Energy Fluctuations In Thermally Isolated Driven Systems

BY

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QUAID-I-AZAM UNIVERSITY
ISLAMABAD, PAKISTAN
2013.

This work is submitted as a dissertation in
Partial fulfillment of the requirement for the degree of

MASTER OF PHILOSOPHY
In
PHYSICS

Department of Physics
Quaid-i-Azam University
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CERTIFICATE

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Dedicated
To
MY BELOVED MOTHER

ACKNOWLEDGEMENT

First and foremost, I want to express my deepest gratitude to Allah Almighty, the most merciful and the the most compassionate, who gave me the opportunity to learn and enabled me to accomplish this research work.

I feel great pleasure in expressing my ineffable thanks to my respectable supervisor **Dr. Kashif Sabeeh** whose personal interest and thought provoking guidance enabled me to complete this tedious work. He has stimulated my mind and gave me insight of research. His sympathetic attitude and encouraging discussion enabled me in broadening and improving my capabilities in physics.

My cordial thanks to all my friends and colleagues for their companionship during the whole span of M.Phil. My deepest sense of acknowledgement goes to my husband and family. I would be pleased to mention here my deepest obligations to my sister Saira for her everlasting love, care and morale boosting. Last but not the least beebu my son whose laughs and cuddles always freshen me up.

May Allah shower His choicest blessings and prosperity on all those who assisted me in any way during completion of my thesis.

(Attiqa Tahir)

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Submitted to the Department of Physics
on 28 January 2013, in partial fulfillment of the
requirements for the degree of
Master of Philosophy (M.Phil)

Abstract

This thesis presents a theoretical review of systems that are thermally isolated and are under the action of some external protocol or drive. Here we have discussed these systems by formulating a Fluctuation-Dissipation relation appropriately describing their physics. Firstly, we have derived the Fluctuation-Dissipation relation using the Fokker-Planck equation and then by using Quantum Crooks equality leading to an expression for the energy fluctuations in the system of interest. We have shown in detail that energy fluctuations in thermally isolated systems that are driven away from equilibrium by some external parameter are universal in nature and follow a non-Gibbsian pattern. We have predicted that there exist two different regimes with a continuous second-order-like transition between them. We have explicitly shown two distinct regimes depending on the value of order parameter η i.e., Gibb's like behaviour for $(\eta < 1)$ and run away like for $(\eta > 1)$. We have verified our approach by applying it to both interacting and non-interacting systems.

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Chapter 1

Introduction

1.1 Motivation

The fluctuations in non-equilibrium systems are under intense theoretical and experimental investigation. Topical 'fluctuation relations' describe symmetries of the statistical properties of certain observables in a variety of models and phenomena. The field has grown beyond expectations, research works and different perspectives are proposed at an ever faster pace. Indeed, understanding fluctuations is important for any theory of non-equilibrium phenomena, as well as for applications, such as those of nanotechnological and biophysical interest.

1.2 Historical background

As it often happens in science, the historical development of theories is quite tortuous. Fluctuation relations are no exception in this respect. Without any intention of providing a thorough and complete historical account, I mention below a few milestones that, in my view, mark crucial steps in the historical development of fluctuation relations.

Sutherland-Einstein (1902,1905,1906) The beginning of the story might be traced back to the early years of the last century, with the work of Sutherland and Einstein, when it was found that the linear response of a system in thermal equilibrium, as it is driven out of equilibrium by an external force, is determined by the fluctuation properties of the system in the initial equilibrium state [1]. They found a relation between the mobility of a Brownian particle (encoding information about its response to an externally applied force) and its diffusion constant (encoding information about its equilibrium fluctuations):

$$D = \frac{R}{N}\frac{T}{6\pi\eta r}$$

Where

D = coefficient of diffusion of the suspended substance

R = universal gas constant

T = absolute temperature

N =avogadro's number

r = radius of suspended particle

η = coefficient of viscosity of liquid

Johnson-Nyquist (1928) Johnson and Nyquist discovered the corresponding relation between the resistance of a circuit and the spontaneous current fluctuations occurring in the absence of an applied electric potential [2],[3]. Statistical fluctuation of electric charge exists in all conductors, producing random variation of potential between the ends of the conductor. The effect of these fluctuations has been measured by a vacuum tube amplifier and thermocouple, and can be expressed by the formula

$$< I^2 >= \frac{2kT}{\pi}\int_0^\infty [R(\omega)|Y(\omega)|^2]d\omega$$

Where

I = observed current in thermocouple

$R(\omega)$ = real component of impedance of conductor

$Y(\omega)$ = transfer impedance of amplifier

$f = 2\pi/\omega$ = frequency

Callen-Welton (1951) The next step was taken by Callen and Welton who derived the previous results within a general quantum mechanical setting [4]. The starting point of their analysis was a quantum mechanical system described by a Hamiltonian H_0. Initially this system stays in a thermal equilibrium state at the inverse temperature $\beta = (k_B T)^{-1}$. This state is described by a density matrix of canonical form; i.e., it is given by a Gibbs state

$$\rho_0 = \frac{e^{-\beta H_0}}{Z_0}$$

Where

$Z_0 = Tr\left(e^{-\beta H_0}\right)$ denotes partition function of unperturbed system

Tr = trace over its Hilbert space

At later time $t > 0$, the system is perturbed by the action of an external, in general, time-dependent force λ_t that couples to an observable Q of the system. The dynamics of the system then is governed by the modified, time-dependent Hamiltonian

$$H(\lambda_t) = H_0 - \lambda_t Q$$

Green-Kubo (1952,1957) The approach of Callen and Welton (1951) was further improved systematically by Green (1952, 1954) and, in particular, by Kubo (1957) [4]. He proved that the linear response is determined by a response function $\Phi_{BQ}(t)$, which gives the deviation $\langle\Delta B(t)\rangle$ of the expectation value of an observable B to its unperturbed value as

$$\langle\Delta B(t)\rangle = \int_{-\infty}^{t} \Phi_{BQ}(t-s)\lambda_s ds$$

Where the response function can be expressed in terms of the commutator of the observables Q and $B^H(t)$ as

$$\Phi_{BQ}(s) = \frac{\langle[Q, B^H(s)]\rangle}{i\hbar}$$

and deduced from it the celeberated quantum fluctuation dissipation theorem

$$\widehat{\Psi}_{BQ}(\omega) = \frac{\hbar}{2i} coth(\frac{\beta\hbar\omega}{2})\widehat{\Phi}_{BQ}(\omega)$$

Where $\widehat{\Psi}_{BQ}(\omega)$ and $\widehat{\Phi}_{BQ}(\omega)$ denotes the Fourier transform of the symmetrized, stationary equilibrium correlation functions $\Psi_{BQ}(s), \Phi_{BQ}(s)$ respectively.

NOTE: The superscript H denotes the Heisenberg picture with respect to the unperturbed dynamics.

Bernard- Callen (1959) Analysis of Kubo opened the possibility for a systematic advancement of response theory, allowing one to investigate the existence of higher order fluctuation-dissipation relations beyond linear regime. This task was soon undertaken by Bernard and Callen, who pointed out a hierarchy of irreversible thermodynamic relationships.

Stratonovich- Efremov Higher order fluctuation dissipation relations were investigated by

- Stratonovich for the Markovian systems
- Efremov (1969) for non-Markovian systems

Hanggi- Thomas For arbitrary systems far from equilibrium the linear response to an applied force can likewise be related to tailored two-point correlation functions of corresponding stationary nonequilibrium fluctuations of the underlying unperturbed, stationary nonequilibrium system. Hanggi and Thomas coined the expression "fluctuation theorems" for these relations. As in the near thermal equilibrium case, in this case higher order nonlinear response can also be linked to corresponding higher order correlation functions of those nonequilibrium fluctuations.

