

**AN INTRODUCTION TO  
MONTE CARLO SIMULATIONS IN  
STATISTICAL PHYSICS**

by

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# Preface

Science is what we understand well enough to explain to a computer.

Donald E. Knuth

Computing facilities - like work stations and PCs, with high speed and large memory are becoming increasingly and easily available to researchers and students since recent times. This is particularly true in our country; the growth has been rapid and is most likely to become more rapid in the coming years. As a result, computer simulation methods are gaining in importance and popularity as viable and useful tools for research and education.

Monte Carlo is an early and an important computer simulation technique. Named after the city (in the province of Monaco, south of France) famous for its (gambling) casinos, the Monte Carlo method makes extensive use of random numbers. It is employed for simulation of a large variety of phenomena in very many different disciplines. However, in this monograph, I shall confine myself to elucidating the technique for simulation of statistical physics systems.

We begin with a quick look at what do we mean by ensembles in general and Gibbs ensemble in particular. We discuss briefly microcanonical ensemble that models isolated system, canonical ensemble that describes closed system and grand canonical ensemble, useful in the study of open system. In the following few sections I present briefly the basic ingredients of the method of Monte Carlo. These include discussions on random numbers, generation and testing of a sequence of pseudo random numbers, random sampling from different distributions, importance sampling and statistical error bars from uncorrelated and correlated data. I have tried to keep the presentation as simple as possible.

These preliminary discussions are followed by a reasonably detailed description of the Monte Carlo methods for simulating a canonical ensemble of microstates of a classical statistical mechanics system. The topics covered are: Markov chains, Metropolis algorithm, Ising model, continuous phase transition, critical exponents, finite size scaling, n-fold way, critical slowing down, cluster algorithms, cluster counting, percolation, histogram techniques, supercritical slowing down, multicanonical /entropic sampling, Wang-Landau algorithm and Jarzynski's equality relating nonequilibrium work done to equilibrium free energies. I have tried to present these topics the way I have seen them, the way I have learnt them and the way I am teaching them.

My first word of thanks goes to Prof. A. K. Bhatnagar, the Central University of Hyderabad and presently the vice chancellor of the Pondichery University. Prof. Bhatnagar met me during a conference in Kurukshetra and spoke of his plans to start

a post-graduate course on computations in the school of physics at the Hyderabad University. He asked of me if I would be willing to handle the portions on Monte Carlo and Molecular dynamics. I readily agreed. On his invitation I went to Hyderabad during November and December 1998 and gave lectures on Monte Carlo and Molecular dynamics to the first batch of students of the M. Tech. Computational physics programme. On my request Prof. V. S. S. Sastri, Prof. K. Venu, Prof. Bansal and Prof. Srivatsav attended all the lectures and gave me valuable criticisms and suggestions. I take this opportunity to say thanks to them and the students of the course. Prof. Bhatnagar invited me again during January-February 2000 for giving the same course to the second batch of students. While writing this monograph I have drawn heavily from the notes I prepared for the Hyderabad courses. I thank Prof. Bhatnagar for giving me this wonderful opportunity to teach and to learn. I requested Prof. Bhatnagar to give a foreword to this monograph and he readily agreed.

Subsequently I got opportunities to speak on Monte Carlo theory and practice in several places some of which are listed below.

Guru Ghasidas University, Bilaspur (tutorial lecture at the Solid State Physics Symposium: 26-30, December 2000),

Madurai Kamaraj University, Madurai (Seminar on Computer Simulations in Physics, 4-5, February 2002),

Calicut University, Calicut (Refresher course for the college teachers, 25-30 November 2002),

Bharathidasan University, Tiruchirappalli (UGC refresher course in Physics, 10-30 December 2002),

Annamalai University, Annamalai Nagar (UGC sponsored refresher course, 19 December 2002 - 8 January 2003),

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I owe a special word of thanks to my friend Dr. A. Natarajan (Kalpakkam); Dr. Natarajan is a man with very big heart and is genuinely concerned with lives and

careers of his colleagues and juniors; he always finds time to actively involve himself with new ventures of his colleagues and encourage them in their work. Dr. Natarajan read through the entire manuscript carefully and critically; he marked several corrections in the manuscript and suggested revisions in several places to improve the readability. I am extremely thankful to Dr. A. Natarajan.

I have intended this monograph only as an introduction to this vast and rapidly growing field. The aim is to help you obtain a feel for the method and an appreciation for the nuances in the different techniques including the recent ones. I have tried to be simple in the presentation, up-to-date in the coverage of several and important topics, and exhaustive in the bibliography. I hope these notes shall become a useful addition to the bookshelves of researchers and students.

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9 November 2003

K. P. N.



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# 1 Prologue

A macroscopic system consists of a very large number of microscopic constituents. A gas in a container is a simple example. The microscopic constituents are the molecules of the gas. The number of molecules  $N$  is typically of the order of  $10^{23}$ . Each molecule requires three position and three momentum coordinates for complete specification in classical mechanics. The entire macroscopic system at any given instant of time can thus be specified by a string of  $6N$  numbers, which defines, in a sense, a microstate. In a  $6N$  dimensional phase space, the system is represented by a point; or more precisely, by a phase space element of volume  $h^{3N}$  (owing its origin to our *quantum mechanical* inability to specify precisely the position and its conjugate momentum simultaneously). Here,  $h$  is the Planck's constant.<sup>1</sup> It is clear that the number of microstates associated with the system is extremely large. The (equilibrium) system is switching from one microstate to the other all the time. In a classical picture, the point representing the system traces a trajectory in the  $6N$  dimensional phase space as time proceeds. Keeping track of  $6N$  numbers as a function of time is neither feasible nor practical. A statistical approach would be helpful.

Any experimentally measured equilibrium macroscopic property is a time averaged quantity : averaged over the phase space trajectory traced by the macroscopic system during the observation time. Let us assume that during the experimental observation time, the system visits all the (typical?) microstates, consistent with the constraints on volume, number of particles, energy *etc.* This is called ergodicity assumption. This assumption is fine since the observation time scale is very large compared to the time scale over which the system switches from one microstate to the other. We can then equate the 'experimental' time average to an average over a suitable static Gibbs ensemble of microstates. For such a scheme to be successful we must, at the outset, recognize that a macroscopic property is basically statistical in nature. For example, pressure is the average momentum transferred by the molecules colliding with the walls of the container; entropy is the logarithm of the number of microstates accessible to the system; temperature is average energy; specific heat is a manifestation of energy fluctuations; *etc.*

When in equilibrium, the macroscopic properties of a system do not change with time; hence a macroscopic property can be defined as a time average over an underlying (stationary) stochastic process or equivalently an average over a suitably defined Gibbs ensemble; the associated fluctuations are inversely proportional to the square root of the system size and hence are usually negligibly small. This is directly a consequence of the Central Limit Theorem: *the distribution of the sum of  $N$  independent and finite variance random variables converges to a Gaussian in the limit  $N \rightarrow \infty$ , and has a variance proportional to  $N$*  [1].<sup>2</sup> Thus the standard deviation of the arithmetic mean of these  $N$  random variables is inversely proportional to  $\sqrt{N}$ . Physically this implies that the fluctuations of a macroscopic property from its average is extremely small and inversely proportional to the size (number of microscopic constituents) of the system.

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<sup>1</sup>The Planck's constant  $h = 6.626 \times 10^{-34}$  Joules.second or  $4.136 \times 10^{-15}$  electron volts.second.

<sup>2</sup>For an account of the rate of convergence of the sum to a Gaussian random variable see [2]. For an elegant demonstration of the Central Limit Theorem employing renormalization and scaling ideas, see [3].

Clearly it is the largeness of the number of microscopic constituents that gives rise to a certain robustness to the macroscopic behaviour of the system.

## 1.1 What is an ensemble? What is a Gibbs ensemble?

To understand the notion of an ensemble consider an experiment which has more than one outcome. Let us collect all the possible outcomes of the experiment in a set called the sample space  $\Omega = \{\omega_i : i = 1, 2, \dots, \hat{\Omega}\}$ , where  $\omega_i$  denotes an outcome and  $\hat{\Omega}$  the number of outcomes of the experiment. Let  $P(\omega_i) \geq 0$  be the probability of the outcome  $\omega_i$ . We have  $\sum_{i=1}^{\hat{\Omega}} P(\omega_i) = 1$ . Thus the sample space  $\Omega$  and the probability  $P$  define the experiment. Physicists however use a single notion of an ensemble, introduced by Maxwell and denoted by  $\Omega_E$ . The members of the ensemble are drawn from the sample space  $\Omega$ . However an outcome  $\omega_i$  appears in the ensemble  $n(\omega_i)$  times so that  $n(\omega_i)/\hat{\Omega}_E \equiv P(\omega_i)$ , where  $\hat{\Omega}_E$  is the size of the ensemble;  $\hat{\Omega}_E$  is taken adequately large so that all outcomes of the experiment appear in the ensemble in correct proportions. We do not specify any rule for the construction of an ensemble; we can employ Monte Carlo (subject of this monograph) or Molecular Dynamics or for that matter any other technique to construct an ensemble.

A Gibbs ensemble contains microstates of an equilibrium macroscopic system under the macroscopic constraints operating on the system. Depending on the nature of the constraints we have different Gibbs ensembles.

### 1.1.1 Isolated system: Microcanonical ensemble

Consider an isolated macroscopic equilibrium system. The constraints are on : Energy (E), Volume (V) and Number of particles (N). Collect all possible microstates of the system into a set  $\Omega_{IS}$ , called the sample space. All microstates of an isolated system are equally probable.<sup>3</sup> Also, because of the constraints, all the microstates are of the same energy and volume and have the same number of particles. Let  $O(\mathcal{C})$  be a macroscopic property of the system when in its microstate  $\mathcal{C}$ . Formally the average of  $O$  is given by

$$\langle O \rangle = \frac{1}{\hat{\Omega}_{IS}} \sum_{\mathcal{C} \in \Omega_{IS}} O(\mathcal{C}) \quad (1)$$

where  $\hat{\Omega}_{IS}$  is the total number of microstates of the system. In fact the entropy of the system is given by  $S = k_B \ln \hat{\Omega}_{IS}$ , where  $k_B$  is the Boltzmann constant.<sup>4</sup> Thus the probability  $P(\mathcal{C})$  for an isolated system to be in a microstate  $\mathcal{C}$  is  $1/\hat{\Omega}_{IS}$  or  $\exp(-S/k_B)$ , and is the same for all the microstates.

Equivalently, we can construct a microcanonical ensemble  $\Omega_{\mu CE}$  of microstates; a microstate  $\mathcal{C} \in \Omega_{IS}$  occurs in  $\Omega_{\mu CE}$  as often as to reflect its probability  $P(\mathcal{C})$ . In other words, the number of times the microstate  $\mathcal{C}$  occurs in the microcanonical ensemble  $\Omega_{\mu CE}$  divided by the size of the ensemble (denoted by  $\hat{\Omega}_{\mu CE}$ ) equals  $P(\mathcal{C})$ . For an isolated system all microstates belonging to  $\Omega_{IS}$  occur in equal proportions in  $\Omega_{\mu CE}$ .

<sup>3</sup>This is an axiom; the entire edifice of statistical mechanics is built on this axiom.

<sup>4</sup>The Boltzmann constant  $k_B$  equals  $1.381 \times 10^{-23}$  Joules per degree Kelvin or  $8.671 \times 10^{-5}$  electron volts per degree Kelvin.

### 1.1.2 Closed system: Canonical ensemble

Consider now an equilibrium macroscopic system in thermal contact with a heat bath at temperature say  $T$ . Only the volume ( $V$ ) and the number of particles ( $N$ ) are fixed. The energy is not fixed. Instead the temperature of the system equals that of the heat bath when in equilibrium. This is a closed system: the system exchanges energy with the heat bath but not particles. Let  $\Omega_{\text{CS}}$  denote the set of all possible microstates of the closed system at temperature  $T$ .  $\Omega_{\text{CS}}$  is called the sample space of the closed system; since the system can exchange energy with the heat bath, different microstates belonging to  $\Omega_{\text{CS}}$  can have different energies.<sup>5</sup> Also the probability with which a closed system can be found in its microstate  $\mathcal{C}$  is proportional to  $\exp[-\beta E(\mathcal{C})]$  where  $\beta = 1/(k_{\text{B}}T)$ . The probability of occurrence of a microstate  $\mathcal{C}$  in a closed system depends on the energy of the microstate and the temperature of the system. Thus to each  $\mathcal{C} \in \Omega_{\text{CS}}$  we attach a Boltzmann weight  $\exp[-\beta E(\mathcal{C})]$ . The sum of the Boltzmann weights taken over all the microstates belonging to  $\Omega_{\text{CS}}$  is called the canonical partition function  $Z(\beta)$ , given by,

$$Z(\beta, V, N) = \sum_{\mathcal{C} \in \Omega_{\text{CS}}} \exp[-\beta E(\mathcal{C})]. \quad (2)$$

Let  $O(\mathcal{C})$  be a macroscopic property of the closed system when in its microstate  $\mathcal{C}$ . The average of  $O$  is formally given by,

$$\langle O(\beta) \rangle = \frac{1}{Z(\beta, V, N)} \sum_{\mathcal{C} \in \Omega_{\text{CS}}} O(\mathcal{C}) \exp[-\beta E(\mathcal{C})] \quad (3)$$

To calculate  $\langle O(\beta) \rangle$ , we can take an alternate approach. Let  $\Omega_{\text{CE}}$  denote a canonical ensemble of microstates belonging to the closed system. A microstate  $\mathcal{C} \in \Omega_{\text{CS}}$  occurs in the ensemble  $\Omega_{\text{CE}}$  as often as to reflect its probability  $P(\mathcal{C}) = \exp[-\beta E(\mathcal{C})]/Z(\beta, V, N)$ . Thus the number of times a microstate  $\mathcal{C} \in \Omega_{\text{CS}}$  occurs in the canonical ensemble  $\Omega_{\text{CE}}$  divided by the size,  $\hat{\Omega}_{\text{CE}}$  of the ensemble is given by  $P(\mathcal{C})$ . The advantage of constructing a canonical ensemble is that a macroscopic property can be calculated as a simple arithmetic mean,

$$\langle O(\beta) \rangle = \frac{1}{\hat{\Omega}_{\text{CE}}} \sum_{\mathcal{C} \in \Omega_{\text{CE}}} O(\mathcal{C}). \quad (4)$$

The size  $\hat{\Omega}_{\text{CE}}$  of the canonical ensemble is usually taken to be large so that even those microstates with very low probability are present in the ensemble in right proportions. We shall follow the convention of denoting an element of a sample space by script letters, *e.g.*  $\mathcal{C}$  and that of an ensemble by capital letters *e.g.*  $C$ .

### 1.1.3 Open system: Grand canonical ensemble

We can proceed further and consider an open system in which there is an exchange of energy as well as particles with the surrounding bath. The constraints are on the

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<sup>5</sup>There can be many microstates having the same energy  $E$ . Logarithm of this number multiplied by  $k_{\text{B}}$  shall be called suggestively as microcanonical entropy  $S(E)$ . We shall find this terminology useful when we consider entropic/multicanonical sampling in sections (23) and (24).

temperature ( $T$ ), volume ( $V$ ) and chemical potential ( $\mu$ ). Let  $\Omega_{\text{OS}}$  denote the sample space. The open system can be found in a microstate  $\mathcal{C}$  with a probability proportional to the Gibbs factor given by  $\exp[-\beta E(\mathcal{C}) + \mu\beta N(\mathcal{C})]$ , where  $N(\mathcal{C})$  is the number of particles in the open system when it is in its microstate  $\mathcal{C}$ . Thus to each microstate  $\mathcal{C}$  we attach a Gibbs weight  $\exp[-\beta E(\mathcal{C}) + \mu\beta N(\mathcal{C})]$ . The sum of the Gibbs weights taken over all the microstates of the open system is called the grand canonical partition function,

$$\mathcal{Q}(\beta, V, \mu) = \sum_{\mathcal{C} \in \Omega_{\text{OS}}} \exp[-\beta E(\mathcal{C}) + \mu\beta N(\mathcal{C})] . \quad (5)$$

The average of a macroscopic property  $O$  is formally given by,

$$\langle O(\beta, V, \mu) \rangle = \frac{1}{\mathcal{Q}} \sum_{\mathcal{C} \in \Omega_{\text{OS}}} O(\mathcal{C}) \exp[-\beta E(\mathcal{C}) + \mu\beta N(\mathcal{C})] . \quad (6)$$

We can calculate the average by constructing a grand canonical ensemble  $\Omega_{\text{GCE}}$  of microstates; the number of times a microstate  $\mathcal{C}$ , belonging to  $\Omega_{\text{OS}}$  occurs in  $\Omega_{\text{GCE}}$  divided by the size of  $\Omega_{\text{GCE}}$  (denoted by  $\hat{\Omega}_{\text{GCE}}$ ) is given by  $\exp[-\beta E(\mathcal{C}) + \mu\beta N(\mathcal{C})]/\mathcal{Q}$ . Thus  $\langle O \rangle$  is given by a simple arithmetic average,

$$\langle O(\beta, V, \mu) \rangle = \frac{1}{\hat{\Omega}_{\text{GCE}}} \sum_{\mathcal{C} \in \Omega_{\text{GCE}}} O(\mathcal{C}) \quad (7)$$

Besides the microcanonical, canonical and grand canonical ensembles, we can construct other physical ensembles like isobaric-isothermal ensembles *etc.*, depending on the problem under considerations. The choice of the ensemble is purely a matter of convenience dictated by the nature of the physical system under investigation and the nature of the macroscopic properties we want to calculate. Indeed we shall see later that even construction of unphysical ensembles like multicanonical ensemble proves to have certain distinct advantages.

However, in these notes I shall concentrate on the calculation of a macroscopic property as an average over a canonical ensemble of microstates generated by the technique of Monte Carlo.

## 2 What is a Monte Carlo method?

Monte Carlo is a numerical technique that makes use of random numbers to solve a problem. Historically, the first large scale Monte Carlo work carried out dates back to the middle of the twentieth century. This work pertained to studies of neutron multiplication, scattering, propagation and eventual absorption in a medium or leakage from it. Stanislaw Ulam, John von Neumann and Enrico Fermi were the first to propose and employ the Monte Carlo method as a viable numerical technique for solving practical problems. The earliest published work on Monte Carlo is perhaps the paper of Metropolis and Ulam [4] in the year 1949. <sup>6</sup>

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<sup>6</sup>There were of course several isolated and perhaps not fully developed instances earlier, when Monte Carlo has been used in some form or the other. An example is the experiment performed in

Thus, for carrying out a Monte Carlo simulation, we require a sequence of numbers which are random, independent, real and uniformly distributed in the range zero to one. Strictly, we can call a sequence of numbers random, if and only if it is generated by a random physical process like radioactive decay, thermal noise in electronic devices, cosmic ray arrival times, tossing of a coin *etc.* These phenomena are known to be truly random at least according to the present day theories. Generate once and for all, a fairly long sequence of random numbers from a random physical process. Employ this sequence in your Monte Carlo calculations. This is always a safe procedure. Indeed, tables of random numbers were generated and employed in early Monte Carlo practice. Census reports [7], telephone directories [11], spinning wheel [11, 12], automatic electronic roulette [13], radioactive decay [14], thermal noise in a semi-conductor device<sup>7</sup> *etc.*, were employed to generate large tables of random digits.

A table of random numbers is useful if the Monte Carlo calculation is carried out manually. However, for computer calculations, use of these tables is impractical. A computer, having a relatively small internal memory, cannot hold a large table of random numbers. One can keep the random numbers in an external storage device like a disk or a tape; but then, constant retrieval from these peripherals would considerably slow down the computations. Hence it is often desirable to generate a random number as and when required, employing simple arithmetic operations that do not take much computer time and the algorithm itself does not require much memory for storage. These numbers, generated by deterministic algorithms, are therefore predictable and reproducible. Hence by no stretch of imagination can they be called random. We shall call them pseudo random. We shall be content with pseudo random numbers if we find they go through tests of randomness satisfactorily. In fact, it is always a good practice to check if the sequence of random numbers you are going to use in your simulation, goes through several standard tests for randomness. It is also desirable to devise special tests of randomness, depending on the particular application you have in mind. I shall come to tests for randomness a bit later.

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the middle of the nineteenth century, consisting of throwing a needle randomly on a board notched with parallel lines and inferring the numerical value of  $\pi$  from the number times the needle intersects a line; this is known as Buffon's needle problem, an early description of which can be found in [5]. The Quincunx constructed by Galton [6] in the second half of the nineteenth century, consisted of balls rolling down an array of pins and getting collected in the vertical compartments placed at the bottom. A pin deflects the rolling ball randomly and with equal probability to its left or right. The heights of the balls in the compartments approximate a binomial distribution. Perhaps this is an early technique of physically sampling random numbers from a binomial distribution. In nineteen twenties, Karl Pearson perceived the use of random numbers for solving complex problems in probability theory and statistics that were not amenable to exact analytical solutions. Pearson encouraged L. H. C. Tippett to produce a table of random numbers to help in such studies, and a book of random sampling numbers [7] was published in the year 1927.

In India, P. C. Mahalanbois [8] exploited ' random sampling ' technique to solve a variety problems like the choice of optimum sampling plans in survey work, choice of optimum size and shape of plots in experimental work *etc.*, see [9].

Indeed, descriptions of several modern Monte Carlo techniques appear in a paper by Kelvin [10], written nearly more than hundred years ago, in the context of a discussion on the Boltzmann equation. But Kelvin was more interested in the results than in the technique, which to him was *obvious!*

<sup>7</sup>M. Richter: millions of physical random numbers were generated by measuring thermal noise of a semiconductor device; these are available upon an anonymous ftp call to site at [dfv.rwth-aachen.de](http://dfv.rwth-aachen.de)

## 3 How do we generate a sequence of pseudo random numbers?

### 3.1 Congruential Generators

In a linear congruential generator, for example, we start with an integer  $R_1$  and generate successive integers by the recursion,

$$R_{i+1} = a \times R_i + b \pmod{m}, \quad (8)$$

where  $a$ ,  $b$  and  $m$  are integers.  $a$  is called the generator or multiplier,  $b$  the increment and  $m$  the modulus. If the increment  $b$  is zero, we call the generator multiplicative congruential and if  $b > 0$ , it is called the mixed congruential. The above equation means the following. Start with an integer  $R_1$ , between zero and  $m - 1$ . This is your choice. Calculate  $a \times R_1 + b$ . Divide the result by  $m$  and find the remainder. Call it  $R_2$ . Calculate  $a \times R_2 + b$ ; divide the result by  $m$ ; find the remainder and call it  $R_3$ . Proceed in the same fashion and generate a sequence of integers  $\{R_1, R_2, \dots\}$ , initiated by the seed  $R_1$ . Thus  $\{0 \leq R_i \leq m - 1 : i = 1, 2, \dots\}$  is a sequence of pseudo random integers. This sequence can be converted to floating point numbers by dividing each by  $m$ .

A congruential generator is robust, simple and fast; the theory is reasonably well understood. It gives a fairly long sequence of ‘good’ pseudo random numbers. The values of  $a$ ,  $b$  and  $m$  must be chosen carefully. Clearly, whatever be the choice of  $a$ ,  $b$  and  $m$ , the sequence shall repeat itself after utmost  $m$  steps. The sequence is therefore periodic. Hence in applications, we must ensure that the number of random numbers required for any single simulation must be much less than the period. Usually  $m$  is taken to be very large to permit this. We can always get a sequence with full period, if  $m$ ,  $b$  and  $a$  are properly chosen.<sup>8</sup> The modulus  $m$  is usually taken as  $2^{t-1} - 1$ , where  $t$  is the number of bits used to store an integer and hence is machine specific. One of the  $t$  bits is used up for storing the sign of the integer. The choice  $a = 7^5 = 16807$ ,  $b = 0$  and  $m = 2^{31} - 1$ , for a 32 bit machine has been shown to yield good results [15]. The period of this generator is  $2^{31} - 1 = 2.15 \times 10^9$ , which is really not long for several applications. Another popular choice of parameters [16] consists of  $a = 69069$ ,  $b = 1$ , and  $m = 2^{32}$ , which also has a short period of  $4.29 \times 10^9$ . The choice of  $a = 13^{13}$ ,  $b = 0$  and  $m = 2^{59}$  in the generator G05FAF of the NAG library [17] has a much longer period of nearly  $5.76 \times 10^{17}$ . The congruential generators have been successful and invariably most of the present day pseudo random number generators are of this class.

### 3.2 Marsaglia lattice structure

Let  $\xi_1, \xi_2, \xi_3, \dots$  denote a sequence of random numbers from a linear congruential generator. Form from these numbers, a sequence of  $d$ -tuples:  $v_1 = (\xi_1, \xi_2, \dots, \xi_d)$ ,  $v_2 = (\xi_2, \xi_3, \dots, \xi_{d+1})$ ,  $v_3 = (\xi_3, \xi_4, \dots, \xi_{d+2}) \dots$ . View the  $d$ -tuples  $\{v_1, v_2, v_3, \dots\}$  as points in the unit hyper cube of  $d$  dimensions. You would expect these points to

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<sup>8</sup>We must ensure that (i)  $m$  and  $b$  are relatively prime to each other; *i.e.*  $\gcd(m, b) = 1$ ; (ii)  $a \equiv 1 \pmod{p}$  for every prime factor  $p$  of  $m$ ; and (iii)  $a \equiv 1 \pmod{4}$ , if  $m \equiv 0 \pmod{4}$ .



be more or less uniformly distributed in the hyper cube. But invariably you will find that these points are confined to a relatively smaller number of parallel planes, called the Marsaglia lattice structure named after its discoverer [18]. The points on several of the Marsaglia planes form regular patterns. Such a hidden Marsaglia order is an inherent feature of all linear congruential generators. The randomness is truly *pseudo* indeed! Hence you must check very carefully if the inevitable presence of Marsaglia defect in the pseudo random number sequence affects significantly the results of your Monte Carlo application. Hopefully it doesn't. But then one never knows. Somehow the Monte Carlo community has learnt to live with the Marsaglia defect over the last three decades!

You can increase the number of Marsaglia planes by a second order recursion,

$$R_{i+2} = a \times R_{i+1} + b \times R_i \pmod{m}, \quad (9)$$

and choosing properly the recursion parameters  $a$  and  $b$ . Note that the above recursion requires two seeds.

### 3.3 Shift register generators

An alternative that does not suffer from the correlations invariably present in the congruential generators is based on the generalized feedback shift register algorithms [19]. These are also called the Tausworthe generators [20]. Let  $R_1, R_2 \dots$  denote a sequence of random binary integers. We define a recursion as follows,

$$R_i = R_{i-p} + R_{i-1} \pmod{2} \quad q < p < i. \quad (10)$$

It is easily seen that the above addition of binary digits is the same as the exclusive-OR operation ( .XOR. ), which can be carried out in a computer rather fast:

$$R_i = R_{i-p} \text{ .XOR. } R_{i-q}. \quad (11)$$

For proper choice of values of  $p$  and  $q$  one can get a maximal period of  $2^p - 1$ . A standard choice proposed by Kirkpatrick and Stoll [21] consists of  $p = 250$  and  $q = 103$ . This is called the R250 generator; it has a long period of  $2^{250} - 1 \approx 1.81 \times 10^{75}$ . We need to provide 250 seeds for which we can employ another random number generator *e.g.* the linear congruential generator with  $a = 16807$ ,  $b = 1$  and  $m = 2^{31} - 1$  as recommended by Kirkpatrick and Stoll [21]. We shall see more about the R250 generator later on in section 4.3.

There are also several other alternatives that have been proposed. These include for example the inversive [22] and explicit inversive [23] generators which employ nonlinear recursions. I do not want to go into the details of random number generation and instead refer you to [24] for some additional literature on this important topic.

## 4 How do we know that a given sequence of numbers is random?

This is not an easy question to answer, especially when we know that the sequence has been generated by a deterministic algorithm and hence is predictable and reproducible. We take a practical attitude and say that it suffices if we establish that the

pseudo random number sequence is indistinguishable statistically from a sequence of real random numbers. This brings us to tests for randomness.

A randomness test, in a general sense, consists of constructing a function  $\psi(r_1, r_2, \dots)$ , where  $r_1, r_2, \dots$ , are independent variables. Calculate the value of this function for a sequence of pseudo random numbers by setting  $r_i = \xi_i \forall i = 1, 2, \dots$ . Compare this value with the value that  $\psi$  is expected to have if  $\{r_i : i = 1, 2, \dots\}$  were truly random and distributed independently and uniformly in the range zero to unity.

#### 4.1 Test based on calculation of the mean

For example, the simplest test one can think of, is to set

$$\psi(r_1, r_2, \dots) = \frac{1}{N} \sum_{i=1}^N r_i, \quad (12)$$

which defines the average of  $N$  numbers. For a sequence of  $N$  truly random numbers, we expect  $\psi$  to lie between  $.5 - \epsilon$  &  $.5 + \epsilon$  with a certain probability  $p(\epsilon)$ . Notice that for  $N$  large, from the Central Limit Theorem,  $\psi$  is Gaussian with mean 0.5 and variance  $\sigma_\psi^2 = \sigma_r^2/N$ , where  $\sigma_r^2 = 1/12$  is the variance of the random variable  $r$ , uniformly distributed in the interval  $(0, 1)$ . If we take  $\epsilon = 2\sigma_\psi = 1/\sqrt{3N}$ , then  $p(\epsilon)$  is the area under the Gaussian between  $.5 - \epsilon$  and  $.5 + \epsilon$  and is equal to 0.9545.  $\epsilon$  is called two-sigma confidence interval. I shall discuss in details the issue of confidence interval / statistical error very soon. Thus for a sequence of  $N$  truly random numbers, we expect its mean to be within  $\pm\epsilon$  around 0.5 with .95 probability, for large  $N$ . If a sequence of  $N$  pseudo random numbers has an average that falls outside the interval  $(0.5 - \epsilon, 0.5 + \epsilon)$  then we say that it fails the test at 5% level.

#### 4.2 Run test

In practice, one employs more sophisticated tests, by making  $\psi$  a complicated function of its arguments. An illustrative example is the run test which is sensitive to the correlations. The idea is to calculate the length of a run of increasing (run-up) or decreasing (run-down) size. We say a run-down length is  $l$  if we have a sequence of random numbers such that  $\xi_{l+1} > \xi_l < \xi_{l-1} < \xi_{l-2} < \dots < \xi_2 < \xi_1$ . We can similarly define the run-up length.

Let me illustrate the meaning of run-down length by considering a sequence of integers between 0 and 9, given below.

6	4	1	3	4	5	3	2	7	4	8							
	6	4	1	3		4	5		3	2	7		4	8			
				3				1				2				1	

The first row displays the sequence; the second depicts the same sequence with numbers separated into groups by vertical lines. Each group contains  $n + 1$  numbers, the first  $n$  of which are in descending order. *i.e.* these numbers are running down. The descent is

broken by the  $(n + 1)^{\text{th}}$  number which is greater than the  $n^{\text{th}}$  number. The third row gives the run-down length, for each group, which is  $n$ .

