x}{l}\right)}^{\arccos\left(\frac{2x}{l}\right)} d\theta = \frac{2l}{t\pi}\int_0^1 dy\, arccos(y) = \frac{2l}{t\pi}$$

Let N total timesthe needle is thrown and N* is the number of times it crossesthe lines. We can estimate the probability as $P \approx N^*/N$. Then using above Eq. π is evaluated as

$$\pi \approx \frac{2lN}{tN^*}$$

The result becomes more and more accurate asN increases.This is one of the examples of the use of statistical sampling. We can efficiently calculate integrals upto three dimensions using quadrature methods. The Monte Carlo method is however, more efficient than quadrature method for higher dimensions.

An interactive Java applet for the calculation of π by sampling the ratio of needles crossing thelines over the total number of needles is available on internet [2].

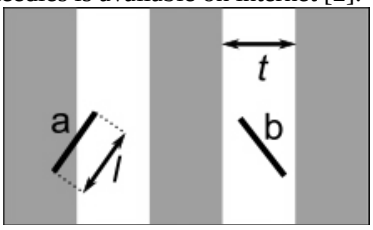

Fig.1: The Buffon's needle: the needle 'a' crosses the line, while the 'b' does not.

Let us consider a function of one variable defined in the interval [0, 1]. It is to evaluate the integral by generating N random numbers $x_1,\ x_2,\ x_3 \ldots\ldots x_N$ in the domain [0, 1].Then

$$I = \int_0^1 f(x)dx \approx \frac{1}{N}\sum_{n=1}^{N} f(x_n) \qquad (1)$$

More generally if the domain of integration is [a,b], above summation can be written as

$$I = \int_a^b f(x)dx \approx \frac{b-a}{N}\sum_{n=1}^{N} f(x_n) \qquad (2)$$

The approximant for a slowly varying function f(x) converges very rapidly to theexact value. However, there are functions which are negligibly small over a large fraction of theintegration domain. Most of the random numbers lie in the part of the integrationdomain where the function is small. Choosing uniform random number distribution for suchfunctions is not a veryefficient procedure asconsiderable computational effort usually ends up with large statistical error. The random numbersneed to be generated in the partof the integration domain where the function f(x) has relatively large value. The procedure for generating random numbers in accordance with integrand is called importance sampling.

The random number generated in the domaindepends on a functionW(x) which is called a density function. It has the following properties W(x) ≥0 in domain [0,1] and

$$\int_0^1 W(x)dx = 1 \qquad (3)$$

Here W(x) dx is the fraction of random numbers generated in the interval[x, x+dx]. Let N be the total number of random numbers generated, then the separation between two of these numbers at position xis given by 1/NW(x). Therefore

$$I = \int_0^1 f(x)dx \approx \frac{1}{N}\sum_{n=1}^{N} \frac{f(x_n)}{W(x_n)} \qquad (4)$$

As an example consider the function $f(x) = e^{-x^2}g(x)$in$[0, +\infty)$, whereg(x) is slowly varying. It is convenient for the Monte Carlo computation of this integral to

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01 – 11

use a Gaussian random number generator, characterizedby a density function $W(x) = \sqrt{2/\pi e^{-x^2}}$. One has

$$I = \int_0^1 f(x)dx \approx \frac{1}{N}\sum_{n=1}^{N}\frac{f(x_n)}{W(x_n)} = \frac{1}{N}\sqrt{\frac{\pi}{2}}\sum_{n=1}^{N} g(x_n) \qquad (5)$$

The domain of integration is unbounded here and the normalization factor is$\sqrt{2/\pi}$

Therefore it is convenient to choose W(x) so that f/W becomes a slow varying function. Mathematically, we can write this condition as the variance σ_I of f/W

$$\sigma_I^2 = \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N}\left(\frac{f(x_i)}{W(x_i)} - \langle f/W\rangle\right)\left(\frac{f(x_j)}{W(x_j)} - \langle f/W\rangle\right) \qquad (6)$$

Here $\langle f/W\rangle$denotes the mean and is the exact value of the integral. The random numbers$(i \neq j)$are independentasthe limit $N \to \infty$

$$\sigma_I^2 = \frac{1}{N}[\langle (f/W)^2\rangle - \langle f/W\rangle] \qquad (7)$$

Thus the error scales as the squared root of the number of sampled points $(\sigma_I \sim 1/\sqrt{N})$. However it can be reduced by minimizing the term in the bracket in Eq.(7). This can be done by choosing W such that f/W is a slowly varying function.Theoptimal case is the one to reduce f/W to a constant, and theterm within the brackets vanishes. But this is not an easy task.Thismeans W(x) = αf(x) and as W(x) is normalized using Eq. (3), we get I = 1/α. This meanswe already know the value of the integral.

II. MONTE CARLO METHODS FOR SYSTEMS IN EQUILIBRIUM

Let a system, in thermal equilibrium with a reservoir at temperatureT, is characterized by some discrete number of microscopic configurations, sayμ. This discrete case can be then generalized to a continuum system, as for instance an interacting gas or a liquid.As we know accordingto one of the basic principles of statistical mechanics, the probability of finding a system in thermodynamicequilibrium in the state μis proportional to $e^{-\beta E_\mu}$ where$E_\mu$is the energy of this configuration and $\beta = \frac{1}{k_B T}$andk_B is the Boltzmann constant.

Let $A_\mu$is an observable of the system. This can be the energy i.e. $A_\mu = E_\mu$ or any other physical quantity.Then the average value of the observable is givenby:

$$\langle A\rangle = \frac{1}{Z}\sum_{\mu} A_\mu e^{-\beta E_\mu} \qquad (8)$$

where $Z = \sum_\mu e^{-\beta E_\mu}$ is called the partition function. (9)

Let usdenote the subset of N configurations by$\{\mu\}$. Then the thermal average $\langle A\rangle$ is given by

$$\langle A\rangle \approx \frac{\sum_{\{\mu\}} A_\mu e^{-\beta E_\mu}}{\sum_{\{\mu\}} e^{-\beta E_\mu}} \qquad (10)$$

The configuration in $\{\mu\}$ is selected, in one way, by Randomsampling. Let us consider an Isingsquare $L \times L$ lattice. Therefore it has a total of L^2spins. Please see section XIXfor a brief introduction on Ising Model. Random sampling procedure generatesindependent configurationsby choosing L^2 spinseither up or down with equal probability. For L=20, we have $2^{400} \approx 10^{120}$ independent configurations. Present day computers can analyse10^{10}configurations within a few hours of CPU time. Therefore this approach is very inefficient for the calculation of $\langle A\rangle$. There is another problem with Random sampling approach is that the sumin Eq. (8) is dominated by particular kind of states. For example in Ising model at low temperatures, in the ferromagnetic phase, large majority of the spins point in thesame direction. However Random sampling generates configurations with small magnetization, as the spins are chosen independently from each other.

Therefore we shall, as in theprevious section, generateconfigurations of the system non-uniformly. Let a given state μ is generated with a probability$W_\mu$then Eq. (8) takes the form

$$\langle A\rangle \approx \frac{\sum_{\{\mu\}} A_\mu e^{-\beta E_\mu} W_\mu^{-1}}{\sum_{\{\mu\}} e^{-\beta E_\mu} W_\mu^{-1}} \qquad (11)$$

This is analogous to the Eq. (4). Choosing $W_\mu = e^{-\beta E_\mu}/Z$, we get

$$\langle A\rangle \approx \frac{\sum_{\{\mu\}} A_\mu}{\sum_{\{\mu\}} 1} = \frac{1}{N}\sum_{\{\mu\}} A_\mu \qquad (12)$$

`Here N is the number of terms in the sum. It is possible to generate states according to the Boltzmann factor $exp(-\beta E_\mu)$using the concept of Markov chain as explained below?