Bochkov- Kuzovlev In the late 1970s Bochkov and Kuzovlev provided a single compact classical expression that contains fluctuation relations of all orders for systems that are at thermal equilibrium when unperturbed. This expression can be seen as a fully nonlinear, exact, and universal fluctuation relation [4]. The fluctuation relation follows from the

- Time reversal-invariance of the equations of microscopic motion
- The system initially resides in thermal equilibrium described by the Gibbs state

The central finding of Bochkov and Kuzovlev is a formal relation between the generating functions for multitime correlation functions of the phase-space functions B_t and Q_t and the generating functions for the time-reversed multitime auto-correlation functions of B_t , expressed as

$$\langle e^{\int_0^\tau dt u_t B_t} e^{-\beta W_0} \rangle_\lambda = \left\langle e^{\int_0^\tau dt \widetilde{u}_t \varepsilon_B B_t} \right\rangle_{\varepsilon_Q \widetilde{\lambda}}$$

Where

$u_\tau =$ an arbitrary test function

$\widetilde{u}_t = u_{\tau-1}$ temporal reverse of u_τ

$W_0 = \int_0^\tau dt \lambda_t \dot{Q}$ where $\dot{Q}$ is the time derivative of $Q_t = Q(\varphi_{t,0}[z_0; \lambda])$

$\langle . \rangle =$ average taken w.r.t Gibbs distribution ρ_0

On the left hand side, the time evolutions of B_t and Q_t are governed by full Hamiltonian $H(z, \lambda_t) = H_0(z) - \lambda_t Q(z)$ in the presence of the forward protocol indicated by the subscript λ, while on the right hand side the dynamics is determined by the time-reversed protocol indicated by the subscript $\varepsilon_Q \widetilde{\lambda}$.

Evans (1993) Gallavotti-Cohen (1995) A new wave of activity in fluctuation relations was initiated by Evans, Gallavotti-Cohen on the statistics of entropy produced in non-equilibrium steady state

Jarzynski-Crooks (1997,1999) Jarzynski and Crooks developed theory of fluctuation relations on the statistics of work performed by a transient, time-dependent perturbation.[5],[6].

Crook's Fluctuation theorem states

$$\frac{P_F(s)}{P_R(-s)} = \exp\left\{\frac{s}{k_B}\right\}$$

Where

$s =$ entropy production of the total system over some time interval

$P_{F/R}(s) =$ probability of a given entropy production along the forward/reversed path

Jarzynski equality is simply a consequence of Crook's relation

$$\left\langle \exp\left[-\frac{W}{T}\right] \right\rangle = \exp\left[-\frac{\Delta F}{T}\right]$$

A detailed account of their work is discussed later in section (3.4).

Since the time of Jarzynski and Crooks the field has generated much interest and flourished. In the present review we have discussed in detail the variance of energy in thermally isolated driven systems (a nonequilibrium phenomenon) first by developing a fluctuation-dissipation relation for such a system and then by directly applying quantum Crooks relation mentioned above.

Chapter 2

Thermally Isolated Equilibrating Systems

2.1 Introduction

In this chapter we consider a thermally isolated system coupled with a heat bath. This model is similar to an oven. Since system is in thermal equilibrium with a heat bath the temperature of the system is defined to be equal to that of the reservoir, and it has strictly no meaning to ask question about the temperature fluctuations. The energy of the system, however, fluctuates as energy is exchanged with the reservoir. Here we have found an expression for the final energy by following the basic formalism of statistical thermodynamics as dicussed in [7]. This gives a distribution of energy i.e., random and follows Gibbs distribution. This result is a corner stone in Statistical physics.

2.2 Classical Formalism

Consider two macroscopic systems A, A'. Their respective energies are E, E' subdivided into equal small intervals δE, $\delta E'$ such that $\Omega(E)$ is the number of states between $E + \delta E$ and $\Omega(E')$ is the number of states between $E' + \delta E'$. Systems are not thermally insulated so that they can exchange energy. External parameters of the system are supported to remain fixed; thus energy tansfer is in the form of heat.

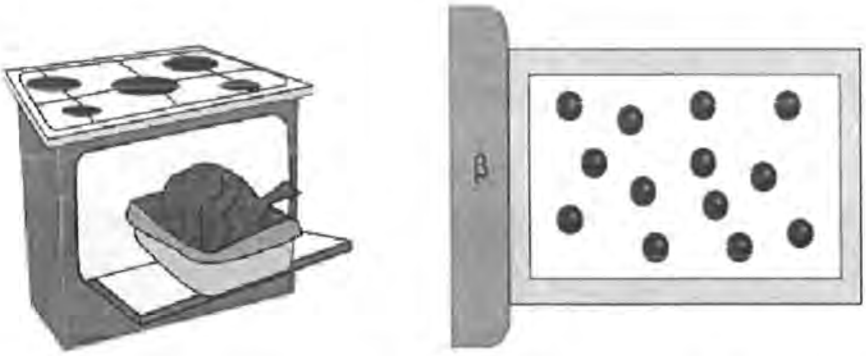

Figure 2-1: Schematic representation of a system coupled to a reservoir of temperature β (oven like setup).

The combined system $A^{(0)} = A + A'$ is isolated and its energy $E^{(0)}$ is therefore constant.

Isolated System: When a system A is not isolated but is allowed to interact with some other system A', it is always possible to reduce the situation to the case of an isolated system by focussing attention on the combined system $A + A'$.

Probability distribution of the system: Let us consider a situation where $A \lll A'$ i.e; when A has many fewer degrees of freedom than A'. Here A' is referred as heat reservoir (as shown in fig. 2-1). By following [7] we find the probability P_r of finding the system A in any of its particular microstate r of energy E_r under equilibrium conditions. Reif [7] assumes weak interaction between A and A' so that their energies are additive. The energy of system A is, of course, not fixed. It is only the total energy of the combined system $A^{(0)}$ which has a constant value in some range between $E^{(0)}$ and $E^{(0)} + \delta E$. The conservation of energy can be written as

$$E_r + E' = E^{(0)} \tag{2.1}$$

Where E' denotes the energy of the reservoir A'. When A has some energy E_r, the reservoir A' must then have an energy near $E' = E^{(0)} - E_r$. Hence, if A is in the one definite state r, the number of states accessible to the combined system $A^{(0)}$ is just the number of states

$\Omega'\left(E^{(0)} - E_r\right)$ accessible to A' when its energy lies in a range δE near the value $E' = E^{(0)} - E_r$. But, according to the fundamental statistical postulate, the probablility of occurrence in the ensemble of a situation where A is in state r is simply proportional to the number of states accessible to $A^{(0)}$ under these conditions. Hence

$$P_r = C'\Omega'\left(E^{(0)} - E_r\right) \tag{2.2}$$

Where

C' = constant of proportionality independent of r.

As usual, it can be determined from the normalization conditon for probabilitics, i.e.,

$$\sum_r P_r = 1 \tag{2.3}$$

Where the sum extends over all possible states of A irrespective of energy.

