Ph.D Thesis

Work fluctuations and free energies in model systems

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Work fluctuations and free energies in model systems

A Thesis submitted to University of Hyderabad for the award of the degree of

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To

My Grandmother

Declaration

I, M. Suman Kalyan, hereby declare that the work presented in this thesis has been carried out by me under the supervision of Prof. K. P. N. Murthy, School of Physics, University of Hyderabad, Hyderabad, India, as per the Ph.D. ordinances of the University. I declare, to the best of my knowledge, that no part of this thesis has been submitted for the award of a research degree of any other University. I hereby agree that my thesis can be deposited in Shodhganga/INFLIBNET.

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The matter embodied in this report has not been submitted to any other University or Institution for the award of any degree or diploma.

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Preface

This thesis addresses a few issues on work fluctuations and the free energies.

The **first** issue we consider is on nonequilibrium work fluctuations. Work and Heat are two methods by which a thermodynamic system transacts energy with its surroundings or with another system. Consider an equilibrium system in state A. It goes to another equilibrium state B by a quasi-static reversible process at constant temperature T. The energy transacted by work W equals free energy change ΔF. *i.e.* $W = \Delta F$, where $\Delta F = F(B) - F(A)$.

Let us say, τ is the time taken to change a thermodynamic property, Λ, that can be controlled from outside from an initial value Λ_1 to a final value of Λ_2. If τ is strictly infinity, the process is quasi-static and reversible. If $\tau < \infty$, the process is irreversible. We call this a switching process.

Let us fix the value of τ at some finite value and carry out the switching process several times following the same protocol. The energy transacted by work shall differ, in general, from one switching experiment to the other. Thus, we have to deal with an ensemble of work values rather than a single value. Let $\rho(W;\tau)$ denote the work distribution describing the ensemble. In the reversible limit of $\tau \to \infty$, we have, $\rho(W;\tau) = \delta(W - \Delta F)$, a result consistent with our thermodynamic wisdom. Of course such a reversible limit is an idealization.

Recently proposed *work theorem* (WT) in nonequilibrium statistical mechanics enables us to calculate equilibrium free energy differences from an ensemble of nonequilibrium work values.

There are also theorems on heat fluctuations and entropy fluctuations. All these are categorized into what one calls fluctuation theorem(FT). FT provides a relation between a thermodynamic property and the fluctuations in the corresponding statistical mechanical random variable. WT relates fluctuations in the work (W) performed during a switching process to equilibrium free energy difference. In this thesis we shall discuss about Jarzynski's equality in detail and show that it can be viewed as a cumulant expansion of work.

The second law of thermodynamics imposes a lower bound on the work done on the system. According to this law, work done on the system is greater than or equals to the free energy difference between the final and initial states. As we mentioned above, the work done equals the free energy difference in a reversible process but this is an idealization. Therefore, in general work done does not equal the change in free energy. In an irreversible process, as work fluctuates about an average value, there is always a possibility of work being less than the change in free energy there by *'violating'* the second law of thermodynamics. Let $p(\tau)$ be the area under the curve of work distribution from $-\infty$ to dF. That means $p(\tau)$ gives the probability of violation

of the second law of thermodynamics. In this thesis, we show analytically that, this quantity $p(\tau)$ increases as τ increases and reaches $\frac{1}{2}$ in the reversible limit.

The **second** issue considered is on a phenomenological free energy which is simultaneously a function of both energy and temperature. Let us denote it by the symbol $F_L(E, T)$. For closed system, when $E = U(T)$, the phenomenological free energy reduces to the familiar equilibrium free energy. The difference between these two free energies gives the penalty we need to incur, if we want to keep the system in an unstable state, with an energy, different from equilibrium energy. Such phenomenological free energies have become accessible to Monte Carlo simulation thanks to the recent developments of non-Boltzmann algorithms like multi-canonical methods, entropic sampling, and Wang-Landau simulation.

Accordingly, we have employed the Wang-Landau Monte Carlo methods to study melting transition in a hair pin model of a DNA in the presence of a constant force that tends to rip the two strands apart. We consider a two dimensional lattice model of a hair pin DNA (hp-DNA). We have employed bond fluctuation model to generate different conformation. Plots of the phenomenological free energy as a function of energy, for temperatures close to the transition temperature show that the transition is discontinuous. We also present results on the force - temperature phase diagram.

The **third** issue considered, concerns calculation of the phenomenological free energy as a function of order parameter. The non-Boltzmann algorithms give only density of (energy) states from which entropy and free energies can be obtained readily. For studying phenomena involving first order phase transition, energy is a good order parameter; hence density of states is adequate. However for phenomena involving second order phase transition energy is not a good order parameter. For example in Ising spins, in the absence of symmetry-breaking external field, the Hamiltonian is invariant under spin flips. For this problem, magnetization is the right order parameter. To calculate free energy as a function of both magnetization and temperature, we need a joint density of states. It is precisely in this context we propose an efficient numerical algorithm to compute joint density of states employing Wang-Landau method. The trick consists of treating the joint density of state as a thermodynamic property of an isolated system and evaluate its average over a microcanonical ensemble, extracted from the production run of the Wang-Landau Monte Carlo simulation. We demonstrate the method on a two dimensional model of Ising spins.

The thesis is organized in six chapters. A brief description of the contents of each chapter is given below.

In chapter 1, we review briefly only those basic concepts of thermodynamics and equilibrium statistical mechanics that are required to appreciate the work reported in the subsequent chapters. We give microscopic description of heat and work. Next we discuss the statistical nature of the second law of thermodynamics and Maxwell's

demon that violates it. This is followed by brief discussion of Crooks fluctuation theorem and Jarzynski equality. We conclude the chapter with a discussion on Landau's theory of phase transitions.

Chapter 2 reviews Monte Carlo techniques. First we give details of Boltzmann sampling *i.e.*, Metropolis algorithm. Canonical ensemble averages of mechanical properties of a thermodynamic system are calculated. Thermal properties, however, are not readily accessible to Metropolis Monte Carlo methods.

To calculate thermal properties there is a need to go beyond Metropolis algorithm. Techniques that accomplish this come under the broad category of non-Boltzmann Monte Carlo methods. Umbrella sampling, Multicanonical Monte Carlo, entropic sampling and Wang-Landau algorithm come under such a category. Of these, we shall describe entropic sampling and Wang-Landau sampling methods.

In chapter 3, we consider work done in reversible and irreversible processes. We discuss the relation between non-equilibrium work fluctuations and free energy differences. We show that Jarzynski equality can be viewed as a cumulant expansion of work and show that in the reversible limit it reduces to standard thermodynamics and close to reversible limit the (thermodynamic) dissipation is proportional to (statistical mechanical) fluctuations as prescribed by Callen-Welton theorem. We derive an expression for the probability of violation of second law of thermodynamics $p(\tau)$. We show that $p(\tau)$ increases with increase of τ and in the asymptotic limit of $\tau \to \infty$, a quasistatic reversible process, it goes to one-half. Further we demonstrate the results on a lattice model of liquid crystalline system.

Wang-Landau sampling provides an elegant method to estimate equilibrium and phenomenological Landau free energies. These form the contents of chapter 4. We consider the problem of melting transition in a hairpin model of DNA subjected to a constant force. First we give a brief introduction to DNA and then we describe a lattice model of DNA-hairpin (hp-DNA). We have employed bond fluctuation model to generate different conformations of hp-DNA. We briefly describe bond fluctuation model. This is followed by details of Monte Carlo simulations based on Wang-Landau algorithm. Then we define a phenomenological free energy which coincides with Landau free energy for temperatures in the neighbourhood of phase transition temperature and with Helmholtz free energy when the system is in equilibrium. We present results on different thermodynamic properties including Landau free energy. We also present force - temperature phase diagram.

In chapter 5, we discuss difficulties of calculating Landau free energy as a function of order parameter. Estimation of joint density of states takes huge amount of computational time. We propose a new technique to calculate joint density of states which involves two steps. In the first step we get density of states in the Wang-Landau iteration run. Then we treat the joint density of states as a thermodynamic property of an isolated system. In the second step we estimate an average of this quantity over

a microcanonical ensemble extracted from entropic ensemble generated in the production run of the Wang-Landau algorithm. This method reduces computational time considerably. We demonstrate this method on a two dimensional Ising model.

In chapter 6, we summarize principal results and conclusions of the thesis and indicate possible future directions.

Contents

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Chapter 1

Introduction

In this chapter we recall a few fundamental concepts of thermodynamics and statistical mechanics that provide the basics for the work reported in this thesis. This also serves the purpose of establishing basic terminologies used in this thesis. We discuss the second law of thermodynamics and its statistical nature in some details. Further we discuss heat and work fluctuation theorems. These developments help relate non-equilibrium measurements to equilibrium properties. Toward the end, we give a brief description of Landau's theory of phase transition.

1.1 First and Second law of thermodynamics

The first law of thermodynamics is about conservation of energy. Its simply says that change in internal energy of a system can be accounted for by the energy transacted with the surroundings by the process of heat and/or work. Any process in which energy is neither created nor destroyed is consistent with first law. For example, let a cold body and hot body be brought into thermal contact with each other. Assume that cold body becomes cooler by transacting energy in the form of heat to hot body which would become hotter. This is very much consistent with first law of thermodynamics. But such a processes does not occur in nature. Heat does not flow from cold to hot spontaneously in nature. The fact that certain kind of processes are never

observed to occur spontaneously is the basis for the second law of thermodynamics. It was first enunciated by Clausius (1850) [3] and Kelvin [1] (1851) [4].

Consider a closed system which is in thermal contact with a heat bath at temperature T. Let us assume that during a reversible process the system absorbs a quantity $đQ_{rev}$ of heat from the heat bath. Here the *bar* on d indicates that the quantity is not a perfect differential. The entropy of the system increases by an amount given by,

$$dS = \frac{đQ_{rev}}{T} \, . \tag{1.1}$$

Since the process is quasi-static and reversible, the entropy of the heat bath is decreased exactly the same amount so that the total change in entropy is zero.

Clausius stated the second law as,

$$dS \geq 0 \, , \tag{1.2}$$

for any thermodynamic process, where dS is the change in entropy of the system plus that in the surroundings. In the above, equality obtains when the process is reversible. If the process is adiabatic, dS is the change in entropy of the system. If the process is reversible $dS = 0$ and if irreverible, $dS > 0$. In statistical Mechanics, Entropy is defined in terms of probabilities of microstates as,

$$S(U, V, N) = -k_B \sum_{i=1}^{\hat{\Omega}} p_i \log(p_i) \, , \tag{1.3}$$

[1]

- *Clausius's statement:* There exists no thermodynamic transformation whose sole effect is to transfer heat from a colder reservoir to a warmer reservoir.
- *Kelvin's statement:* There exists no thermodynamic transformation whose sole effect is to extract heat from a reservoir and to convert that heat entirely into work.

where k_B is now called the Boltzmann constant and p_i is the probability to find the system in microstate i. Ω denotes the set of all possible microstates of the system. $\hat{\Omega}$ is the number of elements in the set Ω.

If we assume that probabilities of all the microstates are equal, *i.e.*,

$$\rho_i = \frac{1}{\hat{\Omega}} \forall\, i\,,$$

we get the famous formula for Boltzmann entropy[2],

$$S = k_B \ln(\hat{\Omega}). \tag{1.4}$$

Thus entropy is statistical in nature. James Clerk Maxwell asserted that, the second law of thermodynamics, which talks of increasing entropy, must also be statistical in character and hence there is a non-zero probability of it being contravened [5].

Statistical nature of second law and Maxwell's demon

To show that the second law of can be contravened, Maxwell proposed a thought experiment [6]. Consider a gas filled vessel which has two partitions A and B and a small door at the partition wall as shown in Figure 1.1. Temperature and pressure are uniform throughout the vessel. Although the temperature of the gas is uniform, the velocities of the gas molecules need not be, since temperature is the average kinetic energy of the molecules. The velocities should in fact vary, because the molecules would be exchanging energy during collisions. The door allows only the molecules with velocity more than average velocity to pass from A to B and less than average

[2]see [7] page no. 53 for a demonstration of the equivalence of Boltzmann entropy and thermodynamic-entropy.

velocity from B to A. Thus, without expenditure of work, temperature of B is raised and that of A is lowered which is contradictory to second law of thermodynamics. Later W. Thomson named it as *'Maxwell's intelligent demon'* [8].

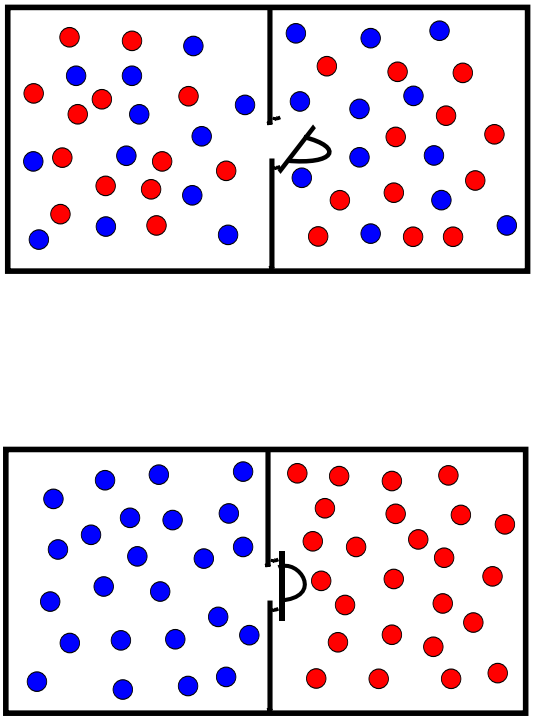

Figure 1.1: Schematic representation of Maxwell's experiment

The subtle purpose of Maxwell's demon can be stated in a simple language: *What the demon purports to accomplish by intent - can it happen by chance?*

To know complete details of birth, death and rebirth of Maxwell's demon refer to [7, 9].

The second law of thermodynamics is regarded as the supreme scientific truth as no exception to it has been observed for a long time. However, this situation has changed over the last two decades. More than two dozen challenges to it have entered the mainstream scientific literature [10]. In chapter 3, we discuss the probability of violation of second law in irreversible processes. We shall determine how this

quantity changes when the process becomes reversible. We provide an analytical derivation of this change and show it numerically on a lattice spin model of liquid crystalline systems.

1.2 Switching experiment

Consider a thermodynamic system which is at equilibrium. Let Λ be a macroscopic property of the system which can be controlled and, let its initial value be Λ_I. Now change Λ from its initial value to a final value Λ_F. This process of changing control parameter from one value to another in a finite duration of time is called switching process or switching experiment [7]. Let Λ be changed from Λ_I to Λ_F in steps of $\Delta\Lambda$. i.e.,

$$\Lambda_F = \Lambda_I + N\,\Delta\Lambda. \tag{1.5}$$

$$\Rightarrow N = \frac{\Lambda_F - \Lambda_I}{\Delta\Lambda}. \tag{1.6}$$

For a given Λ_I and Λ_F, if N is small, the process is irreversible; when $N \to \infty$ we get a quasi-static reversible process. A quasi-static reversible process is thus an idealization. However, we can get an approximate quasi-static reversible process by taking N to be large.

1.3 Heat and Work

Thermodynamics

According to the first law of thermodynamics, the internal energy of the system can be increased by the process of heat and/or work. we express it as

$$dU = đQ + đW\,, \tag{1.7}$$

where U denotes internal energy, $đQ$ and $đW$ are heat and work respectively. The bar on heat and work denote that they are not state variables.

Statistical Mechanics

Thermodynamic internal energy U is given by the average of statistical mechanical energy E; the average is taken over a suitable ensemble, *e.g.* canonical ensemble for a closed system, microcanonical ensemble for a isolated system, grand canonical ensemble for an open system *etc*. Let p_i represents the probability of the system to be in microstate i and E_i the energy of that microstate. The average energy (or internal energy) of the system is given by,

$$U = \sum_i p_i\, E_i\,, \tag{1.8}$$

where the sum runs over all possible microstates of the system. Let us consider a process which results in small changes in the energies and/or probabilities of the microstates. Then, formally, we have

$$
\begin{aligned}
U &= U(p_1, p_2, \ldots, E_1, E_2, \ldots)\,, \\
dU &= \sum_i \frac{\partial U}{\partial E_i}\, dE_i + \sum_i \frac{\partial U}{\partial p_i}\, dp_i\,, \\
&= \sum_i p_i\, dE_i + \sum_i E_i\, dp_i. \qquad (1.9)
\end{aligned}
$$

Note there is a constraint on the probabilities namely: $\sum_i p_i = 1$ and $\sum_i dp_i = 0$. Consider the first term of RHS of above equation, and proceed as follows

$$
\begin{aligned}
\sum_i p_i\, dE_i &= \sum_i p_i \frac{\partial E_i}{\partial V}\, dV\,, \\
&= \frac{\partial}{\partial V} \sum_i p_i E_i\; dV\,, \\
&= \frac{\partial U}{\partial V}\, dV\,, \\
&= -P\, dV\,, \\
&= đW. \qquad (1.10)
\end{aligned}
$$

Thus, work done corresponds to the change in energy of the macroscopic system brought about by changing the energies of its microstates without altering their probabilities [7]. Thus we take $\sum_i p_i dE_i$ as the definition of work and employ this to calculate work in non-equilibrium processes. However as shown above, this reduces to the familiar expression for work, given by $-PdV$ when the process is quasi-static and reversible.