We can calculate the probability distribution of the run-down length as follows. Let  $P(L \geq l)$  be the probability that the run-down length  $L$  is greater than or equal to  $l$ . To calculate  $P(L \geq l)$  we consider a sequence of  $l$  distinct random numbers. There are  $l!$  ways of arranging these numbers. For a sequence of truly random numbers, each of these arrangements is equally likely. Of these, there is only one arrangement which has all the  $l$  numbers in the descending order. Hence  $P(L \geq l) = 1/l!$ . Since  $P(L = l) = P(L \geq l) - P(L \geq l + 1)$ , we get

$$P(l) = \frac{1}{l!} - \frac{1}{(l+1)!} \quad . \quad (13)$$

Alternately, for the probability of run-down length we have,

$$\begin{aligned} P(L \geq l) &= \int_0^1 d\xi_1 \int_0^{\xi_1} d\xi_2 \cdots \int_0^{\xi_{l-1}} d\xi_l \\ &= \int_0^1 \frac{\xi_1^{l-1}}{(l-1)!} d\xi_1 \\ &= \frac{1}{l!} \end{aligned} \quad (14)$$

In the test, we determine numerically, the distribution of the run length on the sequence of pseudo random numbers and compare it with the exact distribution given by Eq. (13). Figure (1) depicts the results of a run-down test.

### 4.3 The rise and fall of R250

Generation and testing of random numbers is a specialized area of research. Several important pieces of work have been carried out in these areas. The field remains active even today. The reason for this is simple: There exists a large number of questions that remain unanswered. In fact, even the very basic issue of what is meant by randomness of a sequence of numbers, is not clearly understood. I shall not discuss these and related issues here and instead, refer you to [25] for some interesting literature on this intriguing subject. For some literature on testing of randomness of a pseudo random number sequence see [26]. The use of pseudo random numbers in a Monte Carlo simulation is perhaps all right for most of the application; in any case we have no other choice; it is always prudent to be watchful; the subtle correlations and patterns present in a sequence of pseudo random numbers may have non trivial effects on the results of your simulation.

The (hi)story of the rise and fall of R250 generator should warn us of how delicate the issue of pseudo random number generation is. I have already talked about the generalized feedback shift register algorithm in section 3.3. R250 is an early implementation of the shift register algorithm [21]. It was introduced in the early nineteen eighties and became an instant hit amongst the Monte Carlo practitioners. Troubles started in the early nineteen nineties. In the year 1992 Ferrenberg, Landau and Wong [27] reported severe problems with the generator in the Monte Carlo simulation of a two

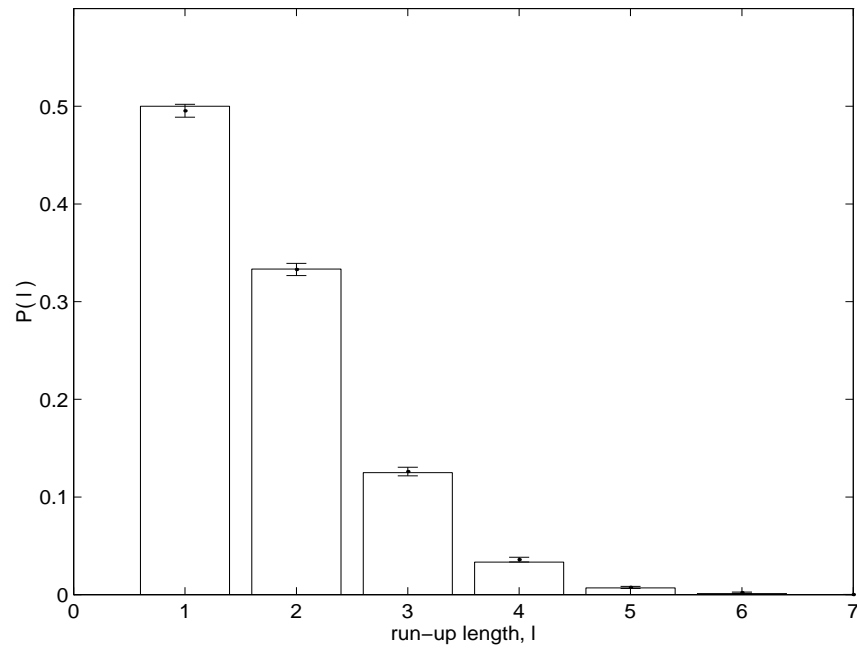


Figure 1: Results of a run-down test. The histogram plot corresponds to what is expected from a sequence of truly random numbers. See Eq. (13). The points with error bars correspond to the ones obtained with random number generator routine RAND of MATLAB version 4.1. The run-down lengths were generated from a sequence of 10,000 numbers. The statistical errors in the calculated values correspond to one-sigma confidence interval.

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dimensional Ising model employing Wolff cluster algorithm.<sup>9</sup> The calculated values of energy and specific heat were erroneous; however, the same algorithm gave correct results when other random number generators were employed. These startling findings were confirmed by Coddington [28] in the year 1994. The culprit was eventually traced to the triplet correlations in R250 in particular [29] and in the shift register algorithms for certain specific choices of the parameters, in general [30]. See also [31] for more literature on how the correlations present in the random numbers would affect the results of the simulations. Perhaps one is tempted to agree with Compagner [32] when, tongue in cheek, he says that “random sequences are easy to generate in a computer except when needed for reliable Monte Carlo simulations” ! But as I said earlier, we have no other choice; we have to depend on deterministic algorithms for generating random numbers. The lesson from the above story of the R250 generator is that do not use your ‘pet’ recursions or algorithms for generating random numbers for your applications. Follow the advise of Janke [33]: Use only well known generators which have been tested and which are being employed by a large number of Monte Carlo practitioners. If such a generator poses problems in your specific application, then you can at least be assured that the Monte Carlo community would work hard to track down the problem and perhaps resolve it, like it did in the case of R250 generator.

## 5 How do we sample from a given distribution?

### 5.1 Analytical inversion and sampling from exponential

Let  $\{\xi_i : i = 1, 2, \dots\}$  denotes the sequence of pseudo random numbers. These are independent, real and uniformly distributed in the range  $(0, 1)$ . From  $\{\xi_i\}$ , we can construct a sequence of independent random numbers,  $\{x_i\}$  having the desired distribution, say  $f(x)$ . Let  $F(x)$  denote the cumulative distribution defined as,

$$F(x) = \int_{-\infty}^x f(x') dx' . \quad (15)$$

Then  $\{x_i = F^{-1}(\xi_i) : i = 1, 2, \dots\}$  constitute an ensemble of real numbers, whose distribution is the desired  $f(x)$ . For example,

$$\{x_i = -\lambda \ln(1 - \xi_i) : i = 1, 2, \dots\}$$

are independent random numbers distributed as per the exponential distribution,

$$f(x) = \begin{cases} \lambda^{-1} \exp(-x/\lambda) & \text{for } x \geq 0 , \\ 0 & \text{for } x < 0 . \end{cases} \quad (16)$$

### 5.2 Fernández-Rivero technique for sampling from exponential

To sample from an exponential distribution, Fernández and Rivero [34] proposed a simple algorithm inspired by statistical physics. Start with  $N$  particles indexed by

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<sup>9</sup>We shall discuss the Ising model and the Wolff cluster algorithm sometime later; see sections 8 and 21.1

integers  $i = 1, 2, \dots, N$ . Initialize  $x(k) = \lambda \forall k$ . The particles ‘interact’ in the following fashion. Select independently and randomly two particles, say  $i$  and  $j$  with  $i \neq j$ . Let  $S = x(i) + x(j)$ ; split  $S$  randomly into two parts, assign them to the particles  $i$  and  $j$  and return. Repeat the above several times until the system *equilibrates*. Some  $4N$  iterations are recommended for *equilibration*, see [34]. After the system has *equilibrated*, every time you select two particles, say  $l$  and  $k$  and  $l \neq k$ , for interaction, you have  $x(k)$  and  $x(l)$  as two independent random numbers distributed exponentially. For more details see [34].

## 5.3 Sampling from Gaussian

### 5.3.1 Fernández-Criado technique

In the same spirit as in section (5.2), set  $x^{(0)}(i) = 1 \forall i$  and let the randomly chosen particles  $i$  and  $j$  with  $i \neq j$  interact in the following fashion,

$$\begin{aligned} x^{(k+1)}(i) &= \eta^{(k)} \frac{x^{(k)}(i) + x^{(k)}(j)}{\sqrt{2}}, \\ x^{(k+1)}(j) &= \eta^{(k)} \frac{x^{(k)}(i) - x^{(k)}(j)}{\sqrt{2}}, \end{aligned} \quad (17)$$

where the superscript is the iteration index and  $\{\eta^{(k)} : k = 0, 1, \dots\}$  are identically distributed independent random variables taking values  $\pm 1$  with equal probabilities. The ‘equilibrium’ distribution of  $x$  is Gaussian with mean zero and variance unity, see [35].

### 5.3.2 Box-Müller algorithm

There is another ingenious way of generating Gaussian random numbers called the Box-Müller method [36]. The Gaussian distribution of zero mean and unit variance is given by,

$$f(x) = \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{x^2}{2}\right). \quad (18)$$

The corresponding cumulative distribution is given by

$$\begin{aligned} F(x) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^x dy \exp\left(-\frac{y^2}{2}\right) \\ &= \frac{1}{2} \left[ 1 + \operatorname{erf}\left(\frac{x}{\sqrt{2}}\right) \right] \end{aligned} \quad (19)$$

where  $\operatorname{erf}(\cdot)$  denotes the error function, which is not analytically invertible. Hence we consider a two dimensional distribution obtained as the product of two identical Gaussians of zero mean and unit variance given by,

$$f_2(x, y) = f_1(x)f_1(y) = \frac{1}{2\pi} \exp\left(-\frac{x^2 + y^2}{2}\right) \quad (20)$$

Let us express the above in terms of polar coordinates  $r$  and  $\theta$  with the transformations defined by:  $x = r \cos(\theta)$  and  $y = r \sin(\theta)$ . We get

$$f_2(x, y) dx dy = \exp\left(-\frac{r^2}{2}\right) r dr \frac{d\theta}{2\pi}, \quad (21)$$

which suggests that the angle  $\theta$  is distributed uniformly between 0 and  $2\pi$  and  $r$  can be sampled by analytical inversion since,

$$\begin{aligned} F(r) &= \int_0^r dr_1 r_1 \exp\left(-\frac{r_1^2}{2}\right) \\ &= 1 - \exp\left(-r^2/2\right) \end{aligned} \quad (22)$$

Thus we get the Box-Müller sampling: from two random numbers  $\xi_1$  and  $\xi_2$ , independently and uniformly distributed in the unit interval  $(0, 1)$  we get two independent Gaussian random numbers,

$$\begin{aligned} q_1 &= \sqrt{-2 \ln \xi_1} \cos(2\pi \xi_2) \\ q_2 &= \sqrt{-2 \ln \xi_1} \sin(2\pi \xi_2). \end{aligned} \quad (23)$$

For Gaussian there is an algorithm directly based on the Central Limit Theorem.

### 5.3.3 Algorithm based on the Central Limit Theorem

According to the Central Limit Theorem, the sum of  $N$  independent random variables each with finite variance, tends to a Gaussian in the limit  $N \rightarrow \infty$ . Let  $y$  be the sum of  $N$  random numbers (independently sampled from uniform distribution in the interval 0 to 1). The distribution of  $y$  tends to a Gaussian with mean  $N/2$  and variance  $N/12$  as  $N \rightarrow \infty$ . Define

$$x = \left(y - \frac{N}{2}\right) \sqrt{\frac{12}{N}}. \quad (24)$$

The random variable  $x$  has mean zero and unit variance. The value of  $x$  is confined between  $-\sqrt{3N}$  and  $+\sqrt{3N}$  and hence  $x$  tends to a Gaussian strictly in the limit of  $N \rightarrow \infty$ . But as shown in [37], even a convenient choice of  $N = 12$  gives good Gaussian random numbers with errors not exceeding one percent or so inside a two sigma interval  $(-2, +2)$ .

A very large number of transformations, tricks and algorithms have been discovered for random sampling from non uniform distributions. In fact this activity continues to be a favorite pastime of the Monte Carlo practitioners. Standard texts on Monte Carlo methods [38, 39, 40, 41] contain detailed descriptions of several random sampling techniques.

## 6 How do we evaluate an integral by Monte Carlo method?

For purpose of illustrating the technique of Monte Carlo, let us consider a simple problem of evaluating the following integral,

$$I = \int_a^b \Phi(x) dx. \quad (25)$$

In a finite difference approximation, we divide the range  $(a, b)$  of  $x$  into  $N$  equal intervals. Let  $x_i$  denote the mid-point of the  $i^{\text{th}}$  interval. The integral is approximated by the sum,

$$I_N \approx \frac{b-a}{N} \sum_{i=1}^N \Phi(x_i), \quad (26)$$

$$x_i = a + \left(i - \frac{1}{2}\right) \frac{b-a}{N}. \quad (27)$$

In the above, instead of choosing  $x_i$  at regular intervals, we can choose them randomly and independently from a uniform distribution in the interval  $a$  to  $b$ . In other words, we set,

$$x_i = a + (b-a) \xi_i : i = 1, 2, \dots, N \quad (28)$$

where  $\{\xi_i\}$  are independent random numbers uniformly distributed in the range  $(0, 1)$ , and carry out the sum in Eq. (26). Let  $\bar{I}_N$  denote the Monte Carlo estimate of the integral, obtained from a sample of size  $N$ . It is intuitively clear that as  $N \rightarrow \infty$  the estimate  $\bar{I}_N \rightarrow I$ . How large should  $N$  be so that  $\bar{I}_N$  is a reliable estimate of  $I$ ? Before we answer this question let us consider the evaluation of the mean of a function  $h(x)$  of a random variable  $X$ .

Formally we have,

$$\langle h \rangle_f = \int_{-\infty}^{+\infty} h(x) f(x) dx, \quad (29)$$

where  $f(x)$  is the probability density function of the random variable  $X$ .  $h(x)$  is usually called the score function. How do we estimate  $\langle h \rangle_f$ ? Let us first consider the so called analogue simulation. We sample randomly a sequence of  $\{x_i : i = 1, 2, \dots, N\}$ , from the density  $f(x)$  and write,

$$\bar{h}_N = \frac{1}{N} \sum_{i=1}^N h(x_i). \quad (30)$$

In the limit  $N \rightarrow \infty$ ,  $\bar{h}_N \rightarrow \langle h \rangle_f$ . Also by the Central Limit Theorem, in the limit  $N \rightarrow \infty$ , the probability density of the random variable  $\bar{h}_N$  tends to a Gaussian with mean  $\langle h \rangle_f$  and variance  $\sigma^2/N$ , where

$$\sigma^2 = \int_{-\infty}^{+\infty} [h(x) - \langle h \rangle_f]^2 f(x) dx. \quad (31)$$



Thus we say that analogue Monte Carlo estimate of  $\langle h \rangle_f$  is given by  $\bar{h}_N \pm \sigma/\sqrt{N}$ , where  $\pm\sigma/\sqrt{N}$  defines the one-sigma confidence interval. This means that with a probability  $p$  given by,

$$\begin{aligned} p &= \frac{\sqrt{N}}{\sigma\sqrt{2\pi}} \int_{\langle h \rangle_f - (\sigma/\sqrt{N})}^{\langle h \rangle_f + (\sigma/\sqrt{N})} \exp\left[-\frac{N(x - \langle h \rangle_f)^2}{2\sigma^2}\right] dx \\ &= \frac{1}{\sqrt{2\pi}} \int_{-1}^{+1} \exp\left[-\frac{y^2}{2}\right] dy \\ &= 0.68268 \end{aligned} \tag{32}$$

we expect  $\bar{h}_N$  to lie within  $\pm\sigma/\sqrt{N}$  around  $\langle h \rangle_f$ , if  $N$  is sufficiently large. First we notice that we do not know  $\sigma$ . Hence we approximate it by its Monte Carlo estimate  $S_N$ , given by,

$$S_N^2 = \frac{1}{N} \sum_{i=1}^N h^2(x_i) - \left[ \frac{1}{N} \sum_{i=1}^N h(x_i) \right]^2. \tag{33}$$

The quantity  $\pm S_N/\sqrt{N}$  is called the statistical error. Notice that the sample size  $N$  must be large for the above estimate of the error (and of course of the mean) to be reliable.

Now, returning to the question of the reliability of  $\bar{I}_N$  as an estimate of the integral  $I$  given by Eq. (25), we immediately see that the associated statistical error is  $\pm S_N/\sqrt{N}$ , where  $S_N^2 = J_N - [\bar{I}_N]^2$ , and

$$J_N = \frac{b-a}{N} \sum_{i=1}^N [\Phi(x_i)]^2. \tag{34}$$

The statistical error is independent of the dimensionality of the integral. The error in a deterministic algorithm, on the other hand, is proportional to  $N^{-1/d}$ , where  $d$  is the dimensionality of the integral. Thus, Monte Carlo method becomes numerically advantageous, for  $d \geq 3$ .

It is clear from the above that the statistical error is directly proportional to  $\sigma$  and inversely proportional to  $\sqrt{N}$ . The computer time however is directly proportional to  $N$ . If the problem on hand has inherently large  $\sigma$ , then for calculating averages within desired (small) statistical error bars, we shall need a very large sample of microstates; generating a large sample is often not possible within meaningful computer time. Then analogue simulation is going to be extremely difficult and most often impossible. We need to resort to techniques that reduce the variance without in any way changing the averages of the desired quantities. These are called variance reduction techniques and in what follows I shall describe one of them called importance sampling.

## 7 What is the basic principle of importance sampling?

Importance sampling helps us sample from the important regions of the sample space. Consider the problem described in section 6; see Eq. (29). Let  $f(x)$  be high where

the score  $h(x)$  is low and  $f(x)$  be low where  $h(x)$  is high. Then, high score regions of  $x$  shall get very poorly sampled. A finite sample Monte Carlo estimate of  $\langle h \rangle_f$  would suffer from poor statistics and would often be erroneous. This is a typical situation whence importance sampling becomes imperative.

Let  $g(x)$  denote an importance density. We decide to sample randomly and independently from the importance density instead of  $f(x)$ . Define a modified score function  $H(x)$  as

$$H(x) = h(x) \frac{f(x)}{g(x)}. \quad (35)$$

The expectation of  $H(x)$  over the importance density  $g(x)$  is identically equal to the expectation of  $h(x)$  over  $f(x)$ :

$$\begin{aligned} \langle H \rangle_g &= \int_{-\infty}^{+\infty} H(x)g(x)dx \\ &= \int_{-\infty}^{+\infty} h(x) \frac{f(x)}{g(x)} g(x)dx \\ &= \int_{-\infty}^{+\infty} h(x)f(x)dx \\ &= \langle h \rangle_f. \end{aligned} \quad (36)$$

Thus we sample  $\Omega_g = \{x_i : i = 1, 2, \dots, N\}$  randomly and independently from the importance density  $g(x)$ . For each  $x_i \in \Omega_g$ , calculate the unweighting - reweighting factor  $f(x_i)/g(x_i)$ . Monte Carlo estimate of  $\langle H \rangle_g$  is given by,

$$\overline{H}_N = \frac{1}{N} \sum_{i=1}^N H(x_i) = \frac{1}{N} \sum_{i=1}^N h(x_i) \frac{f(x_i)}{g(x_i)} \underset{N \rightarrow \infty}{\sim} \langle H \rangle_g \quad (37)$$

Notice that as  $N \rightarrow \infty$ ,  $\overline{H}_N \rightarrow \langle H \rangle_g \equiv \langle h \rangle_f$ .

Let us now calculate the statistical error associated with  $\overline{H}_N$ . It is adequate if we consider the second moment, since we have formally shown that the average value of  $h$  over  $f$ -ensemble is identically equal to the average of  $H$  over  $g$ -ensemble. In other words the mean is preserved under importance sampling. The second moment of the  $H$ , evaluated over the  $g$ -ensemble is given by,

$$\begin{aligned} M_2^B(H) &= \int_{-\infty}^{+\infty} H^2(x)g(x)dx, \\ &= \int_{-\infty}^{+\infty} \frac{h(x)f(x)}{g(x)} \frac{h(x)f(x)}{g(x)} g(x)dx, \\ &= \int_{-\infty}^{+\infty} \left[ \frac{f(x)}{g(x)} \right] h^2(x)f(x)dx. \end{aligned} \quad (38)$$

On the other hand the second moment of  $h$  over the  $f$ -ensemble is given by,

$$M_2^A(h) = \int_{-\infty}^{+\infty} h^2(x)f(x)dx. \quad (39)$$

We find  $M_2^B(H) \neq M_2^A(h)$ . If we choose the importance density function  $g(x)$  properly, we can make  $M_2^B(H)$  to be much less than  $M_2^A(h)$ . In other words we can get substantial variance reduction under importance sampling. The averages estimated employing importance sampling will be statistically more reliable than the ones calculated by sampling from  $f(x)$ . This in essence is the principle of importance sampling.

## 7.1 An illustration of importance sampling

A simple problem would drive home this important point. Let  $f(x) = \exp(-x)$  defined for  $x \geq 0$ . Consider a score function defined as,

$$h(x) = \begin{cases} 0 & \text{for } x < T \\ 1 & \text{for } x \geq T \end{cases} \quad (40)$$

These two functions are depicted in Fig. (2a) for  $T = 5$ . Notice that the score function  $h(x)$  is zero for  $x < T$  - a region of  $x$  where the probability is very high. Hence most of the values of  $x$  sampled from the density  $f(x)$  will all be in this region and the corresponding scores are zero. On the other hand, the score function  $h(x)$  is unity for  $x > T$  - a region of  $x$  where the probability is negligibly small. This high score region is going to be scarcely sampled; often this region is almost never represented in a finite sample. Let us consider an importance density  $g(b, x) = b \exp(-bx)$  defined for  $x \geq 0$  and  $0 < b \leq 1$  where  $b$  is a parameter to be optimized for minimum variance. Fig. (2b) depicts the importance density and the modified score function  $H(x) = h(x)f(x)/g(b, x)$  for  $T = 5$  and  $b = \hat{b} = 0.18$ . For this problem all the statistics

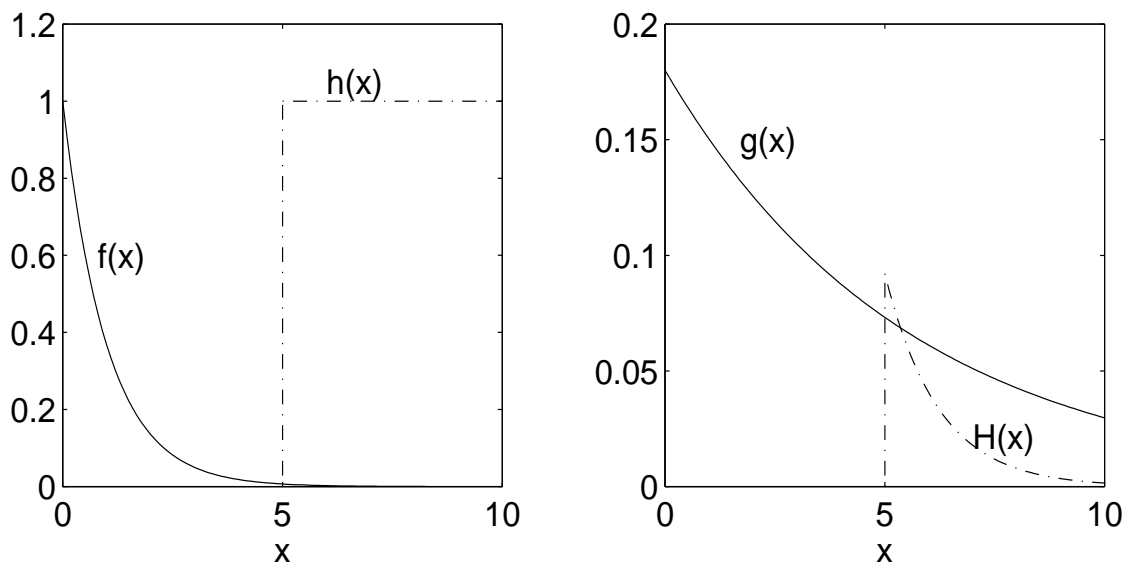


Figure 2: (a) The probability density  $f(x)$  and the score function  $h(x)$  for  $T = 5$ . The score function  $h(x)$  is zero for  $x < 5$ , where the probability is high;  $h(x) = 1$  for  $x > 5$  where the probability is negligibly small. (b) The importance density function  $g(\hat{b}, x)$  and the modified score function  $H(x) = h(x)f(x)/g(\hat{b}, x)$ , where  $\hat{b} = 0.18$ .

can be calculated analytically. The mean and variance of  $h$  over the  $f$ -ensemble are given by,

$$\begin{aligned}\langle h \rangle_f &= \exp(-T) \\ \sigma^2(h) &= \langle h \rangle_f (1 - \langle h \rangle_f)\end{aligned}\quad (41)$$

Table (1) gives the mean and the relative standard deviation of  $h$  over the  $f$ -ensemble for several values of  $T$ . The last column gives the size of the sample required in a Monte Carlo simulation, to estimate the mean within  $\pm 10\%$  statistical error by random sampling from the  $f$ -ensemble. We see from Table (1) that as  $T$  increases  $\langle h \rangle_f$  decreases

Table 1:  $f$ -ensemble: exact analytical results

$T$	$\langle h \rangle_f$	$\sigma(h)/\langle h \rangle_f$	$N = 100\sigma^2(h)/\langle h \rangle_f^2$
3	$4.98 \times 10^{-2}$	4.37	$1.91 \times 10^3$
5	$6.74 \times 10^{-3}$	$1.21 \times 10^1$	$1.47 \times 10^4$
10	$4.54 \times 10^{-5}$	$1.48 \times 10^2$	$2.20 \times 10^6$
20	$2.06 \times 10^{-9}$	$2.20 \times 10^4$	$4.85 \times 10^{10}$

and the relative fluctuation increases. We find that the sample size required to predict the mean within  $\pm 10\%$  statistical error is over 48 billion for  $T = 20$ , a task which is nearly impossible on any computer.

Let us see how the use of importance sampling renders possible the impossible. The mean of  $H$  over the  $g$ -ensemble is identically equal to the mean of  $h$  over the  $f$ -ensemble. However the variance of  $H$  over  $g$ -ensemble is different and is given by,

$$\sigma^2(H, b) = \frac{e^{-T(2-b)}}{b(2-b)} - e^{-2T}. \quad (42)$$

It is now quite straight forward to calculate the value of  $b = \hat{b}$  for which the variance is minimum. We get,

$$\hat{b} = 1 + \frac{1}{T} - \sqrt{1 + \frac{1}{T^2}}. \quad (43)$$

Table (2) presents  $T, \hat{b}, \sigma(H, b = \hat{b})/\langle H \rangle_g$  and the sample size required to estimate the mean within  $\pm 10\%$  statistical error under importance sampling Monte Carlo. We find from Table (2) that use of importance sampling would lead to a considerable reduction of variance especially for large  $T$ . Take the case with  $T = 5$ . Use of importance sampling would reduce the statistical error by a factor five or so. As a consequence a

sample of size 650 is adequate to estimate  $\langle H \rangle_g = \langle h \rangle_f$  whereas from the  $f$ -ensemble we would require to sample 14,700 realizations to estimate the average within  $\pm 10\%$  statistical error. The results for  $T = 20$  are more dramatic and bring home the need and power of importance sampling. The statistical error gets reduced by a factor of 4247 when we employ importance sampling. We need only a sample of size 2687 from the  $g$ -ensemble to estimate the mean within  $\pm 10\%$  of the exact, as compared to the sample of size 48 billion from the  $f$ -ensemble.

Table 2: Importance sampling: exact analytical results

$T$	$\hat{b}$	$\sigma(H, \hat{b}) / \langle H \rangle_g$	$N = 100\sigma^2(H, \hat{b}) / \langle H \rangle_g^2$
3	.28	1.95	381
5	.18	2.55	651
10	.09	3.65	1329
20	.048	5.18	2687

Let us see below if the above conclusions based on analytical theories are borne out by Monte Carlo simulations. We have sampled explicitly 10,000 realizations from the importance density  $\hat{b} \exp(-\hat{b}x)$ , employing analytical inversion technique, described earlier, and calculate  $\langle H \rangle_g$  as,

$$\bar{H}_N = \frac{1}{N} \sum_{i=1}^N H(x_i) \approx \langle H \rangle_g \text{ and } N = 10,000, \tag{44}$$

where,

$$H(x_i) = \begin{cases} \frac{1}{\hat{b}} \exp[-(1 - \hat{b})x_i], & \text{if } x_i \geq T, \\ 0, & \text{if } x_i < T. \end{cases} \tag{45}$$

The statistical error is calculated as,

$$\Delta \bar{H}_N = \pm \frac{1}{\sqrt{N}} \sqrt{\frac{1}{N} \sum_{i=1}^N H^2(x_i) - \bar{H}_N^2}. \tag{46}$$

Table (3) gives the estimated mean  $\bar{H}_N$ , the relative statistical error, and the actual deviation of the Monte Carlo estimate from the exact value  $\langle h \rangle_f$ . We observe from Table (3) that we are able to make a very good estimate of the desired average employing importance sampling. The corresponding results obtained by random sampling from the density  $f(x)$  of 50,000 realizations (five times more than what we have considered

Table 3: Results of Monte Carlo sampling of 10,000 realizations from the  $g$ -ensemble

$T$	$\bar{H}_N$	$\frac{\Delta\bar{H}_N}{\bar{H}_N} \times 100$	$\frac{\bar{H}_N - \langle h \rangle_f}{\langle h \rangle_f} \times 100$
3	$4.94 \times 10^{-2}$	$\pm 2.0\%$	$-0.8\%$
5	$6.76 \times 10^{-3}$	$\pm 2.6\%$	$+0.3\%$
10	$4.52 \times 10^{-5}$	$\pm 3.7\%$	$-0.4\%$
20	$1.96 \times 10^{-9}$	$\pm 5.4\%$	$-4.9\%$

Table 4: Results of Monte Carlo sampling of 50,000 realizations from the  $f$  ensemble

$T$	$\bar{h}_N$	$\frac{\Delta\bar{h}_N}{\langle h \rangle_f} \times 100$	$\frac{\bar{h}_N - \langle h \rangle_f}{\langle h \rangle_f} \times 100$
3	$5.03 \times 10^{-2}$	$\pm 1.9\%$	$+1.8\%$
5	$6.68 \times 10^{-3}$	$\pm 5.5\%$	$-0.9\%$
10	$6.16 \times 10^{-4}$	$\pm 57.7\%$	$+35.7\%$
20	.	.	.

for sampling from the  $g$ -ensemble) are given in Table (4). We find from Table (4) that Monte carlo simulation based on sampling from the  $f$ -ensemble to estimate  $\langle h \rangle_f$  with  $T = 20$  is impossible. On the average, we can expect one in 49 million realizations sampled from the exponential density, to have a value greater than 20. The chance of getting a score in a simulation of 50,000 histories is practically nil.

