

# A Note on Non-equilibrium Work Fluctuations and Equilibrium Free Energies

M. Suman Kalyan<sup>†</sup>, G. Anjan Prasad<sup>\*</sup>, V. S .S. Sastry<sup>†</sup> and K. P. N. Murthy<sup>†</sup>

<sup>†</sup> *School of Physics, University of Hyderabad,*

*Central University P.O., Hyderabad 500 046. Andhra Pradesh, India*

<sup>\*</sup> *Institute for Computational Physics, Stuttgart University,*

*Pfaffenwaldring 27, 70569 Stuttgart Germany*

(Dated: November 22, 2010)

## Abstract

We consider in this paper, a few important issues in non-equilibrium work fluctuations and their relations to equilibrium free energies. First we show that Jarzynski identity can be viewed as a cumulant expansion of work. For a switching process which is nearly quasistatic the work distribution is sharply peaked and Gaussian. We show analytically that dissipation given by average work minus reversible work  $W_R$ , decreases when the process becomes more and more quasistatic. Eventually, in the quasistatic reversible limit, the dissipation vanishes. However estimate of  $p$  - the probability of violation of the second law given by the integral of the tail of the work distribution from  $-\infty$  to  $W_R$ , increases and takes a value of 0.5 in the quasistatic limit. We show this analytically employing Gaussian integrals given by error functions and Callen-Welton theorem that relates fluctuations to dissipation in process that is nearly quasistatic. Then we carry out Monte Carlo simulation of non-equilibrium processes in a liquid crystal system in the presence of an electric field and present results on reversible work, dissipation, probability of violation of the second law and distribution of work

PACS numbers: 05.20.-y; 05.70.-a; 05.70.Ln

Keywords: Classical Statistical Mechanics; Thermodynamics; Non-equilibrium and Irreversible Thermodynamics; Work Fluctuations; Free Energy; Liquid Crystal; Dissipation.

## I. INTRODUCTION

Non equilibrium work fluctuations and equilibrium free energy differences are related to each other through a remarkable identity proposed and proved by Jarzynski [1, 2]. Ever since several studies have been carried out to establish the validity and utility of the identity for various non-equilibrium evolutions - stochastic, see *e.g.* [3, 4] as well as deterministic, see *e.g.* [1, 5]

We show in this paper that 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 quasistatic reversible process. With only the first two cumulants in the expansion, we get Callen-Welton theorem [6]. When we include the third and higher order cumulants we get Jarzynski identity. We derive an analytical expression for probability of violation of the second law, under Gaussian approximation to work fluctuations. We then carry out Monte Carlo simulation of a liquid crystal system in the presence of a varying electric field and report numerical results on free energy changes, dissipation, probability of violation of the second law and distribution of work.

The paper is organized as follows. We start with a brief introduction to a few relevant basic issues of heat and work in a quasistatic 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 quasistatic process it goes to one-half. However dissipation defined as average work minus reversible work becomes smaller when the duration of time of the switching process increases and in the quasistatic limit it goes to zero. We demonstrate the usefulness of Jarzynski identity [1, 2] on a system of liquid crystals in the presence of external electric field. We consider a lattice model with each lattice site holding a headless spin. We calculate the work done when the external electric field is switched from an initial value to a final value following a well specified experimental protocol. We carry Monte Carlo simulation of the non-equilibrium switching process and collect an ensemble of work values. From this ensemble we extract equilibrium properties of the liquid crystalline system employing both Jarzynski identity

and Callen-Welton theorem [6]. Principal conclusions of the study are brought out briefly in the concluding section.

## II. HEAT AND WORK : REVERSIBLE PROCESSES

Consider a closed system in equilibrium at temperature  $T$ . It draws a small quantity  $\delta Q$  of heat by a quasistatic reversible process at constant temperature.  $\delta Q$  is not a perfect differential. However,

$$dS = \frac{\delta Q}{T}, \quad (1)$$

is a perfect differential where  $S$  is entropy. Thus, during a quasistatic reversible process, entropy of the system increases by  $\delta Q/T$ .