From the definition of Boltzmann-Gibbs-Shannon entropy [11] , we have

$$S = -k_B \sum_i p_i \log p_i. \tag{1.11}$$

We know that

$$đQ_{rev} = TdS. \tag{1.12}$$

From above two equations, we can write

$$\begin{aligned} đQ_{rev} &= -k_B T \sum_i dp_i - k_B T \sum_i dp_i \log p_i \,, \\ &= -k_B T \sum_i dp_i \log p_i \,, \\ &= k_B T \sum_i dp_i \left[\beta E_i + \log Z\right] \,, \\ &= \sum_i E_i \, dp_i. \end{aligned} \tag{1.13}$$

where Z denotes the canonical partition function. Here we have used the fact, see [12], that in a canonical ensemble $p_i = Z^{-1} \exp(-\beta E_i)$.

Thus, heat is the change of energy of a closed system brought about by changing the probabilities p_i without altering the energies E_i of the microstates. Thus we take $\sum_i E_i dp_i$ as a definition of heat and employ it to calculate heat in non-equilibrium processes. However it reduces to the familiar expression of heat given by TdS if the process is quasi-static and reversible.

While performing Monte Carlo simulations, we calculate heat and work employing the definitions discussed above. More details can be found in chapter 3.

1.4 Fluctuation theorems

The idea of relating fluctuations to their corresponding response properties was proposed long ago by Einstein [13], Onsager [14, 15], Nyquist [16] and Callen and Welton [17]. These are called Fluctuation-Dissipation Relations (FDRs). These relations are valid in the regime of equilibrium or near equilibrium.

However, over the last two decades, generalised FDRs have been proposed. These are called *fluctuation theorems* (FTs) which are valid even when the system is driven far from equilibrium. The FTs involve negative work tails which are usually very rare: heat flowing from cold to hot, fluids forcing rheometers to move faster, work done being less than reversible work are a few examples.

1.4.1 Crooks fluctuation theorem

The Crooks fluctuation theorem (CFT) [20] predicts a symmetry relation in the work fluctuations when a system is driven away from thermal equilibrium by the action of an external perturbation. This theorem is based on the observation that dynamics is microscopically reversible and therefore its experimental evaluation in small systems is crucial for a better understanding of the phenomenon of non-equilibrium. Let $P_F(W)$ be the probability of work in the forward process and similarly $P_R(-W)$ is the probability of work distribution in the reverse process. Then according to CFT

$$\frac{P_F(W)}{P_R(-W)} = \exp\left(\frac{W-\Delta F}{k_B T}\right) , \tag{1.14}$$

where ΔF is the free energy difference between final and initial equilibrium states; ΔF is also equal to the reversible work associated with this process; k_B is Boltzmann

constant. Here one should ensure that system be in equilibrium before the process starts (either forward or reverse). However, the system need not reach equilibrium at the end of the process. It only requires that the control parameter attains its final value at the end of the process in either case; however, the system would eventually equilibrate to a well defined state, consistent with the final value of the parameter. This latter process occurs without any change of the control parameter, and therefore contributes no work. Eq. 1.14, states that although $P_F(W)$ and $P_R(-W)$ depend on the experimental protocol, their ratio depends only on the value of ΔF. Thus, the value of ΔF can be determined once the work distributions in forward and reverse processes are known. In particular, the two distributions cross at $W = \Delta F$,

$$P_F(W) = P_R(-W) \Rightarrow W = \Delta F\,. \tag{1.15}$$

Although the above equation already gives an estimate of ΔF it is not necessarily very precise as it only uses the local behaviour of the distribution around $W = \Delta F$. Using the whole work distribution increases the precision of the free energy estimate. Crooks fluctuation theorem has been verified experimentally by D. Collin *et al.,* [21] and has been extensively employed in the study of different systems, see eg. [22–24].

1.5 Work theorem or Jarzynski equality

The Jarzynski equality (JE) [25, 26] is perhaps the most simple and general formula discovered recently in statistical physics. It gives a relation between *equilibrium* free energy differences and work done through *non-equilibrium* processes. In its most

common expression it is stated as,

$$\langle e^{-\beta W} \rangle = e^{-\beta \Delta F} \,, \tag{1.16}$$

where $\beta = \dfrac{1}{k_B T}$, with T denoting the temperature of the heat bath to which system is in contact. It is obvious that Crooks theorem implies Jarzynski equality.

Jarzynski equality opens up the possibility of calculating free energies from non-equilibrium processes. One can refer to this approach as non-equilibrium thermodynamic integration, as opposed to the conventional thermodynamic integration based on quasi-static processes for which ΔF equals $\langle W \rangle$. The average of exponential work appearing in JE is dominated by the trajectories corresponding to small work values that arise only rarely. An accurate estimate of free energy, hence, requires suitable sampling of such rare trajectories. Liphardt *et al.* [27] checked JE by carrying out an experiment on the free energy difference (in their case the Gibbs free energy ΔG instead of ΔF) between the unfolded and the folded conformations of a single P5abc RNA molecule, suspended between two handles, in an aqueous salt solution. JE has been illustrated in variety of systems [28–33].

In chapter 3, we show JE as cumulant expansion of work; we also investigate numerically work fluctuations in a lattice spin model of liquid crystalline system.

1.6 Landau theory of phase transitions

In chapters 3 and 4 we would investigating model systems close to phase transitions. In this context we would require a phenomenological free energy which is simultaneously a function of both temperature and energy (or order parameter). Essentially

we would like to estimate free energy penalty we need to incur, if we want to keep a system in a state with energy different from its equilibrium energy. The phenomenological free energy is obtained from the non-Boltzmann Monte Carlo simulations. Such a phenomenological free energy bears close resemblance to Landau free energy for temperatures close to transition temperature T_C. Hence we call the phenomenological free energy obtained from non-Boltzmann Monte Carlo techniques as Landau free energy and denote it as $F_L(T, E)$.

Here, we give a brief description of Landau free energy in the study of phase transitions.

1.6.1 Phase transitions

Phase transitions are ubiquitous in nature. A phase transition occurs when an equilibrium system changes according to the external conditions like temperature, pressure, electric or magnetic field. Here we are interested only in phase transitions that occur due to change of temperature. The information about a system is embedded in the partition function, Z, given by

$$Z = \sum_C \exp\left(-\frac{E(C)}{k_B T}\right) , \tag{1.17}$$

where summation runs over all the microstates of the closed system, k_B is Boltzmann constant and T is temperature. Free energy of the system is given by

$$F = -k_B T \ln Z . \tag{1.18}$$

If we can calculate free energy, we can calculate all the desired thermodynamic properties of the system using appropriate derivatives.

At phase transition, free energy $F(T, V, N)$ becomes non-analytic. That means derivatives of free energy are not defined at certain points called singularities. These singularities contain a lot of information. L. D. Landau came up with a theory to explain second order phase transitions. He noticed that most of the phase transitions involves breaking of discrete or continuous symmetry and he introduced a very important concept to capture the nature and extent of this symmetry breaking : the order parameter. The order parameter (ψ) is zero in disordered phase and has a non-zero value in ordered phase. For example, in ferromagnetic transition the order parameter is average magnetization per unit volume.

1.6.2 Landau free energy

Landau's contribution lies in the series expansion of free energy as a function of order parameter near the critical point [34],

$$F(\psi, T) = F_0(T) + a(T)\psi^2 + \frac{1}{2}b(T)\psi^4 \,, \tag{1.19}$$

where F_0 is an analytic function of temperature. Sixth and higher order terms in ψ could be retained, but are not usually necessary for the behaviour near T_C. The term linear in ψ is absent because, states with $\psi \neq 0$ and $\psi = 0$ have different symmetries. For systems in which the free energy is independent of the sign of ψ i.e., $F(\psi, T) = F(-\psi, T)$ the cubic and higher odd powers are not allowed. For rigorous discussion on Landau free energy, see [35–37].

P. G. de Gennes extended Landau theory to describe discontinuous transitions

while studying the nematic-isotropic transition of liquid crystals [38]. In this case order parameter is no more a scalar but a tensor quantity $S(\vec{r})$. However, the expansion contain only scalar combinations of $S(\vec{r})$ and hence linear term vanishes here also. However, the cubic term does not vanish for transition in liquid crystalline systems. Thus, free energy reads as,

$$\begin{aligned}
\tilde{F} &= F_0 + \frac{1}{2}a(T - T_C^*)S_{ij}(\vec{r})S_{ji}(\vec{r}) + \\
&\frac{1}{3}BS_{ij}(\vec{r})S_{jk}(\vec{r})S_{ki}(\vec{r}) + \frac{1}{4}C_1\left[S_{ij}(\vec{r})S_{ji}(\vec{r})\right]^2 + \\
&\frac{1}{4}C_2S_{ij}(\vec{r})S_{jk}(\vec{r})S_{kl}(\vec{r})S_{li}(\vec{r}) + \\
&\frac{1}{2}L_1\partial_i S_{jk}(\vec{r})\partial_i S_{jk}(\vec{r}) + \frac{1}{2}L_2\partial_i S_{ij}(\vec{r})\partial_k S_{kj}(\vec{r}) \ , \qquad (1.20)
\end{aligned}$$

where T_C^* is a temperature slightly below T_C, $a > 0, B, C_1, C_2, L_1, L_2$ are constants; $i, j, k, l = 1, 2, 3$ denote the components along the three orthogonal axes of the coordinate system; $\partial_i \equiv \dfrac{\partial}{\partial x_i}$ is the partial derivative with respect to spatial coordinate x_i and summation over repeated indices is implied. Detailed discussion about Landau - de Gennes theory can be found in [39–41]. In chapter 4, we present results on Landau free energy of a hairpin DNA close to the melting point, calculated employing non-Boltzmann Monte Carlo techniques.

Calculating Landau free energy for a second order phase transition using Monte Carlo techniques is a highly time consuming process. It calls for calculation of density of states as a function of energy as well as an order parameter. In this thesis we propose a new and efficient method to calculate joint density of states and hence Landau free energy. Detailed description of the method is given in chapter 5. We

have taken Ising spin model for illustrating the method proposed.

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Chapter 2

Monte Carlo methods

2.1 Introduction

Monte carlo methods have been recognized as an important tool in a variety of disciplines. These techniques help us understand macroscopic properties of matter resulting from interplay of large number of atoms. Monte Carlo methods use random numbers to solve a problem. In practice, of course, these numbers are not truly random but are generated by an algorithm; they are called pseudo random numbers [1]. Using these random numbers one can generate a stochastic trajectory in a phase space of the model considered and calculate average properties.

In statistical mechanics one computes average of a macroscopic property O from the Boltzmann distribution [2],

$$\langle O \rangle = \frac{\sum_i O_i \exp(-\beta E_i)}{\sum_i \exp(-\beta E_i)} , \tag{2.1}$$

where i denotes a microstate, O_i is the value of macroscopic property O when the

system is in microstate i; E_i is energy of the system when it is in microstate i and

$$\beta = \frac{1}{k_B T} ,$$

with T the temperature and k_B Boltzmann constant.

The number of microstates is exponentially large in the number of degrees of freedom, N, and so it is quite impractical to perform the sum in Eq. 2.1. In Monte Carlo methods, rather than summing over all the states in Eq. 2.1, we sample a small fraction of these states [3]. This gives an estimate of the average, which will not be exact but will have statistical errors. Sample different microstates from Boltzmann probability distribution and estimate average as [4]

$$\overline{O} = \frac{1}{N} \sum_{n=1}^{N} O_n , \tag{2.2}$$

where N is the number of microtates sampled and O_n is value of O in microstate n. In the limit $N \to \infty, \overline{O} \to \langle O \rangle$.

Statistical error is given by the quantity $\pm S_N/\sqrt{N}$, where S_N is given by

$$S_N = \sqrt{\overline{O^2} - \overline{O}^2} , \tag{2.3}$$

see [4] for details. The above formula for statistical error is valid only if $\{O_i \ : \ i = 1, \ 2, \ \cdots\}$ are independent of each other.

It is clear from the above that the statistical error is inversely proportional to $\sqrt{N}$. 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. Importance sampling is a technique which re-

duces variance without effecting average quantities. We discuss importance sampling in some detail in the next section.

2.2 Importance sampling

Let $f(x)$ be the probability density function of random variable X and $h(x)$ be the property whose average is to be calculated. Formally we have,

$$\langle h \rangle_f = \int_{-\infty}^{+\infty} h(x)\, f(x) dx = \lim_{N \to \infty} \frac{1}{N} \sum_{i=1}^{N} h(x_i) \,, \tag{2.4}$$

where $\{x_i \ = \ 1, 2, \ldots, N\}$ is Monte Carlo sample, sampled randomly from $f-$ ensemble. Let $h(x)$ be high where $f(x)$ is low and $h(x)$ be low where $f(x)$ is high. Then, high score regions of x shall get very poorly sampled. Monte Carlo estimate of $\langle h \rangle_f$ would be associated with large statistical error. Importance sampling becomes imperative in these situations. Basic idea is to estimate average property over the given distribution from an ensemble of another distribution.

Let $g(x)$ denote an importance probability density function and $H(x)$ be modified score function defined as

$$H(x) = h(x)\, \frac{f(x)}{g(x)} \,. \tag{2.5}$$

Now Average of $H(x)$ over g ensemble is given by,

$$\begin{aligned}
\langle H \rangle_g &= \int_{-\infty}^{+\infty} H(x)\, g(x) dx \,, \\
&= \int_{-\infty}^{+\infty} h(x)\, \frac{f(x)}{g(x)}\, g(x) dx \,, \\
&= \int_{-\infty}^{+\infty} h(x)\, f(x) dx \\
, &= \langle h \rangle_f \,. \qquad (2.6)
\end{aligned}$$

Monte Carlo estimate of $\langle H \rangle_g$ is given by,

$$\overline{H}_N = \frac{1}{N} \sum_{i=1}^{N} h(x_i)\, \frac{f(x_i)}{g(x_i)} \,, \qquad (2.7)$$

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

Thus, from $g-$ ensemble, we can calculate $\langle h \rangle_f$ by employing appropriate unweighting and reweighting factors.

2.3 Metropolis algorithm

This algorithm was introduced by Nicolas Metropolis and his co-workers [5] in a paper on simulations of hard-sphere gases and is essentially an importance sampling algorithm.

Consider a closed system and let Ω_{CS} represents set of all the microstates.

$$\Omega_{CS} = \{C_1, C_2, \ldots, C_{\hat{\Omega}_{CS}}\}\,, \tag{2.8}$$

where $\hat{\Omega}_{CS}$ represents the total number of microstates. According to this algorithm, we generate a Markov chain of microstates starting with microstate C_0,

$$C_0 \to C_1 \to \ldots C_n \to C_{n+1} \to \ldots \tag{2.9}$$

Here index n can be viewed as denoting discrete time and $C_i \in \Omega_{CS}$ The term Markov chain 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 in all the previous times. *The past has no influence over the future once the present is specified.* The markov property can be stated as [6, 7]

$$P(C_k|C_{k-1}, C_{k-2}, \ldots, C_1, C_0) = P(C_k|C_{k-1}) \quad \forall\, k = 1, n. \tag{2.10}$$

By restricting ourselves to a time homogeneous Markov chain for which, regardless of the time index k, we have,

$$P(C_{k+1} = C_i|C_k = C_j) = W_{i,j} \quad \forall\, k\,, \tag{2.11}$$

where $W_{i,j}$ is the probability for transition from microstate C_j to microstate C_i in a single step; it is $i,j-$th element of the $\hat{\Omega}_{CS} \times \hat{\Omega}_{CS}$ square matrix. This square matrix W completely specifies the stochastic dynamical evolution of the system given the initial state C_0 at time $n = 0$ and hence called stochastic matrix.

The sequence of states produced follows a time ordered path; it is referred to as

Monte Carlo time. The time-dependent behaviour of the system is described by discrete time master equation

$$P(C_i, n+1) - P(C_i, n) = \sum_{j \neq i} \Big[W_{i,j} P(C_j, n) - W_{j,i} P(C_i, n) \Big] . \tag{2.12}$$

Here $P(C_i, n)$ is the probability of the system to be in microstate C_i at discrete time n. When $n \to \infty$, system reaches a unique equilibrium state. Then we have, for $n \to \infty$,

$$\pi(C_i) = \pi_i = \lim_{n \to \infty} P(C_i, n) \quad \forall\, i. \tag{2.13}$$

Then Eq. 2.12 simplifies to ,

$$\sum_j \Big(W_{i,j} \pi_j - W_{j,i} \pi_i \Big) = 0 \quad \forall\, i. \tag{2.14}$$

This is called the balance condition. We impose a more strict rule by demanding the above to hold good separately for each j. Then we have,

$$W_{i,j} \pi_j = W_{j,i} \pi_i \quad \forall\, i, j. \tag{2.15}$$

This is called the detailed balance condition. The equilibrium probability distribution π_i is given by $\exp(-\beta E(C_i))/Z$, where Z is partition function. From Eq. 2.15,

$$\frac{W_{i,j}}{W_{j,i}} = \frac{\pi_i}{\pi_j} = \exp \Big\{ -\beta \Big[E(C_i) - E(C_j) \Big] \Big\} = \exp \Big[-\beta \Delta E \Big]. \tag{2.16}$$

Thus, we just need the ratio of Boltzmann weights to generate a Markov chain. We do not need to know the partition function. This is the salient feature of Metropolis algorithm.

Metropolis algorithm can be summarized as:

→ Choose an initial microstate C_0; calculate its energy $E(C_0)$.

→ Generate a trial microstate C_t, by making a local change (for example, flip a randomly selected spin in case of Ising spin system or change position and momentum in case of a Harmonic oscillator) and calculate energy $E(C_t)$.

→ Compute $\Delta E = E(C_t) - E(C_0)$

→ Accept the microstate with a probability given by

$$p = \min\Big[1, \exp(-\beta\Delta E)\Big] \ . \tag{2.17}$$

Iterating the above we get a Markov chain of microstates. Generating a microstate C_{k+1} from C_k constitutes a Monte Carlo step. M such Monte Carlo steps constitutes a Monte Carlo Sweep (MCS). M denotes the size of the system. The energy of the microstates is plotted as a function of Monte Carlo steps to check for equilibration. Once the system reaches equilibrium energy fluctuates around a mean value which is a constant.