The key point is that importance sampling helps you pick up rare events - events that have very low probability of occurrence. We need these rare events in our Monte Carlo sample because they have high scores; *i.e.* we are interested in investigating a phenomenon that concerns these rare events. For example we would like to have in our Monte Carlo sample the rare neutrons from a source that manage to penetrate a very thick shield and enter the detector kept on the other side. We shall employ, for example, an importance sampling scheme based on exponential biasing [42,43]. In the problem of Monte Carlo calculation of averages over canonical ensemble, we would like

to sample microstates with high Boltzmann weight. We shall employ the Metropolis importance sampling [46]. In the study of first order phase transition, we would be interested in sampling the rare microstates that describe interfaces between the ordered and disordered phases. We would resort to multicanonical sampling [84]. In fact we can say that without importance sampling techniques, Monte Carlo method is of rather very little practical use for simulation of a large variety of problems, be it in statistical physics or in radiation transport.

With these preliminaries let us now turn our attention to sampling from a canonical ensemble of microstates of a macroscopic system, employing Monte Carlo. I shall illustrate this taking ferromagnetism as an example. We shall consider Ising spin model of magnetism.

## 8 What is an Ising spin model?

Unpaired electron spins couple and align. The sum of such tiny magnetic moments results in macroscopic magnetism. In the year 1923, Prof. Lenz proposed a very simple model of magnetism to his student, Ising, who solved it analytically in one dimension. Ever since, this model is called the Ising model. For an historical introduction to Ising model, see [44]. In the Ising model, a spin has only two states: an *up* state and a *down* state. Let us denote the spin variable by the symbol  $S_i$ , and in the model, we say that  $S_i$  can take only values of  $+1$ , denoting the *up* state ( $\uparrow$ ) or  $-1$ , denoting the *down* state ( $\downarrow$ ). We organize the spins on a lattice and the index  $i$  refers to the lattice site. The lattice can be in general  $d$  dimensional. Let  $i$  and  $j$  refer to two nearest neighbour sites on the lattice and let  $S_i$  and  $S_j$  be the spins on these lattice sites. Energy associated with the pair of nearest neighbour spins is given by  $\epsilon_{i,j} = -JS_iS_j$ . Thus when the two spins are aligned (up or down), the energy associated with them is  $-J$ ; when not, the energy associated with the pair is  $+J$ . The value of  $J$  measures the strength of the spin-spin interaction. If  $J$  is positive, the interaction is ferromagnetic. If  $J$  is negative, the interaction is anti-ferromagnetic. We consider  $J > 0$ . Figure (3) depicts two-spins configurations. There are a total of four possible configurations. The two configurations marked (a) are each of energy  $-J$ , since the spins are aligned. The two configurations marked (b) are each of energy  $+J$  since the spins are not aligned. Consider now Ising spins on a lattice. Energy associated with a spin configuration  $\mathcal{C}$  is given by,

$$E(\mathcal{C}) = -J \sum_{\langle i,j \rangle} S_i(\mathcal{C})S_j(\mathcal{C}) , \quad (47)$$

where, the symbol  $\langle i,j \rangle$  denotes that the sites  $i$  and  $j$  are nearest neighbours. The sum is taken over all pairs of nearest neighbour sites in the lattice. We shall concentrate on ferromagnetism and hence  $J$  is positive. The energy is lowest when all the spins are aligned, either up or down. The Ising Hamiltonian, see Eq. (47), remains the same if all the spins are flipped. An external magnetic field that couples to all the spins, if present, would break this symmetry of the Hamiltonian. Let us consider an external field in the *up*( $\uparrow$ ) direction. The external field couples to each of the Ising spin in the system with a strength  $B$ . The energy of the system when in the configuration  $\mathcal{C}$  is



Figure 3: Two-spins configurations: (a) There are two aligned spin configurations. The energy of each configuration is  $\epsilon_{i,j} = -J S_i S_j = -J$ . (b) There are two configurations in each of which the spins are not aligned. The energy of each configuration is  $\epsilon_{i,j} = -J S_i S_j = +J$ .

given by,

$$E(\mathcal{C}) = -J \sum_{\langle i,j \rangle} S_i(\mathcal{C}) S_j(\mathcal{C}) - B \sum_i S_i(\mathcal{C}), \quad (48)$$

When the temperature is lowered below a critical value, even in the absence of an external field ( $B = 0$ ), the symmetry is broken. This is called spontaneous symmetry breaking.

It is clear that Ising spin system at very low temperature,  $k_B T \ll J$ , will have low energy, aligned spins and large magnetization. On the other hand, at very high temperature, the spin system will have high energy, randomly oriented spins and hence no net macroscopic magnetization. The system transforms from a disordered paramagnetic to an ordered ferromagnetic phase, when the temperature is lowered below a critical value called the Curie temperature.

Ising solved the model in one dimension analytically and showed that there is no phase transition: Magnetization  $M(T)$  decreases slowly and continuously as  $T$  increases. The susceptibility  $\chi = \partial M / \partial T$  is finite at all temperature. There is no divergence, either of the specific heat or of the susceptibility. But, under a mean field approximation, the Ising model exhibits phase transition at  $T = T_C = \eta J / k_B$ , where  $\eta$  is the coordination number of the lattice.<sup>10</sup> This raised a serious doubt whether the statistical mechanics machinery can at all describe the phenomenon of phase transition. After all, one can argue that the phase transition predicted is an artifact of the mean field approximation. This serious dilemma was settled, once and for all, by Onsager [45]. He solved the two dimensional Ising model exactly; it shows phase transition just like real magnets, at finite temperature. Onsager showed that the transition temperature for two dimensional Ising system is given by,  $k_B T_c / J = 2 / \ln(1 + \sqrt{2})$ .

<sup>10</sup>The coordination number  $\eta$  is 2 for one dimensional lattice; 4 for two dimensional square lattice; 6 for two dimensional hexagonal lattice; 6 for three dimensional cubic lattice; *etc.* Under mean field, the critical temperature does not depend on the dimensionality; it depends only on  $\eta$  - the number of nearest neighbour interactions and  $J$  - the strength of interaction.



## 9 How do we simulate an Ising spin system?

Let  $P(\mathcal{C})$  denote the probability with which a microstate  $\mathcal{C}$  (of an Ising spin system) occurs in a closed system at temperature  $T = 1/(k_B\beta)$ . It is given by,

$$P(\mathcal{C}) = \frac{1}{Z(\beta)} \exp[-\beta E(\mathcal{C})] , \quad (49)$$

where the normalization, known as the canonical partition function, is given by

$$Z(\beta) = \sum_{\mathcal{C}} \exp[-\beta E(\mathcal{C})] , \quad (50)$$

and  $E(\mathcal{C})$  is the energy of the microstate  $\mathcal{C}$ . We say that a Boltzmann weight given by  $\exp[-\beta E(\mathcal{C})]$  is associated with the microstate  $\mathcal{C}$ . Let  $V$  denote the total number of spins in the system. It is readily seen that the number of possible spin configurations (microstates) is  $2^V$ . Let us consider a simple minded approach to simulate the system; we shall call this analogue Monte Carlo. It consists of sampling microstates randomly, independently and with equal probabilities. Assemble an ensemble of  $N$  equiprobable microstates; carry out (Boltzmann) weighted average of the macroscopic quantity, say magnetization  $M$ , over the ensemble as given below.

$$\langle M \rangle = \lim_{N \rightarrow \infty} \overline{M}_N = \frac{\sum_{i=1}^N M(C_i) \exp[-\beta E(C_i)]}{\sum_{i=1}^N \exp[-\beta E(C_i)]} . \quad (51)$$

A real magnetic system would contain an extremely large number of spins; *i.e.*  $V$  shall be of the order of  $10^{23}$ . Let us consider a modest model system with some hundred spins on a two dimensional  $10 \times 10$  square lattice. The number of spin configurations is  $2^{100} \approx 10^{30}$ . Even if we assume optimistically that it takes a nano second to generate a spin configuration, the total time required to sample all the spin configurations is nearly of the order of thirty thousand billion years! In a Monte Carlo simulation, we sample only a very small number of spin configurations, say ten thousand or so; with modern high speed computers it may be possible to generate say a few billion microstates. Unfortunately, because of the Boltzmann weight  $\exp[-\beta E(C)]$ , most of the spin configurations randomly generated would contribute very negligibly to the sum. The associated fluctuations shall be very large. Hence we resort to importance sampling.

In importance sampling, the idea is to select spin configurations randomly and independently from the distribution  $P(\mathcal{C}) = \exp[-\beta E(\mathcal{C})]/Z$ . These spin configurations, when sampled adequately large in number, constitute, to a very good approximation, a canonical ensemble. Therefore average of a macroscopic property can be calculated as a simple arithmetic mean over the sampled microstates. But to carry out this task we need to know the partition function,  $Z(T)$ . But then  $Z$  is precisely what we want to calculate in the first place. Thus there is a catch. But then fortunately there is a way out, as shown by Metropolis and his co-workers [46].

Construct a Markov chain of configurations, starting from an arbitrary initial configuration  $C_0$ . Let  $C_0 \rightarrow C_1 \rightarrow \dots \rightarrow C_n \rightarrow C_{n+1} \rightarrow \dots$  represent a Markov chain of spin configurations. The index  $n$  can be viewed as denoting time. If we establish that, for large  $n$ , the set  $\{C_{n+1}, C_{n+2}, \dots\}$  constitutes an equilibrium canonical ensemble, we have done the job.

## 10 What is a Markov chain?

A Markov chain is a discrete time stochastic process. Consider the Ising spin system which can be described at any discrete time  $n$  as being in any one of the microstates (spin configurations) belonging to the closed system at given temperature; the microstates are denoted by the script alphabet:  $\{\mathcal{C}_1, \mathcal{C}_2, \dots, \mathcal{C}_{\hat{\Omega}_{\text{CS}}}\}$ . The set of all microstates are denoted by  $\Omega_{\text{CS}}$  and the number of microstates belonging to the closed system is denoted by  $\hat{\Omega}_{\text{CS}}$ . Let  $C_n$  be the microstate of the system at the discrete time  $n$ .  $C_n$  is random and can be any one of the microstates belonging to  $\Omega_{\text{CS}} = \{\mathcal{C}_1, \mathcal{C}_2, \dots, \mathcal{C}_{\hat{\Omega}_{\text{CS}}}\}$  with certain probabilities. If the system is in equilibrium the probability for  $C_n$  to be  $\mathcal{C}_i$  is given by  $P(C_n = \mathcal{C}_i) = \exp[-\beta E(\mathcal{C}_i)]/Z$ , and is independent of the time index  $n$ .

The system present in microstate  $C_n \in \Omega_{\text{CS}}$  at time  $n$  makes a transition to microstate  $C_{n+1} \in \Omega_{\text{CS}}$  at time  $n+1$ , according to certain probabilistic rules. The discrete time stochastic evolution of the system starting from an initial state  $C_0 \in \Omega_{\text{CS}}$  at time zero until time  $n$  is completely specified by the joint probability  $P(C_0, C_1, \dots, C_n)$ ; this joint probability can be expressed in terms of conditional probabilities<sup>11</sup>, see page 33 and 34 of A. Papoulis listed in [1] as,

$$\begin{aligned}
 P(C_n, C_{n-1}, \dots, C_1, C_0) = & P(C_n|C_{n-1}, C_{n-2}, \dots, C_1, C_0) \times \\
 & P(C_{n-1}|C_{n-2}, C_{n-3}, \dots, C_1, C_0) \times \\
 & P(C_{n-2}|C_{n-3}, C_{n-4}, \dots, C_1, C_0) \times \\
 & \dots \times \\
 & P(C_2|C_1, C_0) \times \\
 & P(C_1|C_0) \times \\
 & P(C_0)
 \end{aligned} \tag{52}$$

The sequence of random variables  $C_0, C_1, \dots, C_n$  constitutes a Markov chain, if

$$P(C_k|C_{k-1}, C_{k-2}, \dots, C_1, C_0) = P(C_k|C_{k-1}) \quad \forall k = 1, n. \tag{53}$$

As a consequence we have

$$P(C_n, C_{n-1}, \dots, C_1, C_0) = P(C_0)P(C_1|C_0)P(C_2|C_1) \dots P(C_n|C_{n-1}). \tag{54}$$

Physically the Markovian assumption implies that the microstate the system is going to visit at time  $n+1$  depends only on the state it is present now at time  $n$  and not where it was at all the previous times.<sup>12</sup> *The past has no influence over the future once the present is specified.* We restrict ourselves to a time invariant or also called a time homogeneous Markov chain for which, regardless of the time index  $k$ , we have,

$$P(C_{k+1} = \mathcal{C}_i|C_k = \mathcal{C}_j) = W_{i,j} \quad \forall k \tag{55}$$

<sup>11</sup>Let  $B$  be an event with non-zero probability,  $P(B) > 0$ . Consider an event  $A$ . We define the conditional probability of  $A$  assuming  $B$  has occurred as  $P(A|B) = P(A \cap B)/P(B)$ . In words,  $P(A|B)$  equals the probability of that part of  $A$  included in  $B$  divided by the probability of  $B$

<sup>12</sup>The Markov process is the stochastic equivalence of the familiar Newtonian dynamics

where  $W_{i,j}$  is the probability for the transition from microstate  $\mathcal{C}_j$  to microstate  $\mathcal{C}_i$  in a single step. Thus  $W_{i,j}$  is the  $i, j$ -th element of the  $\hat{\Omega}_{\text{CS}} \times \hat{\Omega}_{\text{CS}}$  square matrix. The stochastic matrix  $W$  completely specifies the stochastic dynamical evolution of the system given the initial state  $\mathcal{C}_0$  at time  $n = 0$

Let  $P(\mathcal{C}_i, n)$  denote the probability that the Ising spin system is in a configuration  $\mathcal{C}_i$  at time  $n$ . In other words  $P(\mathcal{C}_i, n)$  is the probability that  $\mathcal{C}_n = \mathcal{C}_i$ . Formally we have the discrete time Master equation,

$$\begin{aligned} P(\mathcal{C}_i, n+1) &= \sum_{j \neq i} W_{i,j} P(\mathcal{C}_j, n) + \left(1 - \sum_{j \neq i} W_{j,i}\right) P(\mathcal{C}_i, n) \\ &= \sum_j \left[ W_{i,j} P(\mathcal{C}_j, n) - W_{j,i} P(\mathcal{C}_i, n) \right] + P(\mathcal{C}_i, n) \end{aligned} \quad (56)$$

We need

$$P(\mathcal{C}_i, n+1) = P(\mathcal{C}_i, n) = \pi(\mathcal{C}_i) = \pi_i \quad \forall i, \quad (57)$$

when  $(n \rightarrow \infty)$ , for asymptotic equilibrium. In the above  $\pi(\mathcal{C}_i) = \pi_i$  is the equilibrium probability of the microstate  $\mathcal{C}_i$ . *i.e.*  $\pi_i = \exp[-\beta E(\mathcal{C}_i)]/Z$ . We can ensure evolution to asymptotic equilibrium by demanding that each term in the sum over  $j$  in the RHS of Eq. (56) be zero. Notice that this condition is sufficient but not necessary for equilibration. This is called the detailed balance condition:

$$W_{i,j} \pi_j = W_{j,i} \pi_i, \quad (58)$$

which implies that

$$\frac{W_{i,j}}{W_{j,i}} = \frac{\pi_i}{\pi_j} = \exp \left[ -\beta \{E(\mathcal{C}_i) - E(\mathcal{C}_j)\} \right] = \exp [-\beta \Delta E], \quad (59)$$

The important point is that only the ratios of the equilibrium probabilities appear in the above. These ratios are known; they are just the ratios of the Boltzmann weights; we do not need to know the normalization (partition function) for constructing a transition matrix, see discussions toward the end of section (9).

A task now is to construct an algorithm that takes the system from one microstate to the next as per a transition matrix whose elements obey Eq. (59). We have already seen that the number of microstates of a closed system is  $\hat{\Omega}_{\text{CS}} = 10^{30}$  even for a small system of Ising spins on a  $10 \times 10$  square lattice; the  $W$  matrix for this problem will thus contain some  $10^{60}$  elements! Constructing explicitly such a matrix, storing it, and carrying out operations with it are neither feasible nor required. What we need is an algorithm that takes the system from one microstate to another which in effect mimics the transition induced by the matrix  $W$ . The Metropolis algorithm does this.

## 11 What is the Metropolis Algorithm?

The Metropolis algorithm defines a stochastic dynamics which generates, starting from an arbitrary initial microstate  $\mathcal{C}_0$ , a Markov chain of microstates, given by,

$$\mathcal{C}_0 \rightarrow \mathcal{C}_1 \rightarrow \mathcal{C}_2 \rightarrow \dots \rightarrow \mathcal{C}_k \rightarrow \mathcal{C}_{k+1} \rightarrow \dots \quad (60)$$

Let us see how does the transition:  $C_k \rightarrow C_{k+1}$ , take place as per Metropolis algorithm. We select one of the spins randomly and with equal probability ( $= 1/V$ ); let  $S_i$  denote the selected spin which is at lattice site  $i$ . We flip the selected spin ( $S_i \rightarrow -S_i$ ) and get a trial configuration denoted by  $C_t$ . This step constitutes the selection part of the transition matrix  $W$ . Let  $\Delta E = E(C_t) - E(C_k)$ . We accept  $C_t$  as the next microstate in the Markov chain with a probability given by,

$$\begin{aligned} p &= \min\left(1, \frac{\pi(C_t)}{\pi(C_k)}\right), \\ &= \min\left(1, \exp[-\beta\Delta E]\right). \end{aligned} \quad (61)$$

In other words,

$$C_{k+1} = \begin{cases} C_t & \text{with probability } p \\ C_k & \text{with probability } 1 - p \end{cases} \quad (62)$$

This step constitutes the acceptance / rejection part of the transition  $W$ . Executing these two steps constitutes one Monte Carlo Step (MCS). It is easily verified that the Metropolis transition described above obeys the detailed balance condition.

Let me recapitulate the different steps involved in the practical implementation of the Metropolis algorithm.:

- Start with an arbitrary initial microstate  $C_0 \in \Omega_{CS}$  and evolve it :  $C_0 \rightarrow C_1 \rightarrow C_2 \dots$ .
- select randomly and with equal probability one of the spins in the current configuration,  $C_k$ . Let  $S_i$  denote the selected spin. Flip the spin ( $S_i \rightarrow -S_i$ ) and get the trial configuration  $C_t$ . Calculate  $\Delta E = E(C_t) - E(C_k)$ .
- If  $\Delta E \leq 0$ , accept the trial state;  $C_{k+1} = C_t$
- if  $\Delta E > 0$  draw a random number  $\xi$ 
  - if  $\xi \leq \exp(-\beta\Delta E)$ , accept the trial state;  $C_{k+1} = C_t$
  - if  $\xi > \exp(-\beta\Delta E)$  reject the trial state;  $C_{k+1} = C_k$  <sup>13</sup>

Iterating the above we get a Markov chain of microstates. In a single Monte Carlo Step (MCS) the system switches from the current state  $C_k$  to the next state  $C_{k+1}$ . A consecutive set of  $V$  number of MCS constitutes one Monte Carlo Step per Spin (MCSS). The time scale for the Metropolis dynamics is set by an MCSS. We construct an ensemble of microstates from the Markov Chain by picking up microstates at the end of every MCSS:  $\{C_0, C_V, C_{2V}, \dots\}$ . Discard configurations at the beginning of

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<sup>13</sup>The rejection part of the algorithm is important for realizing equilibrium ensemble; there are however rejection free algorithms; in these, the information on the dynamics is transferred to the time axis; these are called event driven algorithms; the Metropolis algorithm is time driven. We shall discuss an event-driven algorithm called the n-fold way, later. See section (15)

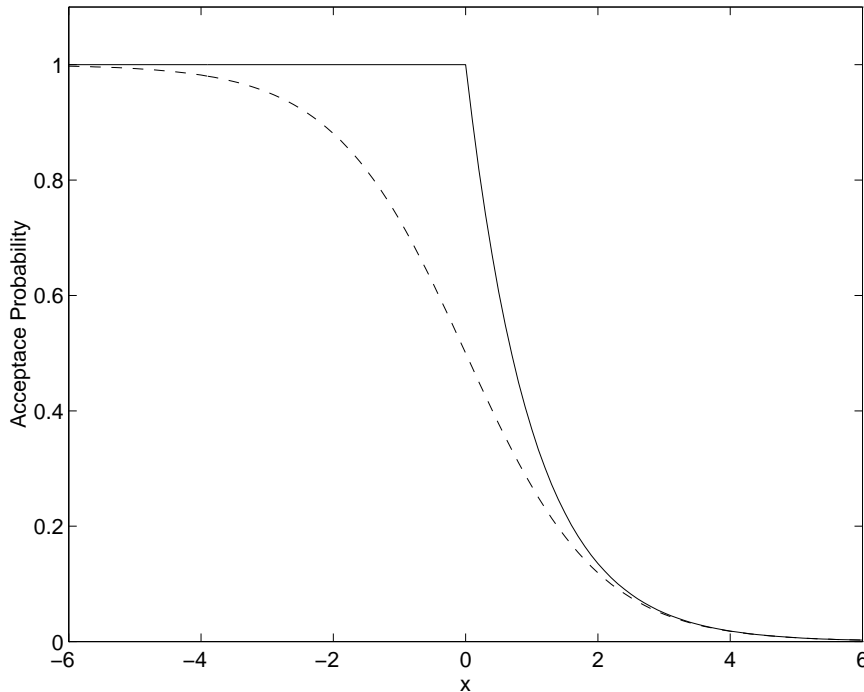


Figure 4: Acceptance probability  $p$ . The solid line refers to Metropolis sampling:  $p = \min\{1, \exp(-x)\}$ . The dashed curve refers to Glauber dynamics:  $p = 1/[1 + \exp(+x)]$ . In the above  $x = \beta\Delta E$ .

the chain; Then the configurations in the asymptotic part of the chain constitute a canonical ensemble, which can be employed for calculating the desired macroscopic properties of the system.

Fig. (4) depicts the probability  $p$  of accepting a trial configuration  $C_t$  produced from the current configuration  $C_k$ , as a function of  $x = \beta[E(C_t) - E(C_k)]$ . It should be remarked that we can devise several other transition matrices consistent with detailed balance. For example, in the Metropolis algorithm, the derivative of the acceptance probability  $p(x)$  is not continuous at  $x = 0$ , see the solid line in Fig. (4). Hence Glauber [50] proposed a dynamics where the probability  $p$  of accepting a trial state  $C_t$ , constructed from the current state  $C_k$ , is given by

$$\begin{aligned}
 p &= \frac{\exp[-\beta E(C_t)]}{\exp[-\beta E(C_k)] + \exp[-\beta E(C_t)]} \\
 &= \frac{1}{1 + \exp[\beta \{E(C_t) - E(C_k)\}]} \\
 &= \frac{1}{1 + \exp(x)}. \tag{63}
 \end{aligned}$$

The above choice of acceptance probability is also consistent with the detailed balance.

There is another dynamics in vogue called the heat-bath algorithm. We define  $h_i = \sum_j S_j$ , where the index  $j$  runs over all the nearest neighbour spins of  $S_i$ . We

define a probability

$$p_i = \frac{\exp(\beta J h_i)}{\exp(\beta J h_i) + \exp(-\beta J h_i)}. \quad (64)$$

The heat-bath algorithm [51] consists of updating the spin  $S_i(k)$  to  $S_i(k+1)$  where  $S_i(k+1) = \pm 1$  with probabilities  $p_i$  and  $1 - p_i$  respectively. This is implemented by drawing a random number  $\xi$  (uniformly distributed in the interval 0 to 1) and setting  $S_i(k+1) = \text{SIGN}(p_i - \xi)$ , where the function  $\text{SIGN}(\eta)$  equals +1 if  $\eta > 0$  and -1 if  $\eta < 0$ . Thus the spin at site  $i$  behaves as if it is in its private heat bath constructed by its nearest neighbours! Let us now cast the Glauber algorithm in the language of the heat-bath algorithm employing  $p_i$ .

In the Glauber algorithm, if  $S_i(k) = +1$ , then the probability  $S_i(k+1) = -1$  is  $p = 1 - p_i$ ; therefore,  $S_i(k+1) = -\text{SIGN}(1 - p_i - \xi)$ . On the other hand if  $S_i(k) = -1$ , then the probability that  $S_i(k+1) = +1$  equals  $p = p_i$  and hence  $S_i(k+1) = \text{SIGN}(p_i - \xi)$ . It is in this sense that the Glauber dynamics differs from the heat-bath algorithm.

However, it readily seen that, in the Glauber algorithm,

$$\begin{aligned} P\left(S_i(k+1) = +1 \mid S_i(k) = +1\right) &= P\left(S_i(k+1) = +1 \mid S_i(k) = -1\right) = p_i \\ P\left(S_i(k+1) = -1 \mid S_i(k) = +1\right) &= P\left(S_i(k+1) = -1 \mid S_i(k) = -1\right) = 1 - p_i, \end{aligned} \quad (65)$$

and these probabilities are identical to those of the heat-bath algorithm; hence the Glauber algorithm differs from the heat-bath algorithm only in a minor and irrelevant technical detail.

I think we understand why do the Metropolis transitions take the system to equilibrium eventually. A system has a natural tendency to lower its energy; hence if a trial microstate has lower energy it is accepted with unit probability. But there are fluctuations present all the time; fluctuations are a part and parcel of an equilibrium system. It is precisely because of these fluctuations that an equilibrium system manages to remain in equilibrium. The fluctuations also correspond to measurable physical properties of the macroscopic system, *e.g.* the specific heat corresponds to energy fluctuations.<sup>14</sup> Hence when the trial microstate is of higher energy, we still accept it but with a probability less than unity; larger the energy increase, lower is the acceptance probability, since in equilibrium larger fluctuations are rarer.

That the Metropolis algorithm assures asymptotic equilibrium can also be shown rigorously mathematically. The transition matrix  $W$ , whether based on the Metropolis dynamics or the Glauber/heat-bath dynamics, has the following properties:  $W_{i,j} \geq 0 \ \forall i, j$  and  $\sum_j W_{j,i} = 1 \ \forall i$ . This second property is just a normalization condition: the system has to be in any one of the microstates including the present one, after a transition. Using the normalization in Eq. (56), we get,

$$P(\mathcal{C}_i, n+1) = \sum_j W_{i,j} P(\mathcal{C}_j, n) \ \forall i. \quad (66)$$

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<sup>14</sup>Fluctuation dissipation theorems relate the equilibrium fluctuations to nonequilibrium or more precisely near equilibrium responses.

The above can be written in a convenient vector notation

$$|P(n+1)\rangle = W|P(n)\rangle \quad (67)$$

where the components of the column vector  $|P(n)\rangle$  are the probabilities of the microstates of the closed system at time  $n$  and the dimension of the vector is equal to the size of the sample space. Specifying the sample space and the probabilities of the microstates of the sample space uniquely defines an ensemble. Hence we shall call  $|P(n)\rangle$  an ensemble at time  $n$ . Thus the transition matrix acts on the ensemble  $|P(n)\rangle$  and transforms it to the ensemble  $|P(n+1)\rangle$ . Let us start with an arbitrary ensemble  $|P_0\rangle$ , such that  $\langle\pi|P_0\rangle \neq 0$ ; in other words the initial ensemble chosen has a non-zero overlap with the equilibrium ensemble. Let  $W$  act on  $|P_0\rangle$  successively some  $n$  times and transform it to  $|P(n)\rangle$ .

$$W^n|P_0\rangle = |P(n)\rangle \quad (68)$$

We want  $|P(n)\rangle \rightarrow |\pi\rangle$  as  $n \rightarrow \infty$  and any subsequent transition should not change the ensemble. For this to happen the largest eigenvalue of  $W$  must be real, non-degenerate<sup>15</sup> and unity;<sup>16</sup> all other eigenvalues must be smaller than unity in modulus; also the eigenvectors of  $W$  must form a complete set. We can then express the initial ensemble in terms of the eigenvectors of  $W$ . Upon repeated operations by  $W$ , only the eigenvector of the largest eigenvalue survives. Hence equilibrium ensemble is the right eigenvector of  $W$  corresponding to the (largest) eigenvalue unity:

$$W|\pi\rangle = |\pi\rangle. \quad (69)$$

$|\pi\rangle$  is called the equilibrium or the invariant distribution of the matrix  $W$ . The Peron - Frobenius theorem [47,48] ensures that such an asymptotic convergence to an equilibrium ensemble is possible if the transition matrix  $W$  has the following properties:

- $W_{i,j} \geq 0 \forall i, j$
- $\sum_j W_{j,i} = 1 \forall i$

A transition matrix  $W$  is called ‘balanced’, if it obeys the above two conditions. In addition we demand the Markov chain to be ergodic:  $(W^m)_{i,j} > 0 \forall i, j$  and  $m < \infty$ . This ensures that every microstate ( $\in \hat{\Omega}_{CS}$ ) is reachable from every other microstate ( $\in \hat{\Omega}_{CS}$ ) in a finite number of transition steps. If the transition matrix obeys a more restricted detailed balance condition, then the above two requirements are automatically fulfilled and hence is ‘balanced’; detailed balance condition is sufficient though not necessary for asymptotic convergence to equilibrium, see below.

There are several Monte Carlo techniques in vogue, that do not satisfy detailed balance condition, see *e.g.* [52], but nevertheless assures march to equilibrium. As we have seen above, the (weaker) balance condition suffices for asymptotic equilibrium, see for *e.g.* [53].<sup>17</sup>

<sup>15</sup>the equilibrium corresponds to a unique ensemble

<sup>16</sup>once the system reaches equilibrium it should remain in equilibrium

<sup>17</sup>In fact we can define a transition matrix  $\widehat{W}$  called the reversal of  $W$  [54] or the  $\pi$ -dual of  $W$  [55].

## 12 How do we calculate Monte Carlo averages and error bars?

We calculate the required macroscopic property by averaging over the ensemble constructed as per the Metropolis rejection technique described earlier. For example, the energy given by,

$$E(\mathcal{C}) = -J \sum_{\langle i,j \rangle} S_i(\mathcal{C}) S_j(\mathcal{C}), \quad (70)$$

when the Ising spin system is in the configuration  $\mathcal{C}$ . Similarly, the magnetization in the microstate  $\mathcal{C}$  is given by

$$M(\mathcal{C}) = \sum_i S_i(\mathcal{C}). \quad (71)$$

The above and any other macroscopic quantity of interest can be averaged over an ensemble generated by the Monte Carlo algorithm.