Let us now make use of the assumption that $A \lll A'$. Then $E_r \ll E^{(0)}$ and Eq.(2.2)can be approximateed by expanding the slowly varying logarithm of $\Omega'(E')$ about the value $E' = E^{(0)}$. Thus

$$\ln\Omega'\left(E^{(0)} - E_r\right) = \ln\Omega'\left(E^{(0)}\right) - \left[\frac{\partial \ln\Omega'}{\partial E'}\right]_0 E_r \tag{2.4}$$

Since A' acts as heat reservoir, $E_r \lll E^{(0)}$ and higher-order terms in the expansion can be neglected. The derivative

$$\left[\frac{\partial \ln\Omega'}{\partial E'}\right]_0 \equiv \beta \tag{2.5}$$

is evaluated at the fixed energy $E' = E^{(0)}$ and is thus a constant independent of the energy E_r of A. It is the constant temperature parameter $\beta \equiv (kT)^{-1}$ characterizing the heat reservoir A'. Physically, this means that the reservoir A' is so large compared to A that its temperature remains uneffected by whatever small amount of energy it gives to A. Hence Eq.(2.4) becomes

$$\ln\Omega'\left(E^{(0)} - E_r\right) = \ln\Omega'\left(E^{(0)}\right) - \beta E_r$$

$$\Omega'\left(E^{(0)} - E_r\right) = \Omega'\left(E^{(0)}\right) e^{-\beta E_r} \tag{2.6}$$

Since $\Omega'\left(E^{(0)}\right)$ is just a constant independent of r, Eq.(2.2) then becomes

$$P_r = Ce^{-\beta E_r} \tag{2.7}$$

Using the normalization condition Eq.(2.3), C is determined by the relation

$$C^{-1} = \sum_r e^{-\beta E_r}$$

So that Eq.(2.7) can also be written explicitly in the form

$$P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \tag{2.8}$$

The exponential factor $e^{-\beta E_r}$ is called the "Boltzmann factor"; the corresponding probability distribution Eq.(2.8) is known as the "canonical distribution". An ensemble of systems all of which are in contact with a heat reservoir of known temperature T, i.e., all of which are distributed over states in accordance with Eq.(2.8), is called a "canonical ensemble".

The above relation Eq.(2.8) gives the probability of finding A in one particular state r of energy E_r. The probability that A has an energy in a small range between E and $E + \delta E$ can be obtained by adding the probabilities for all states whose energy lies in the range i.e.,

$$P(E) = \sum_r P_r \tag{2.9}$$

Where r is such that $E < E_r < E + \delta E$. But all these states are, by Eq.(2.8) equally probable and are characterized by the same exponential factor $e^{-\beta E}$; hence one need simply to multiply the probabilities of finding A in any one of these states by the number $\Omega(E)$ of its states in this energy range i.e.,

$$P(E) = C\Omega(E)e^{-\beta E_r} \tag{2.10}$$

To the extent that A itself is a large system (although very much smaller than A'), $\Omega(E)$ is a rapidly increasing function of E. The presence of rapidly decreasing factor $e^{-\beta E}$ in Eq.(2.10) results then in a maximum of product $\Omega(E)\, e^{-\beta E}$. The larger A is, the sharper is this maximum in $P(E)$;i.e., the more rapidly $\Omega(E)$ increases with E, the sharper this maximum becomes.

Once the probability distribution Eq.(2.8) is known, various mean values can readily be computed. for example, let y be any quantity assuming the value y_r in state r of the system A. Then

$$\overline{y} = \frac{\sum_r e^{-\beta E_r} y_r}{\sum_r e^{-\beta E_r}} \tag{2.11}$$

Where the summation is over all states r of the system A.

Energy fluctuations: Fluctuations are deviation from the mean i.e., mean of square minus square of mean. Energy fluctuations are defined as

$$\Delta E = \overline{E^2} - \overline{E}^2 \tag{2.12}$$

Here mean value of energy is given by Eq.(2.11) i.e.,

$$\overline{E} = \frac{\sum_r e^{-\beta E_r} E_r}{\sum_r e^{-\beta E_r}} \tag{2.13}$$

Where sum is taken over all accessible states r of the system, irrespective of their energies. Eq.(2.13) can be reduced to much simpler form by noting that the sum in the numerator can be readily expressed in terms of the sum appearing in the denominator. Thus

$$\begin{aligned} \sum_r e^{-\beta E_r} E_r &= -\sum_r \frac{\partial}{\partial \beta}\left(e^{-\beta E_r}\right) \\ &= -\frac{\partial}{\partial \beta} Z \end{aligned}$$

Where

$$Z = \sum_r e^{-\beta E_r} \tag{2.14}$$

is just the sum in the denominator of Eq.(2.13). Hence one obtains

$$\begin{aligned} \overline{E} &= -\frac{1}{Z}\frac{\partial Z}{\partial \beta} \\ &= -\frac{\partial \ln Z}{\partial \beta} \end{aligned} \tag{2.15}$$

The quantity Z defined in Eq.(2.14) is called the "sum over states" or the "partition function". (The letter Z is used because the German name is "Zustandsumme.")

Mean of square of energy is

$$\overline{E^2} = \frac{\sum_r e^{-\beta E_r} E_r^2}{\sum_r e^{-\beta E_r}} \tag{2.16}$$

But

$$\begin{aligned} \sum_r e^{-\beta E_r} E_r^2 &= -\frac{\partial}{\partial \beta}\left(\sum_r e^{-\beta E_r} E_r\right) \\ &= \left(-\frac{\partial}{\partial \beta}\right)^2 \left(\sum_r e^{-\beta E_r}\right) \end{aligned}$$

Hence Eq.(2.16) becomes

$$\overline{E^2} = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} \tag{2.17}$$

By using

$$\frac{1}{Z}\left(\frac{\partial^2 Z}{\partial \beta^2}\right) = \frac{\partial}{\partial \beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right) + \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2$$

Eq.(2.17) can be written in a form involving the mean energy $\overline{E}$ of Eq.(2.15). Thus

$$\begin{aligned} \overline{E^2} &= \frac{\partial}{\partial \beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right) + \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2 \\ &= -\frac{\partial \overline{E}}{\partial \beta} + \overline{E}^2 \end{aligned}$$

$\Rightarrow$

$$\overline{E^2} - \overline{E}^2 = -\frac{\partial \overline{E}}{\partial \beta} \tag{2.18}$$

Hence Eq.(2.12) yields

$$\begin{aligned} \overline{(\Delta E)^2} &= -\frac{\partial \overline{E}}{\partial \beta} \\ \overline{(\Delta E)^2} &= \frac{\partial^2 \ln Z}{\partial \beta^2} \end{aligned} \tag{2.19}$$

Since $(\Delta E)^2$ can never be negative, it follows that $\frac{\partial \overline{E}}{\partial \beta} \leqslant 0$ or equivalently, that $\frac{\partial \overline{E}}{\partial T} \geqslant 0$ i.e., the absolute temperature of any system increases with its energy. It allows one to establish the general connection between absolute temperature and the direction of heat flow. Now

$$\overline{\Delta E^2} = -\left(\frac{\partial \overline{E}}{\partial T}\right)_v \frac{\partial T}{\partial \beta}$$

Where

$$C_v = \left(\frac{\partial \overline{E}}{\partial T}\right)_v \tag{2.20}$$

is the specific heat of the system at constant volume (system of interest is kept at constant volume). Hence

$$\delta E^2 = kT^2 C_v \tag{2.21}$$

Which is the required fluctuation-dissipation theorem i.e., "fluctuation of some quantity is related to a certain susceptibility of that quantity". The system is independent of the history i.e., if energy is given at a certain moment then width can be calculated easily using above Eq.(2.21) at that time without knowing previous history of energy change.

2.3 Quantum Analogue

To calculate energy fluctuations for a canonical ensemble of quantum mechanical systems one needs corresponding quantum canonical partition function. We here formulate quantum mechanical version of canonical partition function by following the approach given in [8]. Suppose the Hamiltonian H is a self adjoint operator with a discrete spectrum. The energy levels $\{E_n\}$ are then eigenvalues of H, corresponding to eigenvectors $|\psi_n\rangle$. From the same perspective as discussed for the classical system, the probability of a system from the whole ensemble to be in a particular state $|\psi_n\rangle$ is given as

$$p_n = Ce^{-\beta E_n} \tag{2.22}$$

Where C is some constant.

