Fluctuations in Model Non-equilibrium Processes

Thesis submitted in partial fulfillment of the
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Master of Technology
in
Computational Techniques

by

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To ..

My Family & Friends

DECLARATION

I hereby declare that the work reported in this thesis has been carried out by me independently in the school of physics, University of Hyderabad, under the supervision of **Prof K P N Murthy**, School of Physics. I also declare that this is my own work and effort, and it has not been submitted at any other University or Institution for any degree. Wherever contributions of others are involved, every effort is made to indicate that clearly with due reference to literature, and acknowledgement of collaborative research and discussions.

Place:

Date: **Bharath Ravu**

CERTIFICATE

This is to certify that the project work entitled "**Fluctuations in Model Non-equilibrium Processes**" being submitted to University of Hyderabad by **Bharath Ravu** bearing Reg. No. **09PCMT07**, in partial fulfilment for the award of the degree of Master of Technology in Computational Techniques, is a bonafide work carried out by him under my supervision.

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Bharath Ravu

Abstract

In this thesis, we have studied two model non equilibrium processes employing Monte Carlo simulation and the recent fluctuation theorem. The aim is to explore the relation between the averages over an ensemble of non-equilibrium measurements and equilibrium properties of a closed thermodynamics system. The first problem is shifted harmonic trap, where the center of the trap dragged from one spatial location to another uniformly over a period of time τ. This problem is also amenable to semi analytical treatment. We have calculated average work, fluctuations of work and the probability for the work to be less than reversible work. The last quantity, we denoted by $p(\tau)$. This quantity usually termed as violation of second law of the thermodynamics. We find that $p(\tau)$ goes to 0.5 in the limit of $\tau \to \infty$. However average work minus reversible work called dissipation, goes to zero in the reversible limit.

The second problem is an harmonic oscillator, where in we have taken the spring constant to be a switching parameter. Here $p(\tau)$ for this problem, we find for τ is very small the system is driven to far from equilibrium in this region when we increase τ, $p(\tau)$ decreases. For some values of τ, we find that the work distribution becomes Gaussian in this region, $p(\tau)$ increases with τ and asymptotically acquire a value of 0.5 in the asymptotic reversible limit of $\tau \to \infty$. This behavior is consistent with what we have found in the first problem and some earlier work.

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Chapter 1

INTRODUCTION

Consider a system in equilibrium with a heat bath at temperature T. Let λ be a macroscopic property of the system whose value is λ_1. From time $t = 0$ to time $t = \tau$ the value of λ is changed from λ_1 to λ_2 with a well defined time dependence, called a protocol.

$$\lambda(t) = \lambda_1 + \alpha t \tag{1.1}$$

$$\alpha = \frac{\lambda_2 - \lambda_1}{\tau} \tag{1.2}$$

We call this a switching process because such a process can not be represented in a thermodynamic phase diagram as a continuous curve, when $\tau < \infty$.

- State A : time $t = 0$: $\lambda(t = 0) = \lambda_1$: System is in equilibrium.
- State B : time $t = \tau$: $\lambda(t = \tau) = \lambda_2$: System is not necessarily in equilibrium.

Quasi-static and reversible limit obtains when $\tau \to \infty$. During a quasi-static reversible process, the system remains in equilibrium when λ changes from λ_1 to λ_2. Such a process can be depicted in the thermodynamic phase diagram as a curve.

When $\tau < \infty$, thermodynamics tells us $W \geq \Delta F$, where ΔF is the change in free energy between the two equilibrium states.

$$\Delta F = F(\lambda = \lambda_2) - F(\lambda = \lambda_1) \tag{1.3}$$

If the process is quasi static, $W = \Delta F$. When $\tau < \infty$, the switching process drives the system away from equilibrium. It is precisely because of this reason that when we carry out the switching experiment several times with the same switching protocol and construct an ensemble of work values, some of the members of the ensemble shall be less than ΔF and hence are not consistent with the second law inequality $W \geq \Delta F$. However the value of W averaged over the ensemble shall be consistent with the second law inequality. In other words, $\langle W \rangle \geq \Delta F$.

The recent work fluctuation theorem of Jarzynski [5] addresses these and related issues. In particular, Jarzynski equality relates the distribution of work values in the ensemble, to equilibrium free energy differences.

To appreciate these and related issues we start with a brief introduction to heat and work.

1.1 Heat and Work

We can change the energy of a system by doing work on it or by heating it. Work and heat are two modes of energy transfer to a system.

In heat, energy flows spontaneously from high temperature to low temperature. The first law of thermodynamics is stated as,

$$W = dU - Q \tag{1.4}$$

where W is the work done on the system and dU, the change in internal energy and Q is the heat transferred to the system. The first law is about conservation of energy and is valid for all processes, quasi-static, non-quasi-static, reversible, irreversible or otherwise.

1.1.1 Microscopic description of Work and Heat

Let U denote the thermodynamic energy of a closed system obtained by averaging the statistical mechanical energy E over a canonical ensemble of micro states. Let the micro states be indexed by natural numbers i. Let p_i denote the probability for the system to be in micro state indexed by i whose energy is E_i. The thermodynamic energy U is then given by,

$$U = \sum_i p_i E_i \ ,$$

with the constraint that

$$\sum_i p_i = 1.$$

In the above two equations the sum runs over all the micro states accessible to the system. Let us consider a process in which we make an infinitesimally small change in a macroscopic control variable *e.g.* volume, which results in small changes in the energies and probabilities of the microstates. Then, formally, we have

$$dU = \sum_i \frac{\partial U}{\partial E_i} dE_i + \sum_i \frac{\partial U}{\partial p_i} dp_i$$

$$= \sum_i p_i dE_i + \sum_i E_i dp_i$$

with the constraint that

$$\sum_i dp_i = 0, \qquad \sum_i p_i = 1.$$

Thus, we can change the energy of a system by an amount dU through work W given by $\sum_i p_i dE_i$, and/or through heat, Q given by $\sum_i E_i dp_i$. Thus, work and heat are simply two modes of energy transfer.

1.2 Quasi Static Process

Consider a closed system in equilibrium with its surroundings at temperature T. If we change an external parameter infinitely slowly so that all the time the system shall be in equilibrium with its surroundings then the process is quasi static. Let the system draw a small quantity Q of heat from the surroundings during the process. Claussius introduced an integrating factor $1/T$ and defined a perfect differential,

$$dS = \frac{Q}{T}, \tag{1.5}$$

Where S is the entropy of the system. During the above process the entropy of the system increase by dS.

Let us now look at the above definition of entropy in conjunction with the first law of thermodynamics, usually stated as,

$$dU = Q + W \tag{1.6}$$

where U is internal energy of the system and W, energy exchanged by work and Q, energy exchanged by heat. Substituting for Q in Eq. (1.6), we get,

$$W = dU - TdS \tag{1.7}$$

Since temperature does not change during the process, we have,

$$W = d(U - TS) \tag{1.8}$$

We recognize immediately that the expression $U - TS$ is the Legendre transform of the fundamental relation that expresses internal energy U as a function of entropy, volume and the number of particles in the system: $U = U(S, V, N)$. We transform the independent variable S in favour of the " slope",

$$T(S,V,N) = \left(\frac{\partial U}{\partial S}\right)_{V,N} \tag{1.9}$$

and transform the dependent variable U in favour of the "intercept" denoted by F, to get,

$$F(T,V,N) = U(S,V,N) - TS \tag{1.10}$$

In the above, S can be eliminated by the definition of temperature given in Eq. (1.9). We emphasize that the process considered is quasi static and reversible. Hence we call W as reversible work and denote it by W_R. Thus, the change in free energy equals reversible work.

1.3 Non-equilibrium Process

How does the picture change when the process takes place over a finite duration of time and hence is not quasi static ? Thermodynamics provides but, a qualitative answer to this question expressed by an inequality. Clausius [2] tells us that when the process is not quasi static and reversible ,

$$dS \ > \ \frac{Q}{T}. \tag{1.11}$$

Therefore, $dU \ < \ TdS + W \Longrightarrow W > dU - TdS$, which leads to $W > dF$ or equivalently $W \ > \ W_R$. Hence the work done on the system exceeds the change in free energy. The difference $W - dF$ is called dissipation and is denoted by W_d. Thus we can state the second law of thermodynamics as

$$W_d \geq 0, \tag{1.12}$$

for any thermodynamic process. In the above, equality obtains when the process is quasi static and reversible. What is the value we should assign to W in a switching process? Every time we carry out a switching process we will get a different W. Hence W is not a fixed number. It changes from one experimental realization of a non-equilibrium switching process to another. Therefore the relevant entity is an ensemble of values W obtained from several experiments all of them carried out with the same protocol. It is quite possible that in some of the experiments, W is less that W_R thus "violating" the second law of thermodynamics. Let us calculate the ensemble average of W denoted by $\langle W \rangle$. We recognize that W calculated in a quasi static reversible process is actually the one averaged over equilibrium ensembles of microstates at each stage of quasi static evolution. Hence we should write $\langle W_d \rangle = \langle W \rangle - dF$ and state the second law of thermodynamics in terms of ensemble average as, $\langle W_d \rangle \geq 0$.

Then arises a natural question. Do the higher cumulants of W contribute to dissipation and if so how ? Consider for example a process which is nearly quasi static. Then Callen-Welton [4] theorem also known as fluctuation dissipation theorem tells us

$$\Delta F = \langle W \rangle - \frac{1}{2}\beta\sigma_W^2, \tag{1.13}$$

where σ_W^2 is the second cumulant of W, defined as average of $[W- < W >]^2$. The dissipation W_d is thus proportional to fluctuation σ_W^2. When the switching process drives the system far from equilibrium, we can expect the third and higher order cumulants to contribute to dissipation and inclusion of them naturally leads to the equality derived by

Jarzynski [5].

Clearly, Free energy plays a central role in equilibrium and nonequilibrium phenomena in a closed system. The state of a thermodynamic system is determined by a competition between chance (disordering entropy) and necessity (ordering energy of interaction amongst its microscopic constituents and the interaction with external field when present). At high temperature entropy wins over energy and we get a disordered gaseous state. At low temperatures energy wins over entropy and we get ordered solid phase. Free energy, $F(T, V, N) = U = TS$ provides a neat way expressing the energy-entropy competition with temperature determining their relative influence.

In this thesis we study fluctuation theorems for Brownian particle with Langevin model. These are described in chapters 2 and 3. A brief introduction to Langevin model is presented in the next section

1.4 Langevin model

The observation that, when suspended in water, small pollen grains are found to be in a very animated and irregular state of motion, was first systematically investigated by Robert Brown in 1827, and the observed phenomenon took the name of Brownian motion. Being a botanist, he of course tested whether this motion was in some way a manifestation of life. By showing that the motion was present in any suspension of fine particles glass, mineral, *etc.* he ruled out any specifically organic origin to this motion.

A satisfactory explanation of Brownian motion was given by Einstein in 1905 [18]. There are two key points in Einstein's solution of the problem of Brownian motion.

- The motion is caused by the exceedingly frequent impacts on the pollen grain from the incessantly moving molecules of liquid in which it is suspended.
- The motion of these molecules is so complicated that its effect on the pollen grain can only be described probabilistically in term of exceedingly frequent statistically independent impacts.

Some time after Einstein's work, Langevin [19] presented a new method which is given below,

Acting on a particle, of mass m, there should be two forces:

(i) a viscous force $f(t)$: assuming that $f(t)$ is given by the same formula as in macroscopic hydrodynamics, this is $-m\gamma dx/dt$, with $\gamma = 6\pi\mu a$, μ being the viscosity and a, the diameter of the particle assumed to be spherical.

(ii) a fluctuating force $\xi(t)$, which represents the incessant impacts on the Brownian particle from the molecules of the liquid. What all we know about this force is that it can be both positive and negative and its magnitude is such that it keeps the Brownian particle continuously on the move.