Let  $C_1, C_2, \dots, C_N$  be the  $N$  successive microstates in the asymptotic part of a Markov chain generated by the Metropolis algorithm. Let  $x_i = x(C_i)$  be the corresponding values of a macroscopic property of the system.  $x$  can be  $M, E, M^2, E^2$  etc. An estimate of the average of  $x$  is given by

$$\bar{x}_N = \frac{1}{N} \sum_{i=1}^N x_i, \quad (72)$$

which in the limit of  $N \rightarrow \infty$  gives  $\langle x \rangle$ . We call  $\bar{x}_N$  as a finite sample estimate of  $\langle x \rangle$ . We can estimate from the ensemble, all the macroscopic properties of the Ising spin system like  $\langle E \rangle$ , and  $\langle M \rangle$ ; Employing fluctuation dissipation theorems we can estimate specific heat given by

$$C_V = \frac{\partial E}{\partial T} = \frac{\langle E^2 \rangle - \langle E \rangle^2}{k_B T^2}, \quad (73)$$

and the magnetic susceptibility given by

$$\chi = \frac{\langle M^2 \rangle - \langle M \rangle^2}{k_B T}. \quad (74)$$

The Monte Carlo estimate  $\bar{x}_N$  is always associated with statistical error since  $N$  is finite. The standard deviation of  $\bar{x}_N$  is the one-sigma confidence interval or the statistical

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It is given by,

$$\widehat{W} = \text{diag}(\pi) W^\dagger \text{diag}(1/\pi)$$

where  $\text{diag}(\pi)$  denotes a diagonal matrix whose diagonal elements are the components of the equilibrium vector  $|\pi\rangle$ , and  $W^\dagger$  denotes the transpose of  $W$ . Both the transition matrices  $W$  and  $\widehat{W}$  have the same invariant distributions.  $\widehat{W}$  describes the time reversed markov evolution. If  $W$  obeys the detailed balance condition then  $\widehat{W} = W$ . The matrix  $\widehat{W}$  has been found useful in several recent studies in nonequilibrium statistical mechanics like fluctuation theorems, work-free energy relations, etc., see for e.g. [56].



error associated with  $\bar{x}_N$ . We express the statistical error employing the Central Limit Theorem: we present the Monte Carlo result as

$$\bar{x}_N \pm \frac{\sigma(x)}{\sqrt{N}}, \quad (75)$$

where  $\sigma^2(x) = \langle x^2 \rangle - \langle x \rangle^2$ . The quantity  $\sigma(x)/\sqrt{N}$  is called the statistical error, or one-sigma confidence interval. The key idea is that in the limit  $N \rightarrow \infty$  the random variable  $\bar{x}_N$  becomes Gaussian distributed with mean  $\langle x \rangle$  and variance  $\sigma^2(x)/N$ . Notice that asymptotically ( $N \rightarrow \infty$ ) the statistical error goes to zero as  $N^{-1/2}$ . In other words the distribution of the sample average tends to a delta function in the limit  $N \rightarrow \infty$ .

In calculating the statistical error, replace  $\sigma^2(x)$  by the sample fluctuations, denoted by  $S_N^2$  and given by,  $S_N^2 = \sum_{i=1}^N (x_i - \bar{x}_N)^2 / (N - 1)$ . Equation (75) for the statistical error holds good only if the Ising spin configurations sampled are all uncorrelated. The configurations generated by the Metropolis algorithm at successive MCSS are usually correlated. Hence the actual statistical error would be higher than what is calculated employing Eq. (75). I shall have more to say on this later.

Before we go further and take up more advanced topics there are a few details and few issues we should attend to. For example before taking average over the ensemble, we must ensure that the Markov process has equilibrated, *i.e.*,  $P(\mathcal{C}, t) \rightarrow P(\mathcal{C})$ , as  $t \rightarrow \infty \forall \mathcal{C} \in \Omega_{\text{CS}}$ . The Ising system should have forgotten the arbitrary initial spin configuration. How do we find this? First we must check if the average converges to a constant value: split the data into several bins and calculate the average for each bin. Discard the initial bins which give averages different from the latter. Another way is to calculate the autocorrelation function and from it, the correlation time  $\tau^*$  in units of MCSS. Discard data from the initial, say  $10 \tau^*$  MCSS.

Another problem is related to the issue of ergodicity. The system can get trapped in a region of the configuration phase and not come out of it at all. It is also possible that the dynamics is quasi-ergodic, in the sense that the system gets trapped in local minimum and is unable to come out of it in any finite time due to the presence of high energy barriers. A possible check to detect these is to carry out several simulations starting from different initial spin configurations and see if all of them give more or less the same results within statistical fluctuations.

The next question concerns boundary conditions. Periodic boundary conditions are often employed: the lattice wraps around on itself to form a torus. Consider a two dimensional square lattice of sites. The first site in a row is considered as the right nearest neighbour of the last site in the same row and the last site in a row is considered as the left nearest neighbour of the first site in the same row. The same holds for the top and bottom sites in each column. Periodic boundaries are known to give least finite size effects; we shall see about finite size effects sometime later. There are also several other boundary conditions *e.g.* rigid, skew periodic, anti periodic, anti symmetric, free edge *etc.*, that are implemented depending on the nature of the problem.

### 13 How does an Ising spin system behave in the vicinity of phase transition?

To distinguish one phase from the other we need an order parameter; magnetization  $M$  is a good order parameter to study phase transition in ferromagnetic systems. Usually, the order parameter is zero in the high temperature disordered paramagnetic phase and non-zero in the low temperature ordered ferromagnetic phase. In the Ising model simulation, we shall be interested in the second order phase transition.

The magnetic phase transitions are characterized by critical exponents. In the limit of  $T \rightarrow T_c$ , we have

$$\begin{aligned} \frac{M(T)}{V} &\sim (T_c - T)^\beta \text{ for } T < T_c, \\ \frac{\chi(T)}{V} &\sim |T - T_c|^{-\gamma}, \\ \frac{C_V(T)}{V} &\sim |T - T_c|^{-\alpha}. \end{aligned} \tag{76}$$

In the above  $V$  is the total number of spins in the system.  $\beta$ ,  $\gamma$  and  $\alpha$  are called the critical exponents. For the two dimensional Ising model system  $\beta = 1/8$ ,  $\gamma = 7/4$  and  $\alpha = 0$ . In fact, the specific heat goes like

$$\frac{C_V(T)}{V} \sim 0.4995 \times \ln ( |T - T_c|^{-\nu} ). \tag{77}$$

The correlation length at temperature  $T$ , denoted by  $\xi(T)$ , which measures the typical linear size of a magnetic domain, goes like  $\xi(T) \sim |T - T_c|^{-\nu}$ , and the exponent  $\nu = 1$  for the two dimensional Ising model. The critical exponents are universal in the sense their values do not depend on the details of the model; they depend only on gross features like dimensionality of the problem, the symmetry of the Hamiltonian *etc.* Indeed this is precisely why very simple models like the Ising model are successful in describing phase transition in real systems.

The correlation length  $\xi(T)$  is expected to be of the order of zero when  $T \gg T_c$ . At very high temperature, the spins behave as if they are independent of each other. Spin-spin interactions are irrelevant compared to the thermal fluctuations. Entropy wins over energy completely. The macroscopic properties of the system are determined by entropic considerations only. As  $T$  decreases, the spin-spin interaction becomes more and more relevant and the correlation length diverges as  $T \rightarrow T_c$ . If the system studied is finite, the correlation length, at best, can be of the order of the linear dimension of the system. This brings us to the important topic of finite size effects and finite size scaling.

## 14 What is finite size scaling and how do we implement it?

At the outset, we recognize that *a finite system can not exhibit phase transition*. Consider a square lattice of size say  $L \times L$ . If the correlation length  $\xi(T) \ll L$ , then for all practical purposes, a finite system can be taken as a good approximation to an infinite system. In other words, our simulations on a finite lattice would give good results if the temperature  $T$  is not close to  $T_c$ , *i.e.* if  $\xi(T) \ll L$ . But when  $T$  is close to  $T_c$ , the correlation length becomes of the order of  $L$ . A finite system thus can not show any divergence of the specific heat or susceptibility; we would get a sort of rounded peaks at best, instead of sharp divergence. Of course as  $L$  becomes larger and larger, the peak would become sharper and sharper. We present in Fig. (5), magnetization per spin,  $|M|/V$  (where  $V = L^2$ ), as a function of  $J/k_B T$  for two dimensional square lattices of size  $L = 2, 4, 8, 16, 32$  and  $64$ . It is clear from the figure that the transition becomes sharper as the system size increases. Similar plots for magnetic susceptibility, are shown in Fig. (6). The peak is rounded and broad for smaller system sizes. As the system size increases we find the peak becomes sharper and its height increases. The behaviour of specific heat as a function of temperature for different system sizes are shown in Fig. (7).<sup>18</sup> We recognize that the correlation length for a finite  $L \times L$  system can at best be  $L$ , when  $T$  is close to  $T_c$ . Hence we can write

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

From this we get

$$|T - T_c| \sim L^{-1/\nu} \quad (79)$$

We can now express the magnetization, magnetic susceptibility, and the specific heat as power laws in  $L$ .

$$\begin{aligned} \frac{|M(T)|}{V} &\underset{T \rightarrow T_c}{\sim} (T_c - T)^\beta &&\underset{L \rightarrow \infty}{\sim} L^{-\beta/\nu} \text{ for } T < T_c \\ \frac{\chi(T)}{V} &\underset{T \rightarrow T_c}{\sim} |T - T_c|^{-\gamma} &&\underset{L \rightarrow \infty}{\sim} L^{\gamma/\nu} \\ \frac{C_V(T)}{V} &\underset{T \rightarrow T_c}{\sim} |T - T_c|^{-\alpha} &&\underset{L \rightarrow \infty}{\sim} L^{\alpha/\nu} \\ |T_c(L) - T_c(L = \infty)| &&&\underset{L \rightarrow \infty}{\sim} L^{1/\nu}. \end{aligned} \quad (80)$$

The above finite size scaling is implemented as follows. For a given  $L$ , find the value of  $T$  at which the specific heat peaks. Call that temperature as  $T_c(L)$ . Calculate, for example  $|M(T)|/V$  at  $T = T_c(L)$  for different values of  $L$ . Plot  $\ln [|M(L)|/V]$  against  $\ln(L)$ . The slope of the best fit straight line would give  $-\beta/\nu$ .

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<sup>18</sup>These plots have been obtained from the computer program ISING.FOR, written and tested by my colleague V. Sridhar, MSD, IGCAR, Kalpakkam. The program can be obtained from him by an e-mail to vs@igcar.ernet.in .

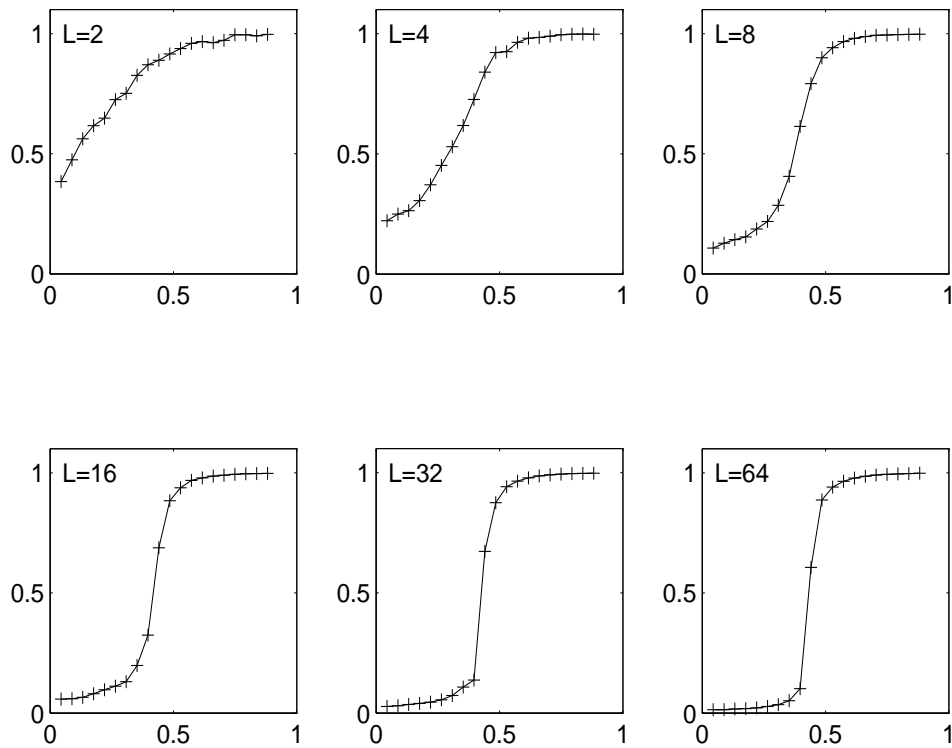


Figure 5: Magnetization per spin ( $|M|/L^2$ ) vs.  $J/k_B T$  for various system sizes  $L$ .

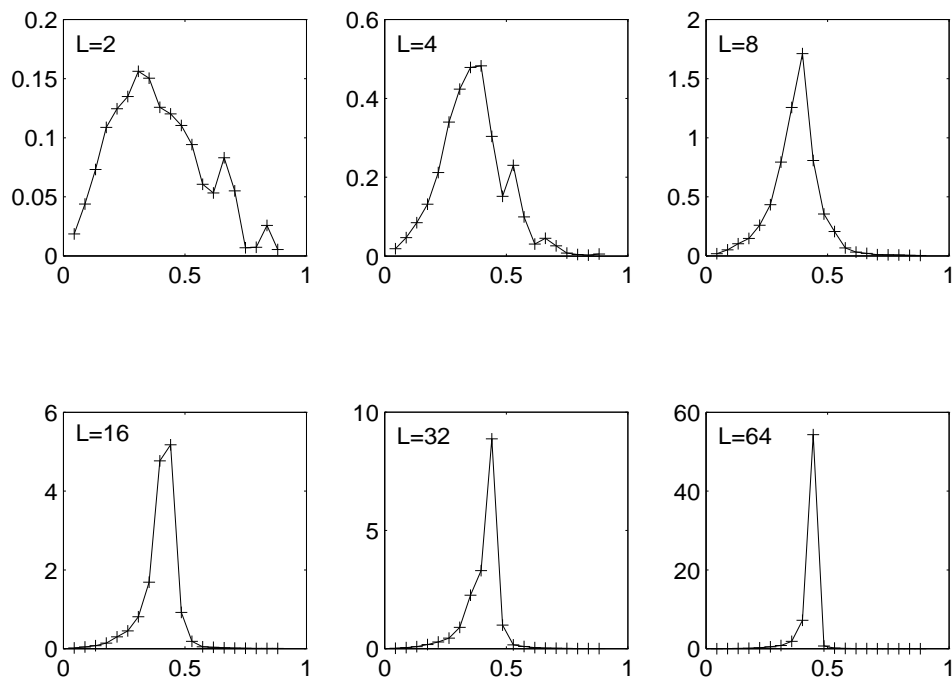


Figure 6: Magnetic susceptibility per spin ( $\chi/L^2$ ) vs.  $J/k_B T$  for various system sizes  $L$ .

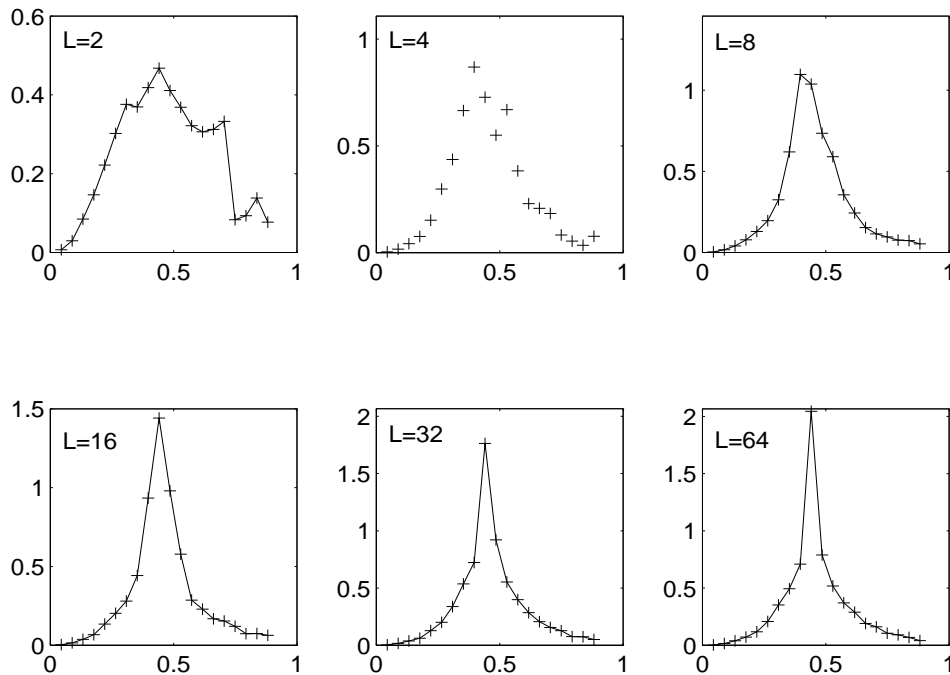


Figure 7: Specific heat per spin ( $C_V/L^2$ ) vs.  $J/k_B T$  for various system sizes  $L$

So far so good; we know now how to assemble, employing random numbers, a Markov chain of microstates each produced from its predecessor through an attempted single flip. What happens when the flipping probability is very very small?<sup>19</sup> The system has a natural tendency to remain stay put in a microstate step after step. Nothing happens to the dynamics for a very long time. But the Monte Carlo clock is ticking all the time. Can such a wastage of computer time be avoided? In other words, can we simulate a very slow dynamics by a fast algorithm? The answer is yes; in the year 1975, Bortz, Kalos and Lebowitz [57] proposed an event-driven algorithm that precisely does this. They called their algorithm the n-fold way.

## 15 What is the n-fold way?

The n-fold way is an event - driven algorithm. We ensure that an event happens at every algorithmic time step. In the context of Ising model simulation, this means that at every MCS we have a new spin configuration. Let  $C_k$  denote the spin configuration at time  $k$ . As we have already explained, this configuration belongs to one of the microstates, say  $C_i$  of the sample space  $\Omega_{CS}$  underlying the closed system. Define  $\lambda_k$  as the probability for the system to persist in its current microstate  $C_i$  for one MCS.  $\lambda_k$  is formally given by  $\lambda_k = W_{i,i} = 1 - \sum_{j \neq i} W_{j,i}$ , where  $W$  is the transition matrix

<sup>19</sup>the flipping probability can become small for several reasons: (a) when the temperature is very low; (b) when the system is in or very close to equilibrium (c) when the system is in a metastable state (d) when the system is very close to a critical state *etc.*

underlying either the Metropolis or the Glauber dynamics. The probability that the system continues to be in the current microstate for the next  $m$  MCS and makes a transition to a different microstate in the  $(m + 1)$ -th step is given by the geometric distribution,

$$p(m) = \lambda_k^m (1 - \lambda_k) \quad (81)$$

The first part of the n-fold way consists of assigning a life time to the microstate  $C_k$ . It is sampled from its distribution, see Eq. (81) by a simple analytical inversion:

$$\tau(C_k) = \frac{\ln \xi}{\ln \lambda_k}, \quad (82)$$

where  $\xi$  is a random number (uniformly distributed in the range 0 to 1); we need the life time in terms of MCS; hence we calculate  $m(C_k) = \lfloor \tau(C_k) \rfloor$  where the RHS denotes the largest integer less than or equal to  $\tau(C_k)$ . Thus in one shot we have advanced the Markov Chain by  $m$  steps:

$$\{\dots, C_k = C_i, C_{k+1} \equiv C_i, C_{k+2} \equiv C_i, \dots, C_{k+m} \equiv C_i, \dots\}.$$

The second part of the n-fold way consists of determining  $C_{k+m+1}$ . This can be obtained in principle from the transition matrix  $W$ . The whole process is repeated and this constitutes the n-fold way of generating a Markov chain of microstates.

I said that  $\lambda_k$  and  $C_k$  can be obtained, in principle, from the transition matrix  $W$ . But in practice, we do not need the transition matrix; also it is not desirable nor feasible to work with the transition matrix since its size is rather large; as we have already seen, even for a small system of Ising spins on a  $10 \times 10$  square lattice, the associated transition matrix would contain some  $10^{60}$  elements! The practical implementation of the n-fold way proceeds as follows. All the spins in the system can be put into  $n$  classes where  $n$  is a small manageable number; Let  $n_i$  be the number of spins in the class  $i$  when the system is in a microstate  $C_k$  at time  $k$ . It is clear  $\sum_{i=1}^n n_i = V$ . What is the value of  $n$  and what are these  $n$  classes? Consider a two dimensional square lattice with periodic boundaries. Let us consider a spin which is oriented *up* ( $\uparrow$ ). Call this the reference spin. The local environment of the reference spin is one of the following five types: (i) all the four nearest neighbours are up; (ii) three nearest neighbours are up and one is down; (iii) two nearest neighbours are up and two are down (iv) one nearest neighbour is up and the other three are down and (v) all the four nearest neighbour spins are down. There are thus five classes when the reference spin is up; When the reference spin is down, there are five more classes, making the total number of classes 10. Thus each of the  $V$  spins in the system belongs to one or the other of these  $n$  classes, hence the name n-fold way, where  $n$  is 10 in the present example. Let us define a local energy for each spin; it is given by the sum of its interaction energies with its four neighbours and with an external field  $B$ . We can flip the spin and calculate the change in the local energy. All the spins belonging to a class have the same local environment, same local energy and cause the same change in energy when flipped. Table (5) presents the ten classes and their common properties. Hence it is quite adequate, see below, if we consider only these ten classes for purpose

Table 5: The ten classes of the 10-fold way for a two dimensional square lattice with periodic boundaries

Class	reference spin	number of nearest neighbour up spins	Local energy	$\Delta E$
1	$\uparrow$	4	$-4J - B$	$+8J + 2B$
2	$\uparrow$	3	$-2J - B$	$+4J + 2B$
3	$\uparrow$	2	$-B$	$+2B$
4	$\uparrow$	1	$+2J - B$	$-4J + 2B$
5	$\uparrow$	0	$+4J - B$	$-8J + 2B$
6	$\downarrow$	4	$+4J + B$	$-8J - 2B$
7	$\downarrow$	3	$+2J + B$	$-4J - 2B$
8	$\downarrow$	2	$+B$	$-2B$
9	$\downarrow$	1	$-2J + B$	$+4J - 2B$
10	$\downarrow$	0	$-4J + B$	$+8J - 2B$

of obtaining  $\lambda_k$  and  $C_{k+m+1}$ . Let  $\Delta E(i)$  be the increase in energy when a spin of the  $i$ -th class is flipped, see the last column of Table (5). This quantity is the same for all the spins belonging to the same class. Let  $p_i$  be the probability of accepting a spin flip in the  $i$ -th class. It is given by,

$$p_i = \begin{cases} \min\left(1, \exp\left[-\beta\Delta E(i)\right]\right) & \text{for Metropolis} \\ \left(1 + \exp\left[\beta\Delta E(i)\right]\right)^{-1} & \text{for Glauber} \end{cases} \quad (83)$$

The value of  $p_i$  depends on whether we use the Metropolis dynamics or the Glauber dynamics. The probability of selecting a class is  $n_i/V$ . Thus the probability of flipping a spin in the system is given by  $q = \sum_{i=1}^{10} n_i p_i / V$ . This immediately gives us  $\lambda_k = 1 - q$ . Once we know  $\lambda_k$  we can sample a life time  $m$  from the geometric distribution as described earlier. We then select a class from the distribution  $\rho_i = n_i p_i / (qV) : i = 1, 10$ ; then a spin is chosen randomly from the selected class and flipped to give  $C_{k+m+1}$ . Calculate the set  $\{n_j : j = 1, 10\}$  for the new configuration. This kind of book-keeping is the time consuming part of the n-fold way; however the changes are confined

to the class indices of the flipped spin and its four nearest neighbours. These changes can be carried out employing simple rules: If the flip is from up ( $\uparrow$ ) to down ( $\downarrow$ ), the class of the flipped spin increases by 5 while that of each of its four nearest neighbours increases by 1. If the flip is from down ( $\downarrow$ ) to up ( $\uparrow$ ), then the class of the flipped spin decreases by 5 and that each of the four nearest neighbours decreases by 1. Having updated the array  $\{n_j\}$  and indexed each spin by its class, we iterate the entire process and get a Markov chain of microstates. The macroscopic properties are calculated from the chain in the usual way described earlier.

Alternately we can store the life times  $\{\tau(C_i)\}$  of each of the microstates belonging to the Markov chain  $\{C_0, C_1, C_2, \dots\}$  where a microstate  $C_i$  is obtained from  $C_{i-1}$  through a spin flip in the n-fold way. While averaging we weight each microstate with its corresponding life time:

$$\langle O \rangle = \lim_{N \rightarrow \infty} \bar{O}_N = \frac{\sum_{i=1}^N O(C_i) \tau(C_i)}{\sum_{i=1}^N \tau(C_i)} \quad (84)$$

Instead of sampling the life time from its geometric distribution one can use the average life time of a microstate  $C_i$ , given by,

$$\bar{\tau}(C_i) = \frac{1 - q(C_i)}{q(C_i)} \quad (85)$$

and employ it as weight while averaging. This completes the discussion on the n-fold way.

The n-fold way is a particular case of a more general technique called the Monte Carlo with Absorbing Markov Chain (MCAMC) [58]. I shall not discuss these techniques here and instead refer you to the beautiful recent review article of Novotny [59].

The n-fold way is a fast algorithm that realizes a slow dynamics. As I said earlier, the dynamics of an equilibrium or near equilibrium system is slow; at very low temperatures the dynamics is slow; many a times the system gets stuck in a metastable state which drastically slows down the dynamics. There exists another phenomenon for which the Metropolis/Glauber dynamics is very very slow: when the system is close to a critical state. This is called critical slowing down - an important issue in the statistical mechanics of continuous phase transition. To this we turn our attention below.

## 16 What do we mean by critical slowing down?

A problem with Monte Carlo simulation is that statistical error decreases with increase of sample size  $N$  only as  $N^{-1/2}$ . This means that to get the numbers to just one extra decimal accuracy, we need to increase the sample size by a factor of hundred. Things are much worse. The error reduction as  $N^{-1/2}$  happens only if the members of the ensemble are independent. But successive Monte Carlo configurations generated by Metropolis rejection technique are usually correlated [60]. Such correlations increase the statistical error. Let us see how this comes about. First notice that  $\bar{x}_N$  given by Eq. (72) is a random variable. The mean of  $\bar{x}_N$  is  $\langle x \rangle$ . The variance of  $\bar{x}_N$  is formally



given by,

$$\sigma^2(\bar{x}_N) = \frac{\sigma^2(x)}{N} \left[ 1 + 2 \sum_{k=1}^{N-1} \left( 1 - \frac{k}{N} \right) \gamma_k \right], \quad (86)$$

where the correlation  $\gamma_k$  is given by

$$\gamma_k = \frac{\langle x_i x_{i+k} \rangle - \langle x_i \rangle \langle x_{i+k} \rangle}{\sigma^2(x)}. \quad (87)$$

In writing the above, we have assumed that the sequence  $x_1, x_2, \dots, x_N$  is stationary. The correlations are estimated from the Monte Carlo Markov chain as,

$$\gamma_k = \frac{N}{N-k} \frac{\sum_{i=1}^{N-k} (x_i - \bar{x}_N)(x_{i+k} - \bar{x}_N)}{\sum_{i=1}^N (x_i - \bar{x}_N)^2} \quad (88)$$

Let us now define the so called integrated correlation time as,

$$\tau^* = \sum_{k=1}^{N-1} \left( 1 - \frac{k}{N} \right) \gamma_k. \quad (89)$$

We can now express the Monte Carlo result as

$$\bar{x}_N \pm \frac{\sigma(x)}{\sqrt{N}} \times \sqrt{1 + 2\tau^*} \quad (90)$$

It is clear that if we have an uncorrelated data set,  $\tau^* = 0$  and the expression for the statistical error given by Eq. (90) reduces to that given by Eq. (75). The value of  $\tau^*$  is a measure of the number of MCSS we need to skip for getting a microstate uncorrelated to the present microstate, after the system has equilibrated. The important point is that the correlation time  $\tau^*$  diverges as  $T \rightarrow T_C$ ; this means that finite sample Monte Carlo estimates of the macroscopic properties of the system become unreliable when the temperature of the system is very close to the critical value. The divergence of  $\tau^*$  as  $T \rightarrow T_C$  is called *critical slowing down*.

Thus we find that the statistical error depends on the correlation time. Is there a way to estimate the statistical error that does not require explicit calculation of the correlation function  $\gamma_k$ ? The answer is *yes* and we shall briefly discuss the so called blocking technique, which is essentially a real space renormalization group technique applied to the one dimensional discrete space of MCSS.

## 17 What is a blocking technique ?

For a lucid account of the blocking technique, see the paper by Flyvbjerg and Petersen [61]. I shall confine myself to discussing the implementation of the technique. We are given a set of correlated data,

$$\Omega_0 = \{x_1^{(0)}, x_2^{(0)} \dots x_N^{(0)}\}. \quad (91)$$

How do we calculate the statistical error associated with the sample mean,

$$m = \frac{1}{N} \sum_{i=1}^N x_i^{(0)} ? \quad (92)$$

Let  $\hat{\Omega}_0$  denote the number of data points in the set  $\Omega_0$ . Note  $\hat{\Omega}_0 = N$ . Calculate the sample variance given by,

$$S^2(\Omega_0) = \frac{1}{\hat{\Omega}_0} \sum_{i=1}^{\hat{\Omega}_0} (x_i^{(0)})^2 - \left( \frac{1}{\hat{\Omega}_0} \sum_{i=1}^{\hat{\Omega}_0} x_i^{(0)} \right)^2. \quad (93)$$

Let  $\epsilon_0^2 = S^2(\Omega_0)/(\hat{\Omega}_0 - 1)$ . Then transform the data to another set of data  $\Omega_1 = \{x_1^{(1)}, x_2^{(1)}, \dots, x_{\hat{\Omega}_1}^{(1)}\}$  which is half as large, *i.e.*  $\hat{\Omega}_1 = \hat{\Omega}_0/2 = N/2$ . In general the equations that relate the data set  $\Omega_k$  to  $\Omega_{k-1}$  are given by,

$$x_i^{(k)} = \frac{x_{2i-1}^{(k-1)} + x_{2i}^{(k-1)}}{2} \quad i = 1, 2, \dots, \hat{\Omega}_k,$$

$$\hat{\Omega}_k = \frac{\hat{\Omega}_{k-1}}{2} \quad k = 1, 2, \dots. \quad (94)$$

Calculate  $\epsilon_k^2$  from the data set  $\Omega_k$ . We get a string of numbers  $\epsilon_0^2, \epsilon_1^2, \epsilon_2^2, \dots$ . These numbers would increase with iterations and eventually reach a constant value within statistical fluctuations beyond certain number of iterations. In other words  $\epsilon_{l+k}^2 = \epsilon_l^2$  for all  $k \geq 1$  and for some  $l$ . In any case the iteration has to stop when the number of data points in the set becomes 2. The desired statistical error (one sigma confidence) of the calculated mean  $m$  is given by  $\epsilon_l$ .