Calculation of average quantities

Let $C_1, C_2, \ldots, C_N$ 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. An estimate of the average of x is given by,

$$\overline{x_N} = \frac{1}{N}\sum_{i=1}^{N} x_i \ , \tag{2.18}$$

which in the limit $N \to \infty$, gives $\langle x \rangle$.

Metropolis algorithm is a simple example of canonical sampling methods. Average mechanical properties of the system can be readily calculated employing Metropolis Monte Carlo sampling. However, calculation of thermal quantities like entropy and free energy is rather difficult, though not impossible, for example see [8]. This is because entropy is not a property of a single microstate rather it is the property of the entire ensemble of microstates. We need to count the distinct microstates of the system which is indeed tedious, see [8]. To calculate thermal properties we need to go beyond Boltzmann Monte Carlo methods.

To this end, non-Boltzmann sampling methods like umbrella sampling [9, 10], multicanonical sampling [11, 12], entropic sampling [13] and transition matrix Monte Carlo[14] were proposed.

2.4 Non-Boltzmann sampling techniques

The Umbrella sampling of Torrie and Valleau is the fore runner to all the non-Boltzmann techniques. For details see see [9, 10]. The multicanonical Monte Carlo methods proposed by Berg comes next, see [11, 12] for details. Entropic sampling proposed by Lee is same is the same as multicanonical Monte Carlo. The latest in the series is Wang-Landau algorithm.

2.4.1 Entropic sampling

In 1993, J. Lee proposed a sampling algorithm called Entropic sampling method [13]. This method is based on sampling of entropy at infinite temperature.

Canonical partition function can be written as

$$\begin{aligned} Z(\beta) &= \sum_{c} \exp(-\beta E(C)) \,, \\ &= \sum_{E} g(E) \exp(-\beta E) \,, \\ &= \sum_{E} \exp\left[\frac{S(E)}{k_B} - \beta E\right] . \end{aligned} \tag{2.19}$$

where $g(E)$ is the density of states and $S(E) = k_B \ln g(E)$ is entropy at energy E. In case of canonical sampling method, we obtain Boltzmann distribution

$$P_B(E) \propto \exp\left(\frac{S(E)}{k_B} - \beta E\right) \,, \tag{2.20}$$

with the help of detailed balance condition given by Eq. 2.16.

By following the same analogy, to obtain an arbitrary distribution

$$P_\alpha(E) \propto \exp\left[\frac{S(E)}{k_B} - \alpha(E)\right] \,, \tag{2.21}$$

we need to impose a similar detailed balance condition given by,

$$\begin{aligned} \frac{W_{ij}}{W_{ij}} &= \frac{P_\alpha(E(C_j))}{P_\alpha(E(C_i))} \,, \\ &= \exp\Big[- \Big\{ \alpha(E(C_j)) - \alpha(E(C_i)) \Big\} \Big] . \end{aligned} \tag{2.22}$$

This condition implies that the acceptance probability of a trial microstate, C_t gen-

erated by modifying the current microstate C_i is given by,

$$p = \min\left(1, \exp\left[- \left\{ \alpha(E(C_t)) - \alpha(E(C_i)) \right\} \right] \right) . \tag{2.23}$$

It is clear that if $\alpha(E(C)) = \beta E(C)$, Eq. 2.21 reduces to Boltzmann probability. Entropic sampling obtains when we set $\alpha(E(C)) = \dfrac{S(E)}{k_B}$.

This renders $P_\alpha(E)$ the same for all E. But then, $S(E)$ is not known a priori. So we start with a guess $\alpha_0(E)$ and update it iteratively $\alpha_1(E) \rightarrow \alpha_2(E) \ldots \alpha_n(E)$. For large n, $\alpha_n(E) \rightarrow \dfrac{S(E)}{k_B}$.

Learning run

Let (E_{min}, E_{max}) be the energy range over which we want to generate microstates with uniform energy distribution. Divide the range into a number of equal width energy bins. Let E_i be the energy of the $i-$th bin. Initialize $\alpha(E_i) = 0 \, \forall \, i$. Now we carry out M number of MCS with the acceptance probability given by Eq. 2.21. In the first iteration every trial move gets accepted. We accumulate h_i, number of visits to the microstates with energy falling in the $i-$th energy bin, after every MCS. After N number of MCS we update $\alpha_i = \alpha(E_i)$ as per the recursion given below,

$$\alpha_i^{(k+1)} = \begin{cases} \alpha_i^{(k)} & \text{if } h_i = 0, \\ \\ \alpha_i^{(k)} + \ln \ h_i & \text{otherwise.} \end{cases} \tag{2.24}$$

In the above, superscript (k) is the iteration index. We continue the iterations until a desired energy range of the energy bins are sampled.

Production run

The final α_i obtained in the learning run is used to collect a large number of microstates. This *entropic ensemble* contains information pertaining to all the temperatures.

Calculation of average quantities

Once we get an entropic ensemble of microstates $\{C_i,\ i = 1, \ldots, N\}$, we can calculate canonical ensemble averages of a macroscopic property say, $O(C)$ at the desired temperature $T = 1/k_B\beta$, by unweighting followed by reweighting,

$$\langle O \rangle_\beta = \lim_{N\to\infty} \overline{O}_N(\beta) = \frac{\sum_{i=1}^{N} O(C_i) \exp\Big[-\beta E_i + \alpha(E(C_i))\Big]}{\sum_{i=1}^{N} \exp\Big[-\beta E_i + \alpha(E(C_i))\Big]} \tag{2.25}$$

We illustrate this entropic sampling method by obtaining probability distribution for for n heads in a toss of N fair coins.

Coin tossing and entropic sampling

Consider N number of fair coins. Our aim is to get probability distribution of n heads in a toss of N coins. n can take values $0, 1, 2, \ldots N$, so there are $N + 1$ values. Therefore, we take $n + 1$ bins and initialize histogram $H(i) = 0$ and density of states with $g(i) = 1$, where i takes values $0, 1, 2, \ldots N$. $H(n)$ and $g(n)$ corresponds to the bin with n heads. Now on tossing N coins, lets say we have n heads, $(N-n)$ tails. We consider this as initial microstate C_0. Let $n_0 = n(C_0)$. Select a coin randomly, flip it and generate a new microstate, say C_t. Call this a trial state. Let $n_t = n(C_t)$. Accept

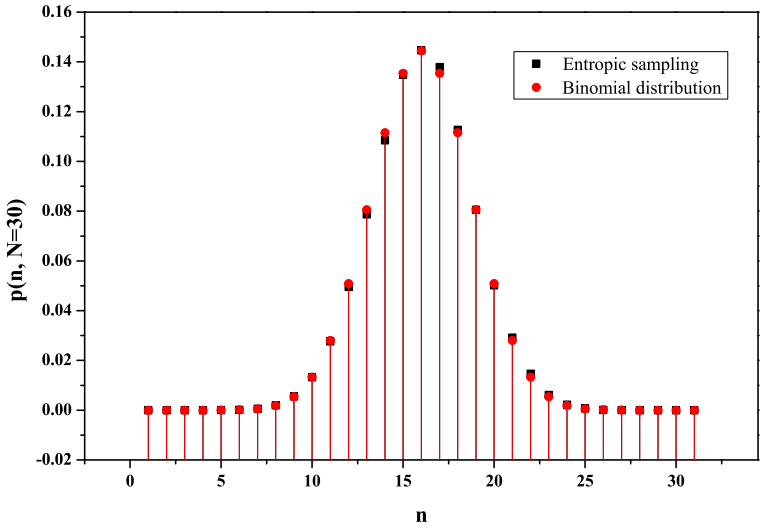

Figure 2.1: probability distribution of n, the number of heads in a toss of N fair coins.

this state with the probability given by Eq. 2.23 and update $H(n_t) \rightarrow H(n_t)+1$ If the trial state is rejected update $H(n_0) \rightarrow H(n_0)+1$. This constitutes a Monte Carlo step. N such steps constitutes a Monte Carlo sweep. After performing certain number of Monte Carlo sweeps, we update density of states $g(i)$, $\forall\, i = 1, n+1$ as given in Eq. 2.24. Then we reset histogram values $h(i) = 0$, $\forall\, i = 1, n+1$ and repeat the whole process for a desired number of iterations.

We have performed simulations for $N = 30$. In this we have considered 8000 Monte Carlo sweeps and 10000 iterations. It is well known that the probability distribution of having n heads in a toss of N coins is given by binomial distribution

$$B(n,N) = \frac{1}{2^N}\frac{N!}{n!(N-n)!}. \tag{2.26}$$

Probability calculated from simulations based on entropic sampling matches with Binomial distribution, see Figure 2.1.

We know that density of states increase exponentially with energy. In this entropic

sampling method, the entries of histogram are done linearly and density of states are updated based on histogram entries. So for large systems, this method is not found to be efficient in obtaining the converged density of states. To this end F. Wang and D. P. Landau proposed a simple and easy-to-implement algorithm that substantially improves the performance of the multicanonical Monte Carlo simulation.

2.4.2 Wang - Landau algorithm

Wang - Landau (W-L) algorithm [15, 16] is also based on the idea of sampling microstates with the acceptance probability proportional to the inverse of density of states, $1/g(E)$ and generate uniform distribution of states in energy space. According to this method entropy is updated after every Monte Carlo step by $\alpha(E(C_i)) \rightarrow \alpha(E(C_i)) + \ln(f)$. Here f is called modification or convergence factor and is a positive value. Initially we set $f = f_0 = e$. Once we get flat histogram, we reduce $f_j \rightarrow \sqrt{f_{j-1}}$, where j is the iteration index. We reset histogram values and repeat the process with new convergence factor. Typically we check for flatness after every 10000 MCS. We repeat the whole process till $f_{final} - 1 \approx 10^{-8}$. This method was successfully applied to study a variety of problems, reported in chapter 4 and 5.

We have considered the same coin tossing experiment described in the previous section and employed Wang-Landau algorithm. The probability distribution for n heads in a toss of N coins is compared with binomial distribution, see Figure 2.2

We implemented this algorithm to a more practical issue of studying the thermodynamics properties of DNA hairpin model, see chapter 4.

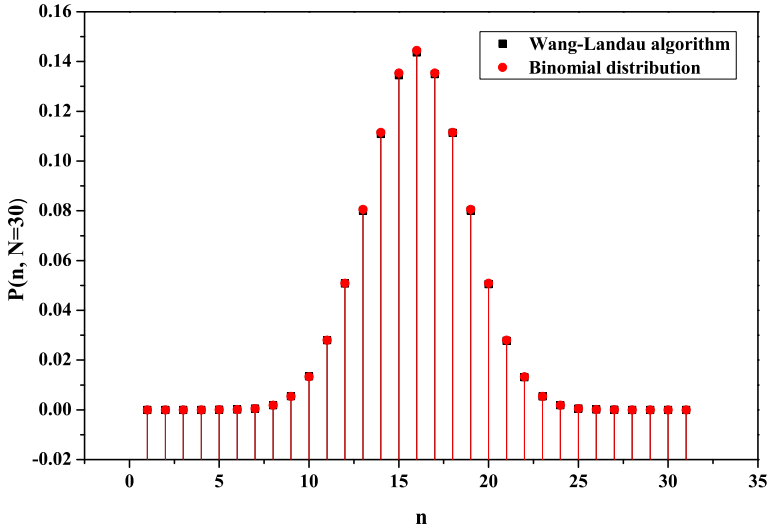

Figure 2.2: probability distribution of n, the number of heads in a toss of N fair coins.

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Chapter 3

Work fluctuations and equilibrium free energies

3.1 Introduction

Relations between equilibrium fluctuations and the response to external fields of physical observables constitutes some of the most important and general results in statistical mechanics. When a thermodynamic system is subjected to an external perturbation, it is thrown out of out of equilibrium. Usually perturbations are described in terms of control parameter Λ. These are a set of external parameters that can be controlled and do not fluctuate. Examples include volume, electric field and magnetic field. Consider a system at equilibrium; drive the system to an out of equilibrium state by a sudden change of an external parameter. The difference of energies of final and initial states gives us the work done, W. If we repeat the above experiment under identical conditions, the system follows different trajectories resulting in different final state and different work value. Repeating the experiment many times results in different values of work and allows us to define a distribution of work $\rho(W)$. When the system size is large, the fluctuations in W are small. In 1928, H. Nyquist has reported that voltage in a resistor display thermal induced fluctuations [1]. Later in 1951, H. B. Callen and T. A. Welton generalised

that intensive quantities indeed show thermal fluctuations [2]. Generalisation of these theorems were proposed in the last two decades. These generalised theorems are known as *fluctuation theorems* (FTs) [3–6]. We have heat, work and entropy fluctuations under transient and as well as steady state conditions.

The FTs which deal with the processes in which system initially in equilibrium and then driven to out of equilibrium by an external perturbation are called Transient fluctuation theorems. Crooks fluctuation theorem [7, 8] and Jarzynski work theorem [9, 10] are examples of such kind of theorems. We shall be interested in Jarzynski work theorem.

We show that the Jarzynski identity can be viewed as a cumulant expansion. When we retain only the first cumulant in the expansion, we get the well-known thermodynamic identity equating the work done on the system to free energy change in a quasi-static reversible process. With only the first two cumulants in the expansion, we get the fluctuation dissipation theorem of Callen-Welton. When we include the third and higher order cumulants we get the Jarzynski identity.

The chapter is organized as follows. We start with a brief introduction to a few relevant basic issues of heat and work in a quasi-static reversible process. Then we consider heat and work in the context of irreversible processes. This is followed by a discussion on the relation between non-equilibrium work fluctuations and equilibrium free energy differences. We show analytically that the probability of violation of the second law increases with increase of time duration of the switching experiment and in the asymptotic limit of a quasi-static process it goes to one-half. We give a brief description of lattice spin model of liquid crystals and demonstrate Jarzynski equality. Further, Monte Carlo simulation results on various properties are presented and principal conclusions of the study are brought out briefly in the concluding section.

3.2 Heat and Work

3.2.1 Reversible process

Consider a closed system in equilibrium at temperature T. It draws a small quantity $đQ$ of energy in the form of heat by a quasi-static reversible process at constant temperature. $đQ$ can not be expressed as a differential of a (thermodynamic state) function. $đQ$ is not a perfect differential. In other words Q is not a content of a body. $đQ$ is not change of a property. To denote this we have used $đ$ in place of d. However,

$$dS = \frac{đQ}{T} \tag{3.1}$$

is an exact differential where S is entropy. dS can be considered as change in a property of the system. S is a state function. Thus, during a reversible process, entropy of the system increases by $đQ/T$.

To calculate the work done on the system, we start with the first law of thermodynamics, usually stated as,

$$W = dU - đQ\,, \tag{3.2}$$

where W denotes the work done on the system and U, the internal energy.

The first law is about conservation of energy and is valid for all processes, quasi-static, non-quasi-static, reversible, irreversible or otherwise. However, if the process

is quasi-static and reversible, then we can replace $đQ$ by TdS, see Eq. (3.1), and write,

$$W = dU - TdS. \tag{3.3}$$

If the process is also isothermal, we have

$$W = d(U - TS). \tag{3.4}$$

We identify the term $U - TS$ as Legendre transform of the fundamental equation $U \equiv U(S, V)$ where we transform the variable S in favour of the 'slope'

$$T(S, V) \quad = \quad \left(\frac{\partial U}{\partial S}\right)_V \tag{3.5}$$

and the variable U in favour of the 'intercept'

$$F(T, V) \quad = \quad U(S, V) - TS. \tag{3.6}$$

$F(T, V)$ is called Helmholtz free energy or simply free energy. Thus the work done equals free energy change :

$$W = \Delta F. \tag{3.7}$$

for a reversible process. We call the above as reversible work and denote it by W_R.

3.2.2 Irreversible process

To obtain the relation between change in free energy and work done when the process is not quasi-static and hence irreversible, we start with the second law inequality, see [11] for an elegant proof, given by

$$dS > \frac{đQ}{T}. \tag{3.8}$$

The above implies

$$đQ < T\,dS \tag{3.9}$$

for an irreversible process. Substitute this in Eq. (3.2) and get,

$$W > dU - TdS \tag{3.10}$$

which for an isothermal irreversible process reduces to

$$W > \Delta F. \tag{3.11}$$

The work done on the system exceeds free energy change, if the process is not quasi-static. This is the best conclusion we can draw from purely thermodynamics considerations. A natural question that arises in this context is about the meaning of the statement $W > \Delta F$. A given process can be realized either in an experiment or in a computer simulation. We recognize that work done, in general, would differ from one experiment or computer realization of the process to another. Let us consider a process in which a parameter of the thermodynamics system is changed from one

value to another, as per a well defined experimental protocol. For example, we can change the volume of a system from one value to another uniformly over a fixed duration of time τ. We call this a switching process. In general, different switching experiments, all carried out with the same protocol, will give rise to different values of W. Only when the switching is done quasi-statically and reversibly does one get the same value of W in all experiments. Hence, in general, we have to deal with an ensemble of values of W and not just a single value. Let us denote this ensemble by $\Omega = \{W_i : i = 1, 2, \dots\}$. It is then quite possible that there can exist realizations for which W is less than ΔF, thereby *violating* the second law [13–17].