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

$$\delta W = dU - \delta Q, \quad (2)$$

where  $\delta W$  denotes the work done on the system and  $U$ , the internal energy.  $\delta W$  is not a perfect differential.

The first law is about conservation of energy and is valid for all processes, quasistatic, non-quasistatic, reversible, irreversible or otherwise. However, if the process is quasistatic and reversible, then we can replace  $\delta Q$  by  $TdS$ , see Eq. (1), and write,

$$\delta W = dU - TdS. \quad (3)$$

If the process is also isothermal, we have

$$\delta W = d(U - TS). \quad (4)$$

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 favor of the ‘slope’

$$T(S, V) = \left( \frac{\partial U}{\partial S} \right)_V \quad (5)$$

and the variable  $U$  in favor of the ‘intercept’

$$F(T, V) = U(S, V) - TS. \quad (6)$$

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

$$dW = dF. \quad (7)$$

For purpose of distinguishing process variables (heat and work) from state variables (energy  $U$ , entropy  $S$  and free energy  $F$ ) we have considered in the above an infinitesimal process.  $dQ$  and  $dW$  are not perfect differentials;  $dU$ ,  $dS$  and  $dF$  are perfect differentials. However the relation between free energy and work, see Eq. (7), holds good for a quasistatic reversible process that takes the system from one equilibrium state, say  $A$  to another equilibrium state, say  $B$ . We have

$$W = F(B) - F(A) \quad (8)$$

We call the above as reversible work and denote it by  $W_R$

### III. HEAT AND WORK : IRREVERSIBLE PROCESSES

To obtain a relation between change in free energy and work done when the process is not reversible, we start with the second law inequality, see [8] for an elegant proof, given by

$$dS > \frac{dQ}{T}. \quad (9)$$

The above implies

$$dQ < T dS \quad (10)$$

for an irreversible process. Substitute this in Eq. (2) and get,

$$dW > dU - TdS \quad (11)$$

which for an isothermal irreversible process reduces to

$$dW > dF. \quad (12)$$

Consider a process that takes the system irreversibly from an equilibrium state  $A$  to another equilibrium state  $B$ . Let  $W$  denote the work done during the process and  $\Delta F = F(B) - F(A)$ . We have

$$W > \Delta F \quad (13)$$

The work done exceeds free energy change, if the process is not reversible. 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 switched 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  $\tau$ . 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 quasistatically 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  $\Omega = \{W_i\}$ . It is then quite possible that there can exist realizations for which  $W$  is less than  $dF$ , thereby *violating* the second law. This should not surprise us since even in the early days of statistical mechanics, Maxwell [9] correctly recognized that the second law is of statistical origin and hence there is a non-zero probability of it being contravened. The demon he created to drive home this point, haunts us even today, see *e.g.* [10].

Let the ensemble  $\Omega$  of work values be formally described by the distribution  $\rho(W; \tau)$  where  $\tau$  denotes the duration of time over which the process takes place;  $\tau$  is the switching time. Typically we switch a macroscopic parameter, denoted by the symbol  $\Lambda$  from an initial value say  $\Lambda_I$  to a final value say  $\Lambda_F$ . This switching can be carried out in any way. The discussions below and the Jarzynski identity described in the next section hold good for any protocol of switching. However we consider the switching to take place at constant rate, over a pre specified duration of time,  $\tau$ . Then by considering different values of  $\tau$  we can describe different switching scenarios: if  $\tau$  is small, we have fast switching; if  $\tau$  is large we have slow switching; in the limit of  $\tau \rightarrow \infty$ , we have a quasistatic reversible switching. Thus

$$\Lambda(t) = \Lambda_I + (\Lambda_F - \Lambda_I) \times \frac{t}{\tau}, \quad 0 \leq t \leq \tau. \quad (14)$$

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

$$p(\tau) = \int_{-\infty}^{W_R} dW \rho(W; \tau), \quad (15)$$

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

$$\langle W \rangle \geq dF . \quad (16)$$

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

$$\langle W \rangle = \int_{-\infty}^{\infty} dW W \rho(W; \tau) \quad (17)$$

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

$$W_d = \langle W \rangle - W_R \quad (18)$$

as dissipation and state the second law as described in the next section

$$W_d \geq 0 \quad (19)$$

for all processes. In the above, equality obtains when the process is quasistatic and reversible.