III. MARKOV CHAIN

A Markov chain is a discrete stochastic process of transforming the state of system starting from a configuration μat time t = 0 to new configuration at a time t + Δt in such a way that each transition depends only on the current state of the system and not on the previous history or states. This property is called as Markov's property.

$$\mu \to \gamma \to \nu \cdots \qquad (13)$$

The evolution is stochastic i.e. is governed by transitionprobabilities $P(\mu \to \nu) \geq 0$. The transition probabilities $P(\mu \to \nu)$ satisfy the following normalization condition

$$\sum_{\nu} P(\mu \to \nu) = 1 \qquad (14)$$

Let the probability of system being in the state μ is p_μ. Then the probability of finding the system at a later timet + Δtin a state visgiven by

$$p_\nu(\mathrm{t} + \Delta\mathrm{t}) = \sum_{\mu} p_\mu(t) P(\mu \to \nu) \qquad (15)$$

Where the summation is over all states μ from where the transition to state ν is possible. If the system has N states,p_μ's can be represented by a vector with N components. Using this vector of dimensionN, we can rewrite Eq. (15) in the form of a vector-matrix product

$$p(t + \Delta t) = Pp(t) \qquad (16)$$

It is obvious that the matrix P will have $N \times N$ elements $P_{\mu\nu} = P(\nu \to \mu)$ .The differential form of

Eq.(16) can be written using the limit $\Delta t \to 0$.This form is also known as the Master equation(please see Section XX).

The sum of each column of the matrix isequal to 1 because of the normalisation condition in Eq.(14). The vector pis called as a stochastic vector if 1) it has non-negative elements $p_\mu \geq 0$ and2)$\sum_\mu p_\mu = 1$. A square matrix with non-negative elements and such that the sum ofall columns is equal to 1 is called stochastic matrix. The stochasticmatrix, in general, is not symmetric i.e. $P(\mu \to \nu) \neq P(\nu \to \mu)$.

It can be easily shown that if p is a stochastic vector and P a stochastic matrix, then

(1) Ppis a stochasticvector.
(2) P has at least an eigenvalue λ= 1.
(3) All other eigenvalues will be suchthat$|\lambda_k|$<1.

As an example, consider a system composed of 3 statesμ, νand γ. Let the elements of the probability matrixare given by P($\mu \to \nu$) = a, P($\nu \to \gamma$) =P($\gamma \to \nu$) = b (a, b <1). Rest of the elements of P corresponding to processes $\mu \to \gamma$, $\gamma \to \mu$, $\nu \to \mu$ are zero. Then the stochastic matrix P is given by

$$P = \begin{pmatrix} 1-a & 0 & 0 \\ a & 1-b & b \\ 0 & b & 1-b \end{pmatrix} \quad (17)$$

It is evident that eigenvalues are$\lambda_1 = 1$, $\lambda_2 = 1 - a$and$\lambda_3 = 1 - 2b$. Therefore the matrix is in agreement with the previous proposition. An eigenvalue is equal to $\lambda_1 = 1$,while the two others $|\lambda_2|$, $|\lambda_3|$<1.

The eigenvector associated to $\lambda_1 = 1$is$\omega = \left(0, \frac{1}{2}, \frac{1}{2}\right)$. This is a stochastic vector. This eigenvector describes a stationary state of the system i.e. theprobability of finding the system in any of the possible configurations does not evolvewith time as from Eq. (16) follows

$$\omega(t + \Delta t) = P\omega(t) = \omega(t) \quad (18)$$

Therefore, given an initial state, the system will evolve towards astationary state in which it spends half of the time in ν and half inγ. Here,$\omega_\mu = 0$, i.e the probability finding thesystem in the state μ is zero because system has evolved to final states νandγ.

IV. ERGODICITY

This is an important property of the Monte Carlo procedures. The procedure adopted or the algorithm should be such that any state of the system should be reachable from any other state. The transition rates may be zero between two arbitrary states μ and νbut there should exist at least a connecting path of transitionwith non-zero rates.

$$\mu \to \gamma \to \delta \to \rho \to \cdots \to \nu \quad (19)$$

The stochastic process given in the above example is non-ergodicas$P(\gamma \to \mu) = P(\nu \to \mu) = 0$. Therefore it is impossible to reach the state μfromany other state of the system.

V. DETAILED BALANCE

The inverse problem is to generate a stochastic dynamics with a stationary state ω. A given stochastic vector ω is stationary if it is eigenvector of the generator of dynamicsP with eigenvalue equal to1, which means

$$P\omega = \omega$$

$$\text{Or}\omega_\nu = \sum_\mu \omega_\mu P(\mu \to \nu) \quad (20)$$

Using Eq. (14) we can rewrite this condition as

$$\sum_\mu \omega_\nu P(\nu \to \mu) = \sum_\mu \omega_\mu P(\mu \to \nu) \quad (21)$$

This is known as the global balance condition. The condition states that ω is stationary if the total probabilityof transition from ν toany configurationof the system ($\sum_\mu \omega_\nu P(\nu \to \mu)$ is equal to the probability of the transition $\sum_\mu \omega_\mu P(\mu \to \nu)$from any other configurationtoν).

Therefore if the probabilities satisfy the following condition, called the detailed balance condition

$$\omega_\nu P(\nu \to \mu) = \omega_\mu P(\mu \to \nu) \quad (22)$$

then Eq. (21) necessarily holds. However the opposite may not be true that Eq. (21) is valid but Eq. (22) is violated. It is easier to implement detailed balance condition.

Let $\omega = \frac{1}{6}(1\ 4\ 1)$be the stationary state of a system with three states. Using detailed balance condition (Eq. (22)) we can write:

$$\frac{P(1\to2)}{P(2\to1)} = \frac{\omega_2}{\omega_1} = 4\frac{P(3\to2)}{P(2\to3)} = \frac{\omega_2}{\omega_3} = 4\frac{P(1\to3)}{P(3\to1)} = \frac{\omega_3}{\omega_1} = 1 \quad (23)$$

Further as we know the sums of all columns must add up toone. One possible solution is

$$P = \frac{1}{5}\begin{pmatrix} 0 & 1 & 1 \\ 4 & 3 & 4 \\ 1 & 1 & 0 \end{pmatrix} \quad (24)$$

The matrix P has ω as its eigenvector with eigenvalue equal to 1 i.e. $P\omega = \omega$.

The detailed balance condition for dynamics to Boltzmann distribution $\omega_\mu = exp(-\beta E_\mu)/Z$ becomes

$$\frac{P(\nu \to \mu)}{P(\mu \to \nu)} = e^{-\beta(E_\mu - E_\nu)} \quad (25)$$

Therefore there is freedom on the specific choice of transition probabilities satisfying detailed balance as it only fixes the ratio of transition probabilities as seen in the above examples. It is therefore simple to implement in practice.

VI. THE METROPOLIS ALGORITHM

Therefore the stochastic Markov chain needs to fulfill the conditions of Ergodicity and Detailed balance in order to converge to thermodynamic equilibrium. Theprobabilitiesshould also satisfy the normalization condition of Eq. (14). Setting $\nu = \mu$ in Eq. (22) we get 1 = 1, i.e. the detailed balance condition is alwayssatisfied for any choice of$P(\mu \to \mu)$which means for an absence of transition and also the normalization condition is also satisfied for the absence of transition i.e. a stationary state case.

Therefore the optimal choice for the quick convergence to equilibriumrequires $P(\mu \to \nu)$ beingas large as possible. However it should satisfy the conditions lay down by Eqs. (22) and (14).