A "density matrix" is in general associated with any quantum mechanical ensemble. We can write density matrix for the above system as

$$\begin{aligned}\rho &= \sum p_n \left|\psi_n\right\rangle \left\langle\psi_n\right| \\ &= \sum Ce^{-\beta E_n} \left|\psi_n\right\rangle \left\langle\psi_n\right|\end{aligned}$$

For a density operator $Tr\left(\rho\right) = 1$ is always true, so we obain

$$Tr\left(\rho\right) = C\underbrace{\sum e^{-\beta E_n}}_{Q} = 1$$

Which implies that

$$C = \frac{1}{\sum e^{-\beta E_n}} = \frac{1}{Q}$$

Where

$Q =$ quantum mechanical counterpart of the canonical partition function

Now density matrix takes the form

$$\rho = \frac{\sum e^{-\beta E_n} \left|\psi_n\right\rangle \left\langle\psi_n\right|}{\sum e^{-\beta E_n}}$$

$\Rightarrow$

$$\rho = \frac{e^{-\beta H}}{Tr(e^{-\beta H})} \tag{2.23}$$

Since energy eigenvalues diverge, the corresponding operator is unbounded, so we can exponentiate the Hamiltonian H by invoking Borel functional calculus. Alternatively, one can simply assume that to be the exponential power series.

The quantity $Tr(e^{-\beta H})$ is the quantum mechanical version of the canonical partition function, a normalization factor for the state of interest. If A is a physical observable, then its expected value is given by the density matrix as

$$\langle A\rangle = Tr\left(\rho A\right) \tag{2.24}$$

Now expected value of H is

$$\begin{aligned} E &= \langle H \rangle \\ &= Tr\left(\rho H\right) \\ &= \frac{TrHe^{-\beta H}}{Tr(e^{-\beta H})} \\ &= \frac{TrHe^{-\beta H}}{Q} \end{aligned} \tag{2.25}$$

Taking derivative w.r.t. β

$$\begin{aligned} \frac{\partial \langle H \rangle}{\partial \beta} &= \frac{\partial}{\partial \beta}\left(\frac{TrHe^{-\beta H}}{Q}\right) \\ &= \frac{1}{Q} TrH \frac{\partial}{\partial \beta} e^{-\beta H} + TrHe^{-\beta H} \frac{\partial}{\partial \beta}\left(\frac{1}{Q}\right) \\ &= -\frac{TrH^2 e^{-\beta H}}{Q} - \frac{1}{Q^2} TrHe^{-\beta H} \frac{\partial Q}{\partial \beta} \\ &= -\frac{TrH^2 e^{-\beta H}}{Q} - \frac{TrHe^{-\beta H}}{Q^2} \frac{\partial}{\partial \beta}\left(Tre^{-\beta H}\right) \\ &= -\frac{TrH^2 e^{-\beta H}}{Q} + \frac{TrHe^{-\beta H} . TrHe^{-\beta H}}{Q^2} \end{aligned}$$

Hence

$$-\frac{\partial \langle H \rangle}{\partial \beta} = \langle H^2 \rangle - \langle H \rangle^2 = \delta E^2 \tag{2.26}$$

By using definition of patition function

$$\begin{aligned} \frac{\partial Q}{\partial \beta} &= \frac{\partial}{\partial \beta}\left(Tre^{-\beta H}\right) \\ &= -Tre^{-\beta H} H \\ &= -Q \langle H \rangle \end{aligned}$$

$\Rightarrow$

$$\begin{aligned} \langle H \rangle &= -\frac{1}{Q}\frac{\partial Q}{\partial \beta} \\ &= -\frac{\partial}{\partial \beta}\ln Q \end{aligned} \tag{2.27}$$

$$\frac{\partial \langle H \rangle}{\partial \beta} = -\frac{\partial^2}{\partial \beta^2}\ln Q \tag{2.28}$$

Comparing Eq.(2.26) and Eq.(2.28) we get

$$\delta E^2 = \frac{\partial^2}{\partial \beta^2}\ln Q \tag{2.29}$$

By using Eq.(2.20) and Eq.(2.27) we have

$$C_v = \frac{\partial E}{\partial T} = \frac{\partial E}{\partial \beta}\frac{\partial \beta}{\partial T} = -\beta^2\frac{\partial E}{\partial \beta} = \beta^2\frac{\partial^2 \ln Q}{\partial \beta^2}$$

$\Rightarrow$

$$\frac{\partial^2 \ln Q}{\partial \beta^2} = T^2 C_v$$

By using the above result in Eq.(2.29)

$$\delta E^2 = kT^2 C_v \tag{2.30}$$

Hence for a quantum mechanical system we get the same result as Eq.(2.21), showing that energy fluctuations in a thermally isolated system, brought into contact with a heat bath are independent of the microscopic details of the system and also the interactions between the system and bath. Energy fluctuations are universal and independent of the history as at any instant can be calculated with just the value of energy at that time using above relation Eq.(2.30).

2.4 Results

- The magnitude of fluctuations in a constant temperature system are dependent just on the macroscopic heat capacity. This expression is valid for any system, since no approximations were involved in its derivation.

- Since C_v and E both are extensive (i.e., growing linearly with the size of the system) we find

$$\begin{aligned}\frac{\Delta E}{\overline{E}} &= \frac{\sqrt{C_v k_B T^2}}{\overline{E}} \\ \frac{\Delta E}{\overline{E}} &\sim \frac{\sqrt{N}}{N} \\ \frac{\Delta E}{\overline{E}} &\sim \frac{1}{\sqrt{N}}\end{aligned} \tag{2.31}$$

In other words, relative magnitude of fluctuations decreases as the inverse square root of the system size. For macroscopic systems (large N) we can imagine the internal energy to be well defined when the system is in thermal contact with a heat bath even though, of course, it is only absolutely precisely determined for an isolated system.

- In thermodynamical limit ($N \to \infty$), we see that the relative width becomes very small, therefore, we expect the system to be almost the same of that in the microcanonical ensemble (where energy is actually constant). This result is usually referred to as "equivalence of ensembles".

- When bath is large enough as compared to the system energy distribution becomes Gaussian (explained by Eq.(2.10)) with a canonical width given by Eq.(2.21) and Eq.(2.30), as shown in the graph below.

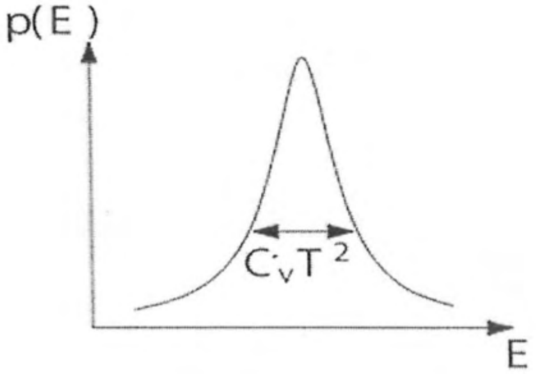

Figure 2-2: Graphical representation of energy distribution for a system equilibrating with a reservoir

Chapter 3

Driven Isolated Systems

3.1 Introduction

In this chapter we consider a thermally isolated system which is driven away from its equilibrium state by an external parameter e.g., electromagnetic field in the case of microwave or the motion of piston. The drive leads to an uncertainity in the final energy of the system. **Bunin**, **Alessio**, **Kafri** and **Anatoli** [9] showed that when the changes in energy are small and slow (but still irreversible) the energy fluctuations are insensitive to almost all microscopic details of the system (universal), depending only on the average energy flow from the drive to the system as a function of time and on the density of states. They predicted the existence of two qualitatively different regimes with a continuous second order like transition between them. Later they proved the same results by using quantum Crooks fluctuation theorem.