If  $\tau$  is very large but not infinity,  $\rho(W; \tau)$  would be sharply peaked and Gaussian. Consider a process that takes a system from an equilibrium state  $A$  to another equilibrium state  $B$ . Let the process be nearly quasistatic. We have  $\Delta F = F(B) - F(A) = W_R$ . The time taken for the process,  $\tau$ , is large. For such a process, dissipation is proportional to fluctuations, and from Callen-Welton theorem [6] we get,

$$\Delta F = W_R = \zeta_1 - \frac{1}{2} \beta \zeta_2 \quad (20)$$

where

$$\zeta_1 = \langle W \rangle \quad (21)$$

is the first cumulant and

$$\zeta_2 = \sigma_W^2 = \langle W^2 \rangle - \langle W \rangle^2 \quad (22)$$

is the second cumulant (or variance) of  $W$ . Thus we have  $W_d = \beta\zeta_2/2$  from Eq. (20): dissipation ( $W_d$ ) is proportional to fluctuation ( $\zeta_2$  or  $\sigma_W^2$ ).

Measuring energy in units of  $k_B T = \beta^{-1}$ , we get, from Eq. (20),

$$-\beta dF = (-\beta) \zeta_1 + \frac{1}{2!} (-\beta)^2 \zeta_2 . \quad (23)$$

The above relation is for a process which is nearly quasistatic. The distribution of work for such a switching protocol is Gaussian. For a Gaussian, the third and higher order cumulants are all identically zero. We contend that in a general process, which is not necessarily quasistatic or near quasistatic, there should be additional terms in the Right Hand Side (RHS) of the above equation involving third and higher cumulants. Once we include these higher cumulants we get Jarzynski identity, as shown in the next section.

#### IV. NON-EQUILIBRIUM WORK AND EQUILIBRIUM FREE ENERGIES

Including the terms involving the third and higher order cumulants in the RHS of Eq. (23), we get,

$$-\beta dF = (-\beta) \zeta_1 + \frac{(-\beta)^2}{2!} \zeta_2 + \sum_{n=3}^{\infty} \frac{(-\beta)^n}{n!} \zeta_n . \quad (24)$$

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,

$$\chi(\beta) = -\beta dF \quad (25)$$

or equivalently

$$\exp(\chi) = \exp(-\beta dF). \quad (26)$$

The moment generating function of  $W$  is defined as

$$\begin{aligned} \phi(\beta) &= \int_{-\infty}^{+\infty} dW \exp(-\beta W) \rho(W; \tau) \\ &= \langle \exp(-\beta W) \rangle . \end{aligned} \quad (27)$$

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

$$\chi(\beta) = \log [\phi(\beta)] . \quad (28)$$

We see immediately that Jarzynski identity given by,

$$\langle \exp(-\beta W) \rangle = \exp(-\beta dF), \quad (29)$$

follows naturally from this.

## V. GAUSSIAN WORK DISTRIBUTION

We shall derive an expression for the probability of violation of the second law formally given by Eq. (15). For large  $\tau$  the work distribution  $\rho(W; \tau)$  would be a sharply peaked Gaussian with mean  $\langle W(\tau) \rangle$  and variance  $\sigma_W^2(\tau) = \langle W^2(\tau) \rangle - \langle W(\tau) \rangle^2$ . Substituting the Gaussian in Eq. (15) for  $\rho(W; \tau)$  we get,

$$\begin{aligned}
 p(\tau) &= \frac{1}{\sigma_W(\tau)\sqrt{2\pi}} \int_{-\infty}^{W_R} dW \exp\left(-\frac{1}{2} \frac{[W - \langle W(\tau) \rangle]^2}{\sigma_W^2(\tau)}\right) \\
 &= \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\frac{W_R - \langle W(\tau) \rangle}{\sigma_W(\tau)\sqrt{2}}} d\xi \exp(-\xi^2) \\
 &= \frac{1}{2} - \frac{1}{2} \operatorname{erf}\left(\frac{\langle W(\tau) \rangle - W_R}{\sigma_W(\tau)\sqrt{2}}\right), \tag{30}
 \end{aligned}$$

where, the error function is defined [11] as,

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x d\xi \exp(-\xi^2) \tag{31}$$