In practice we split the probability or rates of transition as follows:

$$P(\mu \to \nu) = g(\mu \to \nu)A(\mu \to \nu) \quad (26)$$

Here $g(\mu \to \nu)$ specifies which states are generated by the algorithm from a given initial state and is called the selection probability. $A(\mu \to \nu)$ is the fraction of times the actualtransition takes place and is called the acceptance ratio

A new state is generated byselecting a spin at random out of a total of M spins in the lattice in Ising model. Therefore the selection probability is $g(\mu \to \nu) = 1/M$ ifthe two states differ by a single spin, while $g(\mu \to \nu) = 0$ otherwise.The acceptance ratio in Metropolis algorithm is given by

$$A(\mu \to \nu) = \begin{cases} e^{-\beta(E_\nu - E_\mu)} & if\ E_\nu > E_\mu \\ 1 & \text{otherwise} \end{cases} \quad (27)$$

Therefore if an update selected according to the rule defined by $g(\mu \to \nu)$ leads to alowering of the energy, it is always accepted. Otherwise it is accepted with a probability proportional to $e^{-\beta(E_\nu - E_\mu)}$ which is the Boltzmann factor associated to the energy difference between thefinal and initial state.

Itiseasy to show that the Metropolis acceptance ratio (Eq. (27)) satisfies detailed balance(Eq.(22)) for any symmetric choice of selection probability $g(\mu \to \nu) = g(\nu \to \mu)$

VII. EQUILIBRATION

The dynamics of the system converges to equilibrium state provided the conditions of Ergodicity and detailed balance of Markov's chain are satisfied.The initial state is chosen at random and it takes the system to reach the equilibrium state in small time.

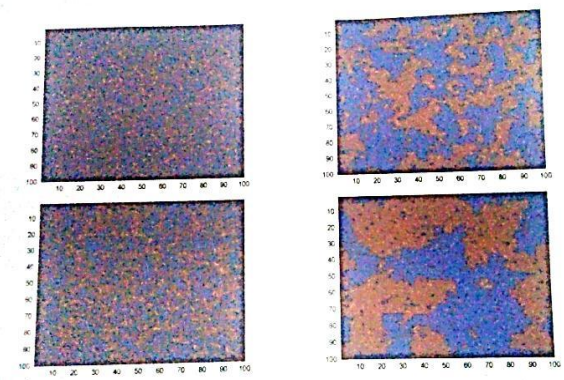

Figure 2: Configurations of a 100×100 Ising lattice at T = $0.88T_c$ obtained from the Metropolis algorithm at different time steps.

The equilibration time τ_{eq} in a simulation is the time required by the system to reach an equilibrium state.Time in a simulation is usually measured in terms of attempted flips per lattice site.It enables us to compare two simulations of lattices of different sizes. A physical quantity(like the total magnetization in an Ising lattice)is plotted as function of time. This quantity starts fluctuating around a constant value as the thermal equilibrium is reached. Fig.2 shows the Metropolis algorithm at different time steps. The initial state of the system configuration is shown in the figure at the top left, followed by the state at 10^4Monte Carlo steps in bottom left, then the state at 10^5MC steps at Top right and in the end near the equilibrium state after 10^6MC steps in the Bottom right. The lattice size is 100x100, therefore ifwe measure the time in sweepse.g. MC steps per spin, the times shown corresponds to 1,10 and 100 sweeps. Differentsnapshots of configurations of the Ising model are obtained at different simulation times. The topleft figure is the random initial configuration. As the temperature is below the criticalone the spins tend to align (ferromagnetic phase). Larger andlarger domains with aligned spins are formed in the course of time, until these domainsreach a characteristic size. This size does not change further.The magnetization, as shown in Fig.3, reaches an average value after about t = 3000 Monte Carlo steps per lattice site. Time in simulation is measured in terms of attempted flips per Lattice site so that a comparisonofsimulations of two lattices of different sizes can be done.

VIII. CORRELATION TIME

Markov chain should gothrougha sufficiently large series of independent statesfor a minimum error in the average of a physical quantity as in Eq. (12). A consistent average is the basic requirement for an efficient simulation process. For example, a single flip at each time step in the Metropolis algorithm discussed above for Ising model gives excellent results.

Therefore the change in magnetization $m = \frac{1}{N}\sum_i s_i$ (28)

for a Lattice with N spins in Ising model at each Monte Carlo step is of the order of 1/N. This means there is strong correlation between the two consecutive steps or configurations. Therefore the loss of this correlation requires many steps.

This correlation is measured in terms of what is known as the correlation time.

Let us suppose that wehave let the simulation run for a sufficient time so to have reached equilibrium. Allthe physical quantities fluctuate around their average equilibrium values.

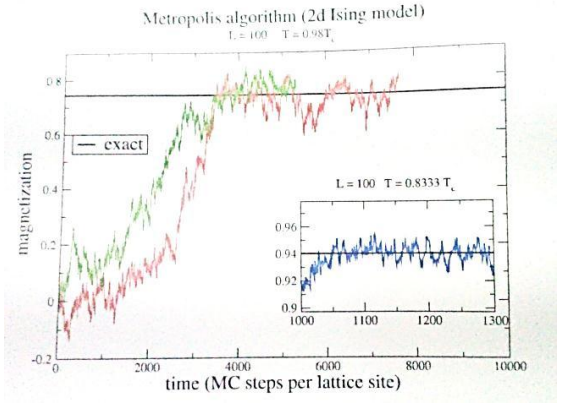

Figure 3: Magnetization of a 100×100 Ising model in the ferromagnetic phase asa function of the simulation time. In the main frame two random differentinitialconfigurations were simulated at T = $0.98T_c$. After about 3000 Monte Carlo sweepsthe two curves converge to the same average value. The solid line is the exact value ofthe magnetization of the 2d Ising model. **Inset:** A similar run for a lower temperatureT = $0.8333T_c$. Note that the equilibrium magnetization is reached faster ($\tau_{eq} \approx 1000$)compared to the T = $0.98T_c$case. Fluctuations around the average magnetization are also much smaller.

 ISSN: 2454-4248
01 – 11

This fluctuation is measured in terms of an autocorrelation function[7]

$$\chi(t) = \int dt' \left[m(t') - \langle m \rangle\right]\left[m(t'+t) - \langle m \rangle\right] \quad (29)$$

Here m(t) is the magnetization of the Ising model at time t, $\langle m \rangle$ is the average magnetization value over all values measuredduring the Monte Carlo run. Here we have chosenthe property of magnetisation for Ising model. HoweverEq.(29) is more general and is applicable to any other physical quantity.Howeverfor a very small value of t, $m(t'+t) \approx m(t')$and the integrand in above equation will have a positive value, that is $\chi(t) > 0$. However $\chi(t)$ is expected to decay to zero after sufficiently long time because $m(t'+t)$ becomes uncorrelated to $m(t')$. Thefluctuationsinmareabove or below its average value at times $t'+t$. The positive and negative contributions will cancel on integration with respect to dt' and therefore integral $\chi(t)$will vanish. This is because integration is the area under the curve and the net area for an uncorrelated region of the curve with both positive and negative values add up to zero. This happensasymptotically as

$$\chi(t) \sim e^{-t/\tau} \quad (30)$$

The dynamics describedby the Markov chain (Eq. (15)) justifies this exponential behavior. Let vector p(0) describes the initialconfiguration at time t = 0. This can be written in terms of eigenvectors of Pas$p = \sum_k c_k \omega^{(k)}$. The state vector $p(t)$ at a later time $t = n\Delta t$ is obtained by using Eq.(15) by multiplying with P^n i.e.

$$p(t) = P^n p(0) = \sum_k c_k \lambda_k^n \omega^{(k)} \quad (31)$$

whereλ_k are the corresponding eigenvalues.