3.2 Basic Formalism For The Calculation Of Energy Fluctuations

3.2.1 System's Description

Consider a thermally isolated system undergoing a repeated cyclic process e.g., piston in (fig. 3-1) is moved with a given cyclic protocol. In adiabatic limit quasistatically there is no opportunity for significant heat exchange so energy will remain constant every time cycle is

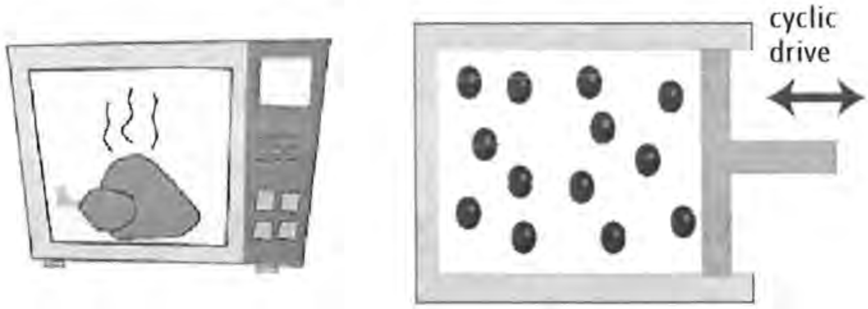

Figure 3-1: Schematic representation of a thermally isolated system subjected to external driving protocol i.e., motion of the piston (microwave oven)

is completed (see fig. 3-2a). But in our case non-adiabatic limit (non-quasistatic change) the dynamics of the system are effected by the detailed microscopic state and repeating the same experiment will lead to different out comes. Specifically, a measurement of the energy as a function of time will yield different results (see fig. 3-2b). The variations between experiments could be averaged out in large thermodynamic systems (see fig. 3-2c), or when driving protocol applied is quasi-static. However they can be significant when the drive is not quasi-static (system is not in equilibrium during the process) and in small or for mesoscopic systems.

3.2.2 Fundamental Questions

The following fundamental questions are of interest in this review:

1. Which features of the energy distribution are universal and which features depend on details of the system and driving protocol?
2. To what extent can the width of the distribution be controlled? e.g., can one dynamically increase the energy of an isolated system without increasing the uncertainity in the final energy?
3. Can the fluctuation-dissiation relations, which determine the energy width in the oven-like setup, be extended to the microwave-like setup?
4. What is the width of the final energy distribution and shape of the graph.

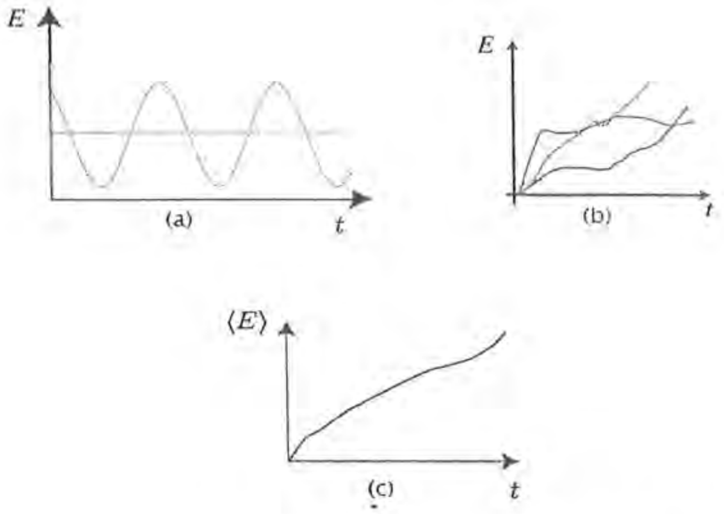

Figure 3-2: Variance in energy distribution for repeated experiments for (a): adiabatic process (b) irreversible process (c) results in (b) averaged for large systems

3.2.3 Derivation Of Main Result

Bunin, **Alessio**, **Kafri** and **Anatoli** found answer to the above questions in [9]. They formulated an expression for the energy fluctuations in such systems by taking into account Fokker-Planck equation, from which they derived generalized fluctuation-dissipation relation and then by invoking saddle-point approximation the main result for the energy fluctuations is obtained. Here I will review their approach step by step as below.

How Does a Fokker-Planck Equation Arise? What is Purpose of using it?

Introduction In case of Brownian motion we have to solve all the microscopic equations of the system in order to find a complete solution of a macroscopic system. It is very tedious to follow this formalism so we use a stochastic description, i.e., we state the system by macroscopic parameters which variate in a stochastic way. The Fokker-Planck equation is just an equation of motion for the distribution function of fluctuating macroscopic variables. The Fokker-Planck equation is of course not the only equation of motion for the distribution function. There exist other equations like the Boltzmann equation and master equation. The Fokker-Planck equation is one of the simplest equations for continuous macroscopic variables. It usually appears for variables describing a macroscopic but small subsystem, like the position and velocity for the Brownian motion of a small particle, a current in an electrical circuit, the electrical field in a laser and energy in our case of single isolated driven system. If the subsystem is larger the fluctuations may then usually be neglected and thus one has a deterministic equation. In those cases, however, where the deterministic equations are not stable, a stochastic description is then necessary even for large systems [10].

Derivation of Fokker-Planck Equation Instead of inquiring simply how mean value of energy E changes with time t, according to [7] I take into account more detailed question concerning the time dependence of the probability $P(E,t)\,dE$ that the energy at time t lies between E and $E + dE$. It is assumed that the probability does not depend on the entire past history and can be determined if one knows $E = E_\circ$ at some earlier time $t_\circ$ (Markoff process). The importance of Markoff process is not that all physical processes are Markoff, but that the analysis of a markoff process is considerably simpler.

Explicitly P can be written as a conditional probability which depends on $E_\circ$ and $t_\circ$ as parameters i.e.,

$$PdE = P\left(Et'/E_\circ t_\circ\right) dE \tag{3.1}$$

The above equation gives the probability with which the energy of the system lies between E and $E + dE$ at time t' if it is known that the energy is $E_\circ$ at some earlier time $t_\circ$. Since nothing in this problem depends on the origin from which the time is measured, P can actually only depend on time difference $t = t' - t_\circ$. Thus to denote the probability that, if the energy has the value $E_\circ$ at any time, it assumes a value between E and $E + dE$ after a time t one can simply write as

$$P\left(Et'/E_\circ t_\circ\right) dE = P\left(E, t/E_\circ\right) \tag{3.2}$$

If $t \to 0$

$$P\left(E, t/E_\circ\right) \to \delta\left(E - E_\circ\right) \tag{3.3}$$

Where dirac delta function on the right side vanishes unless $E = E_\circ$.

On the other hand, if $t \to \infty$, the system must come to equilibrium at temperature T, irrespective of its past history. P then becomes independent of $E_\circ$ and also independent of time; i.e., it reduces to canonical distribution. Thus for $t \to \infty$

$$P\left(E, t/E_\circ\right) dE \to e^{-\beta E} dE \tag{3.4}$$

One can readily write down a general condition that must be satisfied by the probability $P\left(E, t/E_\circ\right)$. In any small time interval τ (driving time), the increase in the probability that the energy lies between E and $E + dE$ must be equal to the decrease in this probability owing to the fact that originally with energy E and $E + dE$, now has a probability $P\left(E', \tau/E\right) dE'$ of changing its energy to any other value between E' and $E' + dE'$ plus the increase in this probability owing to the fact that originally with an energy in any range between E' and $E' + dE'$ has a probability $P\left(E, \tau/E'\right) dE$ of changing its energy to a value in the original range between E and $E + dE$. In symbolic notation this condition becomes

$$\frac{\partial P}{\partial t} dE.\tau = -\int_{E'} P\left(E, t/E_\circ\right) dE \cdot P\left(E', \tau/E\right) dE' + \int_{E'} P\left(E', t/E_\circ\right) dE' \cdot P\left(E, \tau/E'\right) dE \tag{3.5}$$

Where the integral extends over all possible energies E'. The above equation is called "master equation". It is worth noting that all terms in the above equation are real and the time enters linearly in the first derivative, hence master equation does not remain invariant as the sign of the time is reversed i.e., as $t \to -t$. This equation therefore describes the irreversible behaviour of a system.