Let the ensemble Ω be formally described by the distribution $\rho(W;\tau)$ where τ denotes the duration of time over which the process takes place or simply the switching time. Typically we switch a macroscopic parameter denoted by the symbol Λ from an initial value say Λ_I to a final value say Λ_F. This switching of Λ from Λ_I to Λ_F can be carried out in any way. The discussions below and the Jarzynski identity discussed in the next section hold good for any protocol of switching. However, for purpose of fixing our idea , we assume switching to take place at constant rate, over a duration of time denoted by τ. If τ is small, we have fast switching. If τ is large we have slow switching. In the limit of $\tau \to \infty$, we get quasi-static reversible process. Thus

$$\Lambda(t) = \Lambda_I + (\Lambda_F - \Lambda_I) \times \frac{t}{\tau}\,, \tag{3.12}$$

where $0 \leq t \leq \tau$. The probability of violation of the second law, denoted by the symbol $p(\tau)$ is given by the following integral.

$$p(\tau) \;=\; \int_{-\infty}^{W_R} dW\, \rho(W;\tau), \tag{3.13}$$

where W_R denotes reversible work and it equals ΔF.

We note that for every thermodynamic variable there corresponds a random variable in statistical mechanics. The average of the random variable over a suitable ensemble gives the value of the thermodynamic variable. For example $\langle E \rangle$ equals the thermodynamic energy U, where the angular brackets denote average over a canonical ensemble. Hence, strictly we should state the second law as

$$\langle\, W \,\rangle \;\geq\; \Delta F. \tag{3.14}$$

In the above, the angular brackets denote an average over an ensemble of switching experiments, all carried out with the same protocol. In other words it is given by

$$\langle W \rangle \;\;=\;\; \int_{-\infty}^{\infty} dW\, W\, \rho(W;\tau). \tag{3.15}$$

Stated thus, the second law can never be violated. We define

$$W_d \;\;=\;\; \langle W \rangle - W_R \tag{3.16}$$

as dissipation and state the second law as,

$$W_d \;\geq\; 0 \tag{3.17}$$

for all processes. In the above, equality obtains when the process is quasi-static and reversible.

If τ is very large but not infinity, $\rho(W;\tau)$ would be sharply peaked Gaussian. In fact, for a process which is nearly quasi-static and reversible (τ is very large), dissi-

pation is proportional to fluctuations and from Callen-Welton theorem [2] we get,

$$\Delta F = W_R = \zeta_1 - \frac{1}{2}\beta\,\zeta_2 \tag{3.18}$$

where

$$\zeta_1 = \langle W \rangle \tag{3.19}$$

is the first cumulant and

$$\zeta_2 = \sigma_W^2 = \langle W^2 \rangle - \langle W \rangle^2 \tag{3.20}$$

is the second cumulant (or variance) of W. Thus we have $W_d = \beta\zeta_2/2$ from Eq. (3.18).

Measuring energy in units of $k_B T = \beta^{-1}$, we get, from Eq. (3.18),

$$-\beta\,\Delta F = (-\beta)\,\zeta_1 + \frac{1}{2!}\,(-\beta)^2\,\zeta_2\,. \tag{3.21}$$

For a Gaussian, the third and higher order cumulants are all identically zero. For a general process the third and higher order cumulants are not zero.

3.3 Jarzynski identity

Adding the terms involving the third and higher order cumulants on RHS of Eq. (3.21), we get,

$$-\beta\,\Delta F = (-\beta)\,\zeta_1 + \frac{(-\beta)^2}{2!}\,\zeta_2 + \sum_{n=3}^{\infty}\frac{(-\beta)^n}{n!}\,\zeta_n. \tag{3.22}$$

We recognize immediately the Right Hand Side (RHS) of the above equation as the cumulant expansion of W.

Let $\chi(\beta)$ denote the cumulant generating function. Thus we have,

$$\chi(\beta) \;=\; -\beta\Delta F \tag{3.23}$$

or equivalently

$$\exp(\chi) \;=\; \exp(-\beta\Delta F). \tag{3.24}$$

The moment generating function of W is defined as

$$\varphi(\beta) \;=\; \int_{-\infty}^{+\infty} dW\ \exp(-\beta W)\,\rho(W;\tau)\,,$$

$$=\; \langle\, \exp(-\beta\ W)\,\rangle. \tag{3.25}$$

The moment and cumulant generating functions are related to each other. We have

$$\chi(\beta) = \log\left[\varphi(\beta)\right]. \tag{3.26}$$

We see immediately that Jarzynski identity given by,

$$\langle \exp(-\beta W) \rangle = \exp(-\beta \Delta F), \tag{3.27}$$

follows naturally from this.

3.4 Gaussian Work Distribution

We shall derive an expression for the probability of violation of the second law formally given by Eq. (3.13). For large τ the work distribution $\rho(W;\tau)$ would be a sharply peaked Gaussian with mean $\langle W(\tau)\rangle$ and variance $\sigma^2_W(\tau) = \langle W^2(\tau)\rangle - \langle W(\tau)\rangle^2$. Substituting the Gaussian in Eq. (3.13) for $\rho(W;\tau)$ we get,

$$\begin{aligned} p(\tau) &= \frac{1}{\sigma_W(\tau)\sqrt{2\pi}} \int_{-\infty}^{W_R} dW \exp\left(-\frac{1}{2}\frac{[W - \langle W(\tau)\rangle]^2}{\sigma^2_W(\tau)}\right), \\ &= \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\dfrac{W_R - \langle W(\tau)\rangle}{\sigma_W(\tau)\sqrt{2}}} d\xi \exp(-\xi^2)\,, \\ &= \frac{1}{2} - \frac{1}{2}\,\mathrm{erf}\left(\frac{\langle W(\tau)\rangle - W_R}{\sigma_W(\tau)\sqrt{2}}\right), \end{aligned} \tag{3.28}$$

where, the error function is defined [18] as,

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x d\xi \exp(-\xi^2). \tag{3.29}$$

For large τ, we have Callen-Welton theorem [2] which tells us

$$\langle W(\tau)\rangle - W_R = \frac{1}{2}\beta\sigma_W^2(\tau). \tag{3.30}$$

Substituting for dissipation in terms of fluctuations in Eq. (3.28) we get

$$p(\tau) \;=\; \frac{1}{2} - \frac{1}{2}\mathrm{erf}\left(\frac{\beta\sigma_W(\tau)}{2\sqrt{2}}\right). \tag{3.31}$$

Note $\mathrm{erf}(\infty) = 1$ and $\mathrm{erf}(0) = 0$. From Eq. (3.31) we see that $p(\tau)$ increases when τ increases. In the limit of $\tau \to \infty$, $p(\tau)$ equals one-half.

This result can be understood as follow [19]. In the quasi-static limit of $\tau \to \infty$, $\rho(W;,\tau)$ becomes more and more sharply peaked such that $\langle W\rangle \to W_R$ and $\sigma_W \to 0$. By Callen - Welton theorem $W_d \propto \sigma_W^2$. This implies that $\sigma_W \gg W_d$ as $W_d \to 0$. Thus W_d and σ_W both tend to zero, with $\sigma_W \gg W_d$. In other words $W_d \to 0$ faster than $\sigma_W \to 0$. This leads to $p(\tau) \to \frac{1}{2}$ in the reversible limit.

However, dissipation is defined as $W_d = \langle W\rangle - W_R$. In the reversible limit of $\tau \to \infty$, we have $\langle W\rangle = W_R$ and hence dissipation is zero. In what follows we demonstrate the above numerically on a model system.

3.5 Work fluctuations in liquid crystalline system

3.5.1 Liquid crystals

Liquid crystal is a matter of phase that is intermediate between Solids and liquids. Solids have spatial order and long range correlation length and liquids do not have

spatial ordering and have short range correlation length. Liquid crystals exhibit long range correlation lengths and have partial ordering. These can be divided into two categories namely thermotropic and lyotropic liquid crystals. See [20, 21] for more details of liquid crystals and applications. In the present work, we consider rod-like molecules with uniaxial symmetry along long axis. Liquid crystal molecules can be considered as headless spins *i.e.,* we cannot differentiate head from tail. Two spins interact with each other and interaction can be modelled through a suitable potential. Lebwohl-Lasher potential is a successful and widely used potential in studying the properties of liquid crystals. We describe this model in the following subsection.

3.5.2 Lebwohl-Lasher Model

Lebwohl-Lasher lattice spin model [22] of liquid crystalline systems is a simple lattice model. In this model, headless spins representing a liquid crystal molecule is located at $L\times L\times L$ cubic lattice. Each spin has continuous rotational degrees of freedom. The nearest molecules interact through a potential which depends on the angle between the two molecules, given by,

$$H = -J\sum_{\langle i,j\rangle} P_2(\cos\theta_{i,j}). \tag{3.32}$$

In the above, the symbol $\langle i,j\rangle$ denotes that i and j are nearest neighbour lattice sites. The sum runs over all distinct pairs of nearest neighbour sites. $\theta_{i,j}$ denotes the angle between the spins and J measures the strength of interaction. In the simulation we express energy in units of J and hence set $J = 1$. $P_2(\eta)$ is the second Legendre

polynomial given by,

$$P_2(\eta) \quad = \quad \frac{3\cos^2(\eta) - 1}{2}. \tag{3.33}$$

Besides, each spin interacts with the external electric field, which is taken as the switching parameter. Without loss of generality we take the external field to be in the z axis direction and switch its magnitude. The energy due to the external electric field is given by,

$$\varepsilon = -\frac{\mathscr{E}^2}{2} \sum_i P_2(\cos\theta_i). \tag{3.34}$$

$\mathscr{E}$ is the amplitude of the external electric field and θ_i, the angle between the spin at lattice site i and the external electric field. So total energy of the system is

$$E = -J \sum_{\langle i,j \rangle} P_2(\cos\theta_{i,j}) - \frac{\mathscr{E}^2}{2} \sum_i P_2(\cos\theta_i). \tag{3.35}$$

We carry out Monte Carlo simulation of the response of the system to a process of switching $\mathscr{E}$ from say $\mathscr{E}_0$ to a value of $\mathscr{E}_f$.

3.6 Monte Carlo simulation of the switching process

Start with an arbitrary initial microstate (spin configuration) and employing Metropolis algorithm [23], equilibrate the system at the desired value of β with $\mathscr{E} = \mathscr{E}_0$. Select randomly a microstate from the equilibrium ensemble. Calculate the energy. Keep the microstate the same and switch the field from $\mathscr{E}_0$ to $\mathscr{E}_1 = \mathscr{E}_0 + \Delta\mathscr{E}$. This is called the work step. The resulting change in energy, called work is denoted by ω_1. Then implement a heat step *via* Metropolis algorithm over one Monte Carlo sweep

as described below.

Select randomly a spin and change its orientation by a random amount. This can done by the procedure suggested by Barker and Watts [24]. Call the resultant microstate as trial state. If the energy of the trial state is less than that of the current state accept the trial state as the next microstate in the Markov chain. If the trial state energy is more, then calculate $p = \exp[-\beta\Delta E]$ where ΔE is the energy of the trial state minus that of the current state. Draw a random number (uniformly and independently distributed in the range zero to unity) and if it less than p accept the trial state; otherwise reject the trial state and take the current state as the next state in the Markov Chain. Carry out the above rejection/acceptance step L^3 number of times and this constitutes a Monte Carlo sweep. The heat step is followed by a work step on the micro state obtained at the end of the heat step. During the work step the field changes from $\mathscr{E}_1$ to $\mathscr{E}_2 = \mathscr{E}_1 + \Delta\mathscr{E} = \mathscr{E}_0 + 2\Delta\mathscr{E}$. The work done is ω_2. The work and heat steps are repeated until $\mathscr{E}$ attains a pre - determined value, say $\mathscr{E}_f$.

Let n be the number of work steps required to switch the field from an initial value of $\mathscr{E}_0$ to a final value $\mathscr{E}_f$. In other words,

$$\mathscr{E}_n = \mathscr{E}_f = \mathscr{E}_0 + n\,\Delta\mathscr{E}\ ,$$

where $\Delta\mathscr{E} = (\mathscr{E}_f - \mathscr{E}_0)/n$. The switching time τ is thus given by n. We have

$$W = \sum_{i=1}^{n} \omega_i. \tag{3.36}$$

We carry out the simulation independently for a large number of times with the same switching protocol and construct a work ensemble $\{W_i\}$ from which all the required statistics described below are calculated. In the simulation, we have taken $\mathscr{E}_0 = 0$

and $\mathscr{O}_f = 2$. The field is directed along the positive z-direction. The results presented in this chapter are for $L = 3$. We have taken the size of the system small because fluctuations play an important role when the system is small in size. The size of the Monte Carlo ensemble of work values generated is one million.

3.7 Results and discussions

Figure 3.1 depicts results on free energy difference (or reversible work) calculated from Jarzynski identity as a function of τ with $\beta^{-1}(= \frac{k_B T}{J}) = 1.5$.

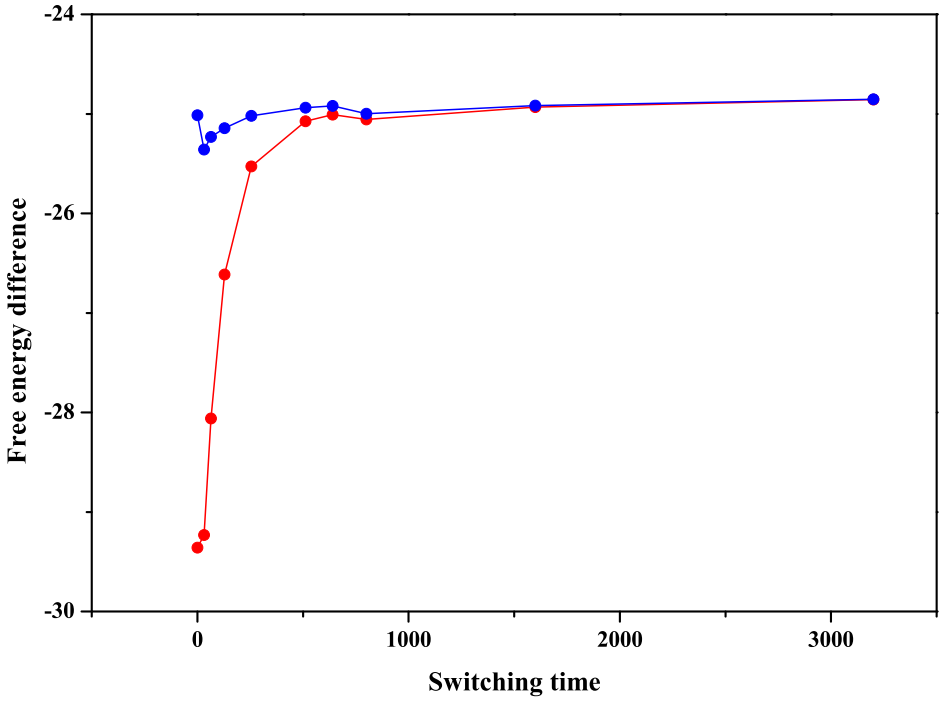

Figure 3.1: Free energy difference ΔF *versus* switching time τ. The upper curve (blue) denotes ΔF^J calculated from Jarzynski identity. The lower curve (red) denotes ΔF^{CW}, calculated from Callen-Welton theorem.

We have also plotted in the same graph the free energy change from Callen-Welton theorem. As expected, Callen-Welton theorem does not predict free energy change

correctly for small switching time when the system is driven far from equilibrium. As τ increases the results from Callen-Welton theorem converges to that from Jarzynski identity.

In Figure 3.2, we have plotted dissipation given by Eq. 3.16 and denoted as W_d^J, as a function τ. This has been calculated from the ensemble of work values generated by the Monte Carlo simulation of the switching process. The dissipation is large for small τ. This is because the system is driven far from equilibrium. However as the switching time increases the process becomes more and more quasi-static. Dissipation decreases. In the limit of $\tau \to \infty$ dissipation goes to zero. For large τ, dissipation can also be calculated from fluctuations employing Callen-Welton theorem. We have $W_d^{CW} = \beta\sigma_W^2/2$. The inset in Figure 3.2 shows $W_d^{CW} - W_d^J$. This quantity is large for small τ. It decreases with increases of τ and eventually goes to zero.

In Figure 3.3, we have depicted the probability of violation of the second law, calculated from the Monte Carlo ensemble of work values. Let $p^{MC}(\tau)$ denote this quantity which is calculated as follows.