Reconsidering the Ising model example, let mis the magnetization and m_μ is the value of the observable in the stateμ, its average value over a state given by the vector p will be

$$m = \sum_\mu m_\mu \, p_\mu = M.p \quad (32)$$

As $\sum_\mu m_\mu \, p_\mu = M.p$ the scalar product of p with M. Now substituting from Eq.(31) weget

$$m(t) = M.\omega^{(1)} + \sum_{k>1} c_k \lambda_k^n M.\omega^{(k)} \quad (33)$$
$$= \langle m \rangle + \sum_{k>1} c_k \lambda_k^n M_k$$

As we know the magnetization in the stationary state is equal to $\langle m \rangle$and the eigenvalue for the stationary state is one i.e. $\lambda_1^n = 1$. Here we have used $M_k = M.\omega^{(k)}$. As $n = \frac{t}{\Delta t}$ and defining relaxation times

$$\tau_k = -\frac{1}{\log|\lambda_k|} \quad (34)$$

We can write the above equation as

$$m(t) - \langle m \rangle = \sum_{k>1} c_k M_k e^{-t/\tau_k} \quad (35)$$

This is true not only for the Ising model and the properties of the magnetization, but Eq. (29) is applicable to all systems. In general we find

$$\chi(t) = Ae^{-t/\tau_1} + Be^{-t/\tau_2} + \cdots \quad (36)$$

Therefore $\chi(t)$ decays exponentially as written in Eq.(30). The Eq.(36), therefore is more general and appropriate for fitting in simulations.

As we see in above example, the Eigen values of stochastic matrix

$$P = \begin{pmatrix} 1-a & 0 & 0 \\ a & 1-b & b \\ 0 & b & 1-b \end{pmatrix}$$

are $\lambda_1 = 1$, $\lambda_2 = 1-a$ and $\lambda_3 = 1-2b$. The stationarystateis$v^{(1)} = \left(0, \frac{1}{2}, \frac{1}{2}\right)$. The two otherEigenvectors are $v^{(2)} = (-b,\ b-a, a)$ and $v^{(3)} = (0,\ 1, -1)$.It can be verified that the sum of the elements of thevectors$v^{(2)}$and $v^{(3)}$is zero. It can be shown that it is a general property of any stochasticmatrix? Let us now assume that the system is initially instate$p = \left(\frac{1}{3}, \frac{1}{3}, \frac{1}{3}\right)$. Thelinear combination

$$p = \sum_{k=1}^{3} c_k \, v^{(k)} = v^{(1)} - \frac{1}{3b} v^{(2)} + \left(\frac{1}{6} - \frac{a}{3b}\right) v^{(3)} \quad (37)$$

Since there is always an equilibrium state we expect for any stochastic matrixc_1= 1.

The data for averaging as taken in Eq.(12) should be determined at time intervals larger than the autocorrelation time τ. However, it significantly reduces the number of data points. Therefore, one should take data at fixed time intervals ΔT.Thestandard deviation on the mean of nexperimental points, taken at uncorrelated intervals, is given by [3]

$$\sigma = \sqrt{\frac{1}{n-1}\left(\overline{m^2} - \overline{m}^2\right)} \quad (38)$$

The same measurements taken [4] at intervals ΔT yields

$$\sigma = \sqrt{\frac{1 + 2\tau/\Delta T}{n-1}\left(\overline{m^2} - \overline{m}^2\right)} \quad (39)$$

It can be seen that this equation reduces to Eq. (38)for$\Delta T \gg \tau$.

IX. CRITICAL SLOWING DOWN: THE DYNAMICAL EXPONENT

Various physical properties of a system in equilibrium show power law singularities near the vicinity of the critical point. These laws are governed by some critical exponents. As an example, the magnetization vanishes near the critical temperature in Ising model, following a power law with a critical exponent β

$$m \sim \left(\frac{T_c - T}{T_c}\right)^\beta \quad (40)$$

Another example, the specific heat diverges as we approach the critical temperature following a power law with critical exponent α

$$c \sim \left|\frac{T - T_c}{T_c}\right|^{-\alpha} \quad (41)$$

As we know the spins at a distance $\vec{r}$ are correlated for temperatures above and below T_c as

 ISSN: 2454-4248
01 – 11

$$\langle s_{\vec{\delta}} s_{\vec{\delta}+\vec{r}} \rangle - \langle s_{\vec{\delta}} \rangle \langle s_{\vec{\delta}+\vec{r}} \rangle \sim e^{-|\vec{r}|/\xi} \quad (42)$$

Here ξ is the correlation length. This quantity also diverges as we approach T_c

$$\xi \sim \left| \frac{T - T_c}{T_c} \right|^{-\nu} \quad (43)$$

Similar is the case for susceptibility with a critical exponentγ. The values of α, β, ν and γ are independent of the type of lattice considered (e.g. triangular, squared . . .) but depend on the dimensionality of the model. In the 2d Ising model one has α= 0 and therefore a logarithmic singularity. Also for this model $\beta = \frac{1}{8}$, $\nu = 1$ and $\gamma = 7/4$.

The typical size of cluster of spins pointing in the same direction (Fig.4) is denoted by the correlation length ξ. As the temperature of the algorithm approaches T_c, the size of the clusters increases and spins become increasingly coupled to each other. It becomes impossible to flip a single spin out of this large cluster. This is because neighboring numerous spins which are coupled to this spin, resist this change. Therefore the Metropolis Monte Carlo algorithm suffers from a so called critical slowing down near the critical temperature T_c. Thereforeit affects the correlation time τwhich diverges as we approach the critical point T_c

$$\tau \sim \left| \frac{T - T_c}{T_c} \right|^{-z\nu} \quad (44)$$

This algorithm dependent exponent Z is called the dynamical exponent. Its value indicates how the correlation time of the algorithm behaves near the critical point. Optimal performance of an algorithm near T_c indicates a small value of Z.

As T_c is known for a 2d Ising model, we can evaluate Z by setting $T = T_c$. As we know for a finite lattice of Length L the correlation length.$\xi \sim \boldsymbol{L}$and is therefore non-diverging.Therefore using Eq.(43) and (44) we get

$$\tau \sim \xi^z \sim \boldsymbol{L^z} \quad (45)$$

Metropolis algorithm for 2d Ising model gives $Z \approx 2.17$. The critical slowing down is visible also from the runshown in Fig.3. The average magnetization value fluctuates in correlatedfashionfor longer times at $T = 0.98T_c$ as compared to$T = 0.833T_c$.

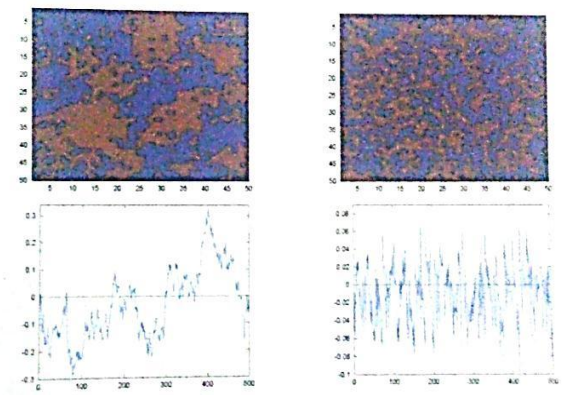

Figure 4: Metropolis algorithm typical spin configurations (top) and magnetization vs. time plots (bottom) for Ising model. Bigger clusters on left are for temperature T=2.5 which isnear $T_c \approx 2.26$.They have an increased autocorrelation time. Smaller clusters are observed for T=5.0 in the fig. on right.

X. CLUSTER ALGORITHMS: THEWOLFF ALGORITHM FOR THE ISING MODEL

U Wolff in 1989 [5] introduced a cluster based algorithm which overcomes the problem of critical slow down as discussed above.It is based on the concept that the whole cluster of spins is flipped in one move unlike a single spin as in Metropolis algorithm. There are more such cluster based algorithms, we are not discussing here

Consider a single spin at random, called the seed spin. Now add all neighboring spins with the same sign as the seed spinin the cluster. The spins are added with a probability P_{add}. The probability of their exclusion is 1-P_{add}. Spins of opposite direction or sign than the seed spin are excluded.