Thus, the equation of Brownian motion for the position of the particle is given by Newton's law

$$m\frac{d^2x}{dt^2} = -m\gamma\frac{dx}{dt} + \xi(t) \tag{1.14}$$

The fluctuating force ξ is modelled as δ correlated Gaussian white noise with vanishing mean,

$$\langle\xi\rangle = 0, \tag{1.15}$$

and variance given by the fluctuation dissipation theorem,

$$\langle\xi(t)\rangle\langle\xi(t')\rangle = 2\gamma k_B T\delta(t - t') \tag{1.16}$$

Chapter 2

Shifted Harmonic Trap(SHT)

2.1 Introduction

Consider a colloidal particle moving in one-dimension through a viscous liquid with a harmonic trap. The motion of the trap is specified by the control parameter $\lambda(t)$. The center of the trap, is changed from an initial value λ_I at time $t = 0$ to a final value λ_F at time $t = \tau$, see Figs. (2.1 and 2.2). During the translation, the trap is felt by the particle as a quadratic external potential with force constant k.

$$U(x,t) = \frac{k}{2}[x - \lambda(t)]^2, \tag{2.1}$$

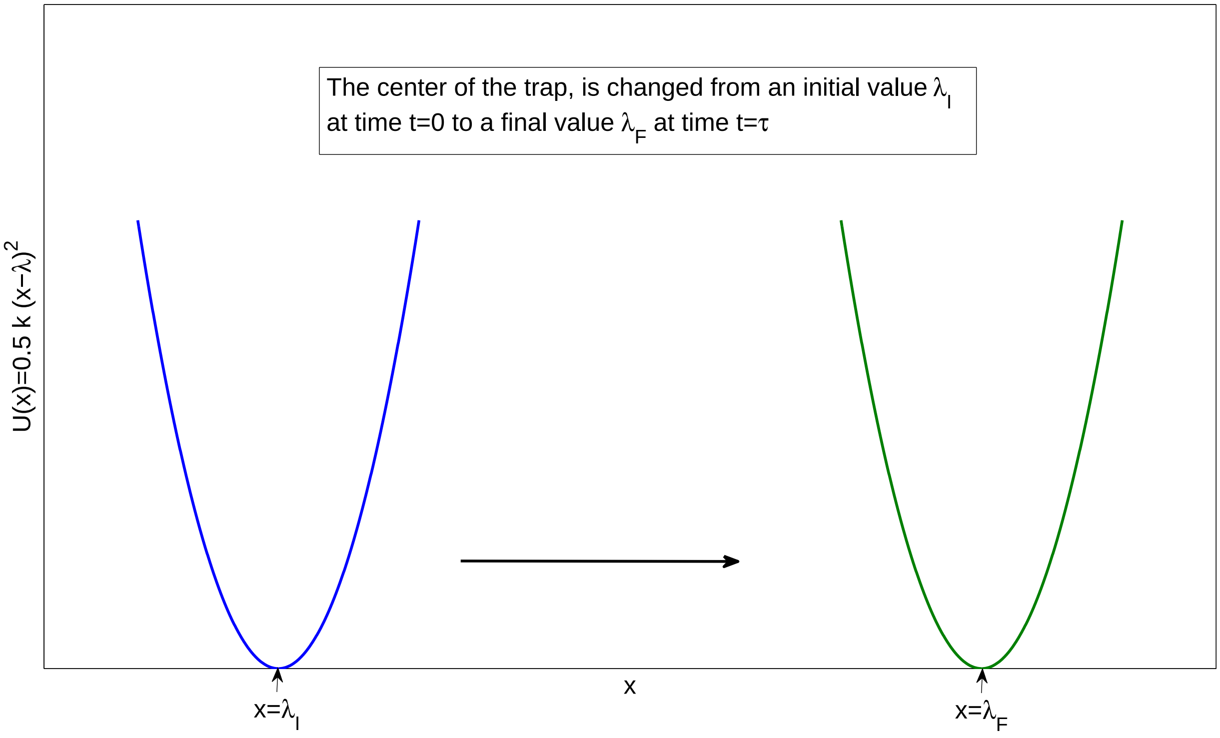

Figure 2.1: Potential energy *versus* position of the particle

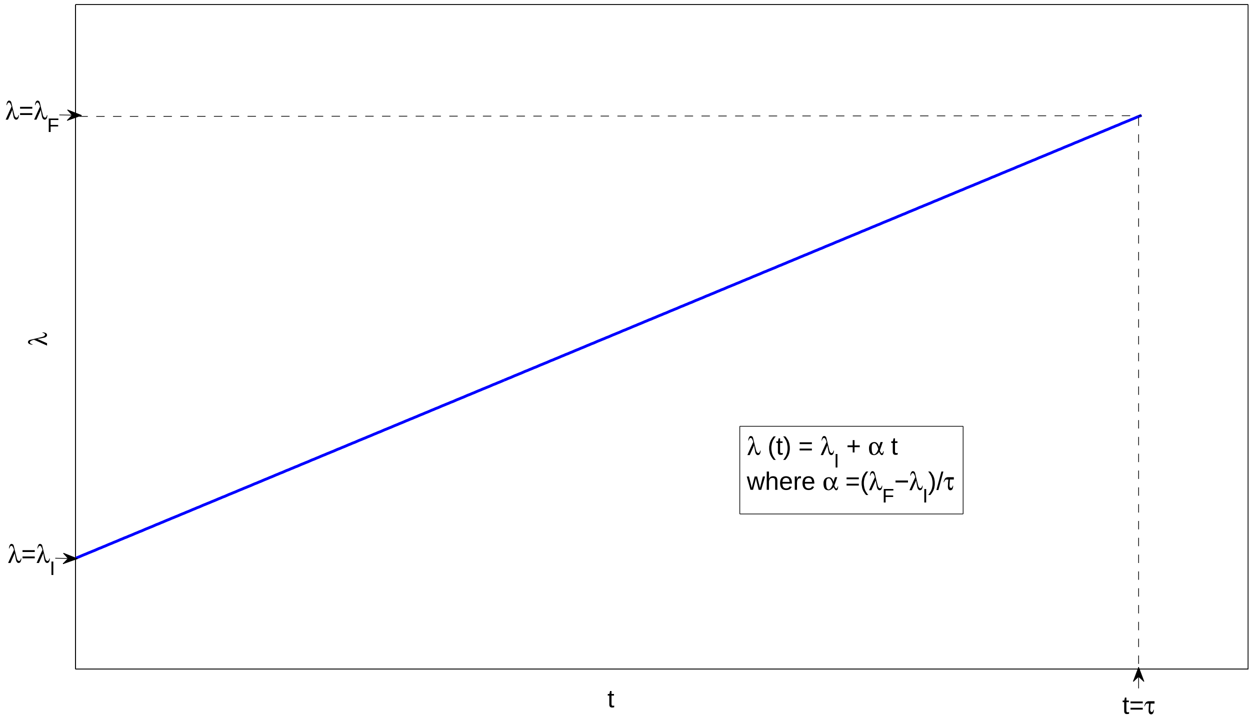

Figure 2.2: External parameter λ *versus* time

where x denotes the position of the particle. For sufficiently large friction, the motion of the particle can be described by an over-damped Langevin equation.

$$\gamma \frac{dx}{dt} = f + \xi, \tag{2.2}$$

where γ is friction coefficient and

$$f = -k[x - \lambda(t)]$$

is the external force. The random force ξ is modelled as delta correlated Gaussian white noise with vanishing mean, $\langle \xi(t) \rangle = 0$, and a variance given by the fluctuation-dissipation theorem,

$$\langle \xi(t)\xi(t') \rangle = 2\gamma k_B T \delta(t - t').$$

The diffusion constant D is related to the friction coefficient by the Einstein relation

$$D = \frac{k_B T}{\gamma}.$$

Note that for this model, the free energy does not depend on the trap position, therefore the free energy difference between the equilibrium states corresponding to the initial and final positions of the trap vanishes; in other words $\Delta F = 0$. Also, the forward and backward processes are identical and lead to the same work distribution.

The stochastic equation of motion can be integrated in the small time steps δt under the assumption that the force $f(x)$ is constant during the time step. The Difference equation is

$$x_{i+1} = x_i + \beta D\Delta t f(x_i) + \delta_{i+1} \tag{2.3}$$

where δ_i, is a random variable drawn from a Gaussian distribution with zero average and a variance of $2\beta D\delta t$. This over damped Langevin dynamics is Markovian.

2.2 Semi analytical treatment of SHT

We draw an initial value of x from Gaussian distribution with mean $\langle x_0\rangle = \lambda_I$ and variance $\sigma^2(0) = 1/\beta k$. In this processes, we will change the external parameter in discrete steps. Change of external parameter is called a work step. Then we calculate the new position including the random noise term. This constitutes a heat step.

Let $\lambda_0(=\lambda_I),\ \lambda_1,\ \lambda_2,\ \cdots,\ \lambda_n(=\lambda_F)$ denote the values of external parameter at discrete time steps at 1, 2, 3.., thus we have $\lambda_n = \lambda(t = n\Delta t)$

If we substitute force $f = -k(x - \lambda(t))$ in the difference equation, we get,

$$x_{m+1} = x_m(1 - \beta D\Delta t k) + \delta_{m+1} + \beta D\Delta t k\lambda_{m+1} \tag{2.4}$$

At time $t = 0$, we change the value of external parameter from λ_0 to λ_1 with the given initial position of the particle x_0 drawn from a Gaussian with mean $< x_0 >= \lambda_I$ and variance $\sigma^2(0) = 1/\beta k$. We use Eq. (2.4) to get the next position of the particle x_1. We continue this process until we reach the final value of $\lambda = \lambda_F$. Fig. (2.3) depicts the switching protocol

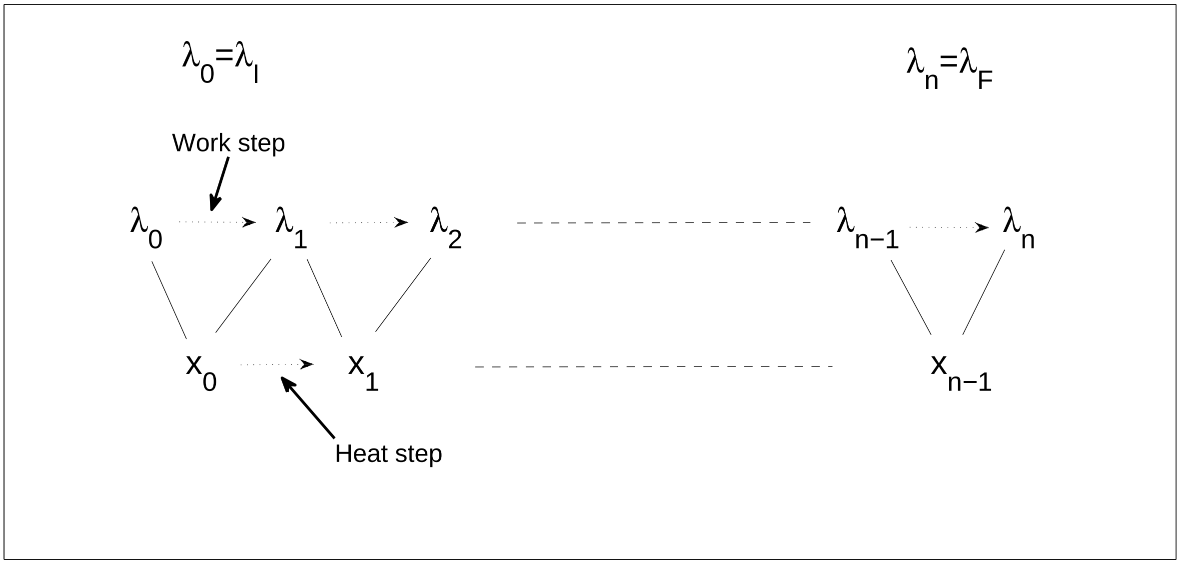

Figure 2.3: Heat and work steps

in terms of work and heat steps. Whenever we change the external parameter we calculate the work done in that step. Total work done in the process is formally given by

$$W = w_1 + w_2 + ... + w_n. \tag{2.5}$$

w_j is the work done when changing the external parameter from λ_{j-1} to λ_j at x_{j-1}

$$w_j = \frac{1}{2}k(x_{j-1} - \lambda_j)^2 - \frac{1}{2}kx_{j-1} - \lambda_{j-1})^2 \tag{2.6}$$

In the whole process we use n independent standard Gaussian random numbers (zero mean and unit variance). One Gaussian number for picking up the initial position and the other

$(n-1)$ numbers for determining the noise term at each time step.