We count how many of the switching experiments give rise to a value of W less than W_R. This number divided by the total number of switching experiments carried out, gives $p^{MC}(\tau)$. We find that $p^{MC}(\tau)$ increases with increase of τ as expected from the analytical results discussed in section 1.4. This can be explained as follows. In the quasi-static limit, $\rho(W; \tau \to \infty)$ is more and more sharply peaked such that mean tends to W_R and $\sigma_W \to 0$. By Callen- Welton theorem $W_d \propto \sigma_W^2$. This implies that $\sigma_W \gg W_d$ as $W_d \to 0$. Thus W_d and the σ_W both tend to zero. $W_d \to 0$ faster than $\sigma_W \to 0$. This leads to $p(\tau) \to \frac{1}{2}$ in the reversible limit. However, we find that $p(\tau)$ increases slowly as τ increases beyond 1500 or so. We could do the numerical

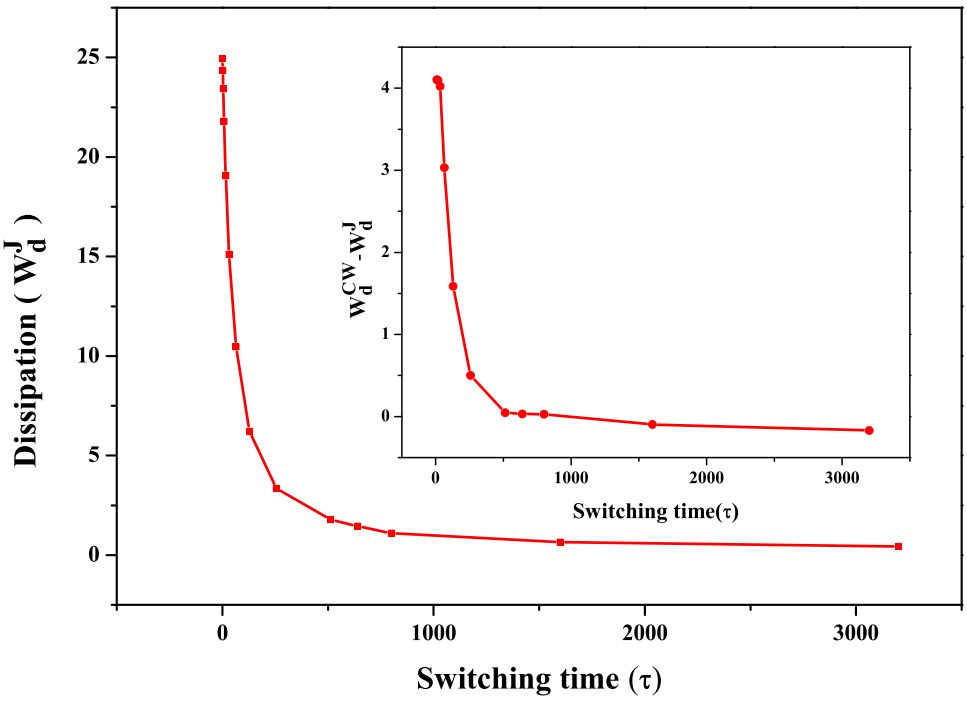

Figure 3.2: Dissipation defined as $W_d^J = \langle W \rangle - W_R$ calculated from Jarzynski identity. The inset shows $W_d^{CW} - W_d^J$, where W_d^{CW} is dissipation calculated from Callen-Welton theorem.

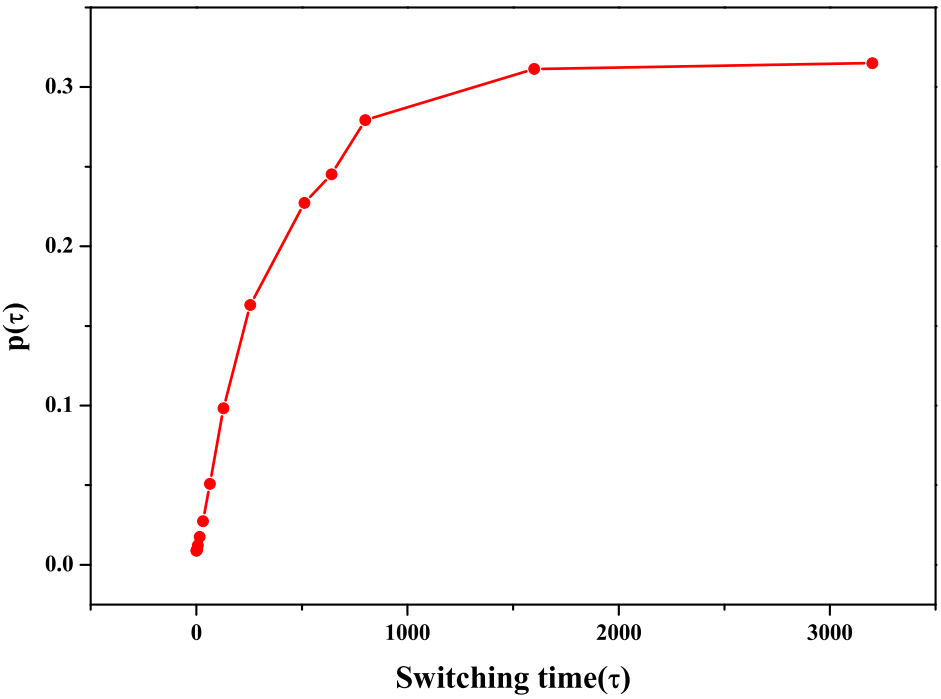

Figure 3.3: The probability of second law violation for various value of τ. calculated from the Monte Carlo ensemble.

work for τ upto 3200. We expect $p(\tau)$ to increase extremely slowly when τ increases beyond 3200, and eventually reach 0.5 as predicted by theoretical analysis.

The work distributions for representative values of τ are depicted in Figure 3.4. For small values of τ we find the distribution is broad. As τ increases the distribution becomes more and more sharply peaked. The distribution is expected to be Gaussian from Central Limit Theorem and see also [25] .

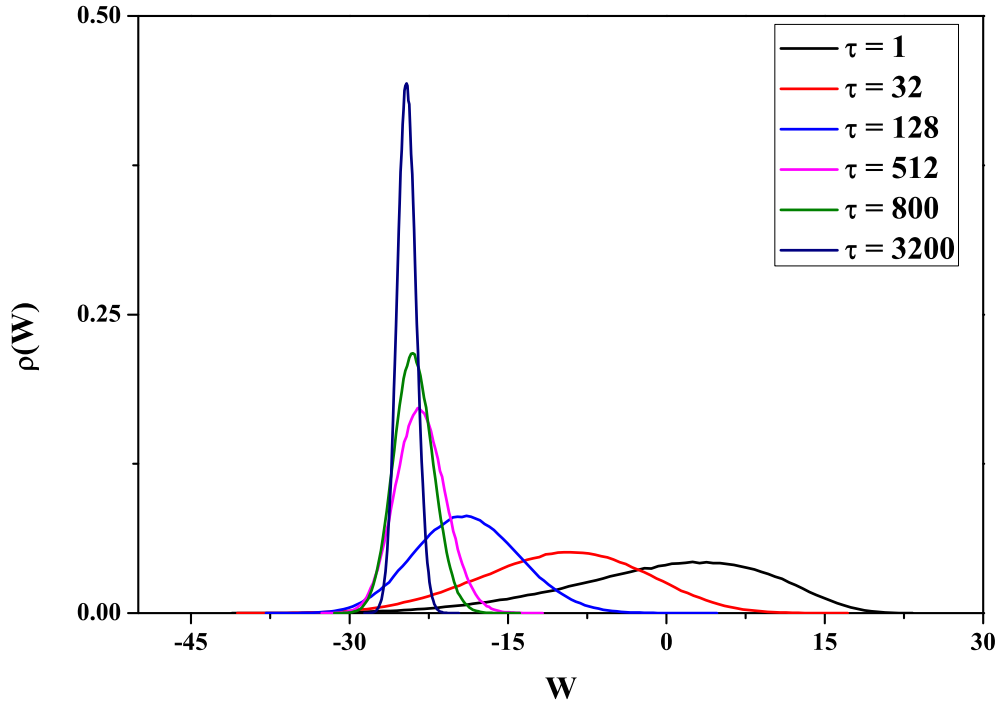

Figure 3.4: Distribution of work for $\tau = 1,\ 16,\ 64,\ 256,\ 800$ and 3200, from right to left.

3.8 Conclusions

Recent developments in non-equilibrium statistical mechanics embodied in various fluctuation theorems give us an insight into the foundational aspects of statistical

mechanics and thermodynamics. There are several other methods which provide us a tool to calculate equilibrium quantities from non-equilibrium measurements. For example Sadhukhan and Bhattacharjee [26] have shown that Barkhausen noise process, repeated many times give adequate data to construct, in conjunction with work fluctuation theorem, a special matrix whose principal eigenvector provides equilibrium distribution.

Transient fluctuation theorem of Evans and Searles [3, 4], heat fluctuation theorems of Crooks [7], and the fluctuations theorems of Gallavotti-Cohen [5, 6] for steady state systems also can be employed to estimate equilibrium quantities from non-equilibrium measurements.

In this chapter we have employed work fluctuation theorem for estimating free energy differences. We have carried out Monte Carlo simulation of the lattice model of liquid crystalline system. Monte Carlo is best suited for lattice spin models. If the Hamiltonian involves continuous degrees of freedom then Molecular Dynamics simulations would be appropriate. We find that dissipation defined as the excess of work done on the system over equilibrium free energy change tends to zero in the asymptotic limit of $\tau \to \infty$. $p(\tau)$ is given by the area under the work distribution in the tail region extending from $-\infty$ to W_R. We have shown analytically that the value of p increases with increase of τ. In the quasi-static limit of $\tau \to \infty$, $p(\tau) = 1/2$.

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Chapter 4

Force induced melting of DNA-hairpin

In the previous chapter we have discussed a method of calculating Helmholtz free energy differences using fluctuations of work in a non-equilibrium process. In this chapter we shall describe a method for calculating Landau free energy employing Wang-Landau algorithm. We obtain Landau free energy profile of a DNA-hairpin (hp-DNA) subjected to a constant force.

The chapter is organized as follows. Brief introduction to DNA is given in section 4.1. In section 4.2, we describe lattice model of hp-DNA. This is followed by a description of bond fluctuation model (BFM) with four site occupation, see section 4.3. Monte Carlo simulations, based on Wang-Landau algorithm, were carried out. The details of the simulations are presented in section 4.4. We define a phenomenological free energy (as a function of both temperature and energy), which coincides with Landau free energy near the transition temperature. The details are given in section 4.5 We present results on energy, extension, heat capacity and free energy in section 4.6. The variation of free energy as a function of energy shows that the transition from closed state to open state is discontinuous. The principal results are summarized in section 4.7.

4.1 DNA: A genetic material

Deoxyribonucleic acid (DNA) is an important molecule in living organisms. It has two strands of equal length which are anti parallel to each other and twisted around a common central axis to form right handed double helix structure [1]. The basic units of these chains are known as nucleotides and hence these strands are also called polynucleotides. These nucleotides consists of nucleobases, Adenine (A), Guanine (G), Cytosine (C) and Thymine (T) along with sugar and phosphate groups. In a strand, sugar group of one nucleotide is linked with phosphate group of another

nucleotide resulting in sugar-phosphate backbone. These chemical bonds between sugar and phosphate groups are known as $3' - 5'$ linkage. Adenine of one strand forms bond with Thymine of another strand; similarly Guanine with Cytosine. Figure 4.1 shows the basic form of DNA. For further information see [2, 3].

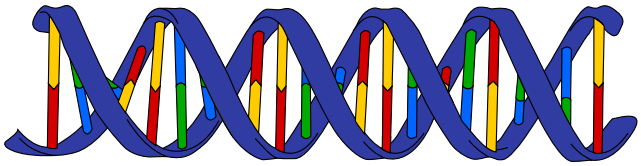

Figure 4.1: Schematic representation of double helix DNA. The vertical lines show the base pairing.

DNA contains gene information in an encoded form. To decode this information, it is necessary to separate the DNA into two single strands. The separation occurs in biological process like replication and transcription. This separation of bonds between two strands is called denaturation. Denaturation can be done by two ways namely unzipping and melting. Unzipping transition is brought about by virtue of force and melting transition by virtue of temperature.

Unzipping was first studied by Bhattacharjee [4]. He showed that Unzipping is a critical phenomenon; a critical force is required to unzip a double strand DNA. Later on unzipping has been studied extensively by several others [5–14]. Melting has also been studied by many authors, see *e.g.* [15–20]. There are a few excellent reviews on denaturation of DNA. For example F. Ritort [21] has reviewed different single molecule experimental methods of unzipping of DNA; a review by Kumar and Li [22] discusses experimental, theoretical and numerical techniques used for investigating the dynamics of biomolecules under the influence of external force; Bhattacharjee, Giacometti and Maritan [23] have reviewed analytical methods in the context of Flory theory.

In this chapter we discuss melting of hp-DNA in the presence of a constant force.

4.2 DNA - Hairpin

Study of properties of hp-DNA gives us an insight into understanding biological processes like replication, transcription, recombination, protein recognition and gene regulation [24–28]. An hp - DNA is single stranded and has sequences with inverted repeats, also called palindromes. It has complementary bases at the ends. The hairpin structure occurs when these two complementary bases form a base pair. There are then two segments: stem and loop. The stem-loop structures are not static. They

change all the time even when the system is in equilibrium. The hairpin conformations can be divided into two categories, i) closed state and ii) open state.

A closed state is of low energy and low entropy because of base pairing in the stem region. The open state is of high energy because there is no base pairing and of high entropy because of the accessibility to a large number of conformations, consistent with the constraints. The transition from closed state to open state occurs when the energy fluctuations are sufficiently large to unbind all the base pairs. We study transition by employing Monte Carlo simulations. To generate all possible conformations, we have employed bond fluctuation model (BFM) which was originally proposed for generating different polymer conformations [29]. Landau free energy profile would give a clear idea of the nature of the phase transition. In the following subsection, we describe a lattice model of an hp-DNA.

Lattice model of an hp-DNA

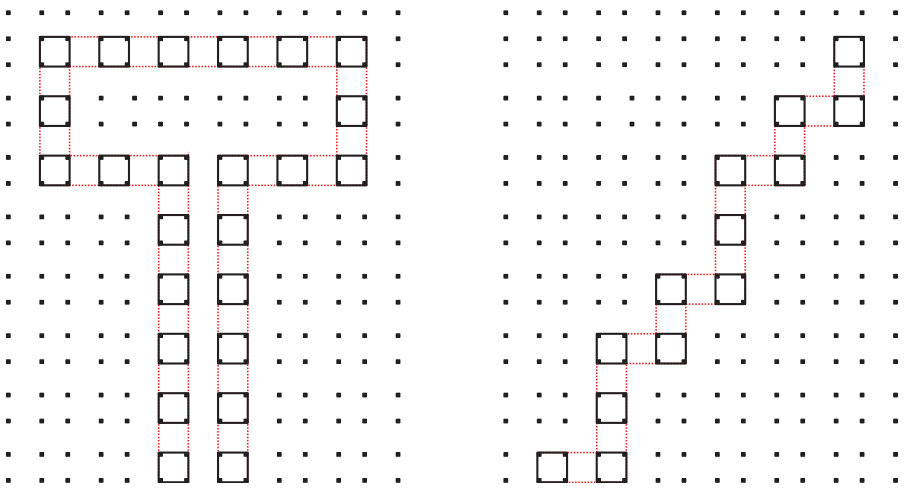

Figure 4.2: Schematic representation of closed (left) and open ((states of an hp-DNA modelled as a four-site occupation bond-fluctuating lattice polymer.

In lattice models, in spite of restricting monomers on lattice sites, a polymer has substantial conformational freedom. It is also observed that lattice models of polymers exhibit qualitatively similar behaviour as real polymers and give results in good agreement with experiments. Excluded volume effect/hard core repulsion can be easily implemented by demanding no lattice site can belong simultaneously to two or more monomers. We consider an hairpin model of DNA on a two dimensional square lattice. The first base pairs with the N-th base; the second with $(N-1)-$th; and so on. We designate these pairs as native contacts. We assign an interaction energy of $-\varepsilon_b$ for each native contact [30, 31]. Without loss of generality we set $\varepsilon_b = 1$. Non-native contacts carry no energy. We apply a force perpendicular to the stem in

the two dimensional plane. The energy due to this applied force is $\varepsilon_f = -\vec{f}\cdot\vec{x}$, where $\vec{x}$ is end-to-end distance. The total energy thus, is

$$E = -\gamma\varepsilon_b - \vec{f}\cdot\vec{x}\,, \tag{4.1}$$

where γ is the number of native contacts in a conformation. In our simulation, we have used chains of length 90, 100 and 110; the stem contains 80 beads (forming 40 base pairs), 90 beads (forming 45 base pairs) and 100 beads (forming 50 base pairs) respectively and the loop contains 10 beads.

4.3 Bond Fluctuation Model

To calculate thermal properties we need to know the total number configurations with all values of order parameter. Conventional growth techniques need large computational time and hence we have chosen bond fluctuation model(BFM) [29]. In this model bond length can fluctuate between permitted values. Fluctuations in bond lengths provide for a more realistic description of DNA dynamics and also makes BFM close to continuous space behaviour as in continuum models. There are two types in BFM; the first is single-site occupation model and the second is four-site occupation model. We have chosen four-site occupation model. The reason for this choice is that this does not suffer from problem of ergodicity, especially at low temperatures. In a single site lattice model there is always a possibility that the system would get struck in a conformation[1]. BFM provides an efficient algorithm to simulate an equilibrium ensemble of lattice polymer conformations. The algorithm helps generate different conformations in an easy manner. To the best of our knowledge, bond fluctuation model has not been employed, so far, in the study of thermodynamic properties of DNA molecules. Implementation of BFM is explained below.

In a four-site lattice model of BFM a monomer occupies four lattice sites. The minimum value allowed for bond-length is 2 to ensure self avoidance. The maximum allowed is taken as less than $\sqrt{16}$ to avoid bond cuts[29]. Thus the allowed values for bond length are 2, $\sqrt{5}$, $\sqrt{8}$, 3, $\sqrt{10}$, $\sqrt{13}$. We start with a closed state of hp-DNA as shown in Figure 1 with the bond length equals to 2 between the beads. Implementing four-site model is a bit difficult as to move a monomer we need to select four positions of the monomer and change their coordinates by one in any one of chosen directions. A simple way is to consider the centre of masses of the monomers. Then the four-site lattice model reduces to a single-site lattice model. However, the conditions for bond length and self avoidance remains the same. We move a randomly selected bead by a lattice spacing along any one of the randomly

[1] see figure 5 in [29]

chosen directions (in a two dimensional lattice model there are four possible directions). If either self avoidance or maximum bond length condition is not satisfied we move the bead to its initial position and carry out the whole process again by selecting a bead and its direction randomly. If both the conditions are satisfied we consider that conformation as a trial conformation and is accepted or rejected on the basis of Wang-Landau sampling, described in the next section.