An immediate issue of concern is the implications of critical slowing down to Monte Carlo simulation. The Metropolis dynamics slows down for  $T$  close to  $T_C$ . The closer  $T$  is to  $T_C$ , the slower does the dynamics become. As we have already seen, this builds up temporal correlations and Monte Carlo estimates of the macroscopic properties become unreliable. Let the divergence of the integrated correlation time  $\tau^*$  with  $T$  be expressed as

$$\tau^*(T) \underset{T \rightarrow T_C}{\sim} |T - T_c|^{-\Delta} \quad (95)$$

We can use finite size scaling arguments and write

$$\tau^*(L) \underset{L \rightarrow \infty}{\sim} L^z \quad (96)$$

where  $z = \Delta/\nu$ . The dynamical critical exponent  $z$  is greater than unity; in fact, for the local update algorithms like the Metropolis, the value of  $z$  is nearly 2 and above. This tells us that for  $T$  close to  $T_C$ , the Monte Carlo error becomes large especially when the system size  $L$  is large. This is indeed a major drawback of the Metropolis Monte Carlo technique. Fortunately this problem of critical slowing down can be very efficiently overcome by employing the so called cluster algorithms, wherein, a large cluster of spins is updated in a single step. Swendsen and Wang [62] derived a cluster algorithm by mapping the spin problem to a bond percolation problem, based on the work of Kasteleyn and Fortuin [63] and developed by Coniglio and Klein [64].

## 18 What is percolation ?

Percolation is a familiar term we use in the context of brewing of coffee: Hot water injected at one end percolates through packed coffee powder and is collected at the other end. In fact percolation was introduced in the year 1957 by Broadbent and Hammersley [65] as a model for the transport of liquid through a porous medium, spread of a disease in a community and other related phenomenon. For an excellent early discussion on percolation see the little book by Hammersley and Handscomb listed under [39]. Let us abstract the notion and consider  $N \times N$  square lattice of sites. Let  $0 \leq p \leq 1$  denote the probability of placing a bond between a pair of nearest neighbour sites. Carry out the following experiment. Select a pair of nearest neighbour sites; select a random number  $\xi$ ; if  $\xi \leq p$  place a bond between the selected pair. Otherwise do not put a bond. Carry out this operation independently on all the nearest neighbour pairs of sites in the lattice. When two nearest neighbour sites are connected by a bond they form a cluster of two sites. When another site gets bonded to one of these two sites then the cluster is of three sites, and so on. At the end, you will have clusters of different sizes. If  $p$  is small, typically, we expect the lattice to contain only small clusters. If  $p$  is close to unity, there will exist a cluster that extend from one end of the lattice to the other. Such a cluster is said to span the lattice. It is called a spanning cluster. Let  $P_L(p)$  denote the probability that a spanning cluster exists on an  $L \times L$  square lattice. For a given  $L$  it is clear that

$$P_L(p) = \begin{cases} 0 & \text{for } p \rightarrow 0, \\ 1 & \text{for } p \rightarrow 1. \end{cases} \quad (97)$$

In fact, we find that the percolation probability  $P_L(p)$  changes sharply from zero to unity at a critical value of  $p = p_C$ . The transition becomes sharper as  $N \rightarrow \infty$ . In other words,

$$P_L(p) \underset{L \rightarrow \infty}{\sim} \begin{cases} 0 & \text{for } p < p_C, \\ 1 & \text{for } p \geq p_C. \end{cases} \quad (98)$$

Thus, there is a geometric phase transition at  $p = p_C$ . The value of  $p_C$  is 0.5 for a two dimensional square lattice in the limit  $N \rightarrow \infty$ . Figure (8) depicts  $P_L(p)$  versus  $p$  for various values of  $L$ . We can clearly see that the transition becomes sharper with increasing system size. Even for  $L = 50$  the transition is already quite sharp. The statistical error in any of the data points plotted in Fig. (8) does not exceed a maximum of  $\pm 5\%$ .

What we have discussed above is called bond percolation, which is of relevance to us in the context of discussions on Swendsen-Wang algorithm. There is also site percolation. For more on percolation read the delightful little book by Stauffer [66]. The most interesting feature of the phenomenon of percolation in the context of our present discussion is that unlike thermal transition, the geometric percolation transition is free from critical slowing down. Every sweep over the lattice generates an independent configuration and hence the correlation time is exactly zero. This is precisely what Swendsen-Wang algorithm makes use of.

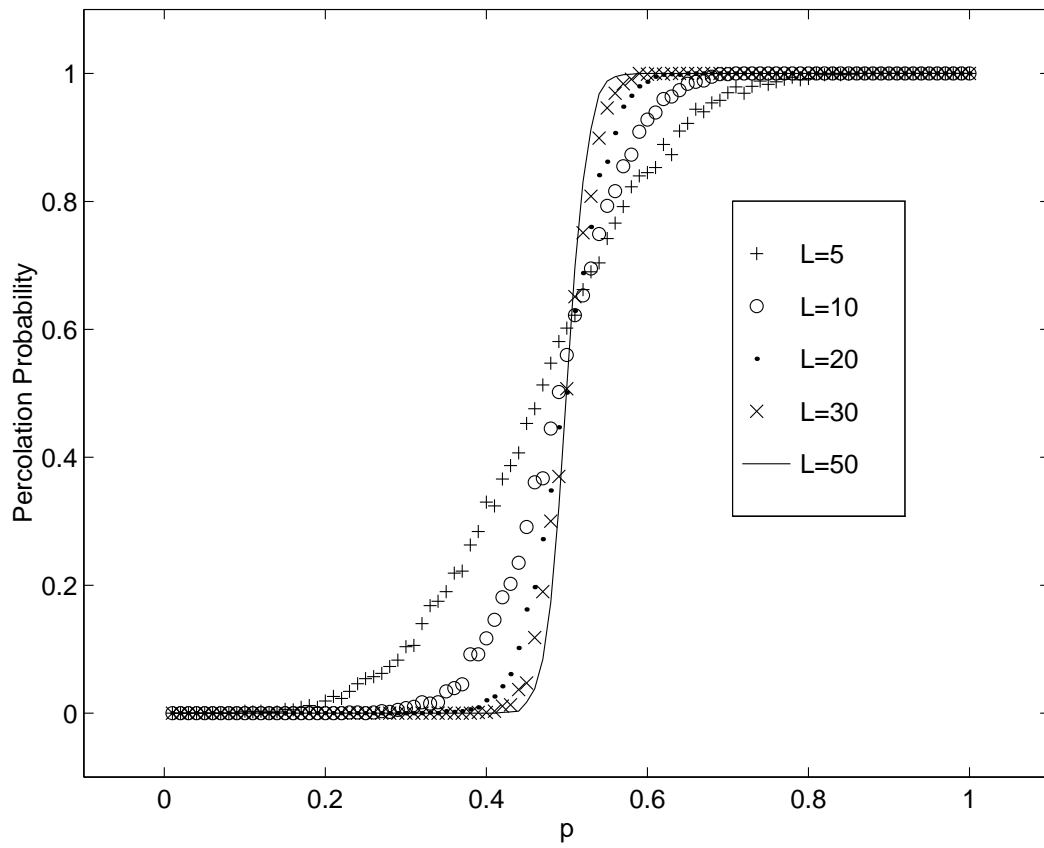


Figure 8:  $P_L(p)$  versus  $p$  for bond percolation. The statistical error is less than 5% for all the points.

## 19 What is Swendsen-Wang algorithm? How do we implement it?

In the Swendsen-Wang algorithm we start with a spin configuration say  $\mathcal{C}$ . Select two neighbouring sites and call them  $(i, j)$ . If  $S_i = S_j$ , then the bond connecting the sites  $i$  and  $j$  becomes eligible for occupation. Such a bond is often referred to as *satisfied* bond. If  $S_i \neq S_j$ , then the bond is not a satisfied bond and hence is never occupied. A satisfied bond is occupied with a probability  $p$ , to be specified later. This is carried out as follows. Select a random number (uniformly distributed between 0 and 1). If it is less than  $p$  occupy the (satisfied) bond. Otherwise do not occupy the bond. Carry out this process for each pair of nearest neighbour sites in the lattice. At the end you will have several clusters of sites connected by occupied bonds. Let us call these Kastelyn - Fortuin - Coniglio - Klein (KF-CK) clusters. Figure (9) depicts an example of KF-CK clusters on a  $10 \times 10$  square lattice. Filled circles denote the up spins and open circles denote the down spins. Occupied bond is denoted by line connecting the neighbouring ‘like’ spins. The clusters are shaded and the spanning cluster is shaded dark. We have used a value of  $J/k_B T = 0.6$ . The critical value,  $J/k_B T_C$ , is 0.4487. I must emphasize that these bonds are fictitious; there is no energy associated with them. They only

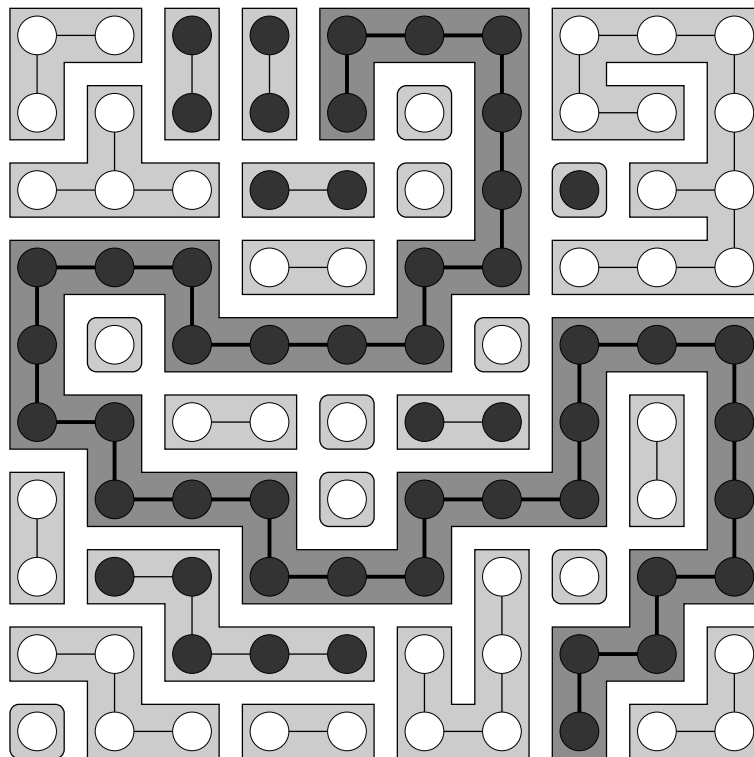


Figure 9: Kastelyn - Fortuin - Coniglio - Klein (KF-CK) clusters on a  $10 \times 10$  square lattice, for the Ising spin system. Filled circles denote up spins; open circles denote down spins. Satisfied and occupied bond is denoted by line connecting nearest neighbour ‘like’ spins. The spin-spin interaction strength  $J/k_B T$  is taken as 0.6. The critical value  $J/k_B T_C$  is 0.4407 for a square lattice. The clusters are shaded. Spanning cluster is shaded dark.

serve to define a cluster. Having thus formed the KF-CK clusters, assign to each cluster a spin variable  $+1$  or  $-1$  independently, randomly and with equal probability. All the spins in a cluster acquire the spin value assigned to the cluster. Remove the fictitious bonds. What you get is a new configuration of spins. Start all over again the process of constructing fresh KF-CK clusters. In other words iterate the whole process and generate a chain of spin configurations; the process obeys detailed balance and is ergodic; hence the configurations in the asymptotic part of the Markov Chain constitute a canonical ensemble of microstates at the desired temperature. Note that temperature enters into picture through the bonding probability  $p = p(T)$ .

### 19.1 What is the appropriate value of the bonding probability $p$ for a given $T$ ?

The interaction energy associated with a pair of nearest neighbour spins is  $\epsilon_{i,j} = -JS_iS_j$ . The energy is  $-J$  when the two spins are aligned and  $+J$ , when not. For convenience, let us set the minimum of the energy scale at zero by defining  $\epsilon_{i,j} = -J(S_iS_j - 1)$ . The Hamiltonian for the spin system can now be written as

$$H(\mathcal{C}) = -J \sum_{\langle i,j \rangle} \left[ S_i(\mathcal{C}) S_j(\mathcal{C}) - 1 \right] \quad (99)$$

and the total energy ranges from 0 to  $+2JN_E$  where,  $N_E$  is the total number of pairs of nearest neighbour spins in the lattice. In the above expression for the Hamiltonian, let us carry out the sum over pairs of nearest neighbour ‘like’ spins and of nearest neighbour ‘unlike’ spins separately and get,

$$H(\mathcal{C}) = 2J \left[ N_E - B(\mathcal{C}) \right] \quad (100)$$

where  $B$  is the number of satisfied bonds (number of pairs of nearest neighbour ‘like’ spins in the spin configuration (microstate)  $\mathcal{C}$ ). The canonical partition function is then given by,

$$\begin{aligned} Z(\beta) &= \sum_{\mathcal{C}} \exp \left[ -2\beta J (N_E - B) \right] \\ &= \sum_{\mathcal{C}} q^{N_E - B} \end{aligned} \quad (101)$$

where  $q = \exp(-2\beta J)$ . Let us define  $p = 1 - q$ . We can select randomly  $b$  bonds from amongst  $B$  satisfied bonds and occupy them. Number of ways of doing this is given by  $\Omega(b, B) = B!/[b!(B-b)!]$ . If we interpret  $p$  as the probability of occupying a satisfied bond, then the probability of having  $b$  occupied bonds in a given a spin configuration  $\mathcal{C}$  is  $P(b, B(\mathcal{C})) = \Omega(b, B(\mathcal{C})) p^b q^{B(\mathcal{C})-b}$ . Notice that  $\sum_{b=0}^B P(b, B) = (p+q)^B = 1$ . Then the canonical partition function can be written in a suggestive form, given by,

$$\begin{aligned} Z(\beta) &= \sum_{\mathcal{C}} q^{N_E - B(\mathcal{C})} (p+q)^{B(\mathcal{C})} \\ &= \sum_{\mathcal{C}} q^{N_E - B} \sum_{b=0}^B \Omega(b, B) p^b q^{B-b} \end{aligned}$$

$$= \sum_{\mathcal{C}} \sum_{b=0}^{B(\mathcal{C})} \Omega(b, B) p^b q^{N_E - b}. \quad (102)$$

From the above it is clear that the correct value of the bonding probability that must be used in the Swendsen-Wang cluster algorithm is given by

$$p = 1 - q = 1 - \exp(-2\beta J). \quad (103)$$

We can construct the same partition sum in a different way. Start with the lattice sans Ising spins. Put randomly  $b$  bonds, each connecting a pair nearest neighbour sites. Number of ways of doing this is  $\Omega(b, N_E) = N_E!/[b!(N_E - b)!]$ . The probability of constructing a single bond is taken as  $p = 1 - \exp(-2\beta J)$ . We call the lattice with a specific arrangement of  $b$  bonds as a graph  $G$ . Let  $N_c(G)$  denote the number of clusters in the graph  $G$ . Note that all the graphs having the same number of bonds need not have the same number of clusters. Consider now the graph  $G$  having vertices equal to the number of lattice sites or Ising spins,  $N_E$  edges (equal to the number of nearest neighbour pairs of spins) and  $b$  bonds. We can now decorate the vertices of  $G$  with Ising spins. While doing so we would like to be consistent so that the bonds we have placed in the lattice are occupied bonds. How many Ising spin configurations are compatible with the graph  $G$ ? It is clear that all the vertices in a given cluster must hold 'like' spins (all 'up'  $\uparrow$  or all 'down'  $\downarrow$ ). Hence there are  $2^{N_c(G)}$  spin configurations compatible with  $G$ . The statistical weight of the graph  $G$  is  $p^{b(G)} q^{N_E - b(G)} 2^{N_c(G)}$ . We can calculate such weights for all the graphs for a given  $b$  and then for all  $b$  ranging from 0 to  $N_E$ . The canonical partition function, see Eq. (102), can now be written equivalently as a sum of the weights of all possible graphs and is given by,

$$Z(\beta) = \sum_G p^{b(G)} q^{N_E - b(G)} 2^{N_c(G)} \quad (104)$$

Thus the interacting Ising spin problem has been mapped on to a noninteracting correlated random bond percolation problem, see [62, 63, 64, 66, 67]. The spontaneous magnetization in the Ising model corresponds to the percolation probability in the percolation problem; the magnetic susceptibility is analogous to the average number of spins per KF-CK cluster; energy and specific heat are like the number of occupied bonds and its fluctuations; the correlation length in Ising system corresponds to the linear size of cluster in the correlated random bond percolation model. Purely from a practical point of view the Swendsen-Wang technique based on KF-CK clusters has emerged as a powerful tool in Monte Carlo simulation of large systems. For a  $512 \times 512$  lattice system the value of  $\tau^*$  can be made as small as ten which is some ten thousand times smaller than that for the single flip Metropolis algorithm. This completes the discussion on Swendsen-Wang algorithm.

For implementing the cluster update Monte Carlo we need a fast algorithm to identify the clusters. An ingenious technique of cluster counting was proposed by Hoshen and Kopelman [68]. The technique is straight forward, easy to implement and quite fast.

## 20 What is the basis of the Hoshen-Kopelman cluster counting algorithm?

The general principle of the Hoshen-Kopelman algorithm is as follows. Consider an arbitrary dimensional lattice with arbitrary coordination number. The lattice sites are occupied by the relevant species - like atoms or spins. Lattice sites linked by suitably defined neighbourhood conditions constitute a cluster. The linkage can be due to presence of same type of atoms on neighbouring sites (site percolation) or the presence of a bond between two neighbouring sites (bond percolation) or any other definition dictated by the nature of the problem under investigation. In a lattice there can be many clusters. Ideally one can assign distinct labels to the clusters and associate with these labels the corresponding cluster sizes. A straight forward procedure would be to scan the lattice row by row and then layer by layer. The first time we hit a ‘relevant’ site we assign a label, say 1 to the site and associate with the label a number  $LL(1) = 1$ . If the next site in the row is linked to this site through the neighbourhood relation, then it is assigned with the same label and the array  $LL$  is updated,  $LL(1) = LL(1) + 1$  signifying that the cluster in its process of ‘growth’ has acquired one more site. On the other hand if the next site is not linked to the site previously examined, then it is assigned with a new label, say 2 and  $LL(2) = 1$ . The process of labelling the sites and updating the array  $LL$  is continued. A conflict starts when we go down the rows or the layer; we come across a site, say X, whose neighbouring sites to which this site is linked carry different labels, say  $l_1, l_2, l_3, \dots, l_n$ . Physically this means that the present site under examination is the link through which the clusters seemingly carrying different labels, coalesce. In other words, the different clusters coalesce at this site to form a big cluster. Therefore we would like to assign a single label to all the sites belonging to the coalesced big cluster. This would mean that we should go over all the previous sites examined and relabel them; the associated  $LL$  also should be changed accordingly. In other words, all the sites carrying the labels  $(l_1, l_2, \dots, l_n)$  should be assigned a common label, say  $l = l_k = \min(l_1, l_2, \dots, l_n)$  where  $1 \leq k \leq n$ . Also we must set  $LL(l) = LL(l_1) + LL(l_2) + \dots + LL(l_n) + 1$ . This kind of backward relabelling is the most time consuming part of the algorithm. Hoshen and Kopelman avoided the backward relabelling completely. The current site X under examination is assigned the label  $l = l_k$ ; However we set  $LL(l_i) = -l, \forall i = 1, n$  and  $i \neq k$ . Therefore  $LL(j)$  denotes the size of the cluster only if it is positive. If it is negative then  $-LL(j)$  denotes the label of the cluster it would start belonging to from now. A label  $k$  is proper if  $LL(k) > 0$ ; if  $LL(k) < 0$  then the label  $k$  is called improper. When we come across a site whose neighbours carry improper labels then by examining the corresponding entries in the array  $LL$ , we can find the proper label. All these issues would become clear when we consider a concrete example, in bond percolation.

Consider a two dimensional square lattice. The aim is to assign a cluster label to each site so that at the end of scanning we have sites having the same label belonging to a cluster; we shall have different clusters having distinct cluster labels. To this end we decide to scan the lattice sites from left to right in a row and then go to the next row below. We start with the first row, see Fig. 10. We assign cluster label ‘1’ to the first site and set  $LL(1) = 1$ . The next site is bonded to the previous site; hence



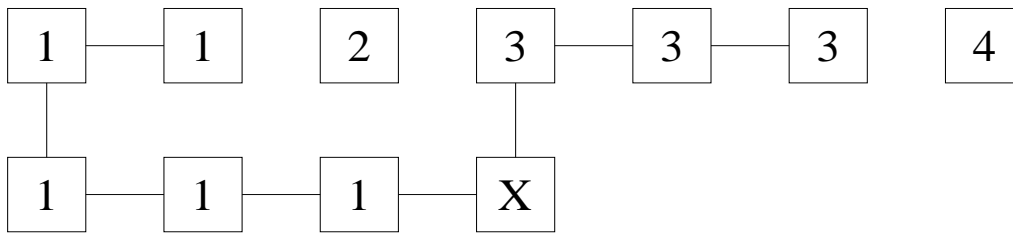


Figure 10: Hoshen-Kopelman cluster counting algorithm: We have to assign a cluster label to the site marked X. Before labelling the site X, we have  $LL(1) = 5$ ,  $LL(2) = 1$ ,  $LL(3) = 3$ ,  $LL(4) = 1$ . The conflicting labels are  $l_1 = 1$  and  $l_2 = 3$ . We select the lower of the two labels, namely  $l_1 = 1$  as label for the site X. We update  $LL(1) = LL(1) + LL(3) + 1 = 5 + 3 + 1 = 9$ . We set  $LL(3) = -l_1 = -1$ . Thus the label '3' has become improper. The other entries in the array  $LL$  remain the same. The two clusters 1 and 3 coalesce.

we assign the same cluster label '1' to this site and update  $LL(1) = LL(1) + 1$ . The next site (the third site in the first row) is not bonded to the previous site; hence we assign the next new label '2' to this site and set  $LL(2) = 1$ . We proceed in the same fashion assigning labels and updating the  $LL$  array. We complete the scanning of the first row. We find, see Fig. 10, the first row assigned with labels 1 – 4; Also  $LL(1) = 2$ ,  $LL(2) = 1$ ,  $LL(3) = 3$ , and  $LL(4) = 1$ . Then we start scanning the second row. We consider the first site in the second row and check if it is bonded to the site at its top. If yes, then it assigned with the cluster label of the top site. If not, it is assigned with the next new cluster label. In Fig. (10) the first site in the second row is assigned with the cluster label '1'. While scanning the second row, we need to check if the site under consideration is bonded to the site at its left (the previous site examined) and/or to the site at its top. If only one of these two sites is bonded to the current site then cluster labelling and updating of the array  $LL$  is carried out exactly the same way as described earlier. You may come across a situation when the current site is bonded to both the sites (site at left and at top) with labels, say  $l_1$  and  $l_2$ . If  $l_1 \neq l_2$ , there is a label conflict. What is the cluster label we should assign to the current site,  $l_1$  or  $l_2$ ? Fig. (10) illustrates an example where the current site is marked X. Physically this conflict implies that what we have considered until now as two different clusters are in actuality one and the same. The current site is the link. Such a cluster label conflict can be resolved by a second pass or by a backward relabelling scheme. But then this would be time consuming. The ingenuity of the Hoshen-Kopelman algorithm lies in the fact it avoids completely the second pass or backward relabelling. To understand the algorithm see Fig. (10). The current site marked X is linked to the site at its left (with label  $l_1 = 1$ ) and also to the site at its top (with label  $l_2 = 3$ ). Thus  $l_1 (= 1)$  and  $l_2 (= 3)$  are the conflicting labels. Let  $L = \min(l_1, l_2)$ . In the example of Fig. (10),  $L = l_1 = 1$ . We assign the label  $L = l_1 = 1$  to the current site, update  $LL(L) = LL(L) + LL(l_2) + 1$  and set  $LL(l_2) = -L$ . In the example considered, the current site is assigned label '1';  $LL(1) = 5 + 3 + 1 = 9$  and  $LL(3) = -1$ . The label 3 has now become improper since  $LL(3)$  is negative. Before labelling the site X, the clusters having labels '1' and '3' were distinct. While examining the site X we discover that the two clusters are linked

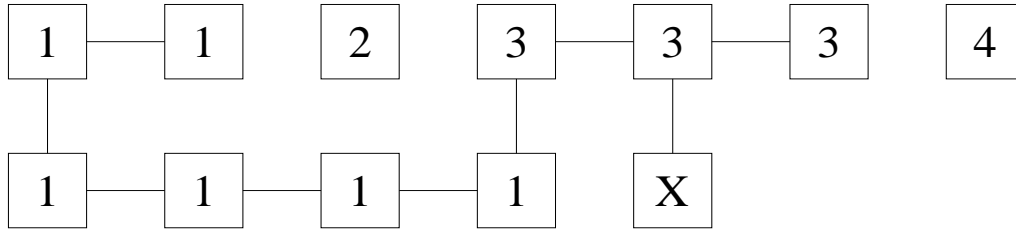


Figure 11: Hoshen-Kopelman cluster counting algorithm: We have to assign a cluster label to the site marked X. Before labelling the site X, we have  $LL(1) = 9$ ,  $LL(2) = 1$ ,  $LL(3) = -1$ ,  $LL(4) = 1$ . The site X is bonded to the site above with label '3'. Hence we should assign label '3' to the site X. But label '3' is improper since  $LL(3) = -1$ . We then check the label '1'. It is proper since  $LL(1) = 9 > 0$ . Hence the root label of 3 is 1. *i.e.*  $l_3^R = 1$ . We assign label '1' to the site X and update  $LL(1) = LL(1) + 1 = 9 + 1 = 10$ .

through the site X and hence are not distinct. The two clusters, so to say, coalesce. We give the lower cluster label ( $L = 1$ ) to the coalesced cluster, store in the array  $LL(L)$  the size of the coalesced cluster and declare the cluster label 3 as improper by setting  $LL(3) = -1$ .  $LL(3)$  takes the role of a pointer. After labelling the current site and updating the LL array we continue with the scanning. There may arise a situation when the current site is bonded to a site with an improper label, say  $l_1$ . In other words we find  $LL(l_1) = -l_2 < 0$ . In such a situation we examine if  $l_2$  is a proper label. If yes, then the root label corresponding to  $l_1$  is  $l_2$ . Let us denote the root label of  $l_1$  by the symbol  $l_{l_1}^R$ . Thus  $l_{l_1}^R = l_2$ . If on the other hand we find that  $l_2$  is again an improper label with  $LL(l_2) = -l_3 < 0$ , the search for the root label continues until we get a proper root label  $l_{l_1}^R$ . This situation is depicted in Fig. (11). The site marked X is bonded to the site above with label  $l_1 = 3$ . But the label  $l_1 = 3$  is an improper label since  $LL(l_1 = 3) = -l_2 = -1 < 0$ . The label  $l_2 = 1$  is a proper label and hence  $l_3^R = 1$ . Hence we assign the label 1 to the current site, update  $LL(1) = LL(1) + 1 = 10$ . If there arises a cluster label conflict, it is resolved exactly the same way as described earlier except that the resolution is done after searching for the corresponding proper root labels. A situation of this type is depicted in Fig. (12). We have to assign a cluster label to the site marked X. Before labelling the site X, we have  $LL(1) = 10$ ,  $LL(2) = 1$ ,  $LL(3) = -1$ ,  $LL(4) = 3$ ,  $LL(5) = -4$ ,  $LL(6) = 5$ . The conflicting labels are  $l_1 = 6$  and  $l_2 = 5$ . The label  $l_1 = 6$  is a proper label. The label  $l_2 = 5$  is however an improper label, since  $LL(5) = -4$ . Hence we examine the label 4. It is proper since  $LL(4) = 3 > 0$ . Therefore  $l_{l_1}^R = l_6^R = 6$  and  $l_{l_2}^R = l_5^R = 4$ . We assign the smaller label '4' to the site, X update  $LL(4) = LL(4) + LL(6) + 1 = 3 + 5 + 1 = 9$ , and set  $LL(6) = -5$ . The label '6' has now become improper. In this fashion we complete scanning the entire cluster. In the end we shall have an array  $\{LL(i) : i = 1, 2, \dots\}$ . The positive entries in this array denote the sizes of the different clusters present in the system. The Hoshen-Kopelman algorithm is quite general and can be easily employed to carry out cluster counting in a general  $d$ - dimensional lattice with arbitrary coordination number. The boundary conditions can also be easily taken care of in cluster counting. In the examples discussed

above we have not considered any boundary conditions. Babalievski [69] has extended the Hoshen-Kopelman algorithm to random and aperiodic lattices. Hoshen, Berry and Minser [70] have proposed an enhanced Hoshen-Kopelman algorithm that enables efficient calculation of cluster spatial moments, radius of gyration of each cluster, cluster perimeter *etc.* Indeed more recently Ahmed Al-Futaisi and Patzek have extended the Hoshen-Kopelman algorithm to non-lattice environments [71]. We can say that the Swendsen-Wang cluster algorithm coupled with the Hoshen-Kopelman counting constitutes a major step forward in Monte Carlo simulation.

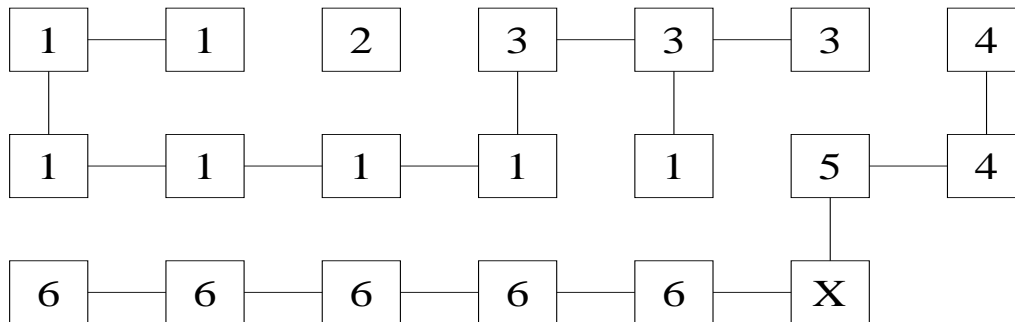


Figure 12: Hoshen-Kopelman cluster counting algorithm: We have to assign a cluster label to the site marked X. Before labelling the site X, we have  $LL(1) = 10$ ,  $LL(2) = 1$ ,  $LL(3) = -1$ ,  $LL(4) = 3$ ,  $LL(5) = -4$ ,  $LL(6) = 5$ . The conflicting labels are  $l_1 = 6$  and  $l_2 = 5$ . The label  $l_1 = 6$  is a proper label since  $LL(6) = 5$ . The label  $l_2 = 5$  is an improper label, since  $LL(5) = -4$ . Hence we examine the label 4. The label ‘4’ is a proper label since  $LL(4) = 3 > 0$ . Therefore the root labels are  $l_6^R = 6$  and  $l_5^R = 4$ . We assign label ‘4’ (the smaller of the two root labels) to the site X, update  $LL(4) = LL(4) + LL(6) + 1 = 3 + 5 + 1 = 9$ , and set  $LL(6) = -5$ . The label ‘6’ has become improper.