From the difference equation it is clear that position of the particle at any discrete time can be written as a linear combination of these n independent Gaussian random variables. Since change of position of trap center determines work, we can express W, as a linear combination of these n independent Gaussian random variables

$$W = c_0\eta + c_1\delta_1 + c_2\delta_2 + ... + c_{n-1}\delta_{n-1} + c_n \tag{2.7}$$

where $c_0, c_1..........c_n$ are constants. η is a gaussian random variable with mean λ_i and variance $1/\beta k$. $\delta_1, \delta_2..........\delta_{n-1}$ are independent Gaussian random variables with mean 0 and variance $2D\delta t$. It is clear that W is Gaussian distribution with mean and variance as given below.

$$\langle W\rangle = c_1\langle\eta\rangle + c_2\langle\delta_1\rangle + c_3\langle\delta_2\rangle + ... + c_n \tag{2.8}$$

$$\langle W^2\rangle = \langle(c_0\eta + c_1\delta_1 + c_2\delta_2 + ... + c_{n-1}\delta_{n-1} + c_n)(c_0\eta + c_1\delta_1 + c_2\delta_2 + ... + c_{n-1}\delta_{n-1} + c_n)\rangle \tag{2.9}$$

where $\eta, \delta_1, \delta_2, ...$ are independent random variables,

$$\langle\eta\delta_i\rangle = \langle\eta\rangle\langle\delta_i\rangle \tag{2.10}$$

$$\langle\delta_i\delta_j\rangle = \langle\delta_i\rangle\langle\delta_j\rangle \tag{2.11}$$

Using Eqs. (2.8, 2.9) we can calculate variance $\sigma_W^2 = \langle W^2\rangle - \langle W\rangle^2$. We thus know mean and variance of the work distribution. Once we specify the external parameter λ at different time steps then we can calculate the work distribution for that protocol by using above method.

2.3 Linear protocol

In our calculations, we take γ =5, k=1, β=1, and Δt = 0.1, We have changed the external parameter (*i.e.* center of the trap) from $\lambda_i = 0$ to $\lambda_f = 1$. We have checked our semi analytical results with the Monte Carlo results and they agree with each other, see Fig. (2.4)

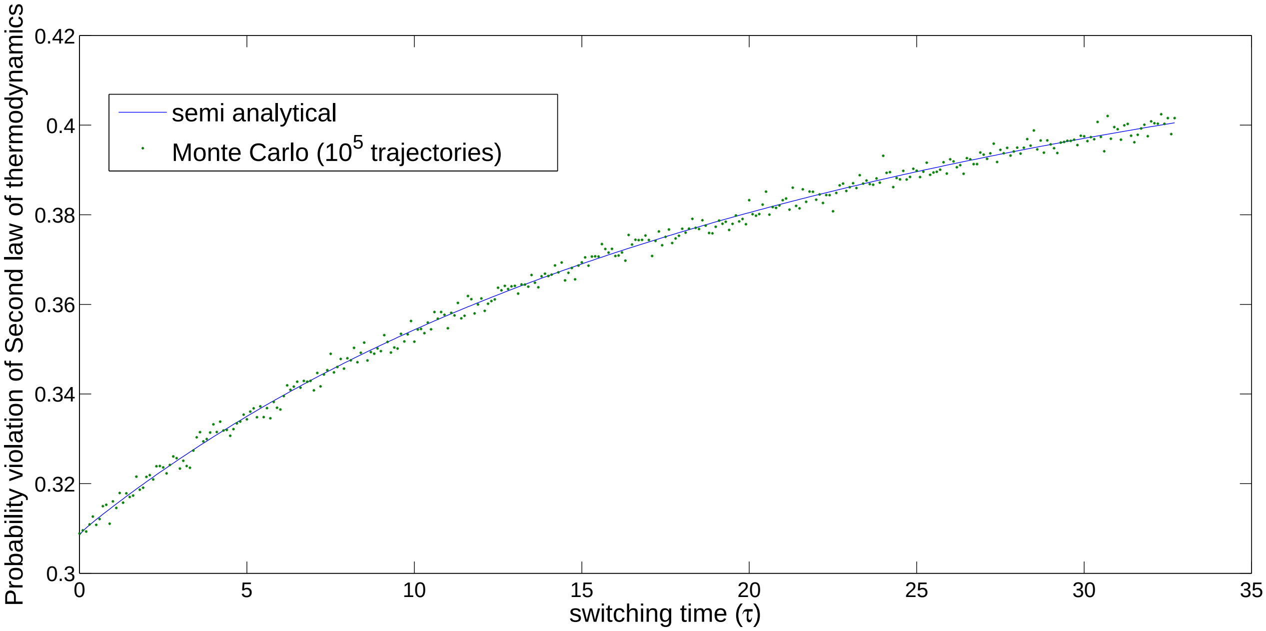

Figure 2.4: Probability violation of the Seconnd law *versus* switching time

We find that the work distribution is Gaussian for all switching times. Free energy does not depend on the center of the trap. Therefore change in free energy is zero. When τ increases the mean and variance of work go to zero, and we have

$$p(\tau) = \int_{-\infty}^{0} dW \rho(W;\tau). \tag{2.12}$$

When τ increases, the distribution becomes sharply peaked and the peak of the distribution move towards the center. In the asymptotic limit of $\tau \to \infty$ the distribution becomes a δ function centered at zero. This in conjunction with Eq. (2.12) imply that $p(\tau) \to 0.5$ when $\tau \to \infty$. Both semi analytic and Monte Carlo results agree with each other.

Figure. (2.5) depicts average work as a function of τ. In this problem since $\Delta F = 0$, average work corresponds to dissipation, Fig.(2.5) shows dissipation as a function of switching time, We find that dissipation goes to zero in the quasi static reversible limit of $\tau \to \infty$ as expected. Both Monte Carlo and semi analytical results give the same answer.

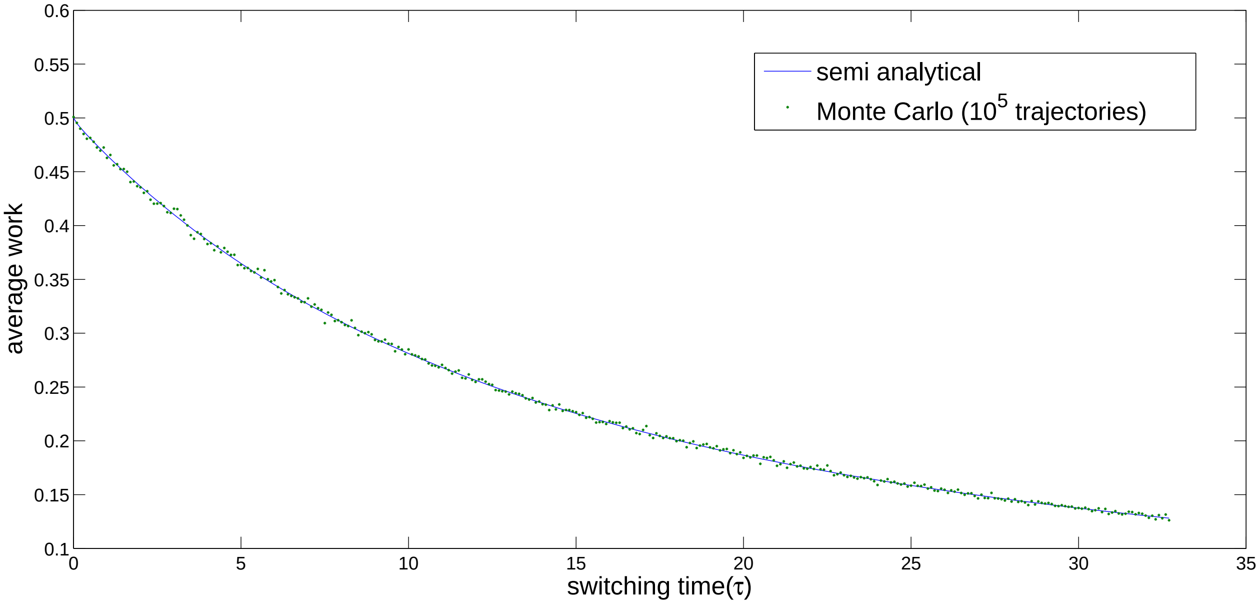

Figure 2.5: Average work *versus* switching time

2.4 Linear and Optimum protocol: Semi analytical calculations

In this section we report results of semi analytical calculations on two switching protocols. The first is a linear protocol discussed in the last section, The second is optimal protocol described below.

For the shifted harmonic trap, the optimal protocol [6] is given by,

$$\lambda^*(t) = \begin{cases} 0 & \text{for } t = 0. \\ \lambda_f \dfrac{kt + 1\gamma}{k\tau + 2\gamma} & \text{for } 0 < t < \tau. \\ \lambda_f & \text{for } t = \tau. \end{cases} \tag{2.13}$$

For the above (Optimal) protocol the average work is minimum. This optimal protocol has two discrete jumps of equal size, given by

$$\Delta\lambda = \frac{\lambda_f \gamma}{k\tau + 2\gamma}$$

at the begining and at the end. Between the two jumps the protocol is linear with slope $\lambda_f k/(k\tau + 2\gamma)$. Thus the jumps are largest for instantaneous switching, τ=0; vanish in the slow switching limit, $\tau \to \infty$.

For a given total time τ, we can find probability violation of second law for linear protocol as well as for optimum protocol. For a given switching time τ, the work distribution $\rho(W;\tau)$

is,

$$\rho(W;\tau) = \frac{1}{\sigma_W(\tau)\sqrt{2\pi}} exp\left(-\frac{1}{2}\frac{[W-<W(\tau)>]^2}{\sigma_W^2(\tau)}\right) \tag{2.14}$$

and the probability violation of Second law is

$$p(\tau) = \int_{-\infty}^{W_R} dW\rho(W;\tau) \tag{2.15}$$

In the present problem, the reversible work, $W_R = 0$.

Figure. (2.6) shows the probability of violation of the second law as a function of τ for linear protocol and for optimum protocol. In the asymptotic, limit both will reach 0.5 because both protocols are same for $\tau \to \infty$. When $0 < \tau < \infty$, $p_{opt}(\tau) > p_{lin}(\tau)$. This is because average work for optimum protocol is less than the linear protocol. The center

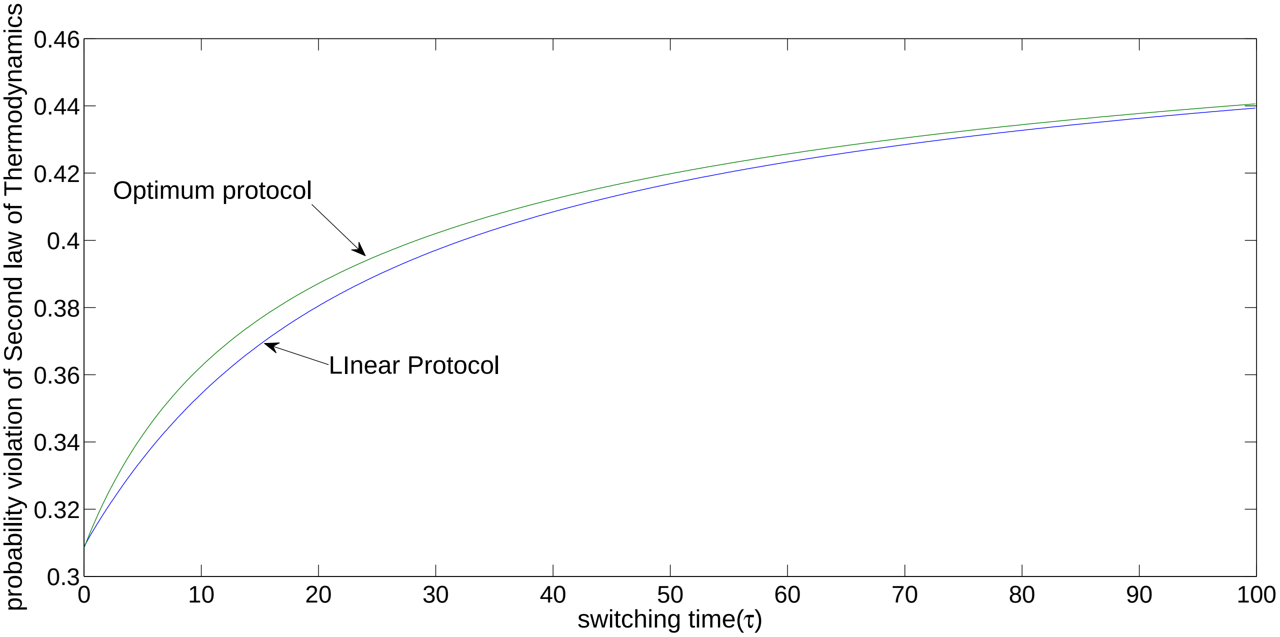

Figure 2.6: Probability violation of 2nd law *versus* switchingtime

of the work distribution for optimum protocol is closer to the zero than the center of the work distribution of the linear protocol. Physically it means that for a given switching time $\tau < \infty$, the optimum protocol leads to least dissipation. This is shown in Fig. (2.7)