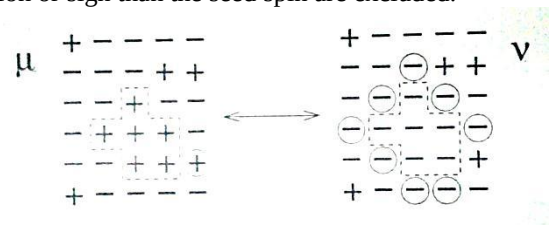

Figure 5: A cluster in the Wolff algorithm is composed of connectedidentical spins. The boundary of the cluster is indicated as a dashed line in the example. Thespins encircled are kept out of the cluster.

The algorithm should fulfillthe detailed balance condition. Let two states μ and ν differ from each other by the flip of a single cluster. The selection probabilities obviously are $g(\mu \to \nu) \propto (1 - P_{add})^m$ and $g(\nu \to \mu) \propto (1 - P_{add})^n$ where m and n are the number of bonds between a spin in the cluster and a spin outside the cluster.

The detailed balance condition reads:

$$\frac{P(\nu \to \mu)}{P(\mu \to \nu)} = \frac{g(\nu \to \mu) A(\nu \to \mu)}{g(\mu \to \nu) A(\mu \to \nu)} = (1 - P_{add})^{n-m} \frac{A(\nu \to \mu)}{A(\mu \to \nu)} = e^{-\beta(E_\mu - E_\nu)} \quad (46)$$

The energy difference for Ising model is $E_\mu - E_\nu = (n - m)2J$. Therefore from above Eq., we have the detailed balance condition as

$$\frac{A(\nu \to \mu)}{A(\mu \to \nu)} = \left[(1 - P_{add}) e^{2\beta J} \right]^{m-n} \quad (47)$$

Choosing

$$P_{add} = 1 - e^{2\beta J} \quad (48)$$

We get $A(\nu \to \mu) = A(\mu \to \nu)$ Let us choose the acceptance ratios $A(\mu \to \nu) =$ 1. This means flipping of the cluster is always accepted. However P_{add} as clear from the above assumption in Eq. (48) is temperature dependent. At high temperatures $\beta \to 0$ and so we get $P_{add} \to 0$ i.e. clusters are very small, consisting of a single seed spin only.Therefore the Wolff algorithm becomes a single spin flipping algorithm at high

 ISSN: 2454-4248
01 – 11

temperatures. Also at very low temperatures $P_{add} \to 0$ as $\beta \to 0$. Therefore clusters are large almost of the size of the lattice.That means system flips betweentotal positive and total negative magnetization values as all spins of the lattice are either up or down. Therefore Wolff algorithm is not successful at very high and at very low temperatures. However Metropolisalgorithm works better at extreme temperatures.Finally let us consider cluster flip τ_{flip} as a unit of time for the algorithm but size of the Wolff cluster is different at different temperatures. Thereforeτ_{flip} is not a reasonable unit of time. Then the time unit for a d dimensional lattice of size L can be defined as

$$\tau = \tau_{flip} \frac{\langle n \rangle}{L^d} \tag{49}$$

Here $\langle n \rangle$ is the average number of spins in the cluster. For low temperatures cluster is as big as the lattice itself and so $\langle n \rangle \to L^d$, and from above Eq. $\tau \approx \tau_{flip}$. This is similar to the time unit of Metropolis algorithm. Further, the correlation time at the critical point in this unit scales as a power law of the lattice size. We get Z≈0.25 for a two dimensional Ising model. Therefore the problem of critical slowing down has been successfully solved by the Wolff algorithm.

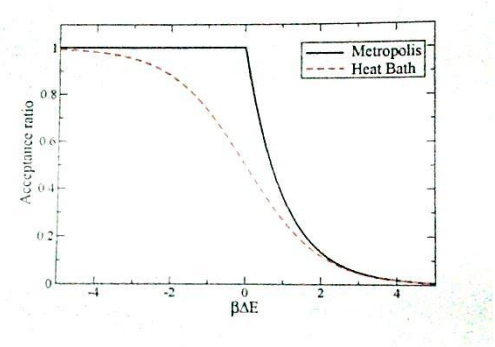

Figure 6: Acceptance ratios as functions of βΔE, where β is the inverse temperature andΔEthe energy difference, for the Metropolis (solid line)and Heat Bath algorithms(dashed line).

XI. THE HEAT BATH ALGORITHM

It is another single spin flip algorithm as it also satisfies the condition of detailed balance (Eq. (22)).The heat bath algorithm for the Ising model has thefollowing form:

$$A(\mu \to \nu) = \frac{e^{-\beta E_\nu}}{e^{-\beta E_\nu} + e^{-\beta E_\mu}} = \frac{e^{-\beta \Delta E}}{e^{-\beta \Delta E} + 1} \tag{50}$$

where$\Delta E = E_\nu - E_\mu$. Comparing with Eq.(27), we see this acceptance ratio matches that of theMetropolis algorithm in the two limiting cases $\beta \Delta E \to -\infty$, where $A \to 1$ and for βΔE large and positive which gives $A \approx e^{-\beta \Delta E}$. However the two algorithms differ for $\Delta E = 0$. The Metropolis acceptance ratio for $\Delta E = 0$ is A = 1. On the other hand for heat bath it is 1/2. This means the acceptance of the flip that does not vary energy is half in heat bath algorithm as compared to that in theMetropolis move.

The Heat Bath algorithm is not very efficient forMonteCarlo simulation of the Ising model however it is a good algorithm forother models like Potts model (Please see section (XIX) for Potts model). In this model the spins can take q different values, as compared to the Ising case in which$s_i = \pm 1$.

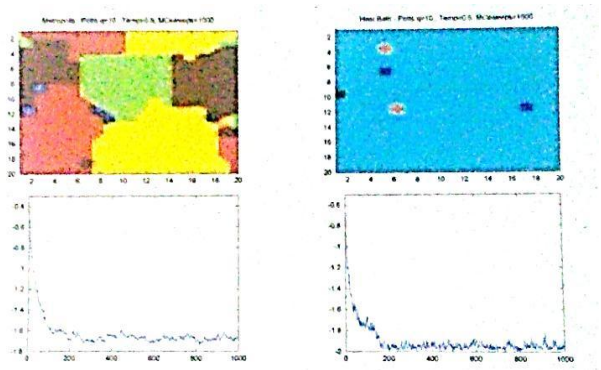

Figure 7: (Top) Comparison of evolution of Metropolis algorithm in the left column and Heat Bath algorithm in the right column for configurations of a 20×20 Lattice 10-state Potts model.The energy vs. time plots in the bottom shows that the Heat Bath algorithm is more efficient than Metropolis forlarge values of q (faster equilibration).

This will be generalization of Eq. (50) to a q state case. Figure 7 shows comparison of Metropolis algorithm andthe Heat Bath algorithm through some snapshots ofconfigurationsfor q = 10 case. The simulated temperature is taken very low, for a better comparison of two algorithms so thatinequilibriumconfiguration almost all spins are aligned to one of the q-values. We can see that theHeat Bath algorithm evolves more rapidly towards the configuration with all alignedspins.

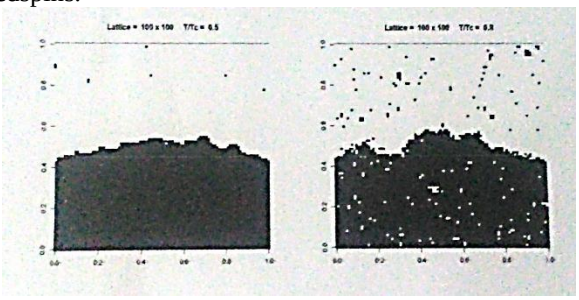

Figure 8: Typical interface configurations in the Ising model at two different temperaturesT = 0.5 T_c on the left whereas T = 0.8 $T_c$on the rightwith Non-local Kawasaki dynamics.