For large  $\tau$ , we have Callen-Welton theorem [6] which tells us

$$\langle W(\tau) \rangle - W_R = \frac{1}{2}\beta\sigma_W^2(\tau). \tag{32}$$

Substituting for dissipation in terms of fluctuations in Eq. (30) we get

$$p(\tau) = \frac{1}{2} - \frac{1}{2} \operatorname{erf}\left(\frac{\beta\sigma_W(\tau)}{2\sqrt{2}}\right). \tag{33}$$

Note  $\operatorname{erf}(\infty) = 1$  and  $\operatorname{erf}(0) = 0$ . From Eq. (33) we see that  $p(\tau)$  increases when  $\tau$  increases. In the limit of  $\tau \rightarrow \infty$ ,  $p(\tau)$  equals one-half.

This result can be understood as follows[7]. In the quasistatic limit of  $\tau \rightarrow \infty$ ,  $\rho(W; \tau)$  becomes more and more sharply peaked such that  $\langle W \rangle \rightarrow W_R$  and  $\sigma_W \rightarrow 0$ . By Callen-Welton theorem  $W_d \propto \sigma_W^2$ . This implies that  $\sigma_W \gg W_d$  as  $W_d \rightarrow 0$ . Thus  $W_d$  and the  $\sigma_W$  both tend to zero, with  $\sigma_W \gg W_d$ . In other words  $W_d \rightarrow 0$  faster than  $\sigma_W \rightarrow 0$ . This leads to  $p(\tau) \rightarrow \frac{1}{2}$  in the reversible limit.

However, dissipation is defined as  $W_d = \langle W \rangle - W_R$ . In the reversible limit of  $\tau \rightarrow \infty$ , we have  $\langle W \rangle = W_R$  and hence dissipation is zero.



## VI. WORK FLUCTUATIONS IN LIQUID CRYSTALLINE SYSTEM

Let us now illustrate the above on a lattice model of a liquid crystalline system. To this end, we consider an  $L \times L \times L$  cubic lattice. Each lattice site holds a headless spin. The spins on nearest neighbor lattice sites interact with each other *via* Lebwohl-Lasher potential [12] see below. 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 Hamiltonian for the nematic system is given by,

$$H = -J \sum_{\langle i,j \rangle} P_2(\cos \theta_{i,j}) - \frac{E^2}{2} \sum_i P_2(\cos \theta_i). \quad (34)$$

In the above, the symbol  $\langle i, j \rangle$  denotes that  $i$  and  $j$  are nearest neighbor lattice sites. The sum runs over all distinct pairs of nearest neighbor sites. We have employed periodic boundary conditions along  $x$ ,  $y$  and  $z$  coordinates.  $\theta_{i,j}$  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  $J = 1$ .  $E$  is the amplitude of the external electric field and  $\theta_i$ , the angle between the spin at lattice site  $i$  and the external electric field.  $P_2(\eta)$  is the second Legendre polynomial given by

$$P_2(\eta) = \frac{3 \cos^2(\eta) - 1}{2} \quad (35)$$

We carry out Monte Carlo simulation of the response of the system to a process of switching  $E$  from say  $E_0$  to a value of  $E_f$ .

## VII. MONTE CARLO SIMULATION OF THE SWITCHING PROCESS

Start with an arbitrary initial microstate (spin configuration) and employing Metropolis algorithm [13], equilibrate the system at the desired value of  $\beta$  with  $E = E_0$ . Select randomly a microstate from the equilibrium ensemble. Calculate the energy. Keep the micro state the same and switch the field from  $E_0$  to  $E_1 = E_0 + \Delta E$ . This is called the work step. The resulting change in energy, called work is denoted by  $\omega_1$ . 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 [14]. 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  $p = \exp[-\beta\Delta\epsilon]$  where  $\Delta\epsilon$  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  $E_1$  to  $E_2 = E_1 + \Delta E = E_0 + 2\Delta E$ . The work done is  $\omega_2$ . The work and heat steps are repeated until  $E$  attains a pre - determined value, say  $E_f$ .