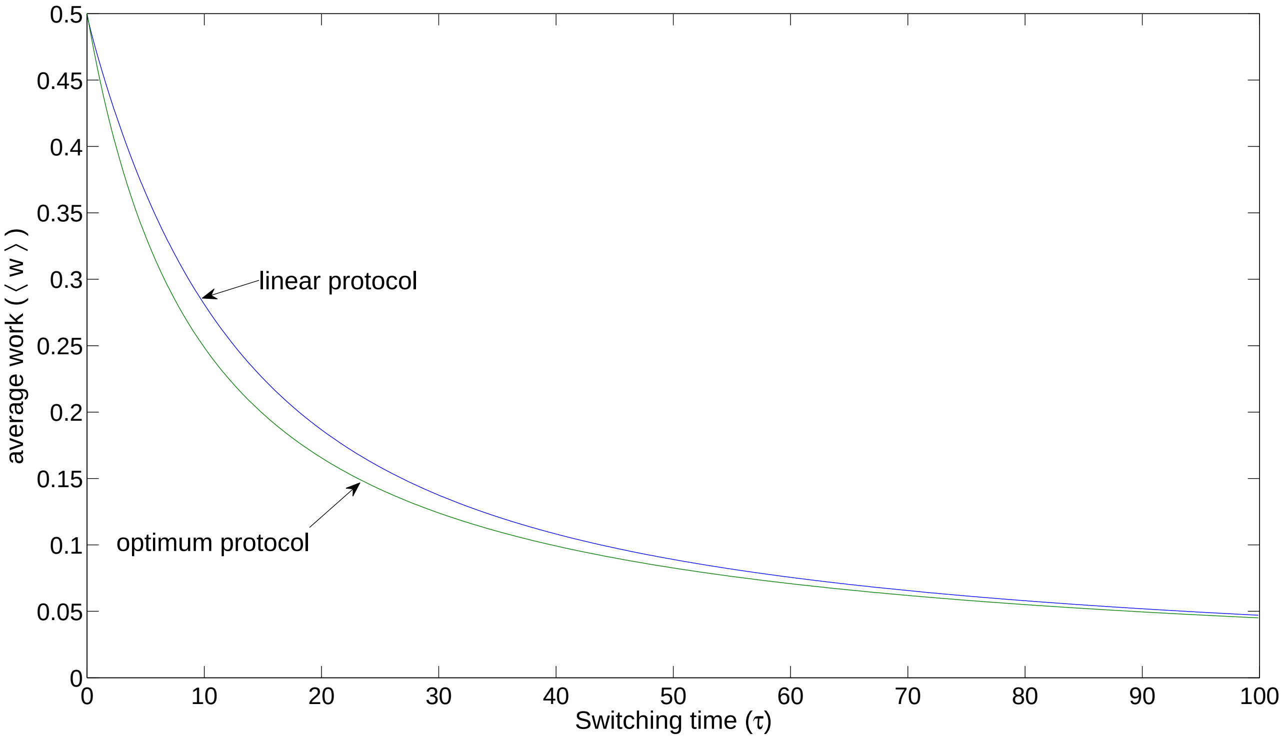

Figure 2.7: Average work *versus* switching time

Next we show that optimum protocol gives smaller fluctuations than linear protocol, see Fig. (2.8).

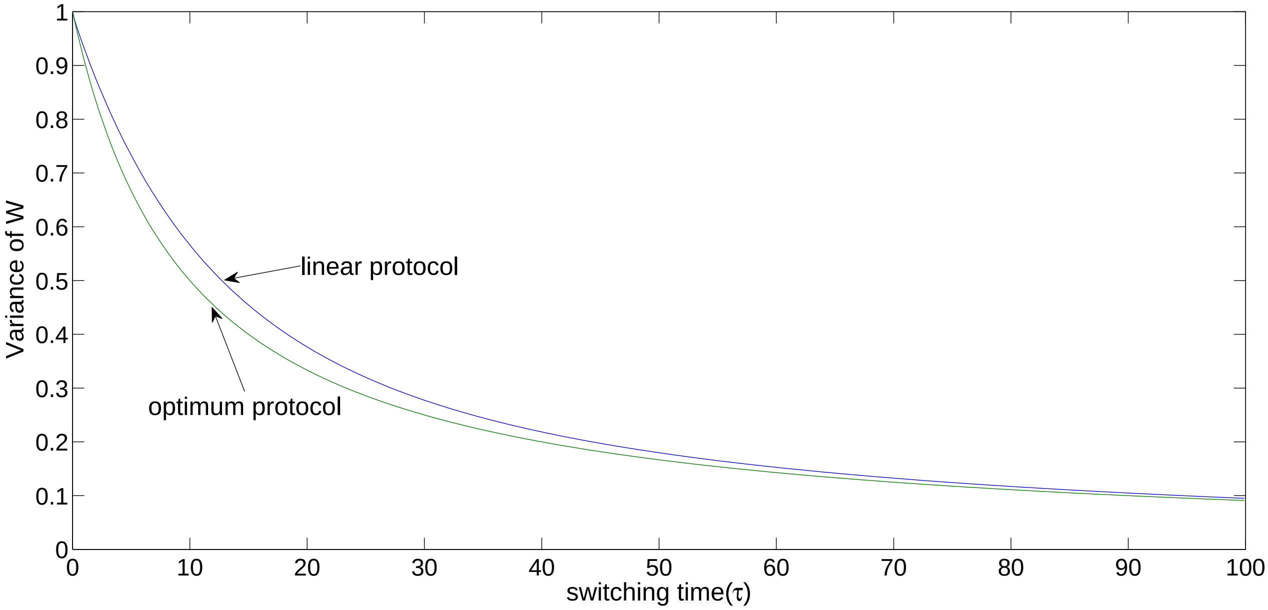

Figure 2.8: variance of work distribution *versus* switching time

We have from Jarzynski equation [5]

$$\langle \exp(-\beta W)\rangle = p(\tau)\langle \exp(-\beta W)\rangle_- + (1-p(\tau))\langle \exp(-\beta W)\rangle_+ = 1; \tag{2.16}$$

$$\langle \exp(-\beta W)\rangle_- = \frac{\int_{-\infty}^{0} dW \exp(-\beta W)\rho(W;\tau)}{\int_{-\infty}^{0} dW \rho(W;\tau)} \tag{2.17}$$

$$\langle \exp(-\beta W)\rangle_+ = \frac{\int_{0}^{\infty} dW \exp(-\beta W)\rho(W;\tau)}{\int_{0}^{\infty} dW \rho(W;\tau)} \tag{2.18}$$

From Fig. (2.9) we observed that $\langle \exp(-\beta W)\rangle_-$ for linear protocol is greater than that from optimum protocol.

From Fig. (2.10), we have observed that $\langle \exp(-\beta W)\rangle_+$ for linear protocol is less than the optimum protocol.