XII. CONSERVED ORDER PARAMETER ISING MODEL

Consider Ising model with two ferromagnetic phases, below the critical temperature T<$T_c$with average magnetization $\pm m(T)$ which approaches unity as $T \to 0$.It is possible that lattice possess two identical symmetrical parts with spins up on one side and spins down in the other. A single spin flip algorithm like the Metropolis algorithm will choose any one of these states with 50% chances and will end up in one single phase. Therefore we need some different algorithm to study the interface between the two ferromagnetic phases.TheKawasaki algorithm is found useful for such situations. The principle of Kawasaki algorithm is similar to spin flip algorithmswith the only difference that it selectpairs of neighboring spins and swaps

them. The acceptance ratio followsthestandard Metropolis rule of Eq. (27). We are only interchanging two spins witheach other, therefore the total magnetization

$$M = \sum_i s_i \tag{51}$$

Isunchanged.The spins in Kawasaki dynamics move diffusively throughout the lattice. Therefore system takes long time before the equilibration is reached. Further improvement is done in the algorithm by choosing far away spins for swapping.Therefore lists of locations of up spins and another list of locations of down spins is prepared. The spins to be swapped are then chosen from two lists with aprobability independent of their physical position in the lattice. The non-local moves lead to a faster equilibration. The acceptance ratio is same as given in Eq. (27).Pairs of equal spins are avoided as we are selecting a plus and a minus spin therefore it saves computer time.

XIII. MONTE CARLO IN CONTINUOUS TIME

There are systems with a defined Markov chain such that thesystem remains locked into certain states for long. For example,

$$\mu \to \gamma \to \gamma \to \cdots \to \gamma \to \nu \cdots\cdots \tag{52}$$

Therefore the dynamics of the system becomes very slow. This problem can be overcome by evaluatingT_γ, the average time spent into a certain state γ and putting an upper limit on the system for this variable. This is the same procedure the continuous time Monte Carlo method adopts to evaluateT_γ ?Consider the probability for transition into γ state itself i.e. $\gamma \to \gamma$ i.e. $p = P(\gamma \to \gamma)$ and then $q = 1 - p = \sum_{\nu \neq \gamma} P(\gamma \to \nu)$(we have used the normalization of Eq. (14)). Then we have

$$T_\gamma = \Delta t \sum_{n=0}^{+\infty} n p^n q = \Delta t \frac{p}{q} \approx \frac{\Delta t}{\sum_{\nu \neq \gamma} P(\gamma \to \nu)} \tag{53}$$

whereΔt is the discrete time unit of the Markov chain and where we have used $q \ll p \approx 1$.The next step after evaluating $T_\gamma$to force the system to use another state sayμ the probability for this transition is

$$g(\gamma \to \mu) = \frac{P(\gamma \to \mu)}{\sum_{\nu \neq \gamma} P(\gamma \to \nu)} \tag{54}$$

However the shortcoming of this method is that for evaluating $T_\gamma$and $g(\gamma \to \mu)$, we need to evaluate all thetransition probabilities $P(\gamma \to \nu)$. This is done by choosing appropriate transitionprobabilities, the continuous time method can be implemented in an efficient way (see for example Ref.[3])

XIV. CONTINUOUS SYSTEMS: LENNARD-JONES FLUIDS

Monte Carlo simulations can be helpful to study classicalfluids, for example Lennard-Jones fluid system. Let certain volume V of the fluid has N particles at a temperatureT. Then as we know, Lennard –Jones pairwise interaction potential is given by

$$V_{LJ(r)} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{55}$$

Here ε is the minimum of the potential and $\sigma$the distancefor zero potential.First term in the bracket is a long-range attraction term decaying as $\frac{1}{r^6}$ and arises because of dispersive Van der Waals forces due to fluctuating dipoles.The second term is a short range repulsion term diverging at short distances as $\frac{1}{r^{12}}$.This short range term is due to Pauli exclusion principle.It is the square of the attraction term and is just chosensobecause of ease of the computation

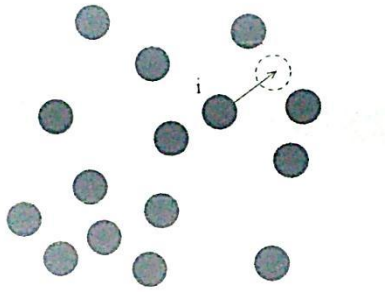

Figure 9: The particle selection in Monte Carlo algorithm for a continuous fluid system is random and a move to a new position is attempted. The acceptance ratio of new configuration is according to the Metropolis rule.

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The partition function of the system is given as an integral over positions $\vec{r_i}$and momenta $\vec{p_i}$ of all as:

$$Z = \int d\vec{r_1} \ldots . d\vec{r_N} d\vec{p_1} \ldots . d\vec{p_N}\, e^{-\beta\left(\sum_i \frac{p_1^2}{2m} + V(\vec{r_1} \ldots . \vec{r_N})\right)} \tag{56}$$

where$\vec{r_i}$ and $\vec{p_i}$ for i = 1,2, … … . Nare the position and the momentum co-ordinates of the N particles.The quantity between the parenthesis in exponential is the total energy of the system. Then the average value of an observable$(\vec{r_1} \ldots . \vec{r_N}, \vec{p_1} \ldots . \vec{p_N})$, a function of position and momentum co-ordinates is given by:

$$\langle A \rangle = \frac{1}{Z} \int d\vec{r_1} \ldots . d\vec{r_N} d\vec{p_1} \ldots . d\vec{p_N}\, A(\vec{r_1} \ldots . \vec{r_N}, \vec{p_1} \ldots . \vec{p_N}) e^{-\beta\left(\sum_i \frac{p_1^2}{2m} + V(\vec{r_1} \ldots . \vec{r_N})\right)} \tag{57}$$

This equation is the same as Eq. (8). Difference is only that A is function of position and momentum coordinates and the summation has been changed to integral. The functions of momenta being Gaussian integrals can be easily integrated. The integration of position-dependent quantities is not so easy and therefore we need numerical simulation methods like Monte Carlo. Lennard-Jones fluid potential is a sum of pair potentials

$$V(\vec{r_1} \ldots . \vec{r_N}) = \sum_{i<j} V_{LJ}(r_{ij}) \tag{58}$$

Here $r_{ij} = \left|\vec{r_i} - \vec{r_j}\right|$. This computationis not easy.As an example to evaluate average distance $\langle \vec{r_1} - \vec{r_2} \rangle$ between two particles,integrationover terms of type $exp\left(-\left(V_{LJ}(r_{12}) + V_{LJ}(r_{13}) + V_{LJ}(r_{14}) \ldots\right)/k_B T\right)$is required. It is really a tough task.

The particle is selected atrandomand a move is attempted $\vec{r_i} \to \vec{r_i'}$(see Fig. 9) in order to perform Monte Carlo simulation on this problem. The shift of the coordinates $\delta_x, \delta_y$and$\delta_z$from a uniform distribution on [-Δ, Δ] is selected. Here Δ is of the order of the inter particle distance. The evaluation of acceptance ratio

requires the computation of the energy difference between new and old configuration.

Let a particle i is moved, the energy difference is given as

$$\Delta E = \sum_{j \neq i} \left[V_{LJ}\left(r'_{ij}\right) - V_{LJ}\left(r_{ij}\right) \right] \quad (59)$$

Here $r'_{ij} = \left|\overrightarrow{r'_i} - \vec{r}_j\right|$.