4.4 Monte Carlo Simulations

As discussed in chapter 2, Wang-Landau algorithm[32] belongs to a class of techniques known as non-Boltzmann Monte Carlo methods. The central idea behind these method consists of biasing the system to visit those regions of energy with lower density of states. Such a biasing technique in a sense cancels the natural tendency the system has, to visit high entropy regions of energy. As a result, the energy-histogram of visited microstates becomes flat. While calculating averages, the effect of such biasses are corrected by employing unweighting and reweighting factors.

Basically we construct a trial microstate C_t by making local change in the current state C_i. The trial microstate is accepted with a probability $p = g(E_i)/g(E_t)$. If accepted $C_{i+1} = C_t$; if not, $C_{i+1} = C_i$. Thus we generate a chain of microstates starting from an arbitrary initial microstate C_0. In our simulation we have taken C_0 as closed state of an hp-DNA as shown in Figure 4.2.

At the beginning of the simulation we set $g_i = g(E_i) = 1 \,\forall\, i$. The histogram of energy is set to zero in all energy bins; *i.e.,* $H_i = H(E_i) = 0 \,\forall\, i$. We generate a sequence of conformations $C_0 \rightarrow C_1 \rightarrow C_2 \rightarrow \ldots \rightarrow C_i \rightarrow C_{i+1} \rightarrow \ldots$ as described above. Whenever a trial state is accepted or rejected, we update the DOS corresponding to the energy of the state C_{i+1} as follows. We multiply $g(E(C_{i+1}))$ by a modification factor $\alpha_0 > 1$. Here we have taken $\alpha_0 = \exp(1.0)$. We also update $H(E(C_{i+1}))$ by incrementing it by unity. This constitutes one Monte Carlo step. A consecutive sequence of N Monte Carlo steps makes one Monte Carlo Sweep where N is length of the chain. We carry out several Monte Carlo sweeps till the histogram becomes flat over a certain energy range. This constitutes one Wang Landau iteration. We say a histogram is flat when the highest and lowest of its entries do not differ from each other by more than 20 percent.

We reduce modification factor to $\alpha_1 = \sqrt{\alpha_0}$, and reset $\{H_i = 0 \,\forall\, i\}$, and carry out the next Wang-Landau iteration with α_1. We continue with Wang-Landau iterations until α_n takes a value very close to unity. Logarithm of the converged DOS gives microcanonical entropy upto an additive constant, from which all other thermodynamic properties can be obtained.

We also carry out a production run with converged DOS and collect a relatively

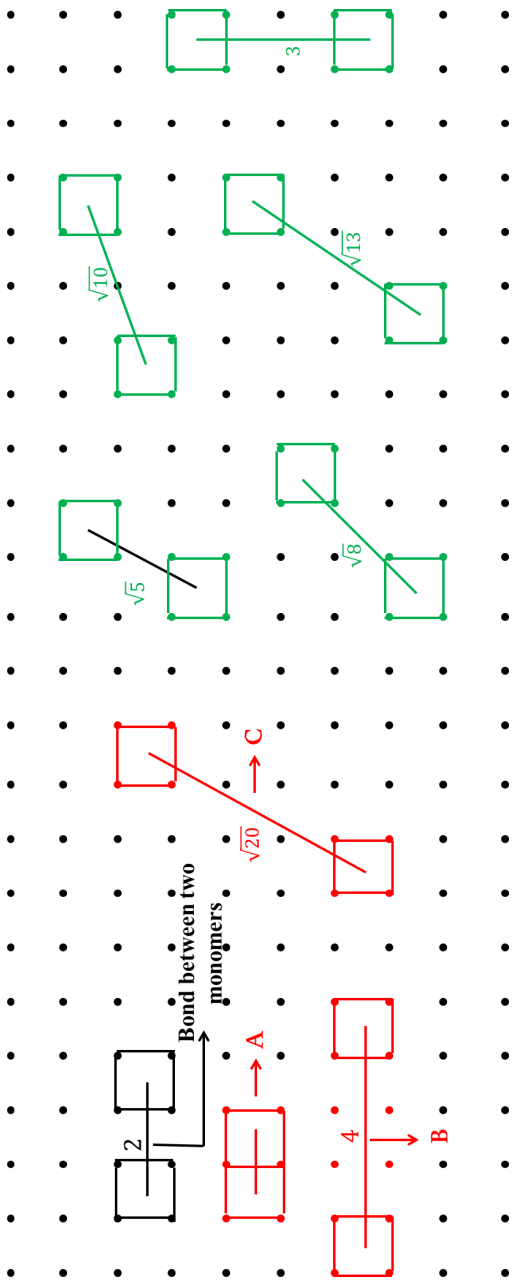

Figure 4.3: Moves that are not permitted (monomers in red colour) and are permitted (Monomers in green colour) in four-site bond fluctuation model.

large number conformations called entropic ensemble. The required thermodynamics properties can be obtained by un-weighting (dividing by $g^{-1}(E(C))$)and reweighting (multiplying by $exp(-\beta E(C))$). For example average energy can be calculated as

$$\langle E \rangle = \frac{\sum_C E(C)\, g(E(C))\, e^{-\beta E(C)}}{\sum_C g(E(C))\, e^{-\beta E(C)}} \,. \tag{4.2}$$

where C belongs to entropic ensemble generated by Monte Carlo in the production run of W-L method. The appropriate order parameter for an hairpin DNA is extension, defined as end-to-end distance. To calculate average extension we have employed the method given by Binder *et al.* [33]. The average extension is calculated as given below.

$$\langle x \rangle_T = \frac{\sum_i \langle x \rangle_{E_i}\ g(E_i)\, e^{-\beta E_i}}{\sum_i g(E_i)\, e^{-\beta E_i}} \,, \tag{4.3}$$

where $\langle x \rangle_E$ is microcanonical ensemble average given by,

$$\langle x \rangle_{E_i} = \frac{1}{H(E_i)} \sum_C x\, \delta(E(C) - E_i) \,. \tag{4.4}$$

4.5 Landau free energy

Helmholtz free energy of a closed system at temperature T is given by

$$F(T, V, N) = -k_B T \ln Q(T, V, N) \,, \tag{4.5}$$

where $Q(T, V, N)$ is the canonical partition function. We can also define so-called microcanonical free energy for an isolated system with energy U, volume V and number of particles N as,

$$F(S, V, N) = U - \left(\frac{\partial U}{\partial S}\right)_{V,N} S \,, \tag{4.6}$$

where S is micro canonical entropy given by $k_B \ln g(E)$. In the above equation we have written left hand side as $F(S, V, N)$ instead of $F(T, V, N)$ because in a microcanonical ensemble temperature is given by,

$$T(S, V, N) = \left(\frac{\partial U}{\partial S}\right)_{V,N} . \tag{4.7}$$

See [34–37] for a discussion on temperature in microcanonical ensemble.

For an equilibrium system, isolated or closed, free energy cannot be simultaneously a function of both energy and temperature. An isolated system with a given energy has a unique temperature (given by Eq. 4.7) and a closed system at a given temperature has a unique energy[2]. However, we are interested in estimating the penalty in terms of excess free energy, required to keep the system in a state with energy different from equilibrium energy for a given temperature. To this end we define a phenomenological free energy denoted by the symbol $F_L(E, T)$, which is simultaneously a function of both energy and temperature. We have $F_L(E, T) \geq F(T)$ for all values of energy. Equality obtains when $E = U(T)$, where $U(T)$ denotes the energy of the system in thermal equilibrium at temperature T. The excess free energy is given by, $\Delta F = F_L(E, T) - F(T)$, where $F_L(E, T)$ is given by,

$$F_L(E, T) = -k_B T \ln \sum_C \delta(E(C) - E) \exp(-\beta E(C)) \,, \tag{4.8}$$

where the summation runs over the entropic ensemble obtained.

Once we know DoS, we can calculate microcanonical entropy as

$$S(E_i) = k_B \ln g(E_i). \tag{4.9}$$

and $F_L(E, T, V)$ as

$$F_L(E_i, T) = E_i - TS(E_i) \,, \tag{4.10}$$

which would correspond to Landau free energy when T is close to transition temperature. We make an estimate of the transition temperature from the data of C_v versus T. The value of T at which C_v peaks is taken as T_C. We have calculated $F_L(E, T, V)$ for values of T in the neighbourhood of T_C. The results are presented and discussed in the next section.

[2]

$$U(T, V, N) = -\frac{\partial \ln Q(T, V, N)}{\partial \beta}$$

4.6 Results and Discussions

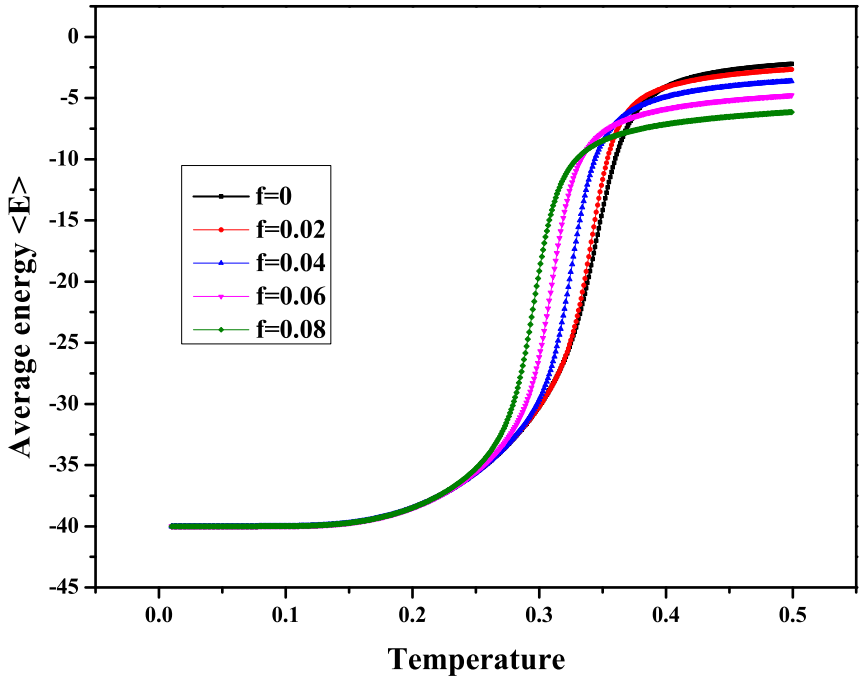

Figure 4.4: Average energy for different force values for chain length of 90.

Figure 4.4. depicts the change of average energy with temperature for different force values. Here temperature is in reduced units of $\frac{k_B T}{\epsilon_b}$. We see that at lower temperatures the average energy is same for different force values and the system is at its lower energy state which is a zipped state. As the temperature increases the energy increases. At higher temperatures, energy saturates to zero for $f = 0$. i.e., without any external force. But energy saturates at a value less than zero if we apply the force as there will be a contribution from second term of energy equation.

In Figure 4.5. we have plotted heat capacity against temperature for different values of external force. The temperature at which the heat capacity is maximum, is taken as the transition temperature. We observe that the transition temperature decreases as the applied force increases.

Figure 4.6. shows extension as a function of temperature for different force values. At lower temperatures, as the system is in a zipped state, the extension tends to the minimum value of 2, expected in a four-site lattice BFM. From the figure we observe that force has negligible effect on unzipping process at low temperatures. However at high temperatures, average extension increases with increase of force.

In Figure 4.7. we have plotted transition temperatures against force applied. The

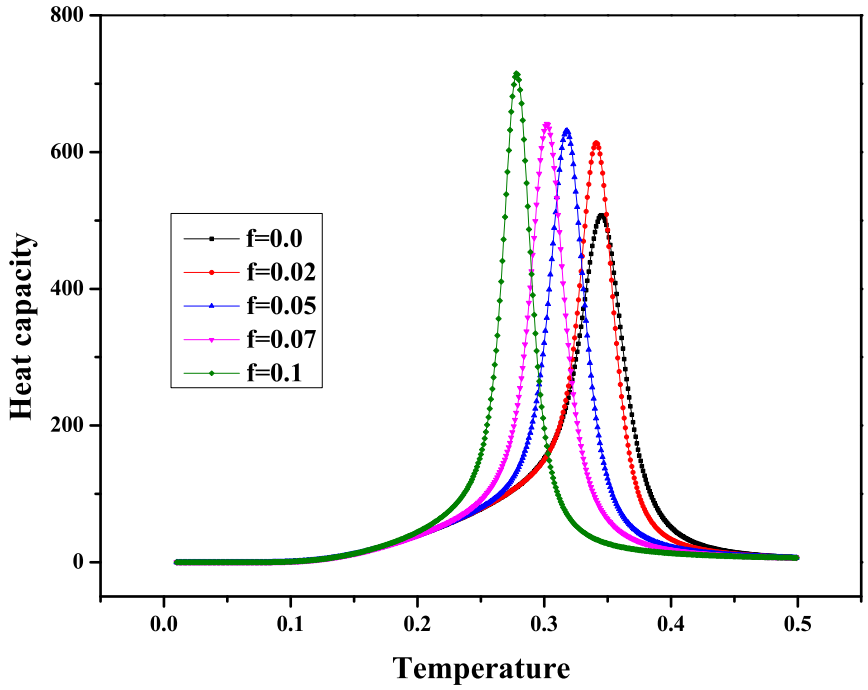

Figure 4.5: Change of heat capacity as a function of temperature for f=0, 0.02, 0.05, 0.07 and 0.1 from right to left for chain length of 90.

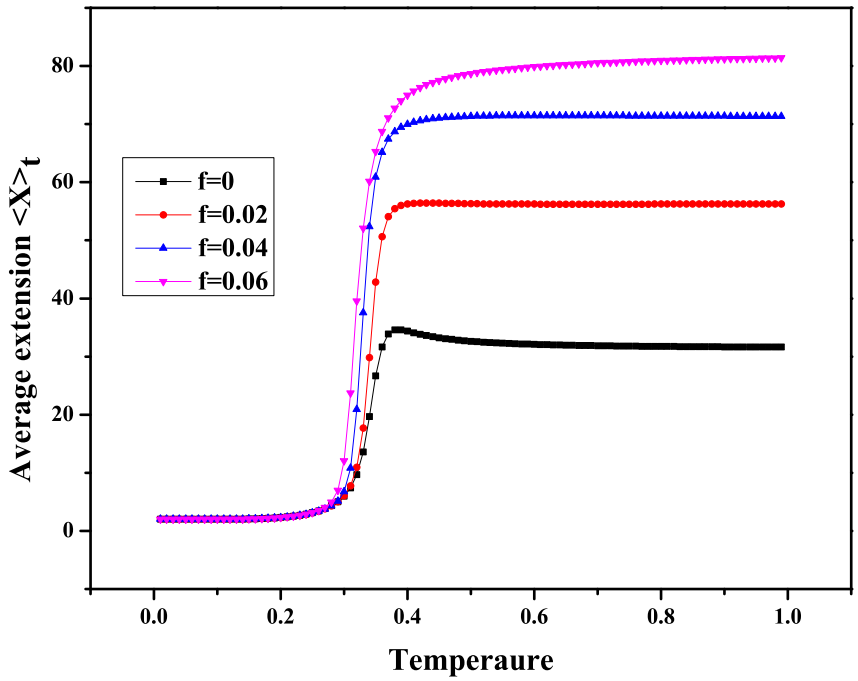

Figure 4.6: Canonical average extension Vs temperature for f=0, 0.02, 0.04 and 0.06 for chain length of 90.

curve separates Temperature-Force plane into two regions. In the region below the curve, the system is in a zipped phase. Above, it is in an unzipped phase.

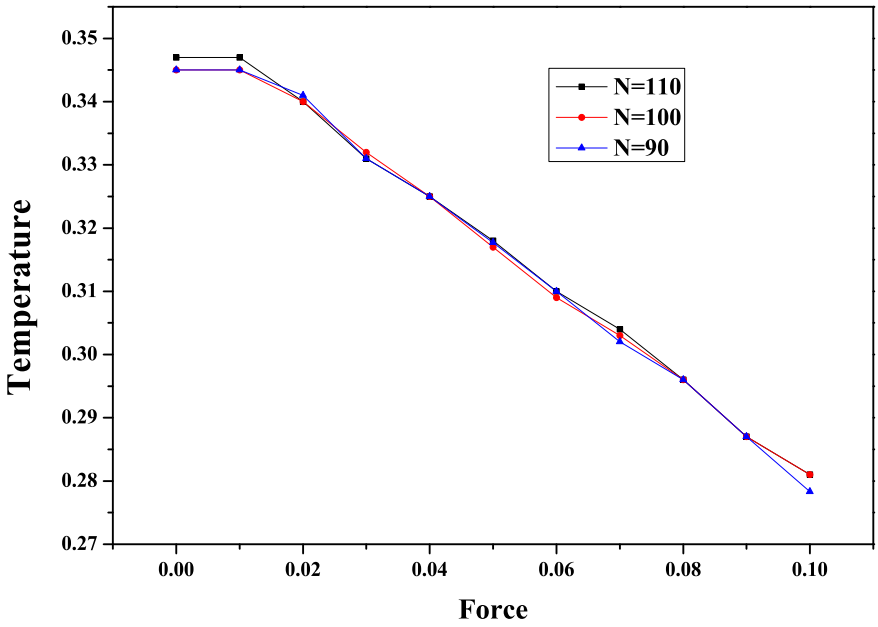

Figure 4.7: Force - Temperature phase diagram.

In Figure 4.8, we have depicted Landau free energy as a function of energy below T_C, above T_C and at T_C where T_C denotes the transition temperature and the applied force is zero. From this figure we observe that the phase transition is discontinuous.