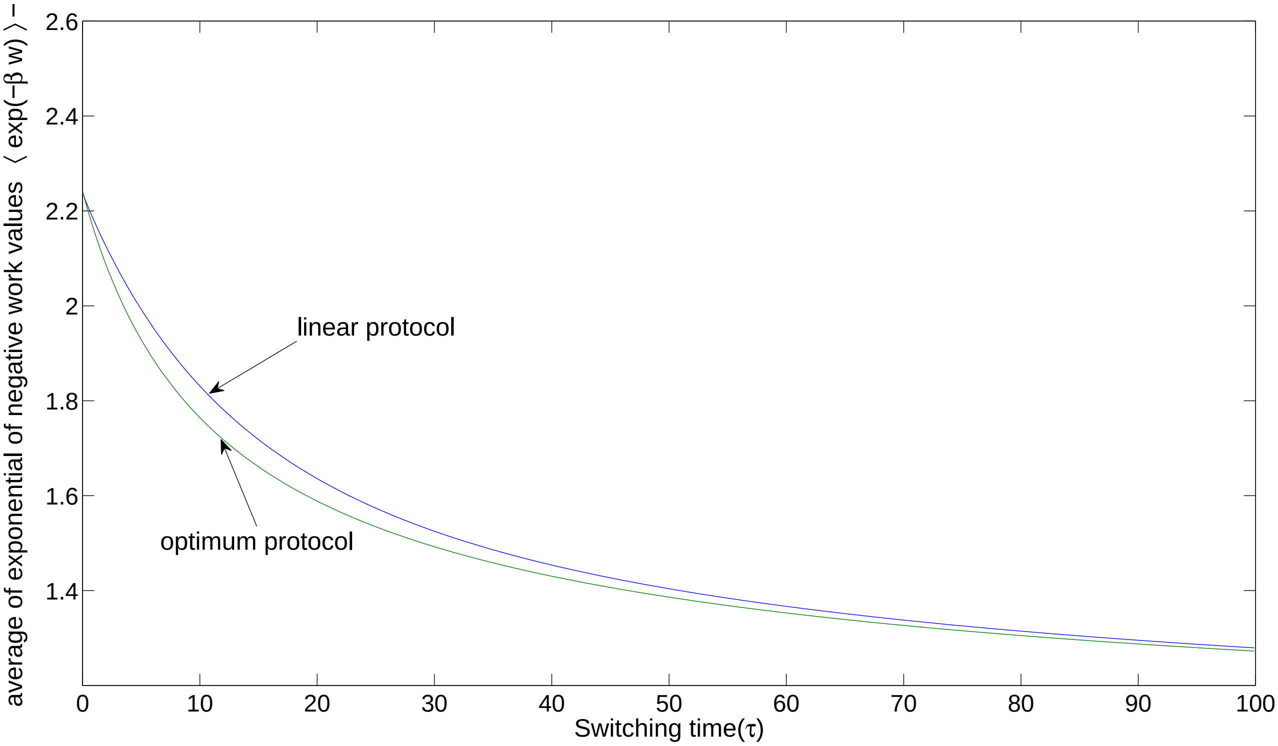

Figure 2.9: Average of exponential of negative work *versus* switching time

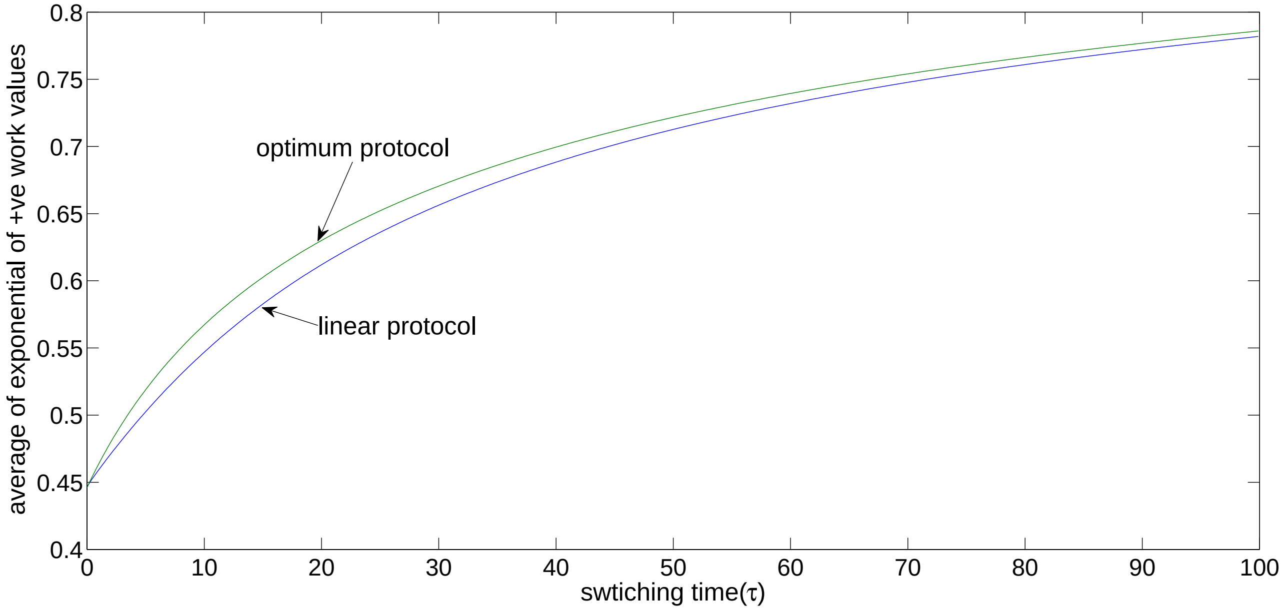

Figure 2.10: Average of exponential of positive work *versus* switching time

In the asymptotic limit of $\tau \to \infty$, $p(\tau) \to 0.5$, $(1 - p(\tau)) \to 0.5$. $\langle \exp(-\beta W) \rangle_{-} \to 1$ and $\langle \exp(-\beta W) \rangle_{+} \to 1$.

Figs. (2.11, 2.12) show, when $\tau \to \infty$, $p(\tau)\langle \exp(-\beta W) \rangle_{-}$ goes to 0.5 and $(1 - p(\tau))\langle \exp(-\beta W) \rangle_{+}$ goes to 0.5. and the sum of this is 1, which is consistent with Jarzynski Identity.

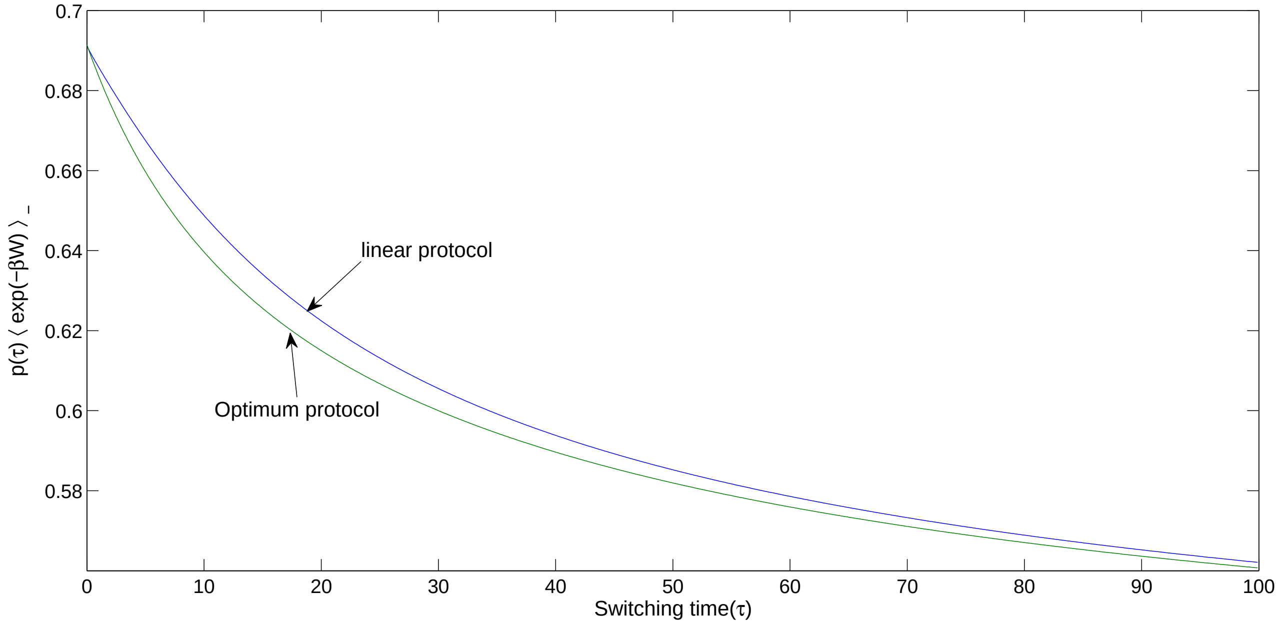

Figure 2.11: Product of probability of violation of second law and average of exponential of negative work values *versus* switching time

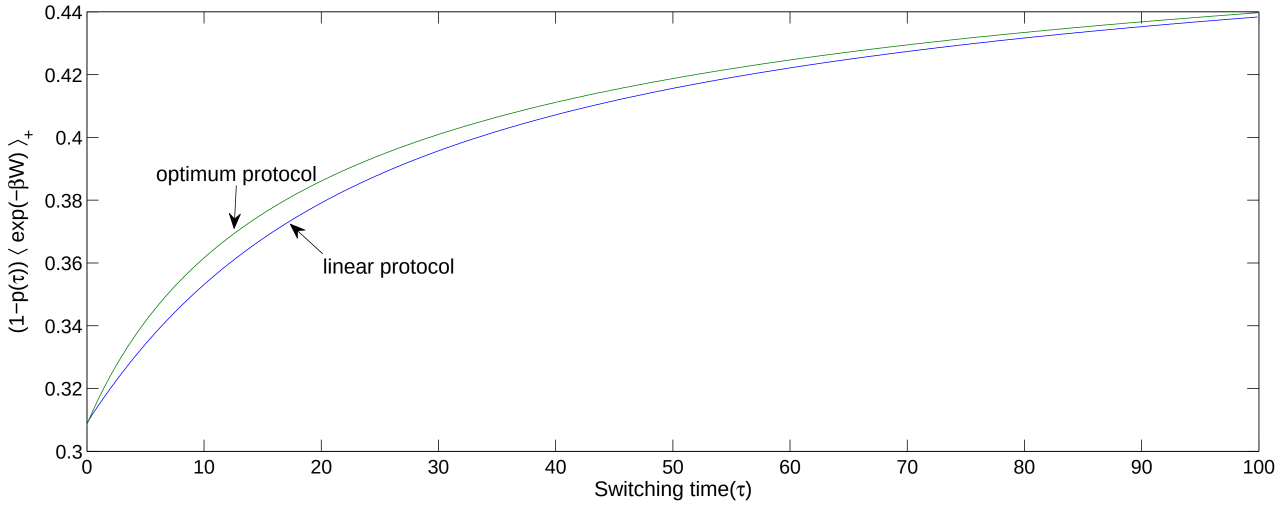

Figure 2.12: Product of $(1 - p(\tau))$ and average of exponential of positive work values *versus* switching time

2.5 Conclusion

In this chapter we have considered the problem of moving harmonic trap. We employed semi-analytical formulation and shown that the work distribution is Gaussian. We have shown that dissipation is always positive and goes to zero in the reversible limit. This result is consistent with second law of thermodynamics. While the average work is always greater than reversible work, there are elements of work ensemble that are less than W_R. The fraction of such work values gives an estimation of the probability of violation of the second law, denoted by $p(\tau)$. For $\tau \to \infty$ we find $p(\tau) \to 0.5$. On the face of it this result appear counter intuitive. However, detailed calculations show that this result indeed is expected and is a simple consequence of the fact that while both $\langle W \rangle$ and σ_W go to zero in the reversible limit, the former goes faster than the latter.

We have also carried out Monte Carlo Simulations and have shown that the results are consistent with semi analytical results.

Chapter 3

Simple Harmonic Oscillator

3.1 Introduction

Consider a particle of unit mass in a potential $V(x)$ given by

$$V(x) = k\frac{x^2}{2} \tag{3.1}$$

where k is a force constant. The particle is in a viscous fluid with friction γ. Equation of motion for that particle is

$$\frac{d^2x}{dt^2} = -kx - \gamma\frac{dx}{dt} + \xi(t) \tag{3.2}$$

The random force ξ is modeled as delta correlated Gaussian white noise with vanishing mean, $\langle\xi(t)\rangle = 0$, and a variance given by the fluctuation-dissipation theorem.

$$\langle\xi(t)\xi(t')\rangle = 2\gamma k_B T\delta(t-t').$$

The Hamiltonian of the system, can be written as:

$$H(x,p) = \frac{p^2}{2} + k\frac{x^2}{2} \tag{3.3}$$

Here we take k as external parameter. Let k be switched from k_1=1 to a final value k_2 =2.

For a given temperature, the partition function of this system is given by

$$Z = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \exp[-\beta(\frac{p^2}{2} + k\frac{x^2}{2})]dxdp = \frac{2\pi}{\beta\sqrt{k}} \tag{3.4}$$

Hence, the free energy difference is

$$\Delta F = -\beta ln(\frac{Z_2}{Z_1}) = -(\beta/2)ln\left(\frac{k_1}{k_2}\right) \tag{3.5}$$

Let β=1. Then,

$$\Delta F = -0.5ln(\frac{1}{2}) = 0.3466$$

We can write the Eq. (3.2) as two first order differential equations,

$$\dot{x}(t) = v(t); \tag{3.6}$$

$$\dot{v}(t) = -kx(t) - \gamma v(t) + \xi(t); \tag{3.7}$$

we have used Brunger-Brooks-Karplus integrator [17] to solve the above equations, see below

$$x(t+\Delta t) = x(t) + v(t)\Delta t + a(t)\frac{\Delta t^2}{2} + \dot{a}(t)\frac{\Delta t^3}{6} + O(\Delta t^4) \tag{3.8}$$

$$x(t-\Delta t) = x(t) - v(t)\Delta t + a(t)\frac{\Delta t^2}{2} - \dot{a}(t)\frac{\Delta t^3}{6} + O(\Delta t^4) \tag{3.9}$$

If we sum Eqns. (3.8, 3.9) we get this,

$$x(t+\Delta t) = 2x(t) - x(t-\Delta t) + a(t)\Delta t^2 + O(\Delta t^4) \tag{3.10}$$

$$x(t+\Delta t) = 2x(t) - x(t-\Delta t) + (-kx(t) - \gamma v(t) + \eta(t))\Delta t^2 \tag{3.11}$$

$$x(t+\Delta t) - x(t-\Delta t) = 2v(t)\Delta t + O(\Delta t^3) \tag{3.12}$$

$$v(t) = \frac{x(t+\Delta t) - x(t-\Delta t)}{2\Delta t} \tag{3.13}$$

If we substitute $v(t)$ in Eq. (3.11) we get,

$$x(t+\Delta t) = \left(\frac{1}{1+\frac{\Delta t}{2}}\right)\left[2x(t) - x(t-\Delta t) + \gamma\frac{\Delta t}{2}x(t-\Delta t) + \Delta t^2(-kx(t) + \eta(t))\right] \tag{3.14}$$

where Δt is a very small interval of time. It requires two previous values to initiate the solution process. We use a simple Euler algorithm to start the solution process. If x_0 and p_0 are the initial conditions. then

$$v_{1/2} = v_0 + (\Delta t/2)(-kx_0 - \gamma v_0 + \eta(0)/\Delta t) \tag{3.15}$$

$$x_1 = x_0 + (\Delta t/2)v_{1/2} \tag{3.16}$$

3.2 Linear protocol

We change the external force linearly from k=1 to k=2. The distribution is not Gaussian for $\tau < \infty$. When τ increases $p(\tau)$ decreases, see Fig. (3.1). When the process is near quasi static (at near quasi static the work distribution will be Gaussian), we expect $p(\tau)$ to increase and go to 0.5 when $\tau \to \infty$. In the asymptotic limit the distribution is a δ function centered at 0.