The acceptance ratio is given by

$$A\left(\vec{r}_i \to \overrightarrow{r_i'}\right) = \begin{cases} 1 & \text{if } \Delta E \leq 0 \\ \exp(-\Delta E / k_B T) & \text{if } \Delta E > 0 \end{cases} \text{and}$$

which is same as the Metropolis Algorithm. Long range interaction demands summing over all pairs of particles, which meansa sum of $N(N-1)/2$ terms. This is a large simulation work with large number of particles.Therefore the range of the interaction is truncated as in the following expression

$$V_{trunc}(r) = \begin{cases} V_{LJ}(r) if r < r_c \\ 0 \qquad otherwise \end{cases} \quad (60)$$

After this modification in the potential only those particles need to be considered which fall within this radius r_c called the truncation radius (typically$r_c \approx 2 - 3\sigma$).

XV. NON- EQUILIBRIUM SYSTEMS

An algorithm needs to satisfy the conditions of ErgodicityandDetailed Balance. As seen in theIsing model there are many algorithms for which these conditions are satisfied. These are single spin flip algorithms like Metropolis, heat bath . . . or are cluster flip type like Wolffalgorithm. However these algorithms are for systems which converge to equilibrium. There can be certain non-equilibrium conditions that one might try to study. But unfortunately there is not such a large choice of algorithms. However the procedure to study non-equilibrium conditions is similar. We build a Markov chain of states with certain transition probabilities like $P(\mu \to \nu)$. Time step Δt is real time and not of an algorithmic type any longer. As for example, the cluster algorithms are not proper to study the dynamical properties in Isingmodel. It isnot a realistic dynamics which shows the buildup of large clusters at low temperatures and single flip situation at high temperatures. Similar is the case with non-local Kawasaki like dynamics which involve the swapping of opposite spins with rates which are independent of their physical locations. Conclusively we need local algorithms totally different from the equilibrium mechanics.Algorithms of Non-equilibrium systems do not rely on physical parameters likepartitionfunctions, free energies etc.Therefore we need to study these systems separately. Following is an example of Monte Carlo simulations applied to non-equilibriumsystems.

XVI. COUPLED CHEMICAL REACTIONS

The coupled chemical reactions, is a non-equilibrium system one may like to study. The reactions may be written in the following general framework

$$m_1 A_1 + m_2 A_2 + m_3 A_3 + \cdots m_r A_r \xrightarrow{k_i} n_1 A_1 + n_2 A_2 + n_3 A_3 + \cdots n_r A_r \quad (61)$$

Here m_i, n_i are stoichiometric coefficients and A_i are different kind of particles i.e. molecules, atoms or ions. Let $k_i t$is the probability the reactant particles react. Let the time interval for reaction is [t,t+dt]. The reaction may be reversible or irreversible. If it is reversible, there will be a forward rate and backward rate.

The Lotka-Volterra model, which deals with these kinds of reactions, is also called as predator-prey model.LetsA_1(the prey) and A_2(the predator) be two particles which react as below:

$$A_1 \xrightarrow{k_1} 2A_1$$
$$A_1 + A_2 \xrightarrow{k_2} 2A_2$$
$$A_2 \xrightarrow{k_3} \emptyset \quad (62)$$

Herek_i, with i = 1,2, 3 are the rates for each reaction.

The system is homogenous, so that spatial effects are negligible. The diffusion is fast enough to efficiently mix the particles. The state of the system at time t can be written as $(X_1, X_2, \ldots . X_N)$where X_i are N non-negative integers. Let M be the total number of chemical reactions occurring in the system.Let $k_i$with$i = 1, 2 \ldots$ M be rates of these M reactions. Let us denote the probability of finding the system in state $(X_1, X_2, \ldots . X_N)$at time tasP$(X_1, X_2, \ldots . X_N, t)$.

Now we are interested to set up a Master equation for P. Consider the first reaction of Eq. (62). Let there are X_1particles of type A_1at time t,thenthetotal probability for first reaction to occurs in [t, t + dt] is equal to $X_1 k_1 dt$. Similarly for the second reaction of Eq. (62), the total probability for reaction to occur is$X_1 X_2 k_2 dt$, where $X_1$and X_2 is the number of particles of type A_1 and A_2respectively.The actual rate for a reaction is

$$a_i = k_i\{\text{number of reagents combinations for reaction i}\} \quad (63)$$

If reaction l is of the type $A_j \to A_i$one has rate of gain of product particles of the form as below:

$$B_l = k_l X_j \mathrm{P}\left(X_1, X_2, \ldots X_j + 1, \ldots X_j - 1, \ldots X_N, t\right) \quad (64)$$

Therefore the Master equation can be written as

$$\frac{\partial}{\partial t}\mathrm{P}(X_1, X_2, \ldots . X_N, t) = -\sum_{i=1}^{M} a_i \mathrm{P}(X_1, X_2, \ldots . X_N, t) + \sum_{i=1}^{M} B_i \quad (65)$$

The first term on the right side is due to the loss of reactants whereas the second term is due to the gain of product particles.

XVII. RATE EQUATIONS

The rate equations is defined as the time evolution of the average number of particlesstarting from the Master equation

One can derive an equation for the averages

$$\langle X_l \rangle = \sum_{\{X\}} X_l \mathrm{P}(X_1, X_2, \ldots . X_N, t) \quad (66)$$

with l = 1,2,…..N.

The problem is to deduce equations in closed form as because of products of particle numbers $X_k$in rate equations (see Eq.(63)), we obtain rate equations in the form

$$\frac{\mathrm{d}}{\mathrm{dt}}\langle \mathrm{X_l} \rangle = \mathrm{g_l}\left(\langle \mathrm{X_1} \rangle, \langle \mathrm{X_2} \rangle, \ldots . , \langle \mathrm{X_N} \rangle \ldots . , \langle \mathrm{X_i X_j} \rangle \ldots , \langle \mathrm{X_k X_p X_q} \rangle, \ldots . \right) \quad (67)$$

These equations can be simplified by neglectingthecorrelation between particle numbers so that we

 ISSN: 2454-4248
01 – 11

can approximate$\langle X_i X_j \ldots X_k\rangle \approx \langle X_1\rangle, \langle X_2\rangle, \ldots., \langle X_k\rangle$. This way we obtain differential equations in closed form. These equations, although not exact, describe the evolution process of $\langle X_k\rangle$in a deterministic way and fluctuations about the average are not observed. The rate equations give an accurate description of the evolution of the system if the number of particles is large i.e..$\langle X_i\rangle \gg 1$. However fluctuationsdominate if the number of particles is low and the rate equation condition is not fulfilled.

As an example for Eqs.(62), the rate equations for Lotka-Volterra model, also known as predator-prey modelcan be written as

$$\frac{d}{dt}X_1 = k_1X_1 - k_2X_1X_2 \quad (68)$$

$$\frac{d}{dt}X_2 = k_2X_1X_2 - k_3X_2 \quad (69)$$

where to simplify the notation the parenthesis $\langle . \rangle$ have been omitted. The two stationary and time independent solutions are$X_1 = X_2 = 0$and$X_1 = \frac{k_3}{k_2}, X_2 = \frac{k_1}{k_2}$. If we trysomesolutionnear the stationary point i.e. $X_1 = \varepsilon + \frac{k_3}{k_2}$and $X_2 = \delta + k_1/\mathrm{k}_2$ .We obtain $\varepsilon(t) = \varepsilon_0 \cos(\omega t + \phi)$, $\delta(t) = \varepsilon_0\sqrt{k_1/k_3}\sin(\omega t + \phi)$, which shows system also has oscillatory solutions.