Landau free energy is usually expressed as a function of a suitably chosen order parameter. In the study of first order phase transition, energy is a good order parameter. The advantage is that Landau free energy can be obtained directly from the density of states. The end-to-end distance is also a good order parameter for the DNA problem considered in this paper. Such a choice would require calculation of joint density of states a function of energy as well as end-to-end distance. Such a calculation is computationally more intensive. We have not taken up such a calculation for the present problem where the transition is discontinuous and hence energy itself is a good order parameter.

We have also plotted Landau free energy when force is applied on the system, see Figures 4.9, 4.10, 4.11 for three chain lengths. We observe that the transition is discontinuous.

Our results shows that the transition from closed state to an open state is discontinuous which is consistent with earlier reports [21, 38]. However, In a recent work Sadhukan and Bhattacharjee [39] have indicated, based on thermodynamics the pos-

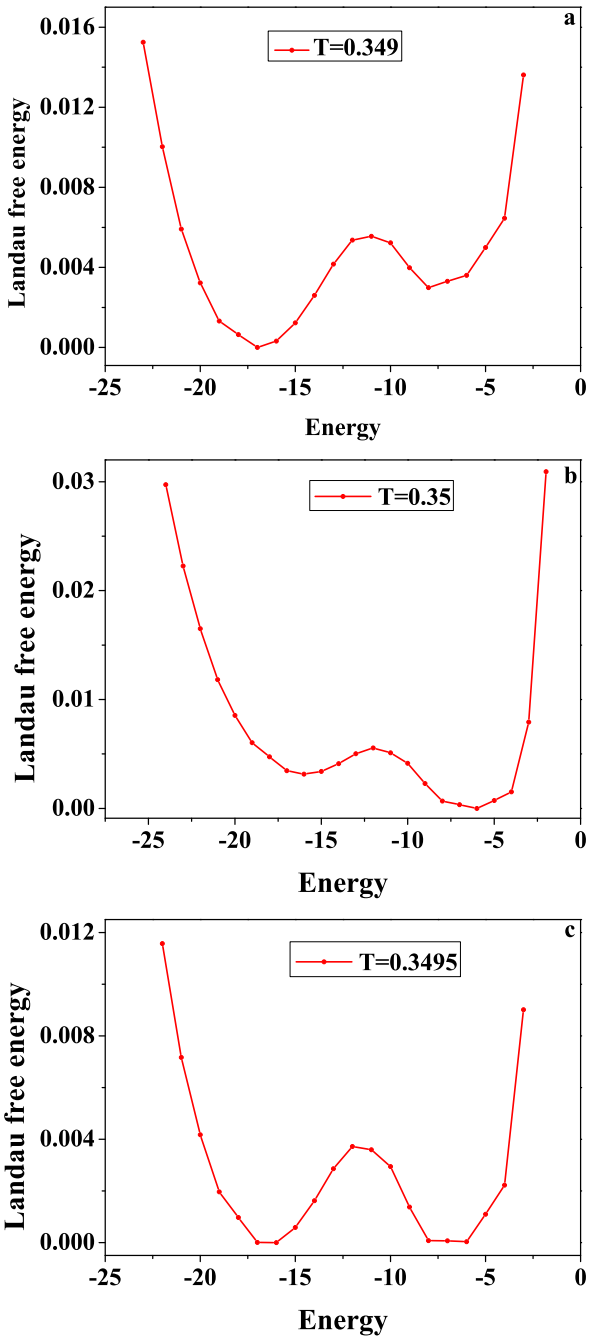

Figure 4.8: Normalized Landau free energy as a function of energy at temperatures below T_C (a), above T_C (b)and at T_C (c) without force for chain of length 90.

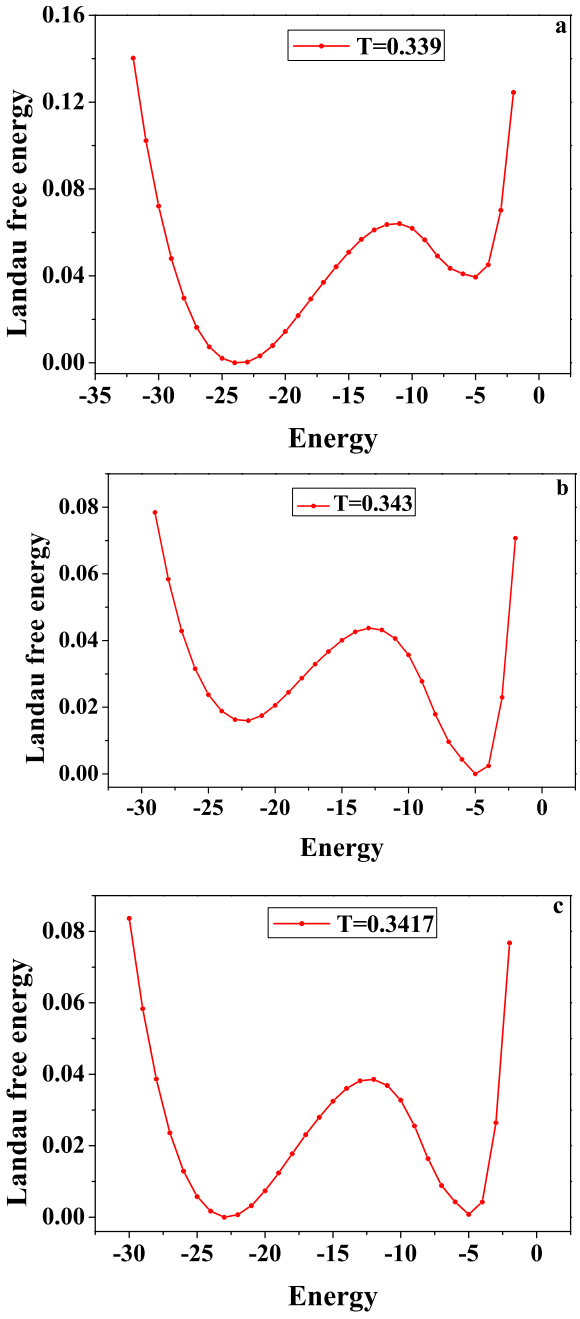

Figure 4.9: Normalized Landau free energy as a function of energy at temperatures below T_C (a), above T_C (b)and at T_C (c) for force f=0.02 for chain of length 90.

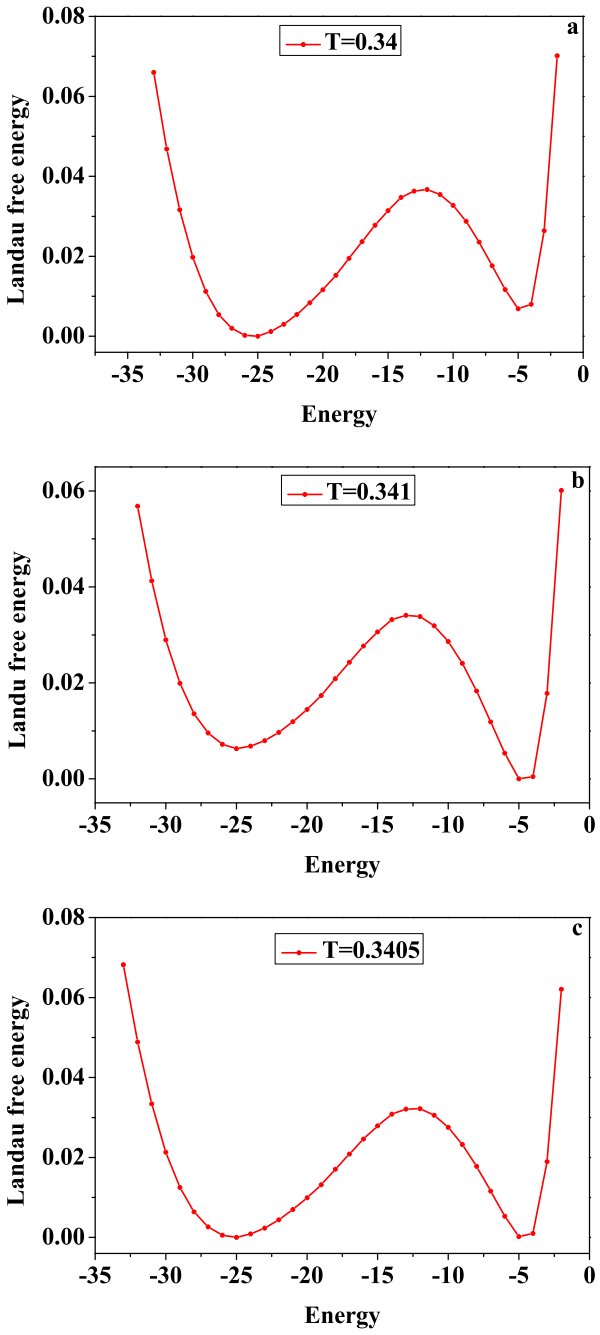

Figure 4.10: Normalized Landau free energy as a function of energy at temperatures below T_C (a), above T_C (b)and at T_C (c) for force f=0.02 for chain of length 100.

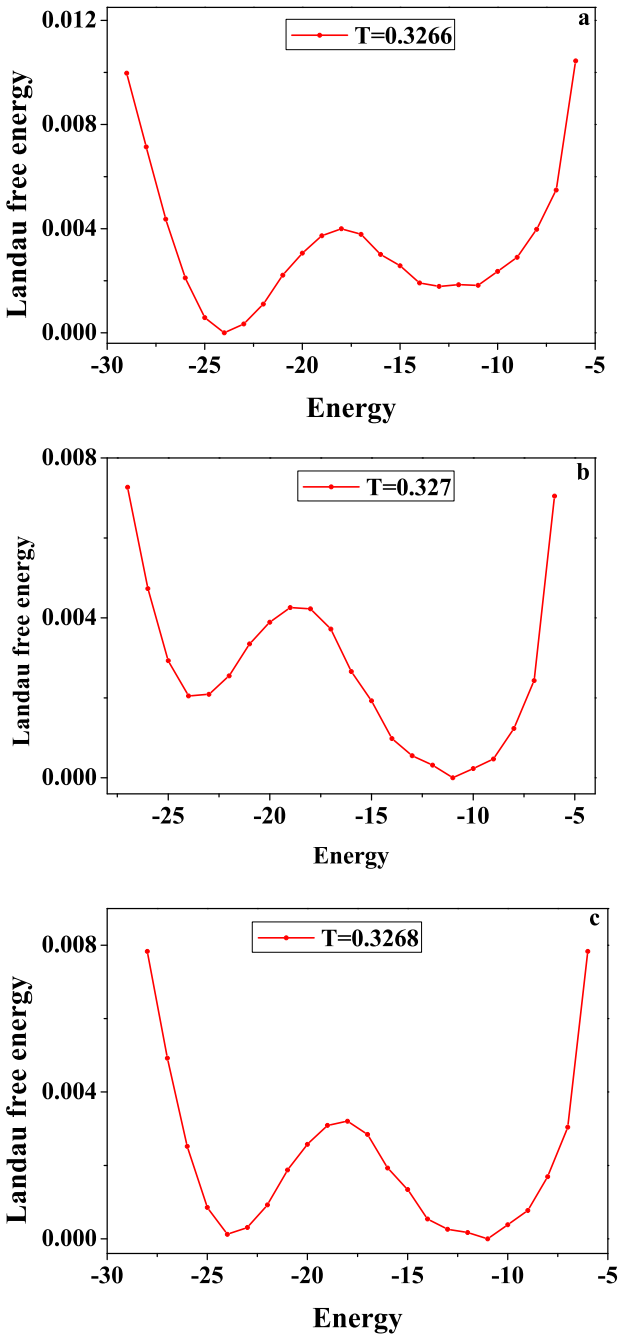

Figure 4.11: Normalized Landau free energy as a function of energy at temperatures below T_C (a), above T_C (b)and at T_C (c) for force f=0.04 for chain of length 110.

sibility of continuous unzipping transition. In our study we have restricted ourselves to small values of external force. The transition may become continuous for higher force values.

4.7 Conclusions

In summary, we have reported the work on thermodynamic properties of a DNA hairpin, investigated employing non-Boltzmann Monte Carlo simulation. Bond fluctuation model was successfully employed for the first time to study melting transition of hp-DNA. It is observed that effect of force on unzipping is negligible at low temperatures. From Landau free energy profile it is observed that the transition is discontinuous, at least for the force values considered.

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Chapter 5

Calculation of joint density of states

WANG-LANDAU (WL) algorithm [1] has emerged as a powerful Monte Carlo technique in statistical physics. It has been applied to various kind of problems which includes polymers [2], Potts model [3], Ising Model [4] and liquid crystals [5, 6] etc. As we discussed in chapter 2, a major advantage of this algorithm is that thermal properties of a system like entropy and free energy can be obtained. These are not accessible to the conventional Markov chain Monte Carlo methods based on Metropolis algorithm.

Often we need to calculate joint density of states(JDoS) $g(E, M)$, where M is order parameter, to calculate certain thermal properties like Landau free energy [7]. To this end, we need to perform random walk both in energy and order parameter spaces to estimate JDoS. But this is computationally expensive.

For a 32×32 Ising spins system, estimation of $g(E, M)$ requires CPU time a factor of 10^3 more than that required for estimating $g(E)$. This extra time required increases with the system size.

In this chapter we propose a simple and efficient method based on Wang-Landau (WL) algorithm to calculate JDoS which takes relatively much less computational

time.

This chapter is organized as follows. In section 5.1 we describe the method of calculating JDoS given by Landau, Tsai and Exler [8] using WL algorithm. We shall refer to this as LTE method. Section 5.2 gives details of our method. We apply both these methods to Ising spin system and study their relative merits. Results are presented in section 5.3. We give concluding remarks in section 5.4.

5.1 Calculation of joint density of states using LTE method

In this section we briefly describe LTE method. We consider Ising spin system [9, 10] on a two dimensional square lattice.

An Ising spin takes a value of $+1$ if it points upwards and -1 if it points downwards. The interaction energy between two spins S_i and S_j which are located at nearest neighbour sites i and j is given by $\varepsilon_{ij} = -JS_iS_j$, where J is the strength of spin-spin interaction. For a two dimensional square lattice, each spin interacts with four nearest neighbours. The total energy of the system is given by

$$H = -J \sum_{\langle i,j \rangle} S_i S_j \,, \tag{5.1}$$

where $\langle i, j \rangle$ denotes that i and j are nearest neighbour sites and the summation runs over all the distinct nearest neighbour pairs with periodic boundary conditions. JDoS is calculated as follows using LTE method.

Initially we set $g(E_i, M_j) = 1, \forall i, j$ and histogram $H(E_i, M_j) = 0 \forall i, j$. Select a spin randomly, flip, and get a trial state. Let E_i be the the energy of the current state and M_i is the order parameter. Let E_t and M_t be the energy and order parameter of the

trial state. We accept the trial state with probability,

$$p = min\left(\frac{g(E_i, M_j)}{g(E_t, M_t)}, 1\right). \tag{5.2}$$

Thus $C_{i+1} = C_t$ with a probability p; $C_{i+1} = C_i$ with a probability $1 - p$. Each time we visit a state with energy E_i and order parameter M_j, we update the corresponding JDoS by multiplying existing value by a modification factor f. *i.e.,* $g(E_i, M_j) = g(E_i, M_j) \times f$. Usually f is taken as $\exp(1.0)$. We also update the histogram by incrementing the existing value by 1. A single acceptance or rejection step is called a Monte Carlo step. L^d number of Monte Carlo steps constitutes one Monte Carlo sweep (MCS), where L is size of lattice and d the dimensionality. We repeat the process till we get a flat histogram. Then we reduce modification factor $f \rightarrow \sqrt{f}$ and reset $H(E_i, M_j) = 0$ and repeat the above process. We repeat the whole process described above till $f \simeq 10^{-8} = 1.00000001$. As $f \rightarrow 1$, $g(E_i, M_i)$ converges to true joint density of states. As discussed earlier it takes huge computational time to get converged JDoS according to LTE method.

5.2 New method to calculate joint density of states

The method we propose consists of two steps.

1. Estimate DoS as a function of energy alone, using WL algorithm. We call this learning run.

2. Estimate JDoS in the production run. We treat $g(E, M)$ as a thermodynamic variable whose average over a microcanonical ensemble is to be obtained. From entropic ensemble we construct a microcanonical ensemble by unweight-

ing and reweighting, see below.

In the production run, we start with a microstate C_0 taken from the last WL iteration of learning run and generate sequence of microstates

$$C_0 \to C_1 \to C_2 \to C_3 \to ....C_i \to C_{i+1} \to ... \to C_N$$

employing WL algorithm with the converged DoS, $g(E)$. In production run we do not update DoS. The above sequence of microstates are taken after every Monte Carlo Sweep *i.e.,* C_{i+1} is a microstate evolved from the microstate C_i after one Monte Carlo Sweep. N is the number of Monte Carlo Sweeps. As this entropic ensemble is collected with the probability proportional to $g^{-1}(E)$, to calculate average of any macroscopic observable O over a microcanonical ensemble, we need to unweight and reweight with suitable factors. In this case the unweighting factor is $g^{-1}(E)$; the reweighting factor is unity since the microstates of the same energy are equally probable. The average is given by,

$$\langle O \rangle_E = \frac{\sum_C O(C) g(E(C))}{\sum_C g(E(C))} , \tag{5.3}$$

where C denotes a microstate belonging to the entropic ensemble, $O(C)$ is the value of macroscopic property O when the system is in microstate C. We can also calculate average over a canonical ensemble by using suitable unweighting and reweighting

factors[1].

Our aim is to calculate average of JDoS over a microcanonical ensemble. This can be done as follows.