In the first integral of Eq.(3.5), $P\left(E, t/E_\circ\right)$ does not depend on E', while $P\left(E', \tau/E\right)$ is a properly normalized probability i.e.,

$$\int_{E'} P\left(E', \tau/E\right) dE' = 1 \tag{3.6}$$

By putting $E' = E - \omega$, Eq.(3.5) then becomes

$$\frac{\partial P}{\partial t}.\tau = -P\left(E, t/E_\circ\right) + \int_{-\infty}^{+\infty} P\left(E - \omega, t/E_\circ\right) \cdot P\left(E, \tau/E - \omega\right) d\omega \tag{3.7}$$

In Eq.(3.7) energy can change abruptly by a very large amount but we are considering the generic case of small work per cycle so energy E can only change by a small amount during the small time interval τ. Hence one can assert that the probability $P(E,\tau/E-\omega)$ can only be appericiable when $|\omega| = |E'-E|$ is sufficiently small. A knowledge of the integrand of Eq.(3.7) for small values of ω should then be sufficient for evaluating the integral. Hence it should be permissible to expand this integrand in a Taylor's series in power of ω about the value $P(E,t/E_\circ)\,P(E+\omega,\tau/E)$ and to retain only the lowest order terms. This expansion becomes

$$P(E-\omega,t/E_\circ)\cdot P(E,\tau/E-\omega) = \sum_{n=0}^{\infty}\frac{(-\omega)^n}{n!}\frac{\partial^n}{\partial E^n}\left[P(E,t/E_\circ)\,P(E+\omega,\tau/E)\right]$$

Hence Eq.(3.7) becomes

$$\frac{\partial P}{\partial t}.\tau = -P(E,t/E_\circ) + \sum_{n=0}^{\infty}\frac{(-1)^n}{n!}\frac{\partial^n}{\partial E^n}\left[P(E,t/E_\circ)\int_{-\infty}^{+\infty} d\omega\cdot\omega^n\cdot P(E+\omega,\tau/E)\right] \quad (3.8)$$

The term $n=0$ in the sum is simply $P(E,t/E_\circ)$ by virtue of the normalization condition in Eq.(3.6). As for the other terms, it is convenient to introduce the abbreviation

$$M_n = \frac{1}{\tau}\int_{-\infty}^{+\infty} d\omega\cdot\omega^n\cdot P(E+\omega,\tau/E) = \frac{\langle[\Delta E(\tau)]^n\rangle}{\tau} \quad (3.9)$$

Where $\langle[\Delta E(\tau)]^n\rangle = \langle[E(\tau)-E(0)]^n\rangle$ is the nth moment of energy increament in time τ. Eq.(3.8) then becomes

$$\frac{\partial P(E,t)}{\partial t} = \sum_{n=1}^{\infty}\frac{(-1)^n}{n!}\frac{\partial^n}{\partial E^n}\left[M_n\cdot P(E,t/E_\circ)\right] \quad (3.10)$$

But when $\tau\to 0$, $[\Delta E(\tau)]^n\to 0$ more rapidly than τ itself if $n>2$. The terms involving M_n with $n>2$ can therefore be neglected in Eq.(3.10). Hence this equation for $P(E,t)$ reduces to

$$\frac{\partial P(E,t)}{\partial t} = -\frac{\partial}{\partial E}(M_1P) + \frac{1}{2}\frac{\partial^2}{\partial E^2}(M_2P) \quad (3.11)$$

This is the so-called "Fokker-Planck" equation. It is a partial differential equation for

$P(E,t)$ and involves as coefficients only the two moments M_1 and M_2 of $P(E,t)$ evaluated for a macroscopically infinitesimal time interval τ.

Moments in terms of Cumulants In probability theory and statistics, the cumulants of a probability distribution are a set of quantities that provide an alternative to the moments of the distribution. The moments determine the cumulants in the sense that any two probability distributions whose moments are identical will have identical cumulants as well, and similarly the cumulants determine the moments. In some cases theoretical treatments of problems in terms of cumulants are simpler than those using moments.

The first four cumulants are called the mean, variance, skewness, and curtosis (kurtosis) of the distribution, respectively, and are obtained from the moments as

$$\begin{aligned}
\langle \omega \rangle_c &= \langle \omega \rangle \\
\langle \omega^2 \rangle_c &= \langle \omega^2 \rangle - \langle \omega \rangle^2 \\
\langle \omega^3 \rangle_c &= \langle \omega^3 \rangle - 3\langle \omega^2 \rangle \langle \omega \rangle + 2\langle \omega \rangle^3 \\
\langle \omega^4 \rangle_c &= \langle \omega^4 \rangle - 4\langle \omega^3 \rangle \langle \omega \rangle - 3\langle \omega^2 \rangle^2 + 12\langle \omega^2 \rangle \langle \omega \rangle^2 - 6\langle \omega \rangle^4
\end{aligned} \tag{3.12}$$

The cumulants provide a useful and compact way of describing a PDF.

In our case first two cumulants are of interest i.e.,

$$\begin{aligned}
A(E) &= \langle \omega \rangle \\
B(E) &= \langle \omega^2 \rangle_c = \langle \omega^2 \rangle - \langle \omega \rangle^2
\end{aligned} \tag{3.13}$$

Here

$A(E)$ = average work per cycle

$B(E)$ = variance of average work per cycle

As its clear that $A(E)$ and $B(E)$ are protocol dependent functions and are a priori independent from each other. Now Eq.(3.11) in terms of cumulants can be expressed as

$$\partial_t P = -\partial_E (AP) + \frac{1}{2}\partial_E^2 (BP) \tag{3.14}$$

The change of the energy distribution in one cycle of the protocol is obtained by integrating above equation over the duration of one protocol, set for simplicity to be unity. Hence under the generic assumptions of absence of correlations between cycles and small work per cycle the time evolution of the probability distribution $\dot{P}(E,t)$ of a thermally isolated driven system is given by the Eq.(3.14).

Fluctuation-dissipation Relation between $A(E)$ and $B(E)$

Given the importance of the Fokker-Planck equation, different analytical and numerical methods have been proposed for its solution. The study of the time-dependent solution is a much more complicated problem. It is well known, that the stationary solution of Fokker-Planck equation can be given in a closed form if the condition of detailed balance holds which states that: "Rate of occurrence of any transition equals the corresponding rate of occurrence of the inverse transition". If we take $P \to P_{st}$; $\frac{\partial P_{st}}{\partial t} = 0$ according to Eq.(3.5) condition of detailed balance holds. Since transition probabilities are dynamical quantities which do not depend on whether the system is in equilibrium or not so the same definition of detailed balance must be quite generally valid even if the system is out of equilibrium.

As a consequence of the global conservation of probabilities i.e., the nomalization $\int P(E)\,dE = 1$ Eq.(3.14) can be written as a conservative law

$$\frac{\partial P}{\partial t} + \frac{\partial J}{\partial E} = 0 \tag{3.15}$$

Where the probability current is given by

$$J = -(AP) + \frac{1}{2}\partial_E (BP) \tag{3.16}$$

In long time limit the distribution P approaches a stationary distribution P_{st}. According to natural boundary conditions i.e., for a closed isolated system we must have $J = 0$, but

$P_{st} = c\Omega\left(E\right)$ so

$$\begin{aligned} AP_{st} &= \frac{1}{2}\partial_E\left(BP_{st}\right) \\ &= \frac{P}{2}\partial_E B + \frac{B}{2}\partial_E P \end{aligned}$$

$\Rightarrow$

$$A = \frac{1}{2}\partial_E B + \frac{B}{2}\frac{1}{P}\partial_E P$$

$$A = \frac{1}{2}\partial_E B + \frac{B}{2}\partial_E\left(\ln P\right) \tag{3.17}$$

By using microcanonical temperature $\beta\left(E\right) = \partial_E \ln \Omega\left(E\right)$; where $\Omega\left(E\right)$ is the density of states, we get the fluctuation-dissipation relation

$$2A = \partial_E B + \beta B \tag{3.18}$$

In general, $A\left(E\right)$ and $B\left(E\right)$ are independent from each other but individually both depend on the driving protocol. As system is thermally isolated its evolution is described by the hamilton's equations of motion giving Eq.(3.15) in the above case. This provides a relationship between $A\left(E\right)$ and $B\left(E\right)$ as shown in the above Eq.(3.18) putting strong restriction on their dependence on each other.