XVIII. STOCHASTIC SIMULATIONS: THE GILLESPIE ALGORITHM

The above reaction rate problems are solved by Gillespie algorithm. Let $P(\tau, j)$ be the probability [6] that system stays in a configuration $(X_1, X_2, \ldots. X_N)$ between time interval $[t\,, t + \tau]$ and that next reaction occurs in the time interval $[t + \tau, t + \tau + d\tau]$and this reaction is of type j. Let $a_j\, d\tau$ is the probability that the reaction j occurs in the interval $[t + \tau, t + \tau + d\tau]$,while $P_0(\tau)$ is the probability that no reactions occur in$[t, t + \tau]$.Then we can write

$$P(\tau, j) = P_0(\tau)a_j\, d\tau \quad (70)$$

The differential equation for $P_0(\tau)$ can be written as

$$P_0(\tau + d\tau) = P_0(\tau)\left[1 - \sum_{i=1}^{M} a_i\, d\tau\right] \quad (71)$$

Let$a_0 = \sum_{i=1}^{M} a_i$ is the total rate that some of the M reactionsoccur. Then integrating Eq.(71) with an initial condition $P_0(0) = 1$, we get

$$P_0(\tau) = e^{-a_0\tau} \quad (72)$$

Gillespie Algorithm can be summarized as

1) The system is in the state $(X_1, X_2, \ldots. X_N)$ at time t.Evaluate the rates $a_i$for all M chemical reactions.Therefore a_i/a_0 is the probability of one of the M reactions.Let$a_0 = \sum_{i=1}^{M} a_i$ is the total rate that M reactionsoccur.

2) A random τis chosen from the distribution $e^{-a_0\tau}$and thetimeis updated to $t = t + \tau$.

3) Update the particle numbers$(X_1, X_2, \ldots. X_N)$accordingly if the reaction chosen is j.Go to step 1.

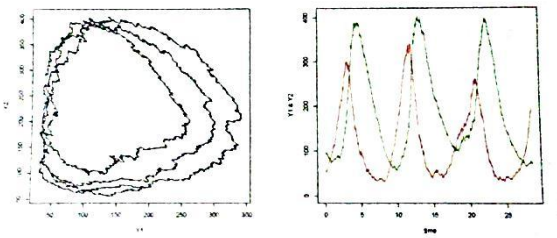

Figure 10: Application of Gillespie algorithm in Simulation of the Lotka-Volterra model.The left figure shows trajectory in the plane Y_1, Y_2. The figure on the right shows plot of $Y_1(t)$and$Y_2(t)$.

XIX. THE ISING AND POTTS MODELS

The Ising model, an important model of classical statistical mechanics,issimple to handle analytically through exact or approximate computations in one and twodimensions.Itis defined on a lattice in ddimensions, whose sites are occupied by a spin taking two values $s = \pm 1$. The energyof a configuration is given by

$$E = -J\sum_{\langle ij\rangle} s_i\, s_j \quad (73)$$

Here the sum is extended to nearestneighborsandJ>0 is the coupling constant of the spins. The model has a phase transition in two and higher dimensions. The transition is from ferromagnetic phase at low temperature to a paramagneticphaseathigh temperature. The transition temperature $T_c$for thetwo dimensional square lattice is

$$T_c = \frac{2J}{In\left(1 + \sqrt{2}\right)} \quad (74)$$

The ferromagnetic phase has a magnetization $m = \langle s_i\rangle \neq 0$ which is the average value of a spin. It is computed exactly for an infinite two dimensional square lattice and is given by

$$m(T) = [1 - \sinh^{-4}(2J/T)]^{\frac{1}{8}} \quad (75)$$

The magnetization shows power-law singularity near T_c

$$m{\sim}(T - T_c)^{\beta} \quad (76)$$

Dimension	α	β	γ	ν	
2	0	1/8	7/4	1	
3	0.12	0.31	1.25	0.64	

Table 1: The critical exponents of Ising model in two and threedimensions evaluated though simulation techniques. The exponents are associated to singularities of specific heat (α), magnetization (β), susceptibility (γ) and correlation length (ν).

The spin-spin correlation function for two spins separated by a distance r in the lattice also follows a power law

$$\langle s_i s_j\rangle{\sim}e^{-r/\xi} \quad (77)$$

The correlation lengthξ, also diverges near $T_c$according as

$$\xi{\sim}|T - T_c|^{-\nu} \quad (78)$$

The model has been simulatedin two dimensions and the exact values of critical exponents are evaluated.However, the value of exponents in three dimensions is known only approximately.

The Potts modelcan be called a generalization of the Ising model as it assumes spins can be found in q states i.e. $s_i = 0, 1, 2 \ldots q-1$.The energy of the q states is given as

$$E = -J \sum_{\langle ij \rangle} \delta_{s_i s_j} \tag{79}$$

HereJ>0 and$\delta_{s_i s_j}$is the Kronecker delta function.Therefore $\delta_{mn} = 1$if m = n and $\delta_{mn} = 0$ otherwise. The q = 2 corresponds to the Ising model because

$$\delta_{mn} = \frac{1}{2}(2m-1)(2m-1) + \frac{1}{4} \tag{80}$$

and this identity is valid for m, n = 0, 1. Potts spins s=0,1 transform to Ising spins $s = \pm 1$ on applying the transformation equation $\hat{s} = 2s - 1$. Therefore we get $E_{Potts}(\{s_i\}) = \frac{1}{2} E_{Ising}(\{\hat{s_i}\}) - \frac{J}{4}$.

Like Ising model, the Potts model shows phase transition from a high temperature phase withrandomlyoriented spins, to an aligned “ferromagnetic" phase. The alignment is along one of the q states.

XX. THE MASTER EQUATION

The stochastic evolution of the system evolving at discrete times Δt is described by (16).

$$p(t + \Delta t) - p(t) = (P_{\Delta t} - I)p(t) \tag{81}$$

Here Iis the identity matrix. Taking limit $\Delta t \to 0$, LHS becomes a time derivative of p(t)

$$\frac{\mathrm{d}}{\mathrm{dt}} p(t) = -Hp(t) \tag{82}$$

$$\text{where } H = \lim_{\Delta t \to 0} \frac{I - P_{\Delta t}}{\Delta t} \tag{83}$$

We have the columnsof P add up to 1 and therefore the elements of the columns of H add up to zero. Also the non-diagonal elements of H are

$$H_{\mu\nu} = -h(\nu \to \mu) \tag{84}$$

Here $h(\nu \to \mu)$ are transition probabilities per unit timefrom the state ν to the state μ i.e. transition probabilities per unit time.

Writing Eq. (82) in terms of matrix elements

$$\frac{d}{dt} p_\mu(t) = -\sum_{\nu \neq \mu} H_{\mu\nu} p_\nu(t) - H_{\mu\mu} p_\mu(t) \tag{85}$$

First term has off diagonal elements whereas the second term has only the diagonal elements of the matrix H. The sum of the elements on each column equals zero.Therefore using Eq. (84) we get what is called as the basic form of the Master Equation

$$\frac{d}{dt} p_\mu(t) = \sum_{\nu \neq \mu} h(\nu \to \mu) p_\nu(t) - h(\mu \to \mu) p_\mu(t) \tag{86}$$

The two terms on the Right hand side of this equation are respectively the“gain" and “loss" terms.

CONCLUSIONS

An algorithm needs to satisfy the conditions of Ergodicityand Detailed Balance. There are many algorithms for which these conditions are satisfied. These are single spin flip algorithms like Metropolis, heat bath . . . or are cluster flip type like Wolff algorithm. However these algorithms are for systems which converge to equilibrium. The simulation of coupled chemical reaction in the Lotka-Volterra model require the application of Gillespie algorithm

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Dr. Dev Raj Mishra won Gold Medal at Graduation for standing First in the University, Did M.Sc. (Physics) from M.D. University, Rohtak (Haryana) and did his Ph.D. in High Temperature Superconductivity from University of Delhi, Delhi. He worked as research fellow during his Ph.D. in Cryogenics Group in National Physical Laboratory and visited for about Eight months in Low Temperature Laboratory at Helsinki University of Technology, Espoo, Finland. Joined as Lecture in Department of Higher Education, Government of Uttarakhand, INDIA in Jan. 2000 and presently posted at Department of Physics, R.H. Govt.P.G. College, Kashipur, US Nagar, Uttarakhand (INDIA) -244713.