Figure. (3.2) shows that when we increase the switching time, average work decreases because dissipation decreases with switching time.

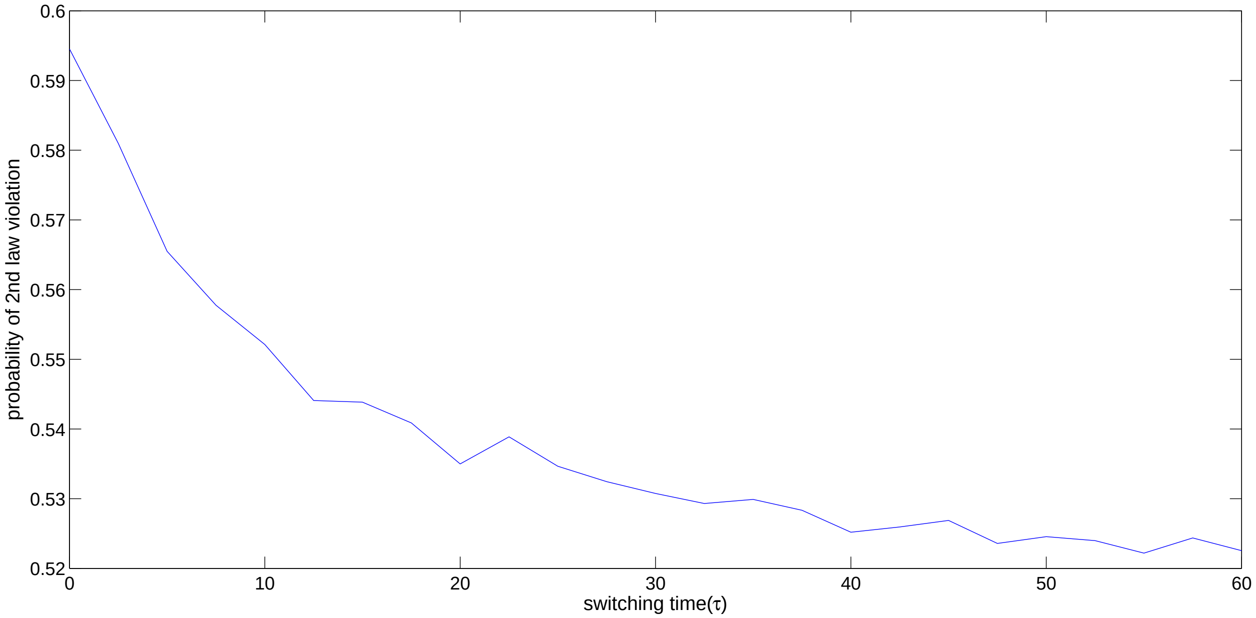

Figure 3.1: probability of violation of second law *versus* switching time

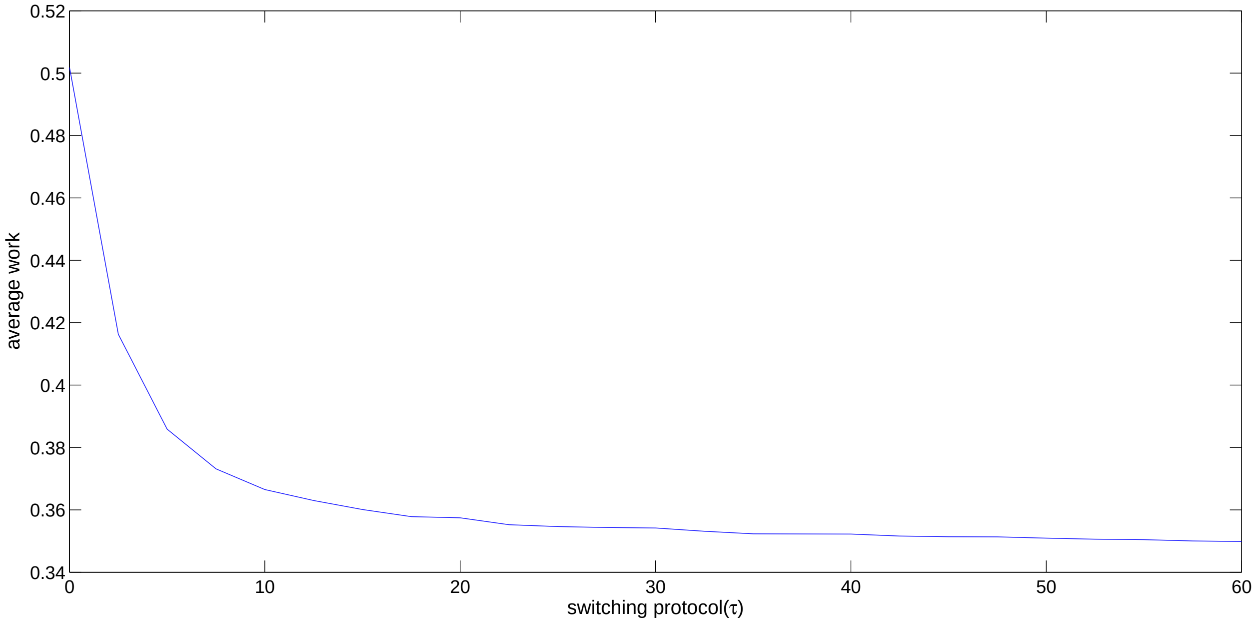

Figure 3.2: Average work *versus* switching time

$$\langle \exp(-\beta(W - W_R)) \rangle = p(\tau)\langle \exp(-\beta(W - W_R)) \rangle_- + (1 - p(\tau))\langle \exp(-\beta(W - W_R)) \rangle_+ = 1 \tag{3.17}$$

Let $W' = W - W_R$. We find that $\langle \exp(-\beta W') \rangle_-$ decreases as $\tau \to \infty$ and goes to 1, see Fig. (3.3).

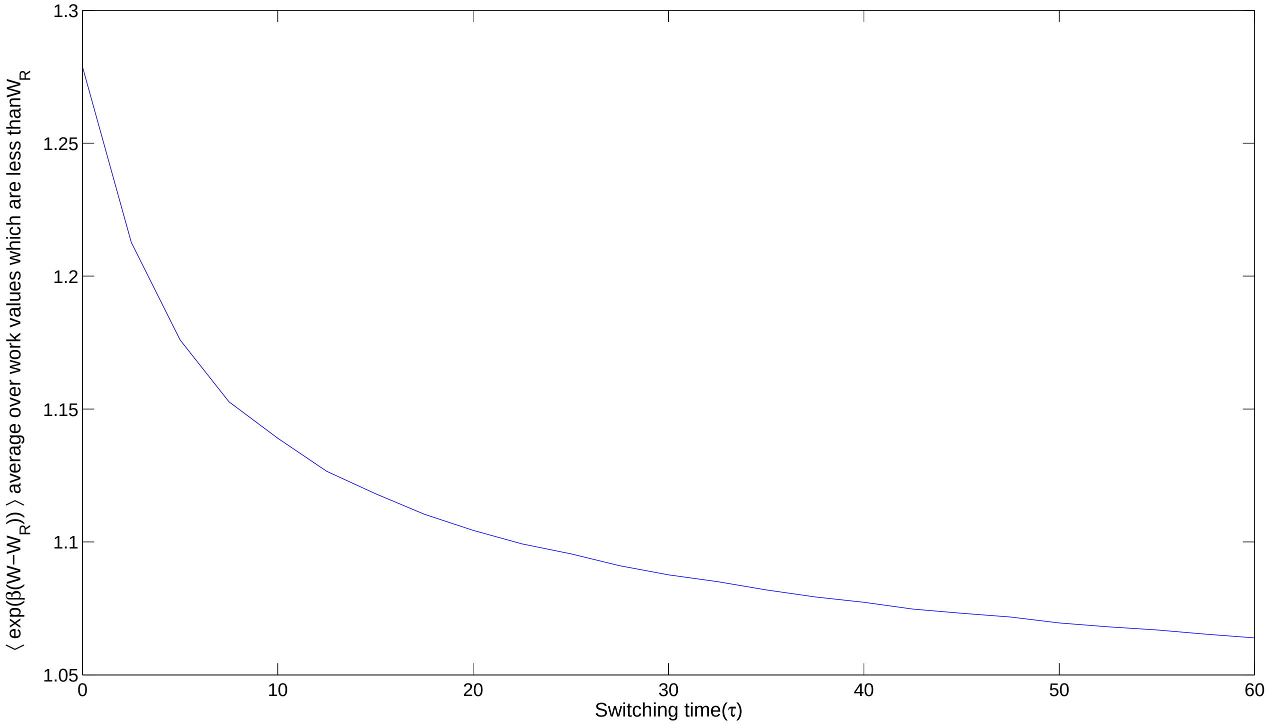

Figure 3.3: $\langle exp(-\beta(W - W_R)) \rangle_-$ *versus* switching time

$\langle \exp(-\beta W') \rangle_+$ increases with τ and asymptotically($\tau \to \infty$) goes to unity. see Fig.(3.4).

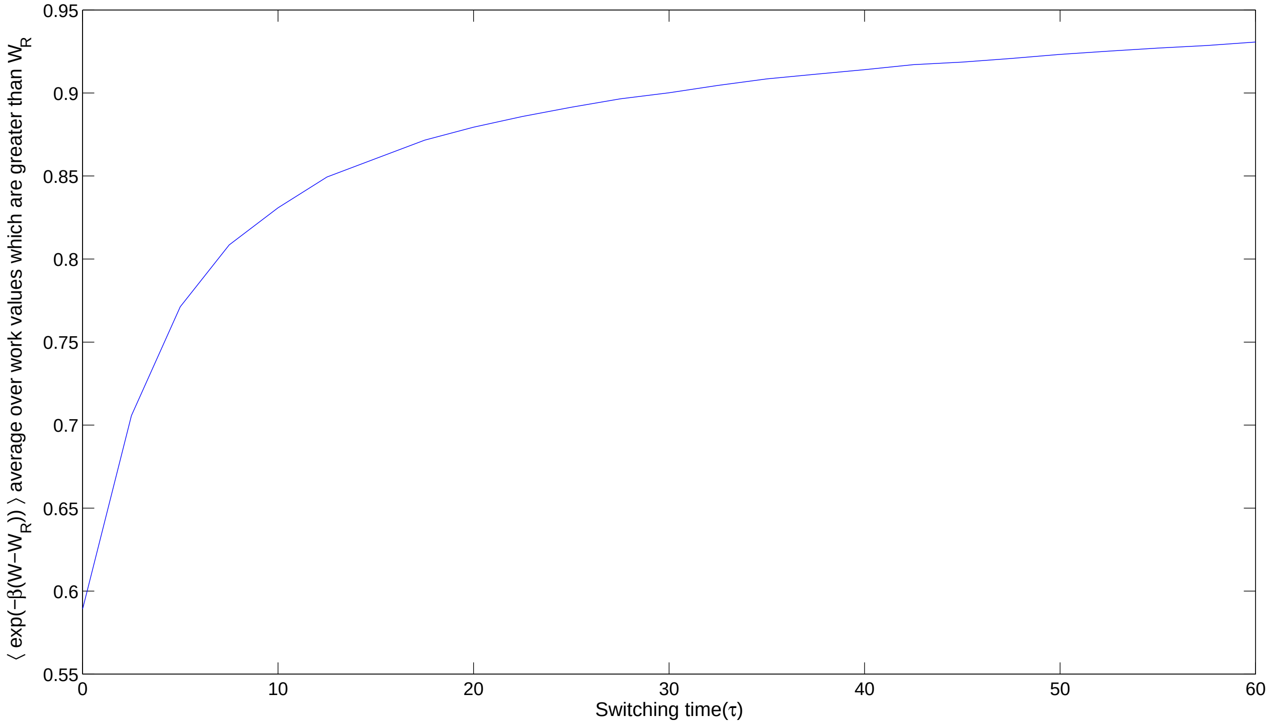

Figure 3.4: $\langle exp(-\beta(W - W_R))\rangle_+$ *versus* switching time

Figures. (3.5 and 3.6) shows that $p(\tau)\langle \exp(-\beta W')\rangle_- \to 0.5$, $(1-p(\tau))\langle \exp(-\beta W')\rangle_+ \to 0.5$ as $\tau \to \infty$.