Let  $n$  be the number of work steps required to switch the field from an initial value of  $E_0$  to a final value  $E_f$ . In other words  $E_n = E_f = E_0 + n \Delta E$ , where  $\Delta E = (E_f - E_0)/n$ . The switching time  $\tau$  is thus given by  $n$ . We have

$$W = \sum_{i=1}^n \omega_i . \quad (36)$$

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  $E_0 = 0$  and  $E_f = 2$ . The results presented in this paper are for  $L = 3$ . Jarzynski identity is valid even for systems which are small. For a small system there would be large fluctuations and hence illustrating various issues, like relating work fluctuations to free energy differences and to dissipation becomes an easy task. This is the reason we have kept the system size small in this work. The size of the Monte Carlo ensemble of work values generated is one million.

## VIII. RESULTS AND DISCUSSIONS

Fig. (1) depicts results on free energy difference (or reversible work) calculated from Jarzynski identity as a function of  $\tau$  with  $\beta^{-1} = 1.5$ .

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  $\tau$  increases the results from Callen-Welton theorem converges to that from Jarzynski identity.

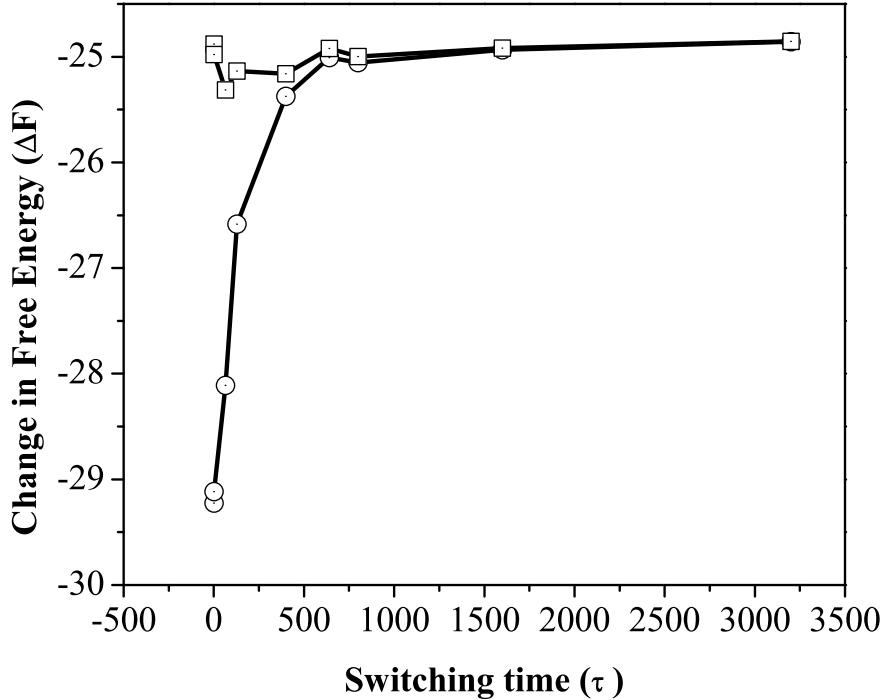


FIG. 1. Free energy difference  $\Delta F$  versus switching time  $\tau$ . The upper curve (squares) denotes  $\Delta F^J$  calculated from Jarzynski identity. The lower curve (circle) denotes  $\Delta F^{CW}$ , calculated from Callen-Welton theorem.

In Fig. (2) we have plotted dissipation given by Eq. (18) and denoted as  $W_d^J$ , as a function  $\tau$ . 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  $\tau$ . This is because the system is driven far from equilibrium. However as the switching time increases the process becomes more and more quasistatic. Dissipation decreases. In the limit of  $\tau \rightarrow \infty$  it goes to zero. For large  $\tau$  dissipation can also be calculated from fluctuations employing Callen-Welton theorem. We have  $W_d^{CW} = \beta\sigma_W^2/2$ . The inset in Fig. (2) shows  $W_d^{CW} - W_d^J$ . This quantity is large for small  $\tau$ . It decreases with increases of  $\tau$  and eventually goes to zero.