## 21 What are the improvements to the Swendsen-Wang cluster algorithm?

### 21.1 Wolff algorithm

In the Swendsen-Wang algorithm, all the clusters, big or small are grown and updated. Small clusters do not influence the critical slowing down and hence computing efforts toward growing them are a waste. This is somewhat eliminated in the algorithm proposed by U. Wolff [72]. A site, say ‘ $i$ ’ is chosen randomly and a single cluster is grown from it as follows. If a neighbouring spin has the same orientation then the bond to it is ‘satisfied’ and hence is occupied with a probability  $p$  given by Eq. (103): Select a random number; if it is less than  $p$  occupy the bond; if not do not occupy. This process is repeated on all the neighbours of the site  $i$  and further on all the neighbours of the new sites that get bonded. The set of bonded sites constitutes a cluster and the cluster grows. The growth of the cluster would eventually terminate. Then all the spins in the cluster are flipped; the bonds are removed; we have a new spin

configuration. The whole process is iterated. The measurement of Monte Carlo time becomes problematic in the Wolff algorithm since the number of spin-flips is different in different steps. Usually the time advanced in a cluster flip is taken as the ratio of the number of spins flipped to the total number of spins in the system.

The Wolff algorithm reduces significantly the correlation times and the dynamical critical exponent  $z$ . Hence for large lattices the Wolff algorithm would prove much better than the local update Metropolis algorithm.

An important point about the Swendsen-Wang/Wolff algorithm is that a KF-CK cluster percolates at the Ising critical point. Indeed one can show that the spin-spin pair correlation function  $\langle S_i S_j \rangle$  is equal to  $\langle \gamma_{ij} \rangle$  - the probability that the sites  $i$  and  $j$  belong to the same cluster. Here  $\gamma_{ij}$  is an indicator function: it is unity if the sites belong to the same cluster and zero otherwise. The average in the above is taken over all spin and bond configurations. This property suggests that there is a natural tendency for the system to self organize itself to criticality; this tendency for selforganized criticality can be captured in an algorithm.

## 21.2 Invaded cluster algorithm

Machta *et al* [73] proposed the invaded cluster algorithm to calculate the equilibrium critical points. This technique is based on the idea of invasion percolation [74]. In invasion percolation we assign random numbers independently to the bonds of the lattice. Growth starts from one or several sites. At each step a cluster grows by the addition of the perimeter bond which has the smallest random number. The growth process stops when a cluster percolates. It is clear that the invasion percolation is a self organized critical phenomenon. In the algorithm of Machta *et al* [73] we grow clusters from every site of the lattice and along the ‘satisfied’ bonds only. Bonds are occupied in a random order until an appropriate stopping condition is fulfilled. The growth process is stopped and each cluster is flipped randomly and independently with equal probability. This gives rise to a new spin configuration; in the new configuration re order the satisfied bonds randomly and start growing invaded clusters. Iterate. For example the stopping condition may be a requirement on the size of the largest cluster. The stopping rule can be devised suitably so that the Invaded Cluster algorithm simulates the system at critical point of the model. Thus the occupied bonds are determined by the stopping rule.<sup>20</sup> Hence the invaded cluster algorithm has a natural feed back mechanism which ensures that the desired equilibrium critical regions are always reached. The phase transition temperature is an output. For more details see [73].

## 21.3 Probability changing cluster algorithm

Tomita and Okabe [75] have proposed an algorithm wherein the system evolves to critical regions but asymptotically remains still a canonical ensemble. They call this a probability changing cluster (PCC) algorithm. The bonding probability is adjusted at

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<sup>20</sup>Note that in the Swendsen-Wang algorithm it is the temperature that determines the occupation of satisfied bonds. See sections (19) and (19.1).

the end of every step or a group of steps so that the spin system is driven to criticality. We start with an Ising spin configuration, and a certain value of the bonding probability  $p$ . As in the Swendsen-Wang algorithm, we grow the KF-CK clusters; then check if there is present a spanning cluster ( $k = 1$ ) or not ( $k = -1$ ). Carry out the cluster-spins-flipping exactly like you did in the Swendsen-Wang algorithm. For the next step change  $p$  to  $p - k\delta p$ . Iterate. It is clear that in the limit  $\delta p \rightarrow 0$ , the PCC ensemble is identical to the canonical ensemble. Hence the algorithm not only drives the system to criticality and hence the critical points can be estimated but also the physical quantities like magnetization, susceptibility, specific heat, *etc* can be evaluated. For more details see [75]

## 21.4 More on clusters and some discussions

I think it is rather clear now why the Swendsen-Wang algorithm in particular and several other cluster algorithms (like the Wolff, invaded cluster and the probability changing cluster algorithms, discussed above) in general are very effective in speeding up the computations; this stems from a very simple observation that a KF-CK cluster contains correlated spins; if a spin is flipped then all the other spins in the same KF-CK cluster have a tendency to flip. It is precisely this tendency for coherent flipping that is exploited when we flip all the spins in a cluster in one shot thus speeding up the dynamics. By the same token, in a physical phenomenon if a KF-CK cluster ceases to represent correlated spins, then the Swendsen-Wang and the related algorithms would fail. An example is the temperature driven first order phase transition studied by Gore and Jerrum [76]; they show that the Swendsen-Wang cluster algorithm is not efficient. The so called super critical slowing down of dynamics in a first order phase transition has its origin in the nature of the canonical distribution: it peaks at two phases and the system switches from one to the other through a rare ‘interface event’. The correlation time  $\tau^*$  is proportional to the residence time in the phases. The ‘interface’ regions are poorly sampled in the local update Monte Carlo algorithm. To handle such super critical slowing down, we need to go beyond Boltzmann sampling, like multicanonical Monte Carlo. I shall say something on these issues later.

For another example consider the following disordered Ising Hamiltonian

$$H = -J \sum_{\langle ij \rangle} (\epsilon_{ij} S_i S_j - 1) , \quad (105)$$

where  $\epsilon_{ij} (= \pm 1)$  is random quenched disorder. If there exists a closed path such that that the product of the disorder parameter  $\epsilon$  over the closed path is -1, then the Hamiltonian is said to contain frustration. A naive application of Swendsen-Wang cluster algorithm to a fully frustrated Ising system will not lead to any improvement whatsoever [77]; it is because, in a frustrated Ising system, a KF-CK cluster does not contain correlated spins. One needs to modify the cluster definition to handle these situations. Several ideas have been proposed to this end and we refer to some of them in [78].

We need to carry out a series of Monte Carlo simulations at different temperatures to obtain the temperature dependence of the desired thermodynamic variable. This can be time consuming. It would be desirable to have a technique that would

give the temperature dependence of a macroscopic variable from a single Monte Carlo run. Also, in the standard Metropolis Monte Carlo technique, it is rather difficult to calculate entropy (or free energy), since the entropy is a function of the probability with which a microstate occurs in a canonical ensemble. The energy distribution in the canonical ensemble,  $P(E) \propto D(E) \exp(-\beta E)$ , is the product of density of states  $D(E)$  which usually increases with increase of energy rather rapidly and an exponential which decreases rather sharply with increase of energy at low temperatures. As a result, microstates with very low or high energies get sampled rather poorly in Metropolis algorithm. If the energy minima are separated by high barriers, the simulation becomes difficult since the system becomes quasi ergodic. Several techniques have been proposed addressing these and related issues. I shall discuss some of them in the remaining part of the talk. First let us consider the so called single histogram technique often used in the context of simulation of critical systems.

## 22 What is an histogram technique ? How do we implement it?

Consider a canonical ensemble of spin configurations generated at inverse temperature  $\beta^*$ . The idea behind histogram technique is to calculate from this ensemble the macroscopic properties of the system at  $\beta \neq \beta^*$ . Let me illustrate the technique by considering energy histogram.

Accordingly, let  $h_i(\beta^*)$  denote the histogram of the energy obtained from a canonical ensemble of spin configurations generated at  $\beta^*$ . In other words,  $h_i(\beta^*)$  is the number of spin configurations with energy in the interval  $\Delta E$  around  $E_i$ . Let  $P(E_i, \beta^*)$  denote the probability density that the system takes an energy  $E_i$ . It is clear that  $P(E_i, \beta^*)$  is proportional to  $h_i(\beta^*)$ . Formally we have

$$P(E_i, \beta^*) = \frac{1}{Z(\beta^*)} D(E_i) \exp(-\beta^* E_i), \quad (106)$$

where  $D(E_i)$  is density of states at energy  $E_i$  and is independent of temperature. Therefore we have

$$D(E_i) \propto Z(\beta^*) h_i(\beta^*) \exp(\beta^* E_i). \quad (107)$$

Let  $P(E_i, \beta)$  denote the probability density of energy at  $\beta \neq \beta^*$ . Formally we have

$$P(E_i, \beta) = \frac{1}{Z(\beta)} D(E_i) \exp(-\beta E_i). \quad (108)$$

In the above, we substitute for  $D(E_i)$  from Eq. (107) and get

$$P(E_i, \beta) \propto \frac{Z(\beta^*)}{Z(\beta)} h_i(\beta^*) \exp[-(\beta - \beta^*) E_i]. \quad (109)$$

Imposing the normalization condition, we get

$$P(E_i, \beta) = \frac{h_i(\beta^*) \exp[-(\beta - \beta^*) E_i]}{\sum_j h_j(\beta^*) \exp[-(\beta - \beta^*) E_j]}. \quad (110)$$

Thus from a single Monte Carlo run at  $\beta^*$  we obtain  $P(E, \beta)$  for various values of  $\beta \neq \beta^*$ . Any energy dependent macroscopic quantity as a function of  $\beta$  can now be obtained from the knowledge of  $P(E, \beta)$ .

Another way of saying the same thing is as follows. We sample a microstate  $\mathcal{C}$  from a probability distribution  $\exp[-\beta^*E(\mathcal{C})]/Z(\beta^*)$ . We say that the microstate  $\mathcal{C}$  is generated with a weight  $\exp[-\beta^*E(\mathcal{C})]$ . We are interested in evaluating the average of a macroscopic quantity  $O(\mathcal{C})$  over a canonical ensemble at  $\beta \neq \beta^*$  *i.e.* from a distribution  $\exp[-\beta E(\mathcal{C})]/Z(\beta)$ . Hence we unweight the sampled microstate and then reweight it at the desired temperature; the unweighting - reweighting factor for the configuration  $\mathcal{C}$  is

$$\frac{\exp[-\beta E(\mathcal{C})]}{\exp[-\beta^* E(\mathcal{C})]} \quad (111)$$

Therefore,

$$\langle O \rangle = \lim_{N \rightarrow \infty} \overline{O}_N = \frac{\sum_{i=1}^N O(\mathcal{C}_i) \exp[-(\beta - \beta^*) E(\mathcal{C}_i)]}{\sum_{i=1}^N \exp[-(\beta - \beta^*) E(\mathcal{C}_i)]} \quad (112)$$

where the sum runs over the microstates sampled from a canonical ensemble at  $\beta^*$ . If  $O(\mathcal{C}_i) = O(E(\mathcal{C}_i))$ , then,

$$\langle O \rangle = \frac{\sum_i O(E_i) h_i(\beta^*) \exp[-(\beta - \beta^*) E_i]}{\sum_i h_i(\beta^*) \exp[-(\beta - \beta^*) E_i]} \quad (113)$$

where the sum runs over the energy bins. The above is identical to energy histogram reweighted average.

The histogram technique is one of the oldest techniques proposed, see for example [79, 80]. But the technique became popular after the publication of a paper by Ferrenberg and Swendsen [81] in 1988. This technique is often referred to as Ferrenberg-Swendsen reweighting technique and is used in almost all Monte Carlo calculations of statistical physics problems, especially the ones dealing with the phenomenon of phase transition, see for example [82].

In the single histogram technique, the estimated  $P(E, T)$  is accurate only for  $T$  close to the reference temperature  $T^*$ . By generating many histograms that overlap we can widen the range of  $T$ . This is called the multi histogram technique [83]. It is also clear that we can increase the range of  $T$  by directly estimating the density of states  $D(E)$ . Multicanonical sampling [84] is an early technique proposed that precisely does this. Multicanonical sampling is a very general technique useful and often the method of first choice for a variety of problems that include critical slowing down near second order phase transition points, nucleation in first order phase transition, and trapping in the metastable minima in systems with rugged energy landscapes. Originally this technique was proposed to tackle the so called super critical slowing down in the first order phase transition and calculation of the interfacial energy for large systems. This problem of super critical slowing down arises due to the fact that the Boltzmann factor suppresses configurations dominated by interfaces between ordered and disordered phases. As a consequence, the quality of the local update Metropolis Monte Carlo results deteriorates exponentially with increase of the system size. Entropic sampling [85] is a technique conceptually equivalent to multicanonical Monte Carlo.

## 23 What is the basic idea behind entropic sampling ?

The canonical partition function is given by,

$$\begin{aligned} Z(\beta) &= \sum_{\mathcal{C}} \exp[-\beta E(\mathcal{C})] , \\ &= \sum_E \exp \left[ \frac{S(E)}{k_B} - \beta E \right] , \end{aligned} \quad (114)$$

where  $S(E)$  is the microcanonical entropy. The probability for the macroscopic system to have an energy  $E$  in the canonical ensemble is given by,

$$P(E) \propto \exp \left[ \frac{S(E)}{k_B} - \beta E \right] . \quad (115)$$

The Metropolis algorithm helps you sample from the above Boltzmann distribution and construct a canonical ensemble of microstates. Instead, if we want to sample from an arbitrary distribution

$$P_{\alpha(E)}(E) \propto \exp \left[ \frac{S(E)}{k_B} - \alpha(E) \right] , \quad (116)$$

it is sufficient to impose, besides ergodicity, a detailed balance condition given by

$$\begin{aligned} \frac{W(B \leftarrow A)}{W(A \leftarrow B)} &= \frac{P_{\alpha(E)} I(E(B))}{P_{\alpha(E)}(E(A))} \\ &= \exp \left[ - \left\{ \alpha(E(B)) - \alpha(E(A)) \right\} \right] . \end{aligned} \quad (117)$$

This implies that a trial configuration  $\mathcal{C}_t$  obtained by a local updating of the current configuration  $\mathcal{C}$ , is accepted with a probability,

$$p = \min \left( 1, \exp \left[ - \left\{ \alpha(E(\mathcal{C}_t)) - \alpha(E(\mathcal{C})) \right\} \right] \right) . \quad (118)$$

It is clear that if  $\alpha(E) = \beta E$ , Eq. (116) is the same as Eq. (115) and we recover the conventional Boltzmann sampling. For other choices of the function  $\alpha(E)$ , we get what one may call non-Boltzmann sampling. The fact that non-Boltzmann sampling can be a legitimate alternative to Boltzmann sampling has been recognized since the early days of Monte Carlo practice. However the practical significance of non-Boltzmann sampling was realized, only in the middle of nineteen seventies for the first time, by Torrie and Valleau [80,86] who proposed the umbrella sampling technique, a forerunner to all the non-Boltzmann sampling technique like the entropic sampling, multicanonical Monte Carlo and its several and recent variants, see below.

Entropic sampling obtains when we set  $\alpha(E) = S(E)/k_B$  that renders  $P_{\alpha(E)}(E)$ , see Eq. (116), the same for all  $E$ . But then, the entropic function is not known *à priori*.



An algorithm to build  $\alpha(E)$  iteratively on the basis of microstates visited during short ‘learning’ runs is usually recommended, see below.

The key point is that entropic sampling gives an ensemble of microstates with energies uniformly distributed over its range. We can say that the algorithm generates a simple random walk in energy space, and hence the presence of energy barriers does not affect the evolving Markov chain of microstates. Since unweighting - reweighting is done while averaging, even a reasonably approximate estimate of the entropic function  $\alpha(E)$  would suffice. The idea is that the closer  $\alpha(E)$  is to  $S(E)/k_B$ , the flatter shall be the energy histogram it generates.

Let  $(E_{\min}, E_{\max})$  be the energy range over which you want to generate microstates with uniform energy distribution. For example this range could include the region of the sample space where the probability is small like the interface region in a first order phase transition. Divide the range into a number of equal width energy bins. Let  $E_i$  be the energy of the  $i$ -th bin. In the first iteration set  $\alpha_i = \alpha(E_i) = 0 \forall i$ . Carry out a small Monte Carlo run, of say  $N$  MCSS. The probability of acceptance of a trial state constructed from locally changing the current state is given by Eq. (118). Since in the first iteration,  $\alpha_i = 0 \forall i$ , every trial move gets accepted. But this will not be so in subsequent iterations. From the microstates visited by the system in the first iteration stage, calculate the histogram  $\{h_i\}$ , where the number of microstates falling in the  $j$ -th energy bin is denoted by  $h_j$ . At the end of the first iteration, calculate  $\{\alpha_i\}$  for the next iteration, as per the recursion given below,

$$\alpha_i^{(k+1)} = \begin{cases} \alpha_i^{(k)} & \text{if } h_i = 0, \\ \alpha_i^{(k)} + \frac{1}{k_B} \ln [h_i] & \text{otherwise.} \end{cases} \quad (119)$$

where the superscript  $(k)$  denotes the iteration index.

Thus, starting from an initial array of  $\{\alpha_i^{(0)} = 0 \forall i\}$  in the zeroth iteration, we successively calculate  $\{\{\alpha_i^{(k)}\} : k = 1, 2, \dots\}$ . We continue the iterations until we find that the histogram of energy accumulated from the microstates visited during the iteration is approximately flat in the desired energy  $(E_{\min}, E_{\max})$ . After the ‘learning’ runs are over, we carry out a long Monte Carlo run, employing the set  $\{\alpha_i\}$ , for calculating the macroscopic properties. We get an *entropic* ensemble of microstates  $\{\mathcal{C}_i : i = 1, N\}$ . Calculate the canonical ensemble average of a macroscopic property say,  $O(\mathcal{C})$  at the desired temperature  $T = 1/[k_B\beta]$ , from the entropic ensemble, by unweighting (divide by  $\exp[-\alpha(E(\mathcal{C}_i))]$ ) followed by reweighting (multiply by  $\exp[-\beta E(\mathcal{C}_i)]$ ),

$$\langle O \rangle_\beta = \lim_{N \rightarrow \infty} \bar{O}_N(\beta) = \frac{\sum_{i=1}^N O(\mathcal{C}_i) \exp[-\beta E(\mathcal{C}_i) + \alpha(E(\mathcal{C}_i))]}{\sum_{i=1}^N \exp[-\beta E(\mathcal{C}_i) + \alpha(E(\mathcal{C}_i))]} \quad (120)$$

Let  $\xi(\beta)$  denote the maximum of  $\{-\beta E(\mathcal{C}_i) + \alpha(E(\mathcal{C}_i)) : i = 1, N\}$ . While reweighting, we have found it necessary to employ the modified but equivalent formula below, when the system size is very large.

$$\langle O \rangle_\beta = \lim_{N \rightarrow \infty} \bar{O}_N(\beta) = \frac{\sum_{i=1}^N O(\mathcal{C}_i) \exp[-\beta E(\mathcal{C}_i) + \alpha(E(\mathcal{C}_i)) - \xi(\beta)]}{\sum_{i=1}^N \exp[-\beta E(\mathcal{C}_i) + \alpha(E(\mathcal{C}_i)) - \xi(\beta)]} \quad (121)$$

Let me repeat: since unweighting - reweighting is any way carried out, there is no need to estimate the entropic function  $\{\alpha_i\}$  accurately. Suffice if the algorithm ensures a relatively flat histogram of energy in the desired range. It is a good idea to increase the number of MCSS in an ‘ $\alpha$  update iteration’ as the energy range covered becomes larger. The important point is that in one shot we get  $\langle O \rangle$  at ‘all’ temperatures, in addition to sampling of rare events.

I said earlier that in principle entropic sampling [85] (described above) is the same as multicanonical sampling technique [84] proposed earlier.

## 24 How is entropic sampling related to multicanonical sampling ?

That entropic sampling is in principle the same as multicanonical sampling has been shown lucidly by Berg, Hansmann and Okamoto [87]. The probability of energy in multicanonical sampling technique is usually parametrized as,

$$P(E) \sim \exp \left[ \frac{S(E)}{k_B} - \tilde{\beta}(E) E + \tilde{\alpha}(E) \right]. \quad (122)$$

The parameter  $\tilde{\beta}$  in the above is given by the derivative of the microcanonical entropy,

$$\tilde{\beta}(E) = \frac{1}{k_B T(E)} = \frac{1}{k_B} \frac{\partial S}{\partial E}. \quad (123)$$

It is precisely because of this the technique is named multicanonical sampling: a microcanonical temperature is defined for each energy. The second parameter  $\tilde{\alpha}(E)$  can be expressed as

$$\tilde{\alpha}(E) = \tilde{\beta}(E) F(E), \quad (124)$$

where  $F(E)$  is microcanonical free energy.

The two parameters  $\tilde{\alpha}(E)$  and  $\tilde{\beta}(E)$  are related:

$$\tilde{\alpha}(E) = -\frac{S(E)}{k_B} + \tilde{\beta}(E) E. \quad (125)$$

Differentiating the above with respect to  $E$ , we get,

$$\frac{d\tilde{\alpha}}{dE} = E \frac{d\tilde{\beta}}{dE}. \quad (126)$$

We have to build up the function  $\tilde{\beta}(E)$  recursively like we built  $\alpha(E)$  in entropic sampling. It is clear that the functions  $\alpha(E)$  of entropic sampling,  $\tilde{\beta}(E)$  and  $\tilde{\alpha}(E)$  of multicanonical sampling are related. Note that  $\alpha(E) = S(E)/k_B$ . Hence,

$$\begin{aligned} \alpha(E) &= \tilde{\beta}(E) E - \tilde{\alpha}(E) \\ \frac{d\alpha}{dE} &= \tilde{\beta}(E). \end{aligned} \quad (127)$$

The recursion for updating  $\tilde{\beta}(E)$  in multicanonical sampling Monte Carlo can be derived from the recursion, see Eq. (119), for updating  $\alpha(E)$  in the entropic sampling Monte Carlo and is given by,

$$\tilde{\beta}_i^{(k+1)} = \tilde{\beta}_i^{(k)} + \frac{1}{k_B \Delta E} \times \begin{cases} \ln(h_i) & \text{if } h_i \neq 0 \text{ and } h_{i-1} = 0 \\ \ln(1/h_{i-1}) & \text{if } h_i = 0 \text{ and } h_{i-1} \neq 0 \\ 0 & \text{if } h_i = h_{i-1} = 0 \\ \ln \left[ \frac{h_i}{h_{i-1}} \right] & \text{if } h_i \neq 0 \text{ and } h_{i-1} \neq 0 \end{cases} \quad (128)$$

where  $\Delta E = E_i - E_{i-1}$ , the suffix  $i$  denotes the energy bin and  $\{h_i\}$  the energy histogram. The corresponding  $\{\tilde{\alpha}_i^{(k+1)}\}$  follows immediately,

$$\tilde{\alpha}_{i-1}^{(k+1)} = \tilde{\alpha}_i^{(k+1)} - E_i \left( \tilde{\beta}_i^{(k+1)} - \tilde{\beta}_{i-1}^{(k+1)} \right) \quad (129)$$

In the above we set  $\alpha_{imax} = 0$  where  $imax$  is the index of the bin of highest energy.

Indeed, one can say that the basic idea behind multicanonical Monte Carlo (and hence entropic sampling) of the nineteen nineties is the same as that of the umbrella and adaptive umbrella sampling of the nineteen seventies. But then it is the work on multicanonical sampling and its remarkable success in the accurate evaluation of the interface tension in the first order phase transition that made popular such non-Boltzmann sampling cum iterative techniques and initiated large scale applications and several new developments. These include flat/broad histogram sampling [88], transition matrix Monte Carlo [89], exchange Monte Carlo [90], simulated tempering [91] and cluster hybrid algorithms [92]. For a comprehensive review see [93]. Multicanonical sampling and its variants have been employed in a variety of studies that include phase coexistence in Ising models [94], Potts spin models [95] liquid-vapour [96] and solid - solid [97] models, systems with complex free energy landscape [98], protein folding [99] and Nematic - Isotropic transition in bulk and confined liquid crystal systems [100] *etc.*, to name a few.

Spanning of energy space in entropic / multicanonical Monte Carlo algorithms and for that matter in broad / flat histogram methods, is achieved through a pure diffusive process on the one dimensional energy axis. Larger the system, wider is its energy range and hence longer it shall take for the system to diffuse from one end of the energy range to the other. The diffusive evolution of the Markov chain is a consequence of the penalty imposed when the system attempts to visit oft-visited energy bins. Also the penalty in a learning run depends on the microstates visited during the immediate preceding learning run. Perhaps increasing the penalty at least during the initial stages and applying the penalty continuously during the stochastic dynamical evolution of the Markov chain would speed up the convergence. To this end Wang and Landau [101] proposed a simple, easy-to-understand and easy-to-implement algorithm that substantially improves the performance of the multicanonical Monte Carlo simulation.

## 25 What is the Wang - Landau algorithm?

In the Wang - Landau algorithm [101], the entropic function  $\alpha(E)$  is directly and continuously updated after every MCS during the stochastic dynamical process. The energy histogram is accumulated but not used in the updating of the entropic function. Instead the updating of the entropic function is carried out as follows. We define a convergence factor  $f$  and set it at  $f = f_0 > 0$  in the beginning. Also we set  $\alpha_i = \alpha(E_i) = 0 \forall i$  in the beginning. Start with an arbitrary microstate and construct a trial microstate by selecting a spin randomly and flipping it. The acceptance/rejection of the trial state is made on the basis of Eq. (118). If the energy of the next microstate lies in the  $i$ -th bin, we set  $\alpha_i = \alpha_i + f$ . The histogram of visited sites is also updated; continue the evolution until the histogram becomes reasonably flat: Let

$$\langle h \rangle = \frac{1}{M} \sum_{i=1}^M h_i \quad (130)$$

denote the average number of entries in the histogram where  $M$  is the number of energy bins. We say the histogram is flat if

$$h_i \geq \epsilon \langle h \rangle \quad \forall i \quad (131)$$

where  $\epsilon$  is taken between 0.75 and 0.95 depending on the problem. Thus the entropic function and the histogram are updated after every MCS. The energy histogram simply plays a passive role and serves as a tool to monitor the convergence. Then we reset  $f = f_1 = f_0/2$  and proceed. A fresh histogram is accumulated and tested for flatness. In the next stage  $f = f_2 = f_1/2$ . It is clear the convergence factor  $f$  decreases exponentially to zero as the number of iterations increases. In fact after twenty five iterations the convergence factor becomes as small as  $3 \times 10^{-8} f_0$  whence we stop the simulation process.  $f_0$  is usually taken as unity. The resultant entropic function will be very close to the true one when normalized on the basis of known information about the system under simulation. For example, in the Ising model, the total number of microstates is  $2^V$  where  $V$  is the number of Ising spins in the system under investigation. Also the ground state of the Ising model is doubly degenerate and this can also be used for normalization purposes. From the normalized entropic function we can calculate the free energy and all other desired macroscopic properties of the system under simulation.

We can employ the unnormalized entropic function in a final production run (when we do not update the entropic function nor do we monitor the energy histogram) and construct an adequately large entropic ensemble, like we did in the production run under entropic/multicanonical Monte Carlo, see section (23). From the entropic ensemble we can calculate the desired macroscopic properties at all temperatures through unweighting and reweighting. The Wang - Landau method has been applied to Ising and Potts spin models [101, 102], quantum mechanical models [103], glassy systems [104] polymer films [105], protein folding [106], models with continuous degrees of freedom [107] and generalized to reaction coordinates [108].

There are a few difficulties with the Wang-Landau algorithm and there are a few issues that remain to be understood. The statistical accuracy of the results can not be improved beyond a certain value, no matter how much additional calculations you

perform. The relation between the convergence factor and the errors in the estimates of the macroscopic quantities is not clear; also it is not clear how flat the energy histogram should be for accurate evaluation of the macroscopic quantities. The algorithm does not satisfy detailed balance condition until the convergence factor  $f$  decays close to zero. Also during the late stages of iteration, the visited microstates do not contribute to the estimate of the entropic function since the convergence factor  $f$  is very small; this means that a lot of information is generated but not used. Consider the situation when we employ the Wang-Landau algorithm to estimate the density of states in a restricted range of energy. What should we do when the transition takes the system to a microstate whose energy falls outside the range? Ofcourse we reject the transition; we do not update either the entropy function or the energy histogram. We proceed with the dynamics and randomly select the next trial microstate. When we do this we find the calculated density of states in the boundary energy bins to be erroneous [101, 109]. However if we update these two quantities in the current energy bin, the errors disappear [110]. The reason for this is not clear. See also [111] for some recent effort toward understanding and updating of the Wang-landau algorithm.

The Wang-Landau algorithm seems to hold great promise. It would indeed worth the effort to put the algorithm on a more rigorous pedestal and devise means of improving its performance through new schemes or by linking it to other existing schemes. For example, already Wang - Landau algorithm has been combined with the  $n$ -fold way [109] for estimating tunneling times in Heisenberg spin models and with multi-bondic method [112] for general discrete models.

## 26 Jarzynski's equality

Estimation of entropy or free energy from simulation or experimental data has always remained a tricky problem. A quantity like energy or magnetization of a macroscopic system can be calculated as an average over a reasonably large sample of microstates drawn from an equilibrium ensemble. However, for estimating entropy or free energies, we have to necessarily consider all the microstates accessible to the equilibrium system and this number is indeed very large. An early ingenious method of calculating entropy from data on dynamics was proposed by S. K. Ma [113], and it is based on counting of coincidence (or repetition) of states along a long phase space trajectory. We have already seen that umbrella sampling and its variants and later improvements like entropic sampling, multicanonical sampling, and Wang-Landau algorithm are some of the useful Monte Carlo techniques that can be adapted for computation of entropy and free energy. In fact, the very formulation of thermodynamics and the definition of entropy and free energies provide us with a method of calculating these quantities, see below.

Consider a classical macroscopic system in thermal contact with a heath bath at temperature  $T$ . Let  $\lambda$  denote a degree of freedom of the system which can be controlled from outside; for example, the system can be a gas contained in a cylinder and the degree of freedom  $\lambda$  can be its volume which can be controlled from outside by moving a piston; the system can be a spin lattice and the parameter can be an external magnetic field whose strength and direction can be changed. To begin with, at time  $t = 0$ , let

$\lambda = \lambda_1$  and the system is in equilibrium with the heat bath. Then switch the value of  $\lambda$  from  $\lambda_1$  to  $\lambda_2$ . What is the change in entropy? Without loss of generality let us assume that the switching of  $\lambda$  from  $\lambda_1$  to  $\lambda_2$  is carried out over a time duration  $t_s$  at a constant rate  $(\lambda_2 - \lambda_1)/t_s$ .