Now to calculate variance in energy $\sigma^2 = \left\langle E^2\right\rangle - \left\langle E\right\rangle^2$, we first multiply Eq.(3.14) by E and E^2 and integrate over all energies. In this way we get the differential equations describing the time evolution of $\left\langle E\right\rangle$ and σ^2

$$\partial_t\left\langle E\right\rangle =.\left\langle A\left(E\right)\right\rangle \tag{3.19}$$

and

$$\partial_t\sigma^2 = \left\langle B\right\rangle + 2\left(\left\langle A\left(E\right)E\right\rangle - \left\langle A\left(E\right)\right\rangle\left\langle E\right\rangle\right) \tag{3.20}$$

Eq.(3.19) and Eq.(3.20) can be combined into a single equation:

$$\frac{\partial\sigma^2}{\partial\langle E\rangle}=\frac{\langle B\rangle+2\left(\langle A\left(E\right)E\rangle-\langle A\left(E\right)\rangle\langle E\rangle\right)}{\langle A\left(E\right)\rangle} \tag{3.21}$$

For narrow energy distributions $P\left(E\right)$, as in the case of large systems, the averages above can be evaluated using a saddle-point approximation and we find

$$\frac{\partial\sigma^2}{\partial\langle E\rangle}=2\beta^{-1}\left(\langle E\rangle\right)+2\frac{\partial_E A\left(\langle E\rangle\right)}{A\left(\langle E\rangle\right)}\sigma^2\left(\langle E\rangle\right) \tag{3.22}$$

Integrating this equation immidiately yields the main result giving the variance of energy distribution $\sigma^2\left(E\right)$ at energy E :

$$\sigma^2\left(E\right)=\sigma_\circ^2\frac{A^2\left(E\right)}{A^2\left(E_\circ\right)}+2A^2\left(E\right)\int_{E_\circ}^{E}\frac{dE'}{A^2\left(E'\right)\beta\left(E'\right)} \tag{3.23}$$

Where

$\sigma_\circ^2$ = initial variance

$E_\circ$ = initial energy of the system

$\beta\left(E\right)=\partial_E\ln\Omega\left(E\right)$ = microcanonical temperature

$\Omega\left(E\right)$ = density of states

$A\left(E\right)$ = average energy change in a cycle at energy E

3.2.4 Regime of validity

Let us now comment on the regime of validity of Eq.(3.23). Since the derivation of Eq.(3.23) is based on the Fokker-Plank equation Eq. (3.14), fluctuation-dissipation relation Eq.(3.18) and saddle-point approximation Eq.(3.22) we discuss validity of each according to [9] as below:

- The validity of Fokker-Planck equation relies on the assumption that the work distribution is narrow and the average work for cycle is small. Two necessary conditions justifying the Fokker-Planck equation Eq.(3.14) and the fluctuation-dissipation relation Eq.(3.18) are:

  (i) The third (and higher order) cumulant of work per cycle are small

$$\left\langle\omega^3\right\rangle_c\ll\langle\omega\rangle=A(E).$$

(ii) The average work per cycle is smaller than the product of temperature and the specific heat C_v:

$$\langle\omega\rangle = A(E) \ll TC_v$$

- Saddle-point approximation in Eq. (3.22) is justified if the energy fluctuations in the system are small. This is the case in large or mesoscopic extensive systems.
- Our derivation implicitly relies on the assumption of ergodicity within the system.

3.2.5 Classes of energy distribution:

The dependence of σ^2 on E displays two qualitatively distinct behaviors with increasing E, depending on whether the integral in Eq.(3.23) diverges or converges as $E \to \infty$ as discussed in [9]. To clearify the different behaviours associated with the dependence of σ^2 on E we follow Bunin, Alessio, Kafri and Anatoli's approach by taking into account the generic case:

$$\beta \propto E^{-\alpha} \qquad\qquad 0 < \alpha \leq 1 \tag{3.24}$$

Where lower limit is required by the fact that the specific heat is always of positive value and upper limit makes sure that the entropy is an increasing unbound function of energy i.e.,$S(E) \propto E^{1-\alpha}$. Time and number of cycles are interchangeable i.e., time is measured in the units of number of cycles carried out.

We also assume a power law behaviour for $A(E)$ as

$$\partial_t(E) = A(E) = cE^s \quad \text{with} \quad s \leq 1 \tag{3.25}$$

Here the limit on s prevents the energy of the system from diverging in a finite time.

Qualitatively We take $\sigma_0^2(E) = 0$

As the energy increases $(E \to \infty)$ the integral in Eq.(3.23):

- Diverges if $2s - \alpha < 1 \Rightarrow$

$$\sigma^2(E) \sim \frac{E}{\beta(E)} \tag{3.26}$$

i.e., protocol independent.

- Converges if $2s - \alpha > 1 \Rightarrow$

$$\sigma^2(E) \sim A^2(E) \tag{3.27}$$

i.e., protocol dependent.

Quantatively We define

$$\eta = 2s - \alpha - 1 \tag{3.28}$$

Also equilibrium canonical width for the above assumptions Eq.(3.24) and Eq.(3.25) becomes

$$\sigma_{eq}^2 = T^2 C_v = -\frac{\partial E}{\partial \beta} \sim \frac{E^{1+\alpha}}{\alpha} \tag{3.29}$$

Depending on the sign of η Eq.(3.23) implies:

Case: 1 When $\eta < 0$;

Using above all approximations in Eq.(3.23) and for simplicity assuming $\sigma_\circ^2 = 0$ and $E_\circ = 0$, we get

$$\begin{aligned} \sigma^2(E) &\sim 2E^{2s} \int_0^E \frac{dE'}{E'^{2s-\alpha}} \\ &\sim \frac{2E^{\alpha+1}}{|\eta|} \end{aligned} \tag{3.30}$$

Comparing the width to the equilibrium canonical width

$$\frac{\sigma^2}{\sigma_{eq}^2} \sim \frac{2\alpha}{|\eta|}$$

The width is Gibbs-like with $\frac{\sigma^2}{\sigma_{eq}^2} \rightarrow \frac{2\alpha}{|\eta|}$, i.e. the ratio $\frac{\sigma^2}{\sigma_{eq}^2}$ asymptotically approaches a constant value that can be either larger or smaller than 1.

Case: 2 When $\eta > 0$;

Here $\sigma_\circ^2 = \frac{2}{\eta} E_\circ^{\alpha+1}$

Eq.(3.23) takes the form

$$\sigma^2(E) \sim \frac{2}{\eta} E_\circ^{\alpha+1} \left(\frac{E}{E_\circ}\right)^{2s} \tag{3.31}$$

Comparing the width to the equilibrium canonical width σ_{eq}^2

$$\frac{\sigma^2}{\sigma_{eq}^2} \sim \frac{2\alpha}{\eta} \left(\frac{E}{E_\circ}\right)^{\eta} \tag{3.32}$$

i.e., the run-away regime as width increases with a higher power of energy than the canonical width: $\frac{\sigma^2}{\sigma_{eq}^2} \sim E^\eta$. The resulting distribution is significantly wider than the canonical one. Given the constraints on the value of s, this regime can only be reached if $\alpha < 1$, in particular this regime is unreacheable for the classical ideal gas.