We have depicted in Fig. (3) 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  $p^{MC}(\tau)$ .

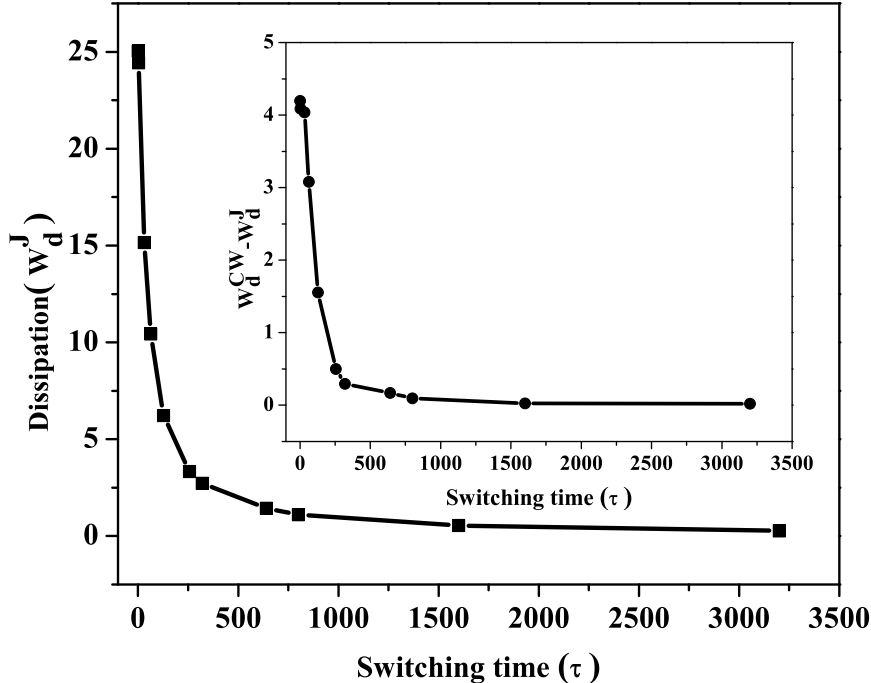


FIG. 2. Dissipation defined as  $W_d^J = \langle W \rangle - W_R$  calculated from Jarzynski identity. The inset shows  $W_d^{CW} - W_d^J$ , where  $W_d^{CW}$  is dissipation calculated from Callen-Welton theorem.

We find that  $p^{MC}(\tau)$  increases with increase of  $\tau$  as expected from the analytical results discussed in section V.

The work distributions for representative values of  $\tau$  are depicted in Fig. (4). For small values of  $\tau$  we find the distribution is broad. As  $\tau$  increases the distribution becomes more and more sharply peaked. The distribution is expected to be Gaussian see [15, 16].

## IX. 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[17] have shown that Barkhausen noise process, repeated many times give adequate data to construct, in conjunction with work fluctuation theorem, a special matrix