Consider first an ideal scenario in which the switching is carried out infinitely slowly; in other words  $t_s = \infty$ ; the system is sort of dragged through a continuous succession of equilibrium states; during the entire process of switching, the system is continuously in equilibrium with the heat bath; such a process is often called a quasi-static equilibrium process; the process is reversible. Under such an ideal thermodynamic process, Clausius defines free energy (change)  $\Delta F = F(\lambda_2) - F(\lambda_1)$  as equal to the reversible work done on the system.<sup>21</sup>

What happens when the switching process takes place over a finite time duration, *i.e.*  $t_s < \infty$ ? The system would all the time be lagging behind the corresponding equilibrium states; the work done will depend on the particular microstate at which the system and the heat bath happen to be present at the precise moment the switching process starts. Hence the work done on the system would differ from one switching experiment to the other.<sup>22</sup> In other words for  $t_s < \infty$ , the work done on the system  $W$  is a random variable; carrying out a switching experiment and measuring the work done is equivalent to sampling  $W$  independently and randomly from its distribution  $\rho(W; t_s)$ . In other words  $\rho(W, t_s)dW$  is the probability that the work done on the system during the switching process lies between  $W$  and  $W + dW$ . Let  $\langle W \rangle$  denote the average work done on the system,

$$\langle W \rangle \equiv \int dW W \rho(W, t_s). \quad (132)$$

In the ideal quasi-static equilibrium limit of  $t_s \rightarrow \infty$ , we have  $\rho(W, t_s \rightarrow \infty) = \delta(W - W_R)$ ;  $W$  does not change from one experiment to the other and it equals  $W_R$ . The reversible work  $W_R$  equals  $\Delta F$ , which is the definition of free energy (change) given by Clausius.

However such reversible thermodynamic processes, very useful though, are idealizations and are not strictly realized in experiments or simulations. In general we have  $\langle W \rangle \geq \Delta F$ , with equality holding good for reversible processes. The difference  $\langle W \rangle - \Delta F$  is called the (irreversible) dissipative work and is denoted by  $W_d$ . Thus, to calculate  $\Delta F$  from experiments/simulation, we need a good estimate of dissipation, in the absence of which, we can, at best provide only an upper limit:  $\Delta F \leq \langle W \rangle$ .

In the year 1951, H. B. Callen and T. A. Welton [115] showed that if the switching process keeps the system all the time very close to equilibrium, then the dissipation

<sup>21</sup>Reversible processes are an idealization; however, in experiments or in simulations, we can be as close to the ideal reversible process as possible; change  $\lambda$  extremely slowly through a succession of infinitesimal increments; estimate the work done during each increment; sum these up and equate the result to the free energy change. There are slow growth algorithms, staged thermodynamic integration methods and thermodynamic perturbation methods to calculate/measure free energies. I do not intend to describe these techniques here and those interested can consult for example [114].

<sup>22</sup>All the switching experiments are carried out with the same protocol: set  $\lambda = \lambda_1$ ; let the system attain thermal equilibrium with the heat bath; start the clock:  $t = 0$ ; switch  $\lambda$  from  $\lambda_1$  to  $\lambda_2$  uniformly until the clock reads  $t = t_s$ ; measure the work done on the system during the switching process; reset  $\lambda$  to  $\lambda_1$ .

$W_d$  is proportional to fluctuations:

$$W_d \equiv \langle W \rangle - W_R \approx \beta \sigma_W^2 / 2 \quad (133)$$

where the fluctuations,  $\sigma_W^2$  is given by,

$$\sigma_W^2 = \int dW W^2 \rho(W; t_s) - \langle W \rangle^2 \quad (134)$$

Recently, in the year 1997, C. Jarzynski, [116] discovered a remarkable and exact identity, valid even when the switching process drives the system far from equilibrium. Jarzynski's identity relating nonequilibrium work to equilibrium free energy differences is given by,

$$\langle \exp(-\beta W) \rangle \equiv \int dW \exp(-\beta W) \rho(W, t_s) = \exp(-\beta \Delta F) . \quad (135)$$

Jarzynski's equality<sup>23</sup> has been rigorously proved for Hamiltonian evolution, [116] as well as stochastic evolution [117]; its validity has been established in computer simulation [117] and more importantly in experiments [118].

Let us express Jarzynski's equality as a cumulant expansion [119],

$$\langle \exp(-\beta W) \rangle \equiv \exp \left[ \sum_{n=1}^{\infty} \frac{(-\beta)^n C_n}{n!} \right] = \exp(-\beta \Delta F) \quad (136)$$

where  $C_n$  denotes the  $n$ -th cumulant of  $W$ . The cumulants and the moments are related to each other. The  $n$ -th cumulant can be expressed in terms of the moments of order  $n$  and less. Given below are first four cumulants expressed in terms of moments.

$$\begin{aligned} C_1 &= \langle W \rangle , \\ C_2 &= \langle W^2 \rangle - \langle W \rangle^2 = \sigma_W^2 , \\ C_3 &= \langle W^3 \rangle - 3\langle W^2 \rangle \langle W \rangle + 2\langle W \rangle^3 , \\ C_4 &= \langle W^4 \rangle - 4\langle W^3 \rangle \langle W \rangle - 2\langle W^2 \rangle^2 + 12\langle W^2 \rangle \langle W \rangle^2 - 6\langle W \rangle^4 . \end{aligned} \quad (137)$$

From the cumulant expansion, see Eq. (136), we get,

$$\Delta F = \langle W \rangle - \frac{\beta \sigma_W^2}{2} + \sum_{n=3}^{\infty} \frac{(-\beta)^{n-1} C_n}{n!} \quad (138)$$

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<sup>23</sup>It may be noticed that since the exponential function is convex,

$$\langle \exp(-\beta W) \rangle \geq \exp(-\beta \langle W \rangle)$$

which in conjunction with Jarzynski's identity implies that,

$$\begin{aligned} \exp(-\beta \Delta F) &\geq \exp(-\beta \langle W \rangle) \\ -\beta \Delta F &\geq -\beta \langle W \rangle \\ \Delta F &\leq \langle W \rangle \end{aligned}$$

which is a statement of the second law, if we modify the switching protocol and let the system equilibrate at  $\lambda = \lambda_2$  at the end of the switching process. In this sense, proof of Jarzynski's identity is a proof of the second law

Consider a quasi-static equilibrium switching process;  $\rho(W) = \delta(W - W_R)$ , by definition. Then, in the above, only the first term (of the cumulant expansion) is non-zero. We get the definition of free energy as given by Clausius:  $\langle W \rangle = W_R = \Delta F$ .

Now consider a switching process, during which the system remains very close to equilibrium; it is reasonable to expect the statistics of  $W$  to obey the Central Limit Theorem; hence  $\rho(W)$  shall be a Gaussian; for a Gaussian, all the cumulants from the third upwards are identically zero; hence in the above expansion only the first two terms survive and we get  $\Delta F = \langle W \rangle - \beta C_2/2 = \langle W \rangle - \beta \sigma_W^2/2$ . This result is identical to the fluctuation dissipation relation of Callen and Welton [115]. However, if the switching process drives the system far from equilibrium, the work distribution would no longer be Gaussian and we need to include contributions from higher order cumulants to calculate the dissipation  $W_d$  and hence free energy:  $\Delta F = \langle W \rangle - W_d$

Jarzynski's equality is helpful to experimenters for measuring free energies; the experimenters do not any more need to keep the system at or close to equilibrium during the switching process. Jarzynski's identity is a powerful tool for calculating free energy, when suitably incorporated in a Monte Carlo or Molecular dynamics programs. A dynamical ensemble of nonequilibrium trajectories all starting off from an equilibrium ensemble is all that is required for free energy computations.

Jarzynski's equality forms a part of recent exciting and important developments in nonequilibrium statistical mechanics. These new developments, related to each other and derivable one from the other, constitute what has come to be known as *Fluctuation Theorems* [56, 116, 117, 118, 121] and have led to fresh insights into nonequilibrium statistical mechanics, reversible and irreversible processes and the second law of thermodynamics.

## 27 Epilogue

All things, good and bad, must come to an end; so must, our Monte Carlo journey, good or bad. I have taken you, randomly though, through the lanes and by-lanes of the Monte Carlo metropolis, confining to those regions relevant for statistical physics applications. Table (6) lists what I consider as milestones in Monte Carlo statistical physics.

In the first leg of our journey we looked at ensembles in general and Gibbs ensembles in particular. We saw details of microcanonical ensemble that describe isolated system; of canonical ensemble that models closed system; and of grand canonical ensemble, useful in the study of open systems. Then we took up the issue of random numbers that fuel the Monte Carlo machine. To our great discomfort we discovered that even today we do not know when can we call a sequence of numbers random except when we know of its origin. This of course did not deter us. We took a pragmatic attitude and settled for pseudo random numbers. We saw how to generate them and how to test them. We learnt how to use them to generate ensemble of random numbers representing the desired distribution - the so called random sampling techniques. We saw explicitly some techniques that help sample from the exponential and Gaussian distributions. For purpose of illustration we saw how to calculate an integral by the method of Monte Carlo. We learnt of Monte Carlo error bars and how to estimate



Table 6: Milestones in Monte Carlo Statistical Physics

When?	What happened?	Who did it and where do I find it?
1951	Linear congruential (pseudo random number) generator	D. H. Lehmer [24]
1953	Metropolis algorithm	N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller and E. Teller [46]
1963	Glauber dynamics	R. J. Glauber [50]
1964	Hand Book on Monte Carlo Methods	J. M. Hammersley and D. C. Handscomb [39]
1969	Random cluster model	P. W. Kasteleyn, C. M. Fortuin [63]
1975	n-fold way	A. B. Bortz, M. H. Kalos and J. L. Lebowitz [57]
1976	Cluster counting algorithm	J. Hoshen and R. Kopelman [68]
1977	Umbrella Sampling	G. M. Torrie and J. P. Valleau [86]
1980	Ising critical droplets	A. Coniglio and W. Klein [64]
1987	Swendsen-Wang cluster algorithm	R. H. Swendsen and J.-S. Wang [62]
1988	Histogram reweighting	A. M. Ferrenberg and R. H. Swendsen [81]
1989	Wolff cluster algorithm	U. Wolff [72]
1991	Multicanonical Monte Carlo	B. A. Berg and T. Neuhaus [84]
1993	Entropic sampling	J. Lee [85]
1995	Absorbing Markov Chain	M. A. Novotny [58]
2000	A Guide to Monte Carlo Simulations in Statistical Physics	D. P. Landau and K. Binder [122]
2001	Wang-Landau algorithm	F. Wang and D. P. Landau [101]

them.

Then we took up the issue of importance sampling and dealt with it in somewhat greater details mainly for two reasons. Importance sampling is an important topic in Monte Carlo theory and practice. Almost all Monte Carlo programmes employ importance sampling in some form or the other and with varying degrees of sophistication. The second reason is that often I find students have difficulties in comprehending what and how does importance sampling achieve what it purports to achieve. One way is to emphasize that importance sampling reduces the variance of the desired statistical variable whose average is what you want to calculate by Monte Carlo simulation. Needless to say that the technique should leave the average unchanged. I have taken this view and elucidated it through a simple example for which all the quantities can be calculated analytically.

Often we need to resort to importance sampling as a matter of necessity; for otherwise, any finite Monte Carlo sample generated should rarely contain microstates of interest to the phenomenon under investigation. Metropolis importance sampling is an example. A randomly chosen microstate belonging to a closed system is most likely to be of high energy <sup>24</sup> and hence contributes negligibly to the canonical partition sum. Hence we have to resort to importance sampling. The Metropolis algorithm generates a Markov chain whose (asymptotic) distribution is the equilibrium canonical distribution at the desired temperature. Indeed it is the Metropolis algorithm that launched the Monte-Carlo-for-statistical-physics business; it remains to date the best algorithm in this field. We took Ising model as an example to illustrate the Metropolis algorithm, continuous phase transition, critical exponents, finite size effects and finite size scaling.

When the actual dynamics slows down, the corresponding time-driven Monte Carlo simulation also becomes slow. Bortz, Kalos and Lebowitz suggested shifting of the (slow) dynamical information to the time axis and derived the so-called n-fold way; this event-driven algorithm is rejection free and helps speed up the computations. Novotny generalized this technique to Monte Carlo with Absorbing Markov Chain (MCAMC). However critical slowing down in continuous phase transition calls for special techniques. We discussed the cluster algorithm of Swendsen and Wang, of Wolff, and of the one based on invasion percolation *etc.* Wolff algorithm became famous for quite another reason also. It was while studying its performance that Ferrenberg, Landau and Wong discovered how dramatically the ‘pseudoness’ of pseudo random numbers can affect your Monte Carlo results and we had a glimpse of the well documented R250 story.

While on clusters we learnt of the celebrated Hoshen-Kopelman cluster counting algorithm; we also discussed blocking technique that helps estimate statistical error bars from correlated data and the histogram technique often employed in the study of systems very close to critical points. The histogram technique helps you calculate macroscopic properties of a system at temperatures different but reasonably close to the simulation temperature by suitable reweighting.

A first order phase transition is associated with the so called supercritical slowing

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<sup>24</sup>the microcanonical entropy increases rather rapidly with increase of energy; more the energy the more is the number of ways of distributing it.

down; we found how non-Boltzmann sampling techniques like entropic sampling/multicanonical Monte Carlo would help. Then we saw of the Wang-Landau algorithm which improves the performance of the multicanonical Monte Carlo methods. We ended our journey with a discussion on the recently proposed Jarzynski's equality and the promise this technique holds for computation of equilibrium free energies from nonequilibrium simulation/experiment.

As you would have rightly noticed, the journey has been somewhat random and in places rather rickety. I made no serious efforts to be otherwise; it had never been my intention to take you through all the topics in this vast and growing field. Nor did I try to place uniform emphasis on the various topics covered in these notes. I just picked up topics that caught my fancy and on which I have some hands-on experience and discussed them in a pedagogic style. Nevertheless I believe these notes cover quite a bit of ground and would serve as an introduction to this fascinating field.

The topics we have not visited include simulation of microcanonical and other ensembles, quantum Monte Carlo, renormalization employing Monte Carlo, replica Monte Carlo, Monte Carlo for vector and parallel computers, off-lattice models, flat/broad histogram sampling, transition matrix Monte Carlo, exchange Monte Carlo, simulated tempering, cluster hybrid algorithms and the whole field of simulation of nonequilibrium phenomena. Perhaps we can visit these topics during another journey on another occasion. Until then bye.

The recent comprehensive book by Landau and Binder [122] should provide an excellent guide.

## References

- [1] A. Papoulis, *Probability Theory, Random Variables and Stochastic Processes*, McGraw Hill Kogakusha Ltd., International Student Edition (1965);  
W. Feller, *An Introduction to Probability Theory and its Applications*, Vols. I and II, John Wiley, New York (1968);  
N. G. van Kampen, *Stochastic Processes in Physics and Chemistry*, North Holland (1981);  
C. W. Gardiner, *A Hand Book of Stochastic Methods for Physics, Chemistry and Natural sciences*, Springer (1985).
- [2] P. A. Pury, *Asymmetry and convergence in the Central Limit Theorem: an approach for physicists*, Am. J. Phys. **58** 62 (1990).
- [3] D. Sornette, *Critical Phenomena in Natural Sciences: Chaos, Fractals, Self-organization and Disorder: Concepts and Tools*, Springer (2000).
- [4] N. Metropolis and S. Ulam, *The Monte Carlo method*, J. Amer. Statistical Assoc. **44** 335 (1949).
- [5] A. Hall, *On an experimental determination of  $\pi$* , Messeng. Math. **2** 113 (1873).
- [6] Francis Galton, *Natural Inheritance* (1889), cited in M. Cundy and A. P. Rollet, *Mathematical Models*, Oxford University Press, Oxford (1961).
- [7] L. H. C. Tippett, *Random Sampling Numbers*, Cambridge University Press (1927).
- [8] P. C. Mahalanobis, *Dialectica* **8**, 95 (1954), cited in [9].
- [9] C. Radhakrishna Rao, *Statistics and Truth : Putting Chance to Work*, second edition, World Scientific (1997).
- [10] Lord Kelvin, *Nineteenth century clouds over the dynamical theory of heat and light*, Phil. Mag.(6), **2**, 1 (1901).
- [11] M. G. Kendall and B. Babington-Smith, *Randomness and random sampling numbers*, J. Roy. Statist. Soc. A **101** 147 (1938).
- [12] M. G. Kendall and B. Babington-Smith, *Second paper on random sampling numbers*, J. Roy. Statist. Soc. B **6** 51 (1938).
- [13] RAND Corporation, *A million random digits with 100000 normal deviates*, The Free Press (1955).
- [14] H. Inoue, H. Kumahora, Y. Yoshizawa, M. Ichimura and O. Miyatake, *Random numbers generated by a physical device*, Applied Statistics **32** 115 (1983).
- [15] W. H. Press, S. Teukolsky, W. T. Vetterling and B. P. Flannery, *Numerical Recipes*, Cambridge (1992).

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- [16] G. Marsaglia, *Applications of Number Theory to Numerical Analysis*, Academic, New York (1972).
- [17] NAG Fortran Library Manual Mark 14, 7 Numerical Algorithm Groups Inc. (1990).
- [18] G. Marsaglia, *Random numbers fall mainly on planes*, Proc. Nat. Acad. Sci. **61** 25 (1968).
- [19] T. G. Lewis and W. H. Payne, *Generalized feedback shift register pseudo random number algorithm*, Journal of the Association for Computing Machinery, **20** 456 (1973).
- [20] R. C. Tausworthe, *Random numbers generated by linear recurrence modulo two*, Math. Comp. **19** 201 (1965).
- [21] S. Kirkpatrick and E. P. Stoll, *A very fast shift-register sequence random number generator*, J. Comput. Phys. **40** 517 (1981).
- [22] J. Eichenauer and J. Lehn, *A nonlinear congruential pseudo random number generator*, Statist. papers **27** 315 (1986);  
J. Eichenauer-Herrmann, *Inversive congruential pseudo random numbers avoid the planes*, Math. Comp. **56** 297 (1991).
- [23] J. Eichenauer-Herrmann, *Statistical independence of a new class of inversive congruential pseudo random numbers*, Math. Comp. **60** 375 (1993);  
J. Eichenauer-Herrmann, *Explicit inversive congruential pseudo random numbers : the compound approach*, Computing **51** 175 (1993).
- [24] D. H. Lehmer, *Mathematical methods in large scale computing units*, Ann. Comp. Lab. Harvard Univ. **26** 141 (1951);  
N. A. Friggario and N. Clark, *Toward Truly Random Numbers*, Report ANL/ES-26 Part 4, Argonne National Laboratory (1978);  
G. Marsaglia, *A current view of random number generators*, in Proc. Computer Sci. and Stat., Sixteenth Symp. on Interface, Elsevier (1985);  
P. l'Ecuyer, *Efficient and portable combination of random number generators*, Comm. ACM **31** 742 (1988);  
F. James, *A review of pseudo random number generators*, Comp. Phys. Comm. **60** 329 (1990);  
M. Luscher, *A portable high-quality random number generator for lattice field theory simulations*, Comp. Phys. Comm. **79** 100 (1994);  
F. James, *RANLUX : A FORTRAN implementation of the high quality pseudo random number generator of Luscher*, Comp. Phys. Comm. **79** 111 (1994);  
G. Marsaglia and A Zaman, *Some portable very-long-period random number generators*, Computers in Physics **8** 117 (1994);  
Shu Tezuka, *Uniform Random Numbers: Theory and Practice*, Kluwer Academic Publishers, Boston (1995);

- F. Gutbrod, *New trends in pseudo random number generation* in Annual Reviews of Computational Physics VI, Edited by D. Stauffer, World Scientific (1999).
- [25] A. N. Kolmogorov, *Foundations of the Theory of Probability*, Chelsea, New York (1950);  
 R. von Mises, *Probability, Statistics and Truth*, MacMillan, New York (1957);  
 M. Kac, *Statistical Independence in Probability, Analysis and Number Theory*, Wiley, New York (1959);  
 J. C. Butcher, *A partition test for pseudo random numbers*, Math. Comp. **15** 198 (1961);  
 P. Martin-Löf, *The definition of random sequences*, Information and Control **9** 602 (1966);  
 R. P. Chambers, *Random number generation on digital computers*, IEEE Spectrum **4** 48 (1967);  
 M. Gardner, *On the meaning of randomness and some ways of achieving it*, Scientific American, July 1968 p. 116 ;  
 R. Coveyou, *Random number generation is too important to be left to chance*, Studies in Appl. Math. **3** 70 (1969);  
 D. Knuth, *The art of computer Programming*, Vol. 2, Reading Mass.: Addison Wesley (1969);  
 P. Martin-Löf in *Intuitionism and Proof Theory*, Eds. A. Kino, J. Myhill and R. B. Vesley, North Holland, Amsterdam (1970)p.73;  
 P. Kirchenmann, *Concepts of randomness*, J. Philosophical Logic **1** 395 (1972);  
 G. J. Chaitin, *Randomness and Mathematical proof*, Scientific American **232** 47 (1975);  
 G. J. Chaitin, *Information, Randomness and Incompleteness*, World Scientific, Singapore (1987);  
 A. de Mattis, *Order out of Chaos in Arithmetics in Dynamical Symmetries and Chaotic behaviour in Physical Systems*, Eds. G. Maino, L. Fronzoni and M. Petteni, World Scientific, Singapore (1989);  
 Ivar Eklund, *Au hasard* Editions du Seuil (1991): English translation : translated by Carol Volk: *Broken dice and mathematical tales of chance*, The university of Chicago Press (1993);  
 A. Bonelli and S. Ruffo, *Modular transformations, order-chaos transitions and pseudo random number generation*, Int. J. Mod. Phys. C **9** (4) (1998);  
 F. J. Resende and B. V. Costa, *Using random number generators in Monte Carlo calculations*, Phys. Rev. E **58** 5183 (1998);  
 G. Chaitin, *Exploring randomness*, Springer, New York (2001).
- [26] J. H. Ahren, U. Dieter and A. Grube, *Pseudo random numbers : a new proposal for choice of multipliers*, Computing **6** 121 (1970);  
 G. Marsaglia, B. Narasimhan and A. Zaman, *A random number generator for PC's*, Comp. Phys. Comm. **60** 345 (1990);  
 K. Kankaala, T. Ala-Nissila and I. Vattulainen, *Bit level correlations in some pseudo random number generators*, Phys. Rev. E **48** R4211 (1993);

- I. Vattulainen, *New tests of random numbers for simulations in physical systems*, arXiv: cond-mat/9411062 (1994);
- I. Vattulainen, T. Ala-Nissila and K. Kanakaala, *Physical tests for random numbers in simulations*, Phys. Rev. Lett. **73** 2513 (1994);
- I. Vattulainen, K. Kanakaala, J. Saarinen and T. Ala-Nissila, *A comparative study of pseudo random number generators*, Comp. Phys. Commun. **86** 209 (1995);
- I. Vattulainen, T. Ala-Nissila and K. Kanakaala, *Physical models as tests of randomness*, Phys. Rev. E **52** 3205 (1995);
- Shu-Ju Tu and E. Fischbach, *Geometric random inner products: a new family of tests for random number generators*, eprint: arXiv : physics/0209032 (2002).
- [27] A. M. Ferrenberg, D. P. Landau and Y. J. Wong, *Monte Carlo Simulations : Hidden errors from "good" random number generators*, Phys. Rev. Lett. **69** 3382 (1992).
- [28] P. R. Coddington, *Analysis of random number generators using Monte Carlo simulation*, Int. J. Mod. Phys. C **5** 547 (1994).
- [29] A. Heuer, B. Dünweg and A. M. Ferrenberg, *Considerations on correlations in shift-register pseudo random number generators and their removal*, Comput. Phys. Commun. **103** 1 (1997).
- [30] L. N. Shchur and H. W. J. Blöte, *Cluster Monte Carlo: Scaling of systematic errors in the two-dimensional Ising model*, Phys. Rev. E **55** R4905 (1997).
- [31] M. Greenberger, *An à priori determination of serial correlation in computer generated random numbers*, Math. Comp. **15** 383 (1961);
- M. Greenberger, Comm. ACM **8** 177 (1965);
- N. A. Friggario and N. Clark, *A random number set for Monte Carlo computations*, Trans. Amer. Nucl. Soc. **22** 283 (1975);
- A. Hoogland, J. Spaa, B. Selman and A. Compagner, J. Comp. Phys. **51** 250 (1983);
- G. Parisi and F. Rapuano, *Effects of random number generator on computer simulations*, Phys. Lett. B **157** 301 (1985);
- G. Marsaglia and A. Zaman, Ann. Appl. Probability **1** 462 (1991);
- P. Grassberger, *Monte Carlo simulation of three dimensional self avoiding walks*, J. Phys. A: Math. Gen. **26** 2769 (1993);
- P. Grassberger, *On correlations in "good" random number generators*, Phys. Lett. A **181** 43 (1993);
- F. Schmid and N. B. Wilding, *Errors in Monte Carlo simulations using shift register random number generators*, Int. J. Mod. Phys. C **6** 781 (1995);
- L. N. Shchur, J. R. Heringa and H. W. J. Blöte, *Simulation of a directed random walk model: The effect of pseudo random number correlations*, Physica A **241** 579 (1997);
- A. Heuer, B. Dünweg and A. M. Ferrenberg, *Considerations on correlations in shift-register pseudo random number generators and their removal*, Comput.

- Phys. Commun. **103** 1 (1997);  
 R. M. Ziff, *Four-tap shift-register-sequence random-number generators*, Computers in Physics **12** 385 (1998);  
 S. Mertens and H. Bauke, *Entropy of pseudo random number generators*, Preprint, Institute for theoretical physics, Otto-von-Guericke Universität, Germany (2003); eprint: arXiv: cond-mat/0305319 (2003);  
 H. Bauke and S. Mertens, *Pseudo random coins show more heads than tails*, eprint: arXiv: cond-mat/0307138 (2003).
- [32] A. Compagner, *Operational conditions for random-number generation*, Phys. Rev. E **52** 5634 (1995).
- [33] W. Janke, *Pseudo random numbers : Generation and quality checks in Quantum Simulations of Complex Many-Body Systems: From Theory to Algorithms*, Lecture Notes, J. Grotendorst, D. Marx and A. Muramatsu (Eds.) John von Neumann Institute for Computing, Jülich, NIC series: vol. 10 (2002)p.447.
- [34] J. F. Fernández and J. Rivero, *Fast algorithms for random numbers with exponential and normal distributions*, Computers in Physics **10** 83 (1996).
- [35] J. F. Fernández and C. Criado, *Algorithm for normal random numbers*, Phys. Rev. E **60** 3361 (1999);  
 see also M. I. J. Probert, *Comment on "Algorithm for normal random numbers"*, Phys. Rev. E **63** 058701 (2001);  
 J. F. Fernández and C. Criado, *Reply to "Comment on 'Algorithm for normal random numbers' "*, Phys. Rev. E **63** 058702 (2001).
- [36] G. E. P. Box and Müller, *A note on the generation of normal random deviates*, Ann. Math. Statist. **29** 610 (1958).
- [37] M. Abramowitz and I. S. Stegun (eds.), *Handbook of Mathematical functions* Dover, New York (1972).
- [38] E. D. Cashwell and C. J. Evert, *A Practical Manual of Monte Carlo Method for Random Walk Problems*, Pergamon, New York (1959);  
 J. Spanier and E. M. Gelbard, *Monte Carlo Principles and Neutron Transport Problems*, Addison Wesley (1969);  
 E. C. McGrath and D. C. Irving, *Techniques for Efficient Monte Carlo Simulation*, Vol. I, II, and III, Report ORNL-RSIC-38, Oak Ridge National Laboratory (1975).
- [39] J. M. Hammersley and D. C. Handscomb, *Monte Carlo Methods*, Chapman and Hall, London (1964);  
 M. H. Kalos and P. A. Whitlock, *Monte Carlo Methods, Vol. 1: Basics*, John Wiley, New York (1986);  
 I. M. Sobol, *The Monte Carlo Method*, Mir, Moscow (1975);  
 Samuel S. M. Wong, *Computational Methods in Physics and Engineering*, Prentice Hall (1992);  
 F. James, *Monte Carlo theory and practice*, Rep. Prog. Phys. **43** 1145 (1980).



- [40] K. Binder (Ed.), Monte Carlo Methods in statistical Physics, *Topics in Current Physics*, Vol. 7, I edition Springer (1970), II edition, Springer (1986);  
K. Binder(Ed.), Applications of the Monte Carlo Method in Statistical Physics, *Topics in Current Physics*, Vol. 36, I edition, Springer (1984), II edition, Springer (1987);  
K. Binder (Ed.), The Monte Carlo Method in Condensed Matter Physics, *Topics in Applied Physics*, I edition 1992, II edition 1995, Springer;  
K. Binder and D. W. Heermann, *Monte Carlo Simulation in Statistical Physics: An Introduction*, Springer (1988);  
Paul Coddington, *Monte Carlo simulation for Statistical Physics*, Report CPS-713, Northeast Parallel Architectures (1996).
- [41] K. P. N. Murthy, *Monte Carlo: Basics*, Monograph ISRP/TD-3, Indian Society for Radiation Physics (2000). (eprint: arXiv : cond-mat/0104215 v1 12 April 2001).
- [42] H. Kahn, *Random sampling Monte Carlo techniques in neutron attenuation problems I*, *Nucleonics* **6** 27 (1950);  
H. Kahn, *Random sampling Monte Carlo techniques in neutron attenuation problems II*, *Nucleonics* **6** 61 (1950);  
J. Spanier, *An analytic approach to variance reduction*, *SIAM J. Appl. Math.* **18** 172 (1970);  
F. H. Clark, *Exponential transform as an importance sampling device - a review*, Report ORNL-RSIC-14, Oak Ridge National Laboratory (1966).
- [43] K. P. N. Murthy, *Exponential biasing - an update* in Proceedings of the National Conference on Radiation Shielding and Protection (RASP-96), Indira Gandhi Centre for Atomic Research, Kalpakkam June 26-28 (1996), Allied Publishers Ltd. (1996)p.70;  
K. P. N. Murthy and R. Indira, *Analytical results on variance reduction characteristics of biased Monte Carlo for deep penetration problems*, *Nucl. Sci. Eng.* **92** 482 (1986);  
K. P. N. Murthy, *Asymptotic survival probability of random walks on a semi-infinite line*, *Pramana - J. Phys.* **25** 231 (1985);  
G. Ananthakrishna and K. P. N. Murthy, *Influence of scattering anisotropy on optimal exponential biasing in Monte Carlo radiation transport: a correlated random walk model*, *Ann. Nucl. Ener.* **12** 195 (1985);  
R. Indira and K. P. N. Murthy, *Effect of scattering anisotropy on optimal choice of parameters for tracklength biasing*, *Ann. Nucl. Ener.* **12** 97 (1985);  
K. P. N. Murthy, *Optimal choice of parameters for tracklength biasing in Monte Carlo deep penetration problems*, *Ann. Nuc. Ener.* **10** 375 (1983);  
K. P. N. Murthy, *A comparative study of different tracklength biasing schemes*, *Ann. Nucl. Ener.* **7** 389 (1980);  
K. P. N. Murthy, *Tracklength biasing in Monte Carlo radiation transport*, *Atomkernenergie.Kerntechnik* **34** 125 (1979).
- [44] S. G. Brush, *History of the Lenz-Ising model*, *Rev. Mod. Phys.* **39** 883 (1967).