From the microcanonical ensemble compute the following

$$\langle g(E_i, M_j)\rangle = \frac{\sum_C \delta(E(C) - E_i)\delta(M(C) - M_j)g(E(C))}{\sum_C \delta(E(C) - E_i)g(E(C))} \quad \forall\, i,\ j. \tag{5.4}$$

In Ising spin system the order parameter is magnetisation, given by

$$M = \sum_{i=1}^{L^2} S_i. \tag{5.5}$$

Once we get the microcanonical average of JDoS, we can calculate the average of any other macroscopic observable over a canonical ensemble as

$$\langle O\rangle_T = \frac{\sum_C O(C) \sum_j \langle g(E(C), M_j)\rangle \exp(-\beta E(C))}{\sum_C \sum_j \langle g(E(C), M_j)\rangle}. \tag{5.6}$$

Also we can calculate Landau free energy as

$$F_L(M_j, T) = -k_B T \ln \sum_i \langle g(E_i, M_j)\rangle \exp(-\beta E_i)\ , \tag{5.7}$$

[1]The unweighting factor is $g^{-1}(E)$ and the reweighting factor is $e^{-\beta E}$. The average is given by

$$\langle O\rangle_T = \frac{\sum_C O(C) g(E(C)) \exp(-\beta E(C))}{\sum_C g(E(C)) \exp(-\beta E(C))}.$$

where we take T to be very close to the transition temperature.

5.3 Results and Discussions

We have considered 10×10 Ising spin system. The JDoS was estimated employing LTE method. It took 6 hours 32 minutes 27 seconds of CPU time. We have done the same calculation by the method proposed here. The calculation took just 1 hour 11 minutes 29 seconds of CPU time. Thus our method takes five times less computational time. We also applied proposed method to Ising spin system of size 32×32. For a 32×32 system, we carried out the simulation by employing LTE method. The time required was very large. We could not get the convergence within a meaningful time with the computational facility accessible to us. However, we could get JDoS for a 32×32 system using our method within ten hours of CPU time.

Average energy can be calculated by substituting $E(C)$ in place of $O(C)$ in Eq. 5.6. In Figures 5.1, 5.2 we have plotted average energy against temperature for systems of size 10×10 and 32×32 respectively. Here temperature is in reduced units of $\frac{k_B T}{J}$. It shows a transition from low energy ferromagnetic state to a high energy paramagnetic state. Table 5.3. compares the average energy calculated from both LTE and our methods at different temperatures. These values match with each other.

We have plotted heat capacity against temperatures in Figures 5.3, 5.4 for 10×10 and 32×32 Ising spin system. The temperature at which heat capacity is maximum is taken as transition temperature.

Using JDoS, we have calculated Landau free energy using Eq. 5.7. Figures 5.5, 5.6 show scaled Landau free energy as a function of order parameter at temperatures

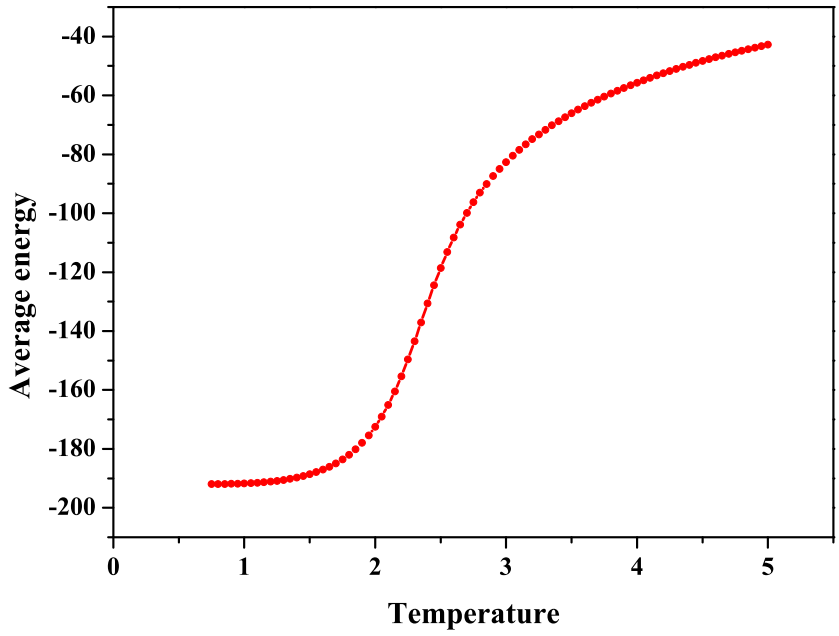

Figure 5.1: Average energy calculated by our method for 10×10 system.

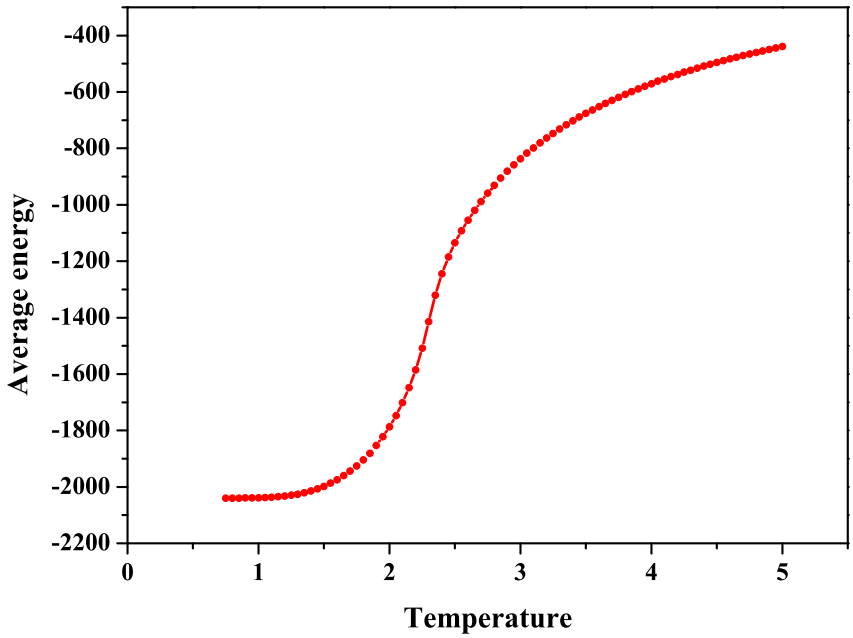

Figure 5.2: Average energy calculated by our method for 32×32 system.

Temperature	$\langle E \rangle$ from LTE method	$\langle E \rangle$ from our method
1	-191.700887	-191.700208
1.5	-188.598623	-188.625694
2	-172.475173	-172.45367
2.5	-118.48199	-118.444848
3	-82.535016	-82.542792
3.5	-66.039919	-66.101456
4	-55.662365	-55.741477
4.5	-48.309297	-48.382036
5	-42.768509	-42.827023

Table 5.1: Comparison of average energies calculated employing LTE method and our method for 10×10 Ising spin sytem.

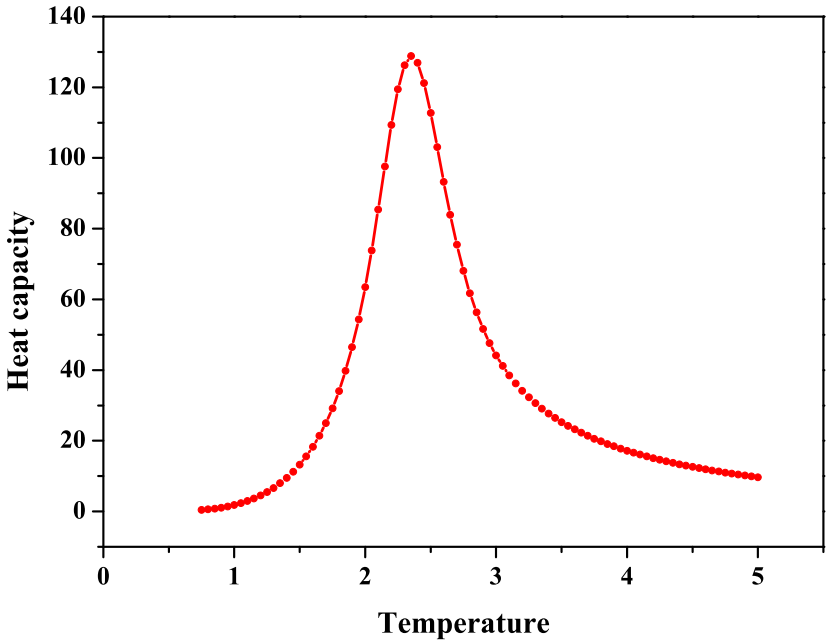

Figure 5.3: Heat capacity as a function of temperature for 10×10 system calculated by employing our method.

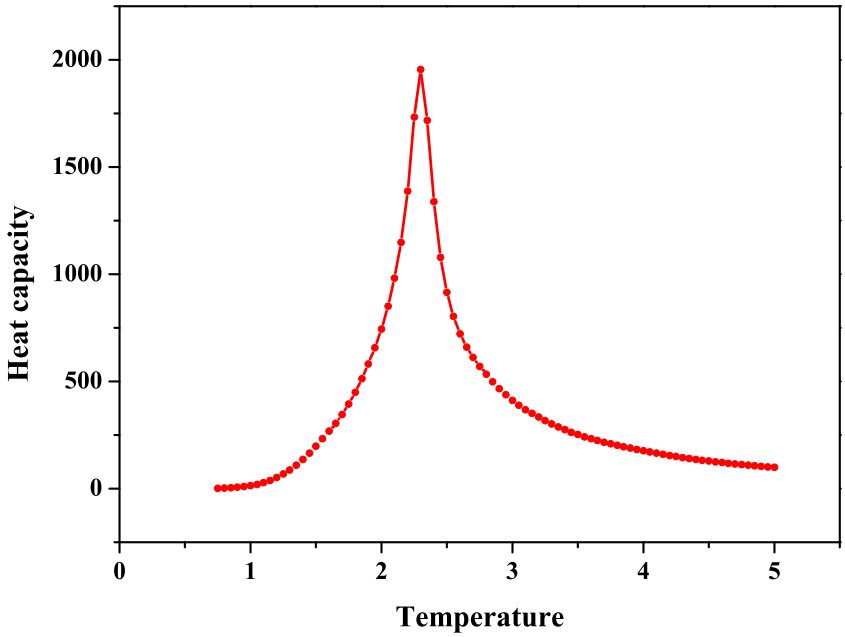

Figure 5.4: Heat capacity as a function of temperature 32×32 system calculated by employing our method.

close to transition temperatures.

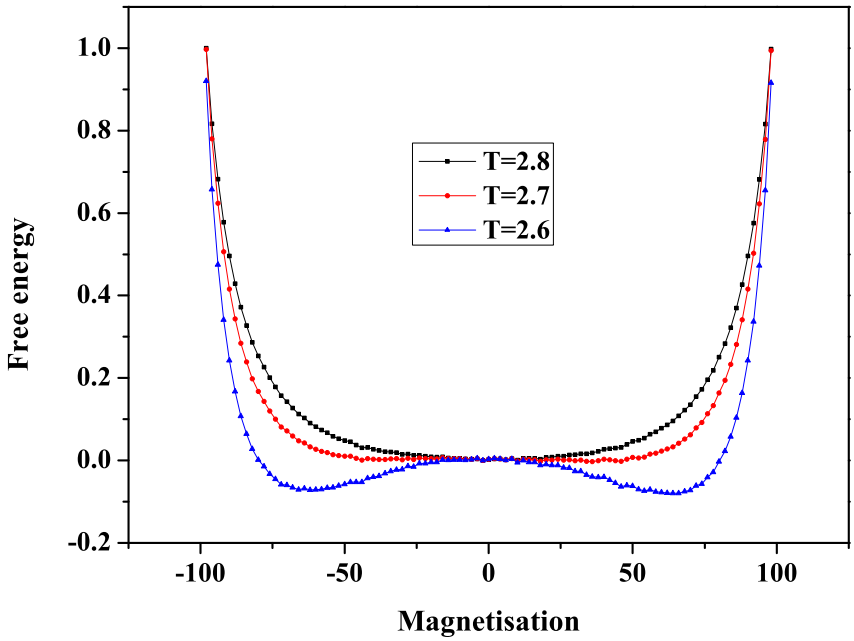

Figure 5.5: Scaled Landau free energy at temperatures around T_c for 10×10 system.

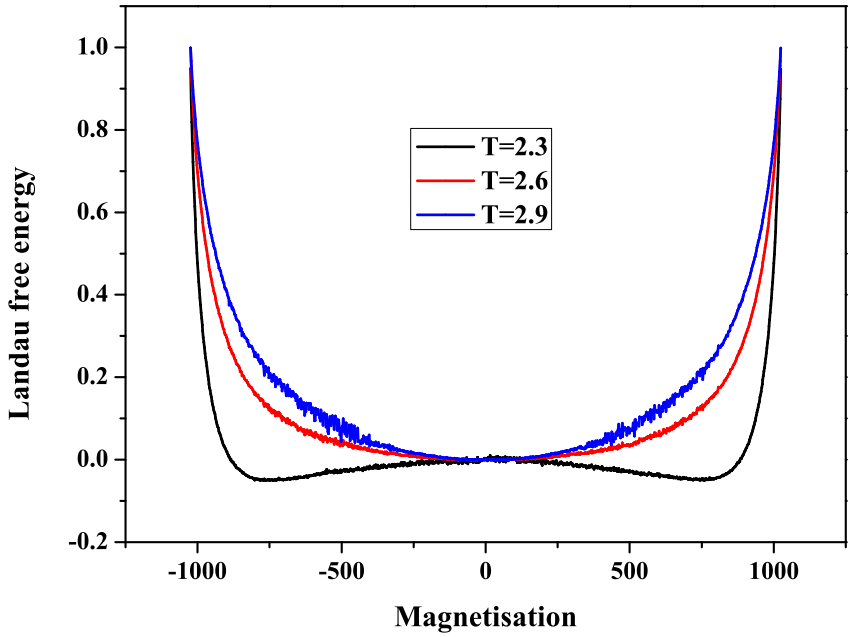

Figure 5.6: Scaled Landau free energy at temperatures around T_c for 32×32 system.

5.4 Conclusions

In summary, we have proposed an efficient and simple method to estimate joint density of states. We have successfully employed this method to two dimensional Ising spin system on a square lattice. For a simple 10×10 Ising spin system, the CPU time required is less by nearly a factor of five.

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Chapter 6

Conclusions

In this chapter we summarize briefly the contents of the thesis highlighiting the principal results and conclusions.

The first issue we considered is on non-equilibrium work fluctuations. The second law of thermodynamics can be stated as $W > \Delta F$, where W is the work done on the system in an actual process and ΔF is that in the corresponding reversible process. Equality obtains when in actual process is reversible. If the process is not reversible, then we have an ensemble of work values. The ensemble average $\langle W \rangle > \Delta F$ for irreversible processes; however some of the elements of the ensemble are less than ΔF. This fraction is denoted by p and gives the probability of violation of second law. p depends on the switching time τ. $p(\tau) \to \frac{1}{2}$ in the limit $\tau \to \infty$. We have shown this analytically in chapter 3. We have also shown this numerically using lattice spin model of liquid crystalline system. However, the dissipation defined as *i.e.* $\langle W \rangle - \Delta F$ goes to zero in the reversible limit.

The second issue we considered is on phenomenological free energy which is a function of both temperature and energy (or order parameter), $F_L(E, T)$. The phenomenological free energy coincides with Landau free energy for T very close to the transition temperatures. We have estimated $F_L(E, T)$ and studied melting of a DNA hairpin. We have employed Wang-Landau Monte Carlo methods to investigate the

melting transition in the presence of a constant force that tends to rip the two strands apart. We have considered a two dimensional lattice model of an hair pin DNA (hp-DNA). We have employed bond fluctuation model to generate different conformation. Plots of Landau free energy as a function of energy, for temperatures close the transition temperature show that the transition is discontinuous. We have also presented results on the force - temperature phase diagram.

The third issue considered in the thesis, concerns calculation of the phenomenological free energy as a function of temperature and order parameter. To this end we need a joint density of states. In this context we propose an efficient numerical algorithm to compute joint density of states employing Wang-Landau method. The trick consists of treating the joint density of state as a thermodynamic property of an isolated system and evaluate its average over a microcanonical ensemble, extracted from the production run of the Wang-Landau Monte Carlo simulation. We demonstrate the efficiency of our method on a two dimensional model of Ising spins. We show that results are consistent with results calculated by the method proposed Landau, Tsai and Exler that involves flattening of histogram surface along energy and order parameter.

The work reported in this thesis can be extended along a few directions. We list some of themin what follows. Reliable estimation of free energy difference is of importance toward understanding a large number of chemical, biological and physical processes. Examples include protein-ligand binding, drug partitioning across cell membrane, atomic clusters *etc.* Several numerical techniques have been proposed based on perturbation theory, and thermodynamic integration. The most recent one is based on Jarzynki identity.

Application of Jarzynski identity for free energy calculation is quite straight for-

ward. The exponential weight would pose a problem. If the work distribution is broad, only trajectories at the lower tail would contribute to the sum. All other trajectories, including the most probable ones, shall have exponentially small weights. Work on importance sampling of trajectories would be very useful.

Recently, Sadhukan and Bhattacharjee, on the basis of thermodynamic analysis, have shown the possibility that the melting transition of a DNA could be continuous. Ofcoure neither experiments nor numerical simulations, as of now support this. May be, if one considers the problem studied in chapter 4 for high force values, one may see a continuous transition. This problem is worth investigating. We shall need to estimate Landau free energy as a function of both temperature and order parameter *i.e.,* end-to-end distance. We plan to take up this problem in the near future.

The method proposed in thesis to estimate joint density of states performs well only for systems with discrete energies. For problems with continuous Hamiltonian, the performance of the algorithm is poor. This could be largely due to the high entropy barriers. It is worthwhile investigating techniques like frontier sampling, simulated annealing, *etc* for problems with continuous Hamiltonian.

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