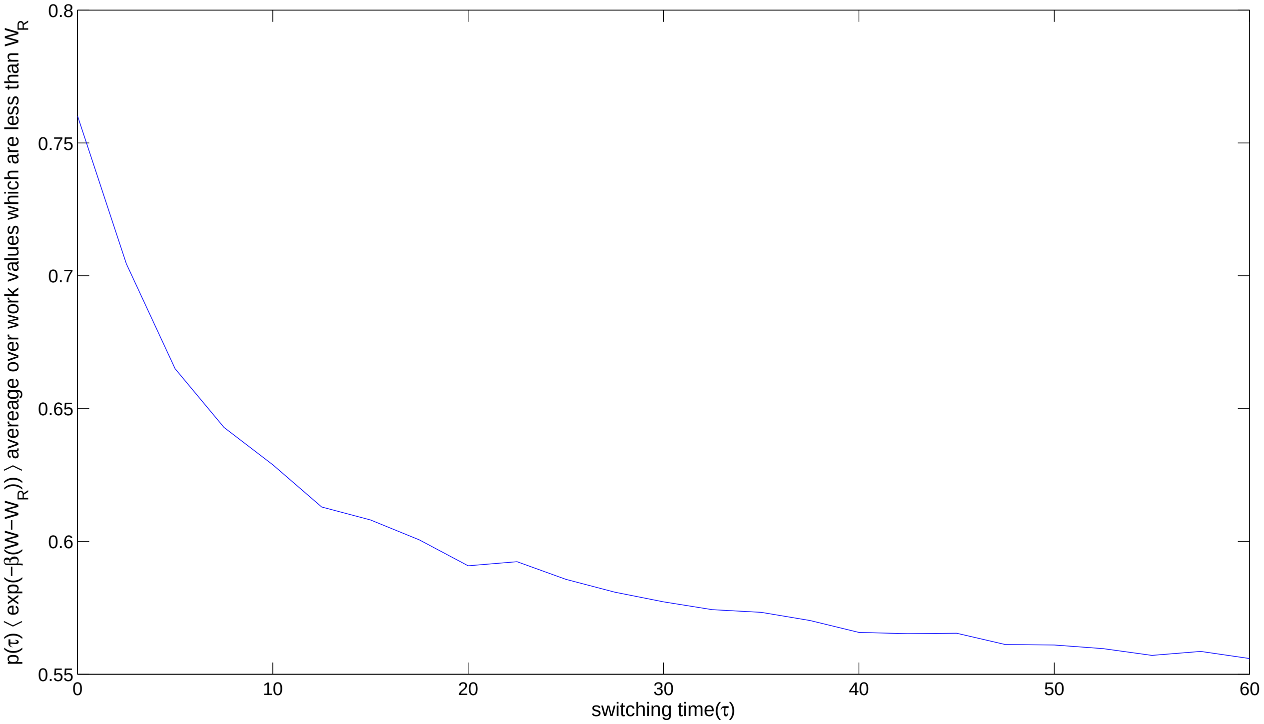

Figure 3.5: $p(\tau)\langle exp(-\beta(W-W_R))\rangle_-$ *versus* switching time

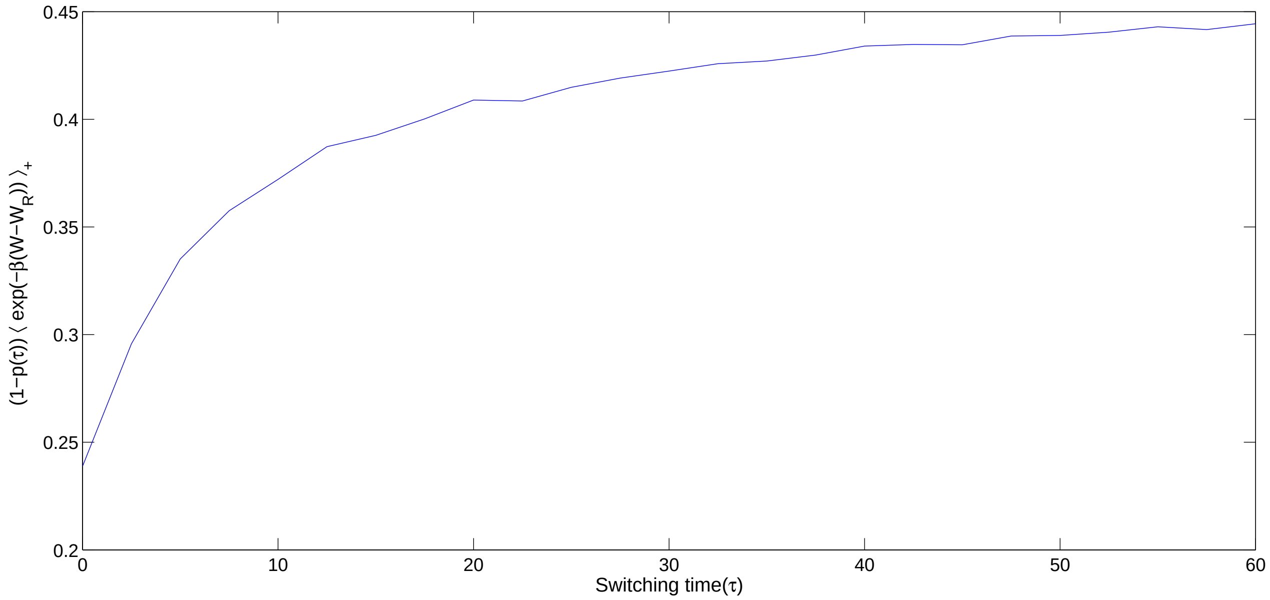

Figure 3.6: $(1 - p(\tau))\langle exp(-\beta(W - W_R))\rangle_+$ *versus* switching time

3.3 Cyclic protocol

In this section, we consider a cyclic protocol $k = 1 \rightarrow 2 \rightarrow 1$. See Fig. (3.7). Initially as τ increases, $p(\tau)$ decreases. The system is far from equilibrium in this range of values of τ. However when τ increases further, the system is driven closer to equilibrium. We find $p(\tau)$ starts increasing with τ. The work distribution for those values of τ is Gaussian. Eventually in the reversibly limit of $\tau \rightarrow \infty$, $p(\tau) \rightarrow 0.5$.

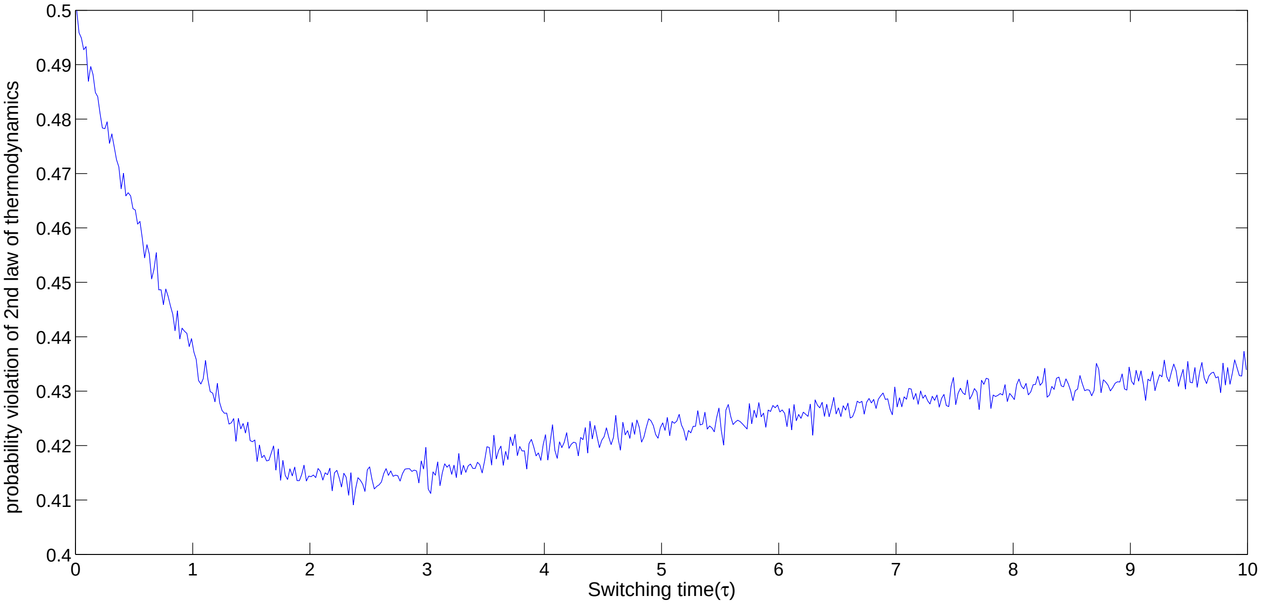

Figure 3.7: probability of violation of second law *versus* switching time

Fig.(3.8) shows when τ increases the average work decreases, since dissipation decreases which the process becomes more and quasi static reversible.

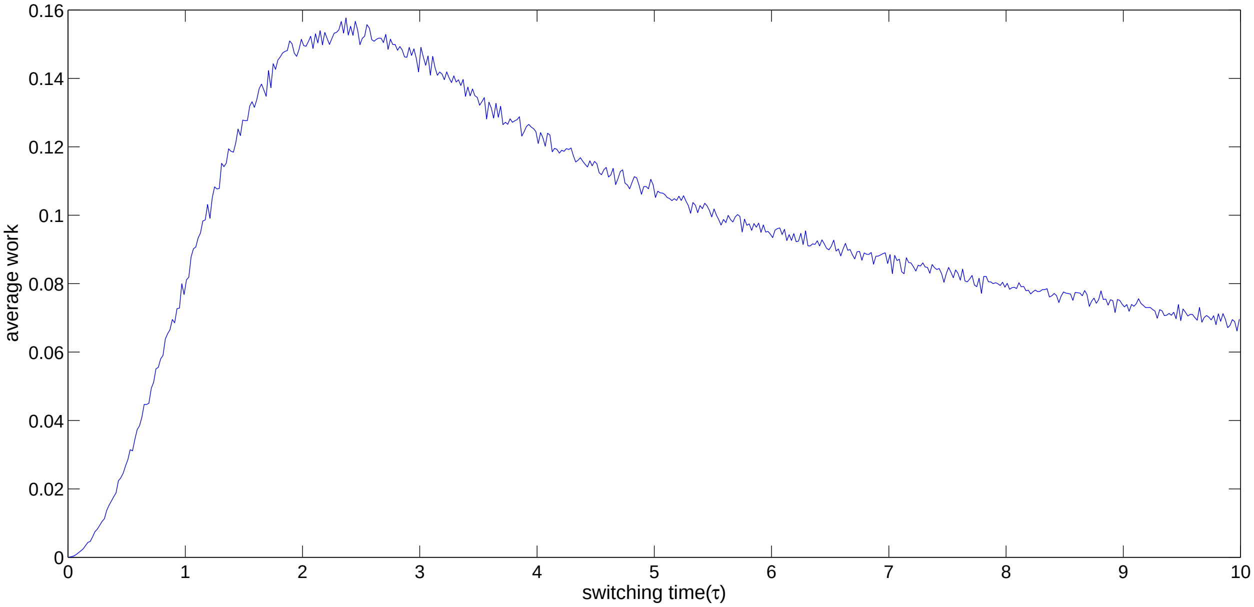

Figure 3.8: Average work *versus* switching time

When τ increase $\langle \exp(-\beta W) \rangle_-$ decreases and then increase, see Fig.(3.9)