- [45] L. Onsager, *Crystal statistics I. A two - dimensional model with an order - disorder statistics*, Phys. Rev. **65** 117 (1944).
- [46] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller and E. Teller, *Equation of state calculation by fast computing machine*, J. Chem. Phys. **21** 1087 (1953);  
For a delightful account of the Metropolis rejection technique through the Monte Carlo game of throwing pebbles randomly on a square with an inscribed circle, see W. Krauth, *Introduction to Monte Carlo algorithm*, eprint: arXiv : cond-mat/9612186, 20 Dec. 1996; see also <http://lps.ens.fr/krauth>
- [47] O. Peron, Math. Ann. **64** 1 (1907).
- [48] F. R. Gantmacher, *Applications of the theory of matrices*, Interscience (1959).
- [49] G. Bhanot, *The Metropolis algorithm*, Rep. Prog. Phys. **51** 429 (1988).
- [50] R. J. Glauber, *Time-dependent statistics of the Ising model*, J. Math. Phys. **4** 294 (1963).
- [51] H. Hinrichsen and E. Domany, *Damage spreading in Ising model*, Phys. Rev. **E56** 94 (1997).
- [52] C. J. Geyer and E. A. Thompson, *Annealing Markov chain Monte Carlo with applications to ancestral inference*, J. Am. Stat. Assoc. **90** 909 (1995);  
D. Frenkel and B. Smit, *Understanding molecular simulations*, Academic, San Diego (1996);  
M. C. Tesi, E. J. Janse van Rensburg, E. Orlandini and S. G. Whittington, *Monte Carlo study of the Interacting Self Avoiding Walk model in three dimensions*, J. Stat. Phys. **82** 155 (1996);  
M. C. Tesi, E. J. Janse van Rensburg, E. Orlandini and S. G. Whittington, *Interacting Self Avoiding walks and polygons in three dimensions*, J. Phys. A **29** 2451 (1996);  
U. E. Hansmann, *Parallel tempering algorithms for conformational studies of biological molecules*, Chem. Phys. Lett. **281** 140 (1997);  
G. Thorleifsson and M. Falcioni, *Improved algorithms for simulating crystalline membranes*, Comp. Phys. Commun. **109** 161 (1998).
- [53] V. I. Manousiouthakis and M. W. Deem, *Strict detailed balance is unnecessary in Monte Carlo simulations*, J. Chem Phys. **110** 2753 (1999).
- [54] J. R. Norris, *Markov Chains*, Cambridge University press (1997).
- [55] J. G. Kennedy, J. L. Snell, and A. W. Knapp, *Denumerable Markov chains*, Springer-Verlag, New York (second edition) (1976).
- [56] G. E. Crooks, *Nonequilibrium measurements of free energy differences for microscopically reversible Markovian systems*, J. Stat. Phys. **90** 1481 (1998);  
G. E. Crooks, *Entropy production fluctuation theorem and the nonequilibrium*

- work relation for free energy differences*, Phys. Rev. E **60** 2721 (1999);  
G. E. Crooks, *Path-ensemble averages in systems driven far from equilibrium*, Phys. Rev. E **61** 2361 (2000);  
G. E. Crooks, *Excursions in Statistical Mechanics*, Ph. D. Thesis, University of California at Berkeley (1999); <http://threeplusone.com/pubs/GECthesis.html>
- [57] A. B. Bortz, M. H. Kalos and J. L. Lebowitz, *A new algorithm for Monte Carlo simulation of Ising spin systems*, J. Comp. Phys. **17** 10 (1975).
- [58] M. A. Novotny, *Monte Carlo with absorbing Markov chains: fast local algorithm for slow dynamics*, Phys. Rev. Lett. **74** 1 (1995); *Erratum*, **75** 1424 (1995); eprint: arXiv: cond-mat/9411081 (1994);  
M. A. Novotny, *A new approach to an old algorithm for the simulation of of Ising-like spin systems*, Computers in Physics **9** 46 (1995).
- [59] M. A. Novotny, *A tutorial on advanced dynamic Monte Carlo methods for systems with discrete state spaces*, eprint: arXiv:cond-mat/0109182 (2001).
- [60] H. Müller Krumbhaar and K. Binder, *Dynamical properties of the Monte Carlo method in statistical mechanics*, J. Stat. Phys. **8** 1 (1973).
- [61] H. Flyvbjerg and H. G. Petersen, *Error estimates on averages of correlated data*, J. Chem. Phys. **91** 461 (1989).
- [62] R. H. Swendsen and J.-S. Wang, *Nonuniversal critical dynamics in Monte Carlo simulation*, Phys. Rev. Lett. **58** 86 (1987).
- [63] P. W. Kasteleyn, C. M. Fortuin, J. Phys. Soc. Japan Suppl. **26** 11 (1969); C. M. Fortuin and P. W. Kasteleyn, *On the random - cluster model: I. Introduction and relation to other models*, Physica(Utrecht) **57** 536 (1972).
- [64] A. Coniglio and W. Klein, *Clusters and Ising critical droplets: a renormalization group approach*, J. Phys. A **13** 2775 (1980).
- [65] S. R. Broadbent and J. M. Hammersley, *Percolation processes*, Proc. Camb. Phil. Soc. **53** 629641 (1957).
- [66] D. Stauffer *Introduction to Percolation Theory*, Taylor and Francis, London (1985). see also: Aharony and Stauffer, *Percolation theory*, Taylor and Francis, London (1994).
- [67] C. -K. Hu, *Correlated percolation and a sub-lattice dilute Potts model at  $T \rightarrow 0$* , Physica A **116** 265 (1982);  
C. -K. Hu, *Exact results for a correlated percolation model*, Physica A **119** 609 (1983);  
C. -K. Hu, *Percolation, clusters and phase transition in spin models*, Phys. Rev. B **29** 5103 (1984).

- [68] J. Hoshen and R. Kopelman, *Percolation and cluster distribution. I. Cluster multiple labelling technique and critical concentration algorithm*, Phys. Rev. B **14** 3438 (1976).
- [69] F. Babalievski, *Cluster counting: The Hoshen-Kopelman algorithm versus spanning tree approaches*, Int. J. Mod. Phys. C **9** 43 (1998).
- [70] J. Hoshen, M. W. Berry and K. S. Minser, *Percolation and cluster structure parameters: the enhanced Hoshen-Kopelman algorithm*, Phys. Rev. E **56** 1455 (1997).
- [71] Ahmed Al-Futaisi and T. W. Patzek, *Extension of Hoshen-Kopelman algorithm to non-lattice environments*, Physica A **321** 665 (2003).
- [72] U. Wolff, *Collective Monte Carlo updating for spin systems*, Phys. Rev. Lett. **62** 361 (1989).
- [73] J. Machta, Y. S. Choi, A. Lucke, T. Schweizer and L. M. Chayes, *Invaded cluster algorithm for equilibrium critical points*, Phys. Rev. Lett. **75** 2792 (1995);  
J. Machta, Y. S. Choi, A. Lucke, T. Schweizer and L. M. Chayes, *Invaded cluster algorithm for Potts models*, Phys. Rev. E **54** 1332 (1996);  
G. Franzese, V. Cataudella and A. Coniglio, *Invaded cluster dynamics for frustrated models*, Phys. Rev. E **57** 88 (1998).
- [74] J. M. Hammersley in *Methods of computational physics*, Academic, New York (1963) vol. I.
- [75] Y. Tomita and Y. Okabe, *Probability changing cluster algorithm for Potts model*, Phys. Rev. Lett. **86** 572 (2001);  
Y. Tomita and Y. Okabe, *Probability-changing cluster algorithm: study of three - dimensional Ising model and percolation problem*, eprint: arXiv : cond-mat/0203454 (2002).
- [76] V. K. Gore and M. R. Jerrum, *The Swendsen-Wang process does not always mix rapidly*, J. Stat. Phys. **97** 67 (1999).
- [77] L. de Arcangelis, A. Coniglio and F. Peruggi, Europhys. Lett. **37** 7384 (1985);  
V. Cataudella, *Percolation transition in systems with frustration*, Physica A **183** 249 (1992);  
P. W. Leung and C. L Henley, *Percolation properties of Wolff clusters in planar triangular spin models*, Phys. Rev. B **43** 752 (1992).
- [78] D. Kandel, R. Ben-Av and R. Domnay, *Cluster dynamics for fully frustrated systems*, Phys. Rev. Lett. **65** 941 (1990);  
D. Kandel and E. Domnay, *General cluster Monte Carlo dynamics*, Phys. Rev. B **43** 8539 (1991);  
D. Kandel, R. Ben -Av and E. Domnay, *Cluster Monte Carlo dynamics for the fully frustrated Ising model*, Phys. Rev. B **45** 4700 (1992);  
V. Cataudella, G. Franzese, M. Nicodemi, A. Scala and A. Coniglio, *Critical*

- clusters and efficient dynamics for frustrated spin models*, Phys. Rev. Lett. **72** 1541 (1994);  
V. Cataudella, G. Franzese, M. Nicodemi, A. Scala and A. Coniglio, *Il Nuovo Cimento D* **16** 1259 (1994);  
V. Cataudella, G. Franzese, M. Nicodemi, A. Scala and A. Coniglio, *Percolation and cluster Monte Carlo dynamics for spin models*, Phys. Rev. E **54** 175 (1996);  
G. Franzese, *Cluster analysis for percolation on a two dimensional fully frustrated system*, J. Phys. A: Math. Gen. **29** 7367 (1996).
- [79] Z. W. Salsburg, J. D. Jackson, W. Fickett and W. W. Wood, *Application of Monte Carlo method to the lattice gas model. I. Two dimensional triangular lattice*, J. Chem. Phys. **30** 65 (1959);  
D. A. Chesnut and Z. W. Salsburg, *Monte Carlo procedure for statistical mechanical calculations in a grand canonical ensemble of lattice systems*, J. Chem. Phys. **38** 2861 (1963);  
I. R. McDonald and K. Singer, *Discuss. Faraday Soc.* **43** 40 (1967);  
I. R. McDonald and K. Singer, *Machine calculation of thermodynamic properties of a simple fluid at supercritical temperature*, J. Chem. Phys. **47** 4766 (1967);  
I. R. McDonald and K. Singer, *Estimation of the adequacy of the 12-6 potential for liquid Argon by means of Monte Carlo calculations*, J. Chem. Phys. **50** 2308 (1969);  
J. P. Valleau and D. N. Card, *Monte Carlo estimation of free energy by multi-stage sampling*, J. Chem. Phys. **57** 5457 (1972);  
G. Bhanot, S. Black, P. Carter and R. Salvador, *A new method for the partition function of discrete systems with applications the 3D Ising model*, Phys. Lett. B **183** 331 (1987);  
G. Bhanot, K. M. Bitar, S. Black, P. Carter and R. Salvador, *The partition function of  $Z(2)$  and  $Z(8)$  lattice gauge theory in four dimensions, a novel approach to simulations of lattice systems*, Phys. Lett. B **187** 381 (1987).
- [80] G. Torrie and J. P. Valleau, *Monte Carlo free energy estimates using non-Boltzmann sampling: application to the sub-critical Lennard-Jones fluid*, Chem. Phys. Lett. **28** 578 (1974).
- [81] A. M. Ferrenberg and R. H. Swendsen, *New Monte Carlo technique for studying phase transition*, Phys. Rev. Lett. **61** 2635 (1988).
- [82] K. Venu, V. S. S. Sastri and K. P. N. Murthy, *Nematic - Isotropic Transition in porous media - a Monte Carlo Study*, Europhys. Lett. **58** 646 (2002).
- [83] A. M. Ferrenberg and R. H. Swendsen, *Optimized Monte Carlo data analysis*, Phys. Rev. Lett. **63** 1195 (1989);  
C. H. Bennet, *Efficient estimation of free energy difference from Monte Carlo data*, J. Comput. Phys. **22** 245 (1976);  
N. A. Alves, B. A. Berg, and R. Villanova, *Ising model Monte Carlo simulations: density of states and mass gap*, Phys. Rev. B **41** 383 (1990).

- [84] B. A. Berg and T. Neuhaus, *Multicanonical algorithms for first order phase transition*, Phys. Lett. B **267** 249 (1991);  
B. A. Berg and T. Neuhaus, *Multicanonical ensemble: a new approach to simulation of first order phase transition*, Phys. Rev. Lett. **68** 9 (1992).
- [85] J. Lee, *New Monte Carlo algorithm: entropic sampling*, Phys. Rev. Lett. **71** 211 (1993); Erratum: **71** 2353 (1993).
- [86] G. M. Torrie and J. P. Valleau, *Nonphysical sampling distributions in Monte Carlo free energy estimation: umbrella sampling*, J. Comp. Phys. **23** 187 (1977);  
G. M. Torrie and J. P. Valleau, *Monte Carlo study of a phase separating liquid mixture by umbrella sampling*, J. Chem. Phys. **66** 1402 (1977);  
I. S. Graham and J. P. Valleau, *A Monte Carlo study of the coexistence region of the restricted primitive model*, J. Phys. Chem. **94** 7894 (1990);  
J. P. Valleau, *Density scaling : a new Monte Carlo technique in statistical mechanics*, J. Comp. Phys. **96** 193 (1991);  
J. P. Valleau, *Density scaling Monte Carlo study of subcritical Lennard - Jonesium*, J. Chem. Phys. **99** 4718 (1993).
- [87] B. A. Berg, H. E. Hansmann and Y. Okamoto, *Comment on "Monte Carlo Simulation of a first-order phase transition for protein folding"* eprint: arXive : chem-ph/9411007 v1 (1994).
- [88] P. M. C. de Olivera, T. J. P. Penna, H. J. Herrmann, *Broad histogram method*, Braz. J. Phys. **26** 677 (1996);  
P. M. C. de Olivera, *Broad histogram relation is exact*, Eur. Phys. J. B **6** 111 (1998);  
B. A. Berg, U. H. E. Hansmann, *Configuration space for random walk dynamics*, Eur. Phys. J. B **6** 395 (1998);  
P. M. C. de Olivera, T. J. P. Penna and H. J. Herrmann, *Broad histogram Monte Carlo*, Eur. Phys. J. B **1** 205 (1998);  
M. E. J. Newman and R. G. Palmer, *Error estimation in the histogram Monte Carlo method*, J. Stat. Phys. **97** 1011 (1999);  
J. -S. Wang, *Is the broad histogram random walk correct ?*, Eur. Phys. J. B **8** 287 (1999);  
J. -S. Wang and L. W. Lee, *Monte Carlo algorithms based on number of potential moves*, Comput. Phys. Commun. **127** 131 (2000);  
J. -S. Wang, *Flat histogram Monte Carlo method*, Physica A **281** 147 (2000);  
P. M. C. de Olivera, *Broad histogram : an overview*, Braz. J. Phys. **30** 195 (2000);  
P. M. C. de Olivera, *Broad histogram : Tests for a simple and efficient micro-canonical simulator*, Braz. J. Phys. **30** 766 (2000);  
M. Kastner and M. Promberger, *Comments on " A comparison between broad histogram and multicanonical methods*, J. Stat. Phys. **104** 893 (2001);  
P. M. C. de Olivera, *Simple dynamics for broad histogram method*, Comp. Phys. Commun. **147** 410 (2002).

- [89] J. -S. Wang, T. K. Tay and R. H. Swendsen, *Transition matrix Monte Carlo reweighting and dynamics*, Phys. Rev. Lett. **82** 476 (1999);  
J. -S. Wang, *Transition matrix Monte Carlo method*, Comp. Phys. Commun. **121-122** 22 (1999);  
R. H. Swendsen, B. Diggs, J. -S. Wang, S. -T. Li, C. Genovese, and J. B. Kadane, *Transition matrix Monte Carlo*, Int. J. Mod. Phys. C **10** 1563 (1999);  
M. Fitzgerald, R. R. Picard and R. N. Selvier, *Monte Carlo transition dynamics and variance reduction*, J. Stat. Phys. **98** 321 (2000);  
M. Fitzgerald, R. R. Picard and R. N. Selvier, *Canonical transition probabilities for adaptive Metropolis simulation*, Europhys. Lett. **46** 282 (1999);  
J. -S. Wang, and R. H. Swendsen, *Transition matrix Monte Carlo Method*, J. Stat. Phys. **106** 245 (2001).
- [90] G. J. Geyer and E. A. Thompson, J. Amer. Stat. Ass. **90** 909 (1995);  
K. Hukushima, H. Takagama and K. Nemoto, *Application of an extended ensemble method to spin glasses*, Int. J. Mod. Phys. C **7** 337 (1996).
- [91] A. P. Lyubartsev, A. A. Martinovskii, S. V. Shevkunov and P. N. Vorontsov - Velyaminov, *New approach to Monte Carlo calculation of the free energy : method of expanded ensembles*, J. Chem. Phys. **96** 1776 (1992);  
E. Marinari and G. Parisi, *Simulated tempering: a new Monte Carlo scheme*, Europhys. Lett. **19** 451 (1992).
- [92] J. A. Plascak, A. M. Ferrenberg and D. P. Landau, *Cluster hybrid Monte Carlo simulation algorithm*, Phys. Rev. E **65** 066702 (2002);  
for some early work on hybrid algorithms see,  
S. Duane, A. D. Kennedy, B. J. Pendelton and D. Roweth, *Hybrid Monte Carlo*, Phys. Lett. B **195** 216 (1987);  
D. W. Heermann, P. Nieaba and M. Revere, *Hybrid molecular dynamics*, Comput. Phys. Commun. **60** 311 (1980);  
F. R. Brown and T. J. Woch, *Over relaxed heat bath and Metropolis algorithms for accelerating pure gauge Monte Carlo calculations*, Phys. Rev. Lett. **58** 2394 (1987);  
M. Cruetz, *Over relaxation and Monte Carlo simulations*, Phys. Rev. D **36** 515 (1987).
- [93] G. R. Smith and A. D. Bruce, *A study of multicanonical Monte Carlo method*, J. Phys. A **28** 6623 (1995);  
E. Marinari, *Optimized Monte Carlo Methods*, Adv. Comp. Simulation (Eds.) J. Kertesz and I. Kondor, Springer (1997) and eprint: arXiv : cond-mat/9612010 (1996);  
A. Gelmann and Xiao-Li Meng, *Simulating normalizing constants: from importance sampling to bridge sampling to path sampling*, Statist. Science **13** 163 (1998);  
G. Besold, J. Risbo and O. G. Mouritsen, *Efficient Monte Carlo sampling by direct flattening of free energy barriers*, Comp. Mater. Sci., **15** 311 (1999);  
B. A. Berg, *Introduction to multicanonical Monte Carlo simulations*, Fields Inst.

- Commun. **26** 1 (2000) and eprint: arXiv : cond-mat/9909236(1999);  
 Y. Iba, *Extended ensemble Monte Carlo*, eprint: arXiv : cond-mat/0012323 v2 (2001);  
 J. -S. Wang, *Efficient Monte Carlo simulation methods in statistical physics*, eprint: arXiv : cond-matt/0103318 (2001);  
 B. A. Berg, *Multicanonical simulations step by step*, Comput. Phys. Commun. **153** 397 (2003).
- [94] B. A. Berg, U. Hansmann and T. Neuhaus, *Simulation of an ensemble with varying magnetic field: a numerical determination of the order - order interface tension in the  $D=2$  Ising model*, Phys. Rev. B **47** 497 (1993);  
 B. A. Berg, U. Hansmann and T. Neuhaus, *Properties of Interfaces in the two and three dimensional Ising model*, Z. Phys. B **90** 229 (1993).
- [95] W. Janke, B. A. Berg, and M. Katoot, *Monte Carlo calculation of the surface free energy for the two-dimensional 7-state Potts model, and an estimate for four dimensional  $SU(3)$  gauge theory*, Nucl. Phys. B **382** 649 (1992);  
 W. Janke, *Multicanonical simulation of the two - dimensional 7-state Potts model*, Int. J. Mod. Phys. C **3** 1137 (1992);  
 K. Rammukainen, *Multicanonical cluster algorithm and the two dimensional 7-state Potts model*, Nucl. Phys. B **390** 621 (1993);  
 C. Borgs and W. Janke, *An explicit formula for the interface tension of 2D Potts model*, J. de Physique I (Paris) **2** 2011 (1992);  
 A. Billoire, T. Neuhaus and B. A. Berg, *A determination of interface free energies*, Nucl. Phys. B **413** 795 (1994).
- [96] N. B. Wilding, *Critical-point and coexistence-curve properties of the Lennard-Jones fluid: a finite-size scaling study*, Phys. Rev. E **52** 602 (1995);  
 N. B. Wilding and Müller, *Liquid - vapour asymmetry in pure fluids: a Monte Carlo study*, J. Chem. Phys. **102** 2562 (1995).
- [97] G. R. Smith and A. D. Bruce, *Multicanonical Monte Carlo study of a structural phase transition*, Europhys. Lett. **34** 91 (1996);  
 G. R. Smith and A. D. Bruce, *Multicanonical Monte Carlo study of solid-solid phase coexistence in model colloids*, Phys. Rev. E **53** 6530 (1996).
- [98] B. A. Berg, *Multicanonical spin glass simulations*, Int. J. Mod. Phys. C **3** 1251 (1992);  
 B. A. Berg and T. Celik, *New approach to spin glass simulation*, Phys. Rev. Lett. **69** 2292 (1992);  
 T. Celik, *Multicanonical simulations of 2D and 3D Ising spin glasses*, Nucl. Phys. B Proc. Suppl. **30** 908 (1993);  
 B. A. Berg, *Multicanonical study of the 3-D Ising spin glass*, Europhys. Lett. **22** 63 (1993);  
 U. H. E. Hansmann and B. A. Berg, *Spin glass ground state investigation by multicanonical ensemble*, Int. J. Mod. Phys. C **5** 263 (1994);  
 B. A. Berg, U. H. E. Hansmann and T. Celik, *Ground state properties of the*



- 3D Ising spin glass*, Phys. Rev. B **50** 16444 (1994);  
B. A. Berg and U. H. E. Hansmann, *Multicanonical study of 3d Ising spin glass at zero temperature*, Nucl. Phys. B Proc. Suppl. **34** 664 (1990);  
K. K. Bhattacharya and J. P. Sethna, *Multicanonical methods, molecular dynamics and Monte Carlo methods: comparison for Lennard-Jones glass*, Phys. Rev. E **57** 2553 (1998).
- [99] U. H. E. Hansmann and Y. Okamoto, *Prediction of peptide conformations by multicanonical algorithm : a new approach to multiple minima problem*, J. Comp. Chem. **14** 1333 (1993);  
M. H. Hao and H. A. Scheraga, *Monte Carlo simulation of a first - order transition for protein folding*, J. Phys. Chem. **98** 4940 (1994);  
U. H. E. Hansmann and Y. Okamoto, *Comparative study of multicanonical and simulated annealing algorithms in the protein folding problem*, Physica A **212** 415 (1994);  
U. H. E. Hansmann and Okamoto, *Multicanonical approach in statistical mechanics of peptides*, Nucl. Phys. B Proc. Suppl. **42** 914 (1995);  
U. H. E. Hansmann and Y. Okamoto, *Monte Carlo simulations in generalized ensemble: multicanonical algorithm versus simulated tempering*, Phys. Rev. E **54** 5863 (1996);  
N. Nakajima, J. Higo, A. Kidera and H. Nakamura, *Flexible docking of a ligand peptide to a receptor protein by a multicanonical molecular dynamics simulation*, Chem. Phys. Lett. **278** 297 (1997);  
N. Nakajima, H. Nakamura and A. Kidera, *Multicanonical ensemble generated by Molecular dynamics simulation for enhanced conformational sampling of peptides*, J. Phys. Chem. B **101** 817 (1997);  
H. Shirai, N. Nakajima, J. Higo, A. Kidera and H. Nakamura, *Conformational sampling of CDR-H3 in antibodies by multicanonical molecular dynamics simulation*, J. Molec. Biol. **278** 481 (1998);  
N. Nakajima, *A selectively enhanced multicanonical molecular dynamics method for conformational sampling of peptides in realistic water molecules*, Chem. Phys. Lett. **288** 319 (1998).
- [100] A. Kalyan Chakravarthy, K. Venu, V. S. S. Sastri and K. P. N. Murthy, *Multicanonical Markov chain Monte Carlo simulation of Nematic - Isotropic phase transition in liquid crystals*, (unpublished) (2003).
- [101] F. Wang, and D. P. Landau, *Multiple range algorithm for calculation of density of states*, Phys. Rev. Lett. **86** 2050 (2001);  
F. Wang and D. P. Landau, *Determining the density of states for classical statistical models: A random walk algorithm to produce a flat histogram*, Phys. Rev. E **64** 056101 (2001);  
F. Wang and D. P. Landau, *Determining the density of states for classical statistical models by a flat-histogram random walk*, Comp. Phys. Commun. **147** 674 (2002).

- 
- [102] C. Yamaguchi and Y. Okabe, *Three - dimensional antiferromagnetic q-state Potts model: application of the Wang-Landau algorithm*, J. Phys. A **34** 8781 (2001).
- [103] M. Troyer, S. Wessel and F. Alet, *Flat histogram methods for quantum systems : algorithms to overcome tunneling problems and calculate the free energy*, Phys. Rev. Lett. **90** 120201 (2003).
- [104] Y. Okabe, Y. Tomita and C. Yamaguchi, *Application of new Monte Carlo algorithms to random spin systems*, Comp. Phys. Commun. **146** 63 (2002).
- [105] T. S. Jain and J. J. de Pablo, *A biased Monte Carlo technique for calculation of the density of states of polymer films*, J. Chem. Phys. **116** 7238 (2002).
- [106] N. Rathore and J. J. de Pablo, *Monte Carlo simulation of proteins through a random walk in energy space*, J. Chem. Phys. **116** 7225 (2002).
- [107] M. S. Shell, P. G. Debenedetti and A. Z. Panagiotopoulos, *Generalization of the Wang - Landau method for off-lattice simulations*, Phys. Rev. E **66** 056703 (2002);  
Q. Yan, R. Faller and J. J. de Pablo, *Density-of-states Monte Carlo method for simulation of fluids*, J. Chem. Phys. **116** 8745 (2002).
- [108] F. Calvo, *Sampling along reaction coordinates with the Wang-Landau method*, Molecular Physics **100** 3421 (2002).
- [109] B. J. Schulz, K. Binder and M. Müller, *Flat histogram method of Wang - Landau and n-fold way*, Int. J. Mod. Phys. C **13** 477 (2002); eprint: arXiv: cond-mat/0112037 v2 3 Dec. (2001).
- [110] B. J. Schulz, K. Binder, M. Müller and D. P. Landau, *Avoiding boundary effects in Wang - Landau algorithm method*, eprint: arXiv : cond-mat/0302123 (2003).
- [111] Q. Yan and J. J. de Pablo, *Fast calculation of the density of states of a fluid by Monte Carlo simulation*, Phys. Rev. Lett. **90** 035701 (2003);  
M. S. Shell, P. G. Debenedetti and A. Z. Panagiotopoulos, *An improved Monte Carlo method for direct calculation of the density of states* eprint: arXiv : cond-mat/0305210 (2003);  
C. Zhou and R. N. Bhatt, *Understanding and improving the Wang - Landau algorithm*, eprint: arXiv : cond-mat/0306711 (2003).
- [112] C. Yamaguchi and N. Kawashima, *Combination of improved multibondic method and the Wang - Landau method*, Phys. Rev. E **65** 056710 (2002).
- [113] S. K. Ma, *Calculation of entropy from data of motion*, J. Stat. Phys. **26** 221 (1981).
- [114] R. W. Zwanzig, *High temperature equation of state by a perturbation method: I. Non polar gases*, J. Chem. Phys. **22** 1420 (1954);  
C. H. Bennet, *Efficient estimation of free energy differences from Monte Carlo*

- data*, J. Comput. Phys. **22** 245 (1976);  
K. K. Mon and R. B. Griffiths, *Chemical potential by gradual insertion of a particle in Monte Carlo simulation*, Phys. Rev. A **31** 956 (1985);  
D. L. Beveridge and F. M. DiCapua, *Free energy via molecular simulation: applications to chemical and biomolecular systems*, Annu. Rev. Biophys. Biophys. Chem. **18** 431 (1989);  
T. P. Straatsma and J. A. McCammon, *Computational alchemy*, Annu. Rev. Phys. Chem. **43** 407 (1992);  
D. Frenkel and B. Smit, *Understanding Molecular Simulation: From Algorithms to Applications*, Academic Press (1996);  
R. J. Radmer and P. A. Kolman, *Free energy calculation methods: a theoretical and empirical comparison of numerical errors and a new method for qualitative estimates of free energy changes*, C. Comput. Chem. **18** 902 (1997).
- [115] H. B. Callen and T. A. Welton, *Irreversibility and generalized noise*, Phys. Rev. **83** 34 (1951).
- [116] C. Jarzynski, *Nonequilibrium equality for free energy differences*, Phys. Rev. Lett. **78** 2690 (1997).
- [117] C. Jarzynski, *Equilibrium free-energy differences from nonequilibrium measurements: a master-equation approach*, Phys. Rev. E **56** 5018 (1997); eprint: arXiv: cond-mat/9707325 (1997).
- [118] G. Hummer and A. Szabo, *Free energy reconstruction from nonequilibrium single-molecule pulling experiment*, Proc. Nat. Acad. Sci. USA **98** 3658 (2001);  
J. Liphardt, S. Dumont, S. B. Smith, I. Tinoco Jr., and C. Bustamante, *Equilibrium information from nonequilibrium measurements in an experimental test for Jarzynski's equality*, Science **296** 1832 (2002).
- [119] R. Kubo, *Generalized cumulant expansion method*, J. Phys. Soc. Japan **17** 1100 (1962).
- [120] S. Park and F. Khalili-Araghi, *Free energy calculation from steered molecular dynamics simulations using Jarzynski's equality*, J. Chem. Phys. **119** 3559 (2003).
- [121] D. J. Evans, E. G. D. Cohen and G. P. Morriss, *Probability of Second law violations in shearing steady states*, Phys. Rev. Lett. **71** 2401 (1993);  
D. J. Evans, D. J. Searles, *Equilibrium microstates which generate second law violating steady states*, Phys. Rev. E **50** 1645 (1994);  
G. Gallavotti and E. G. D. Cohen, *Dynamical ensembles in nonequilibrium statistical mechanics*, Phys. Rev. Lett. **74** 2694 (1994);  
D. J. Searles and D. J. Evans, *Fluctuation theorem for stochastic systems*, Phys. Rev. E **60** 159 (1999);  
E. Mittag, D. J. Searles, and D. J. Evans, *Isobaric-isothermal fluctuation theorem*, J. Chem. Phys. **116**, 6875 (2002);  
D. J. Evans and D. J. Searles, *The fluctuation theorem*, Adv. Phys. **51** 1529

(2002);

D. J. Evans, *A nonequilibrium free energy theorem for deterministic systems*,  
Molecular Physics **101** 1551 (2003).

- [122] D. P. Landau and K. Binder, *A Guide to Monte Carlo Simulations in Statistical Physics*, Cambridge University Press (2000).