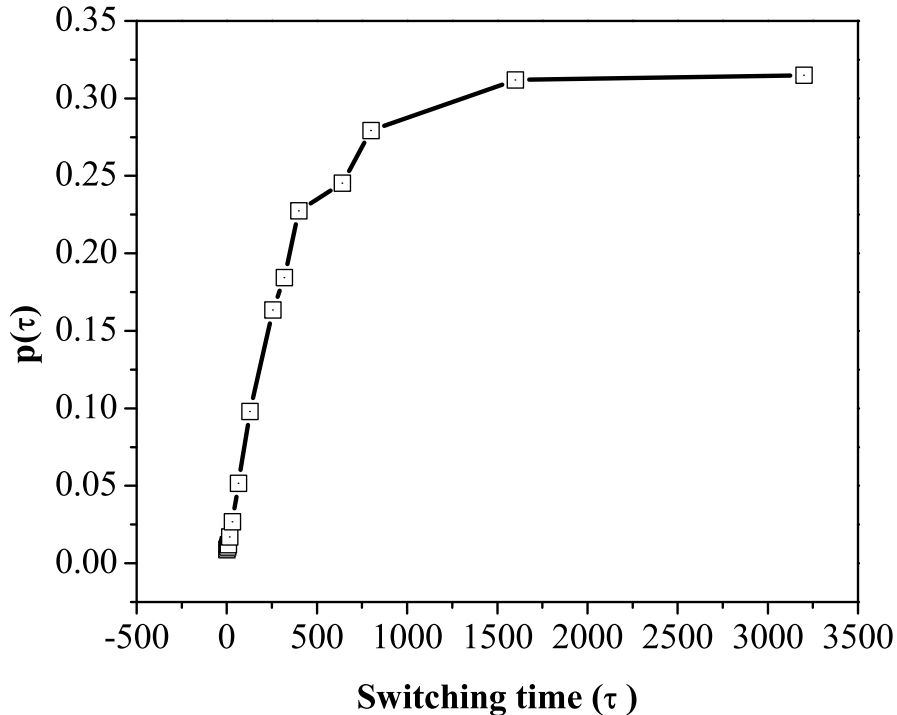


FIG. 3. *The probability of second law violation for various value of  $\tau$ . calculated from the Monte Carlo ensemble*

whose principal eigenvector provides equilibrium distribution. Transient entropy-fluctuation theorem of Evans and Searles [19], heat fluctuation theorems of Crooks[18] and the fluctuations theorems of Gallavotti-Cohen [20] for steady state systems also can be employed to estimate equilibrium quantities from non-equilibrium measurements. In this paper 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  $\tau \rightarrow \infty$ .  $p(\tau)$  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  $\tau$ . In the quasistatic limit of  $\tau \rightarrow \infty$ ,  $p(\tau) = 1/2$ .

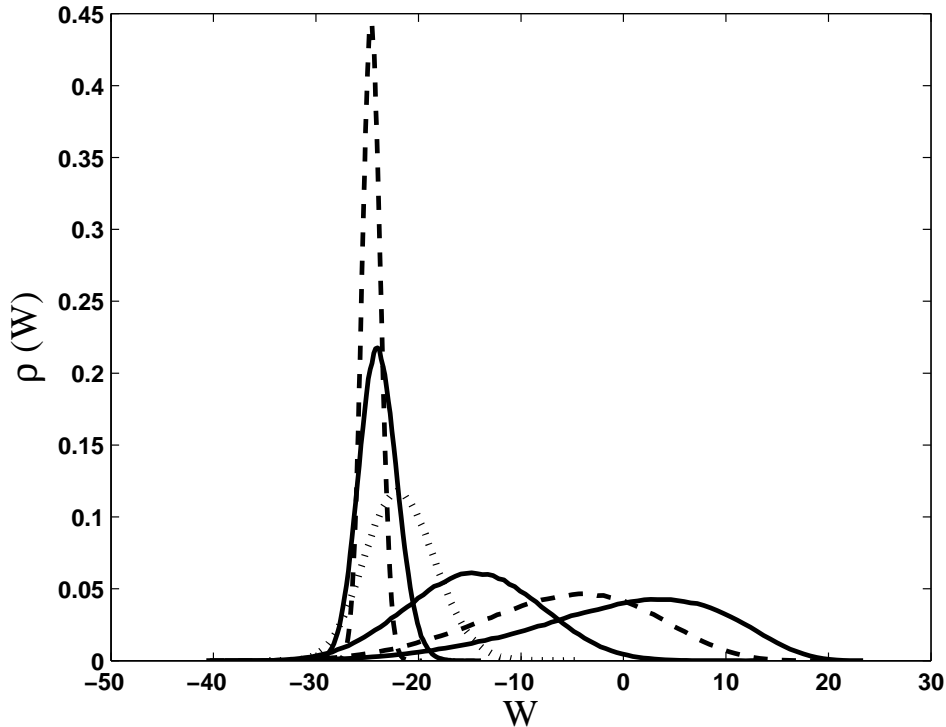


FIG. 4. *Distribution of work for  $\tau = 1, 16, 64, 256, 800$  and  $3200$ , from right to left.*

## X. ACKNOWLEDGEMENTS

MSK would like to thank Center for Advanced Studies, School of Physics, University of Hyderabad for financial support for this work.

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