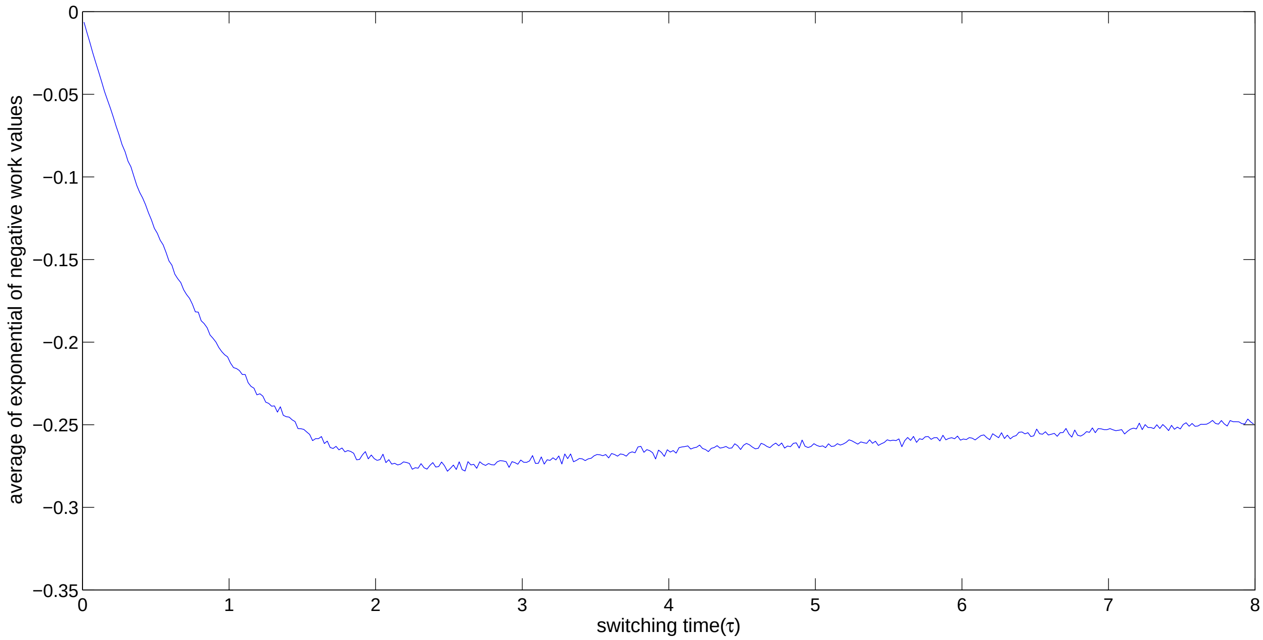

Figure 3.9: $\langle \exp(-\beta W) \rangle_-$ *versus* switching time

When τ increase $\langle \exp(-\beta W) \rangle_+$ increases and then decreases, see Fig.(3.10)

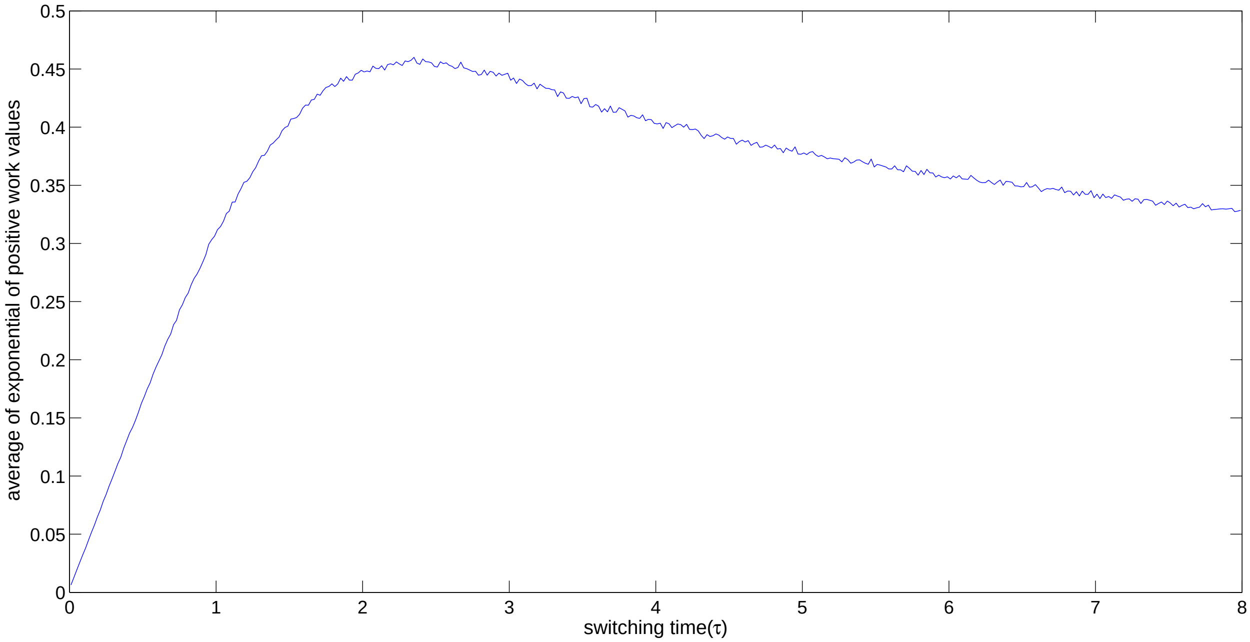

Figure 3.10: $\langle \exp(-\beta W) \rangle_+$ *versus* switching time

When τ increase $p_{-}\langle\exp(-\beta W)\rangle_{-}$ decreases and then increase, see Fig.(3.11)

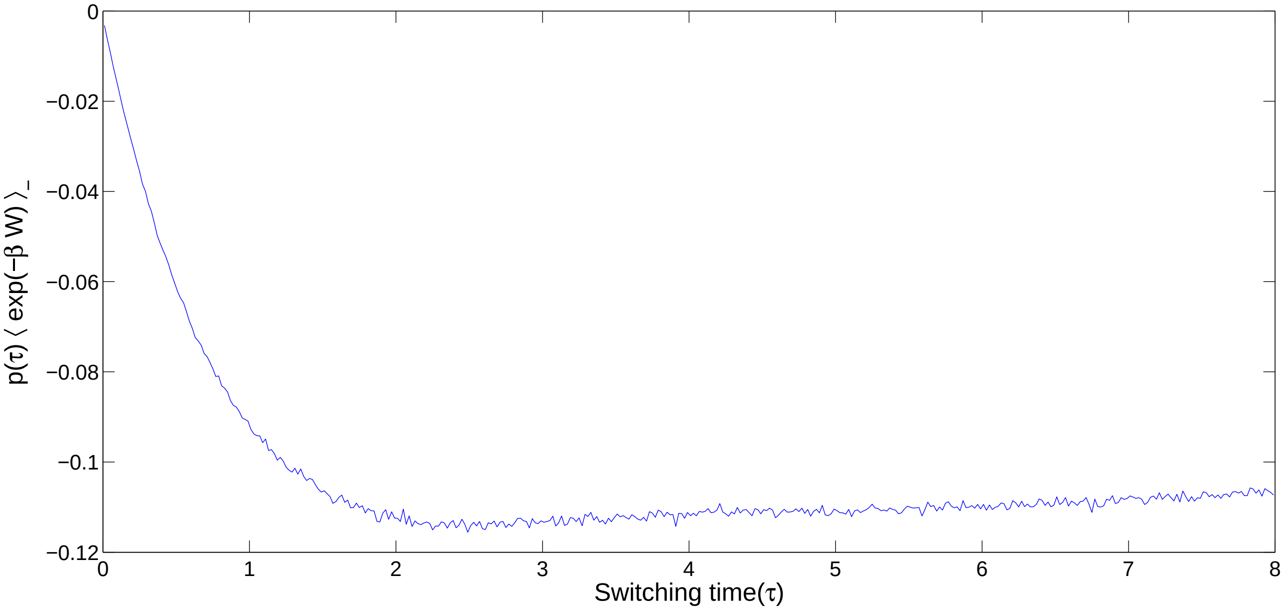

Figure 3.11: $p(\tau)\langle exp(-\beta(W))\rangle_{-}$ *versus* switching time

When τ increase $p_+\langle\exp(-\beta W)\rangle_+$ increases and then decreases, see Fig.(3.12)

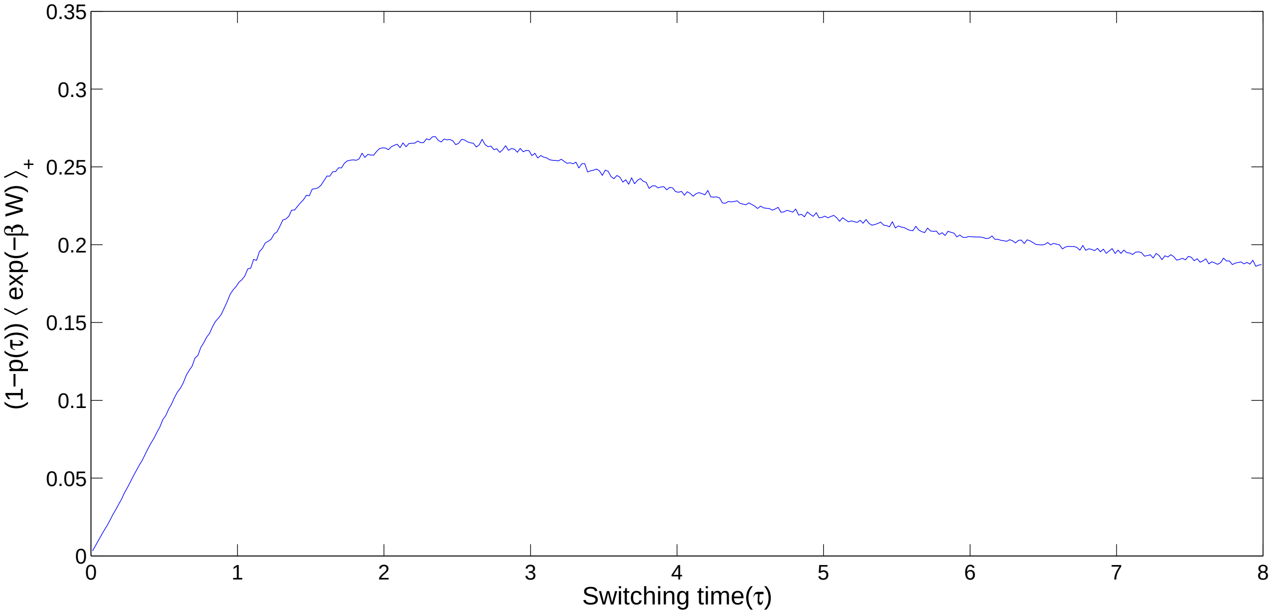

Figure 3.12: $(1-p(\tau))\langle exp(-\beta(W))\rangle_+$ *versus* switching time

Chapter 4

Conclusions

We have considered in this thesis two model switching processes and investigated work fluctuations. The first is a harmonic trap and the trap position is switched. The second process ia a harmonic oscillator with spring constant taken as a switching parameter.

For small switching time the system is driven far from equilibrium. Nevertheless averaging a suitable quantity over an ensemble of switching experiments gives us equilibrium quantities. We show that $\langle W \rangle \geq W_R$ where $\langle \cdots \rangle$ denotes averaging over an ensemble of work values from independent switching experiments all carried out with the same protocol. W_R deontes the reversible work that corresponds to equilibrium free energy difference. W_R can be calculated from the non-equilibrium work ensemble employing Jarzynksi identity. We have also picked up the values of w in the ensemble that are less than W_R. These are usually referred to as second law violating switching scenario. The fraction of such work values is called the probability of second law violation. We show that $p(\tau) \to 0.5$ as $\tau \to \infty$. We present an explanation for this result both qualitatively and quantitatively.

Another important issue we investigated in this thesis is about optimal switching protocol for which average and fluctuations of work are minimum. Jarzynski equality has contributed immensely to our understanding of non-equilibrium phenomena. It gives us a powerful handle to relate non-equilibrium measurements to equilibrium quantities. In this sense we can view Jarzynski equality as a viable numerical technique to calculate free energy differences. Of course for an arbitrary protocol the number of times you have to carry out the switching experiments would be very large and would require prohibitively large computing time. If we manage to derive a switching protocol that keeps the average work and fluctuations of work to small values, Jarzynski equality would become an efficient tool, toward calculating free energy differences. To this end, we have studied optimal switching derived from steepest descent method. We find it helps calculate the free energy differences reasonably efficiently. It would worth the effort to investigate this issue further and come up with efficient switching protocols.

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