Case: 3 When $\eta = 0$;

$\Rightarrow 2s = \alpha + 1$

Here transition between Gibbs-like and run-away regimes occur.(critical point)

Eq.(3.23) takes the form

$$\begin{aligned} \sigma^2(E) &\sim 2E^{\alpha+1} \int_0^E \frac{dE'}{E'} \\ &\sim 2E^{\alpha+1} \log\left(\frac{E}{E_\circ}\right) \end{aligned} \tag{3.33}$$

Comparing the width to the equilibrium canonical width σ_{eq}^2

$$\frac{\sigma^2}{\sigma_{eq}^2} \sim 2\alpha \log\left(\frac{E}{E_\circ}\right) \tag{3.34}$$

TABLE

regime	condition	width
Gibbs-like	$\eta < 0$	$\frac{2\alpha}{\lvert\eta\rvert}$
run-away	$\eta > 0$	$\frac{2\alpha}{\eta}\left(\frac{E}{E_\circ}\right)^{\eta}$
critical	$\eta = 0$	$2\alpha \log\left(\frac{E}{E_\circ}\right)$

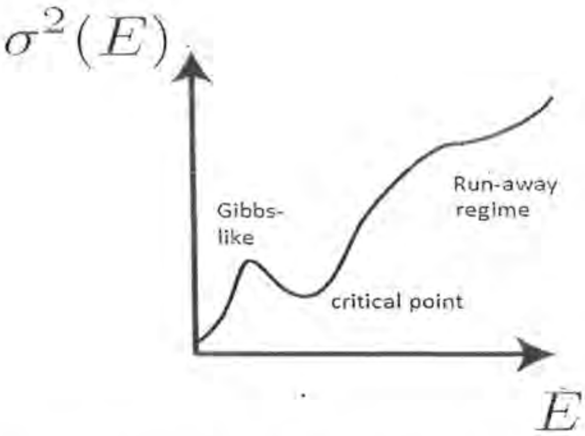

Figure 3-3: Schematic representation of energy distribution for a single isolated driven system.

3.3 Examples

3.3.1 Single particle in a driven chaotic cavity

Let us consider a single particle that is bouncing elastically in a chaotic cavity. When the cavity is not driven externally i.e., in stationary condition the energy of the particle is conserved. Since the cavity is chaotic (of irregular or random shape) there are no other conserved quantities. It is stated that in such a cavity when no drive is applied after a long time limit the particle slows down to a uniform position distribution and an isotropic momentum distribution. Here we consider that the cavity is driven by a cyclic process which deforms it between the two shapes shown in the above figure (see Fig. 3.4) such that at the end of each cycle the cavity returns to its original shape and the system relaxes as described above for a stationary cavity. Let N is the number of degrees of freedom such that $N = 2d$ where d stands for the number of dimensions of the system. In a single collision with the moving wall the particle's kinetic energy can either increase or decrease but on average it will always increase and finally the velocity of the particle will become much larger than that of the wall. Since the work per cycle is associated with the velocity of the wall it will automatically become small and the conditions for the validity of the Fokker-Planck equation are satisfied that are small work per cycle and relaxation time of subsystem is less than that of drive.

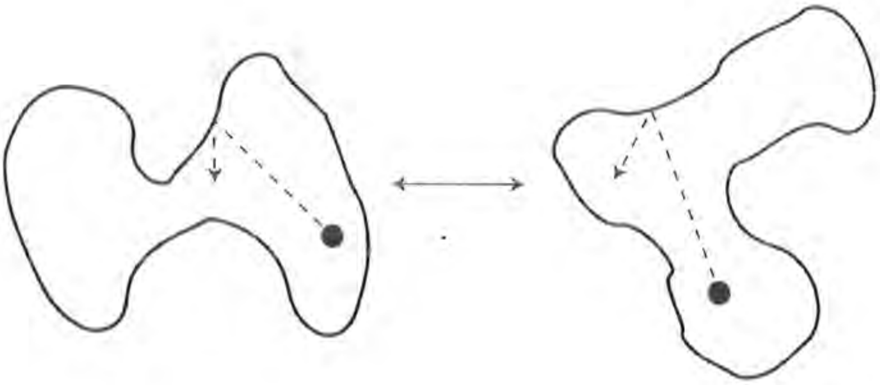

Figure 3-4: An illustration of a single particle bouncing in a deforming cavity of constant volume. The driving protocol consists in repeatedly deforming the cavity between the two shapes shown.

If the cavity is sufficiently chaotic successive collisions are uncorrelated and the formalism holds even if the waiting time between cycles approaches zero. In this case the fundamental equation for the energy distribution, $P(E)$, assumes the Fokker-Planck form of Eq.(3.14) and Jarzynski after a tedious calculation found expression for $A(E)$ and $B(E)$ [16]. Here our purpose is just to check the validity of our approach for such systems so we directly take these values that are

$$A(E) = cE^{1/2} \tag{3.35}$$

$$B(E) = \frac{4c}{d+1}E^{3/2} \tag{3.36}$$

Where c contains information about the mass of the particle, the area or volume of the container and the velocity of the moving walls. Then by Eq.(3.18) we can calculate $\beta(E)$ as

$$\begin{aligned}
\beta B(E) &= 2c\dot{E}^{1/2} - \frac{4c}{d+1}\partial_E E^{3/2} \\
\beta B(E) &= 2cE^{1/2} - \frac{6c}{d+1}E^{1/2} \\
\beta \frac{4c}{d+1}E^{3/2} &= 2cE^{1/2}\left[\frac{d-2}{d+1}\right] \\
\beta &= \frac{d-2}{2E}
\end{aligned} \tag{3.37}$$

Now by comparing Eq.(3.24) and Eq.(3.25) with Eq.(3.35) and Eq.(3.37) we get

$$\alpha = 1 \text{ and } s = 1/2 \tag{3.38}$$

Using these values in Eq.(3.28) we have $\eta = 1$ so we invoke the relation Eq.(3.32) i.e., for $\eta > 0$, this gives

$$\frac{\sigma^2}{\sigma_{eq}^2} \rightarrow 2 \tag{3.39}$$

This result is identical to the single particle result as obtained in [18].

3.3.2 Single particle in a time dependent potential

As a second example we consider a single classical particle in a harmonic trap. This setup explains that how a system could be drived with a local perturbation which in general acting independently on many different particles. Let our particle is a part of a larger system, which could be a set of N identical particles (see fig. 3.5). The energy of the entire system is taken as (E) and the corresponding microcanonical temperature is defined by $\beta(E)$. Within the duration of a cycle, the coupling to the rest of the system is assumed weak and unimportant similar to the example of weakly-interacting particle gas as described above. The particle's energy ε between cycles is given by

$$\varepsilon = \frac{1}{2}kx^2 + \frac{1}{2}mv^2 \tag{3.40}$$

For simplicity we work in one dimension. For large N the probability distribution for (x, v)

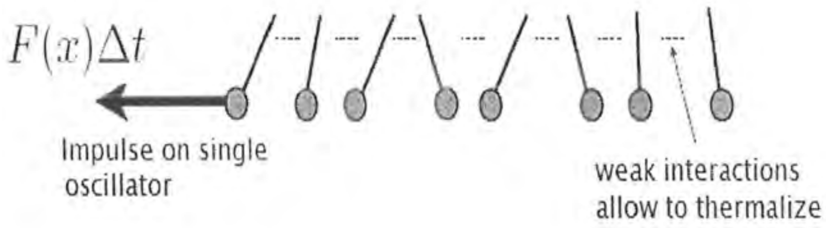

Figure 3-5: An illustration of a single particle that is trapped in a harmonic trap.

before the drive is

$$\rho(x, v) \propto \exp\left(-\beta(E)\varepsilon\right) \tag{3.41}$$

We consider that an impulse of magnitude $F(x)\Delta t$ is acting on the particle as a driving protocol for a time interval of t. The driving time is short enough so that the change in the position of the particle is insignificant which further assures weak coupling to the rest of the system during a cycle. Under the action of this impulse the velocity of the particle changes from v to $v + F(x)\Delta t$. By averaging over initial positions in Eq.(3.40) we obtain $\left[(v + F(x)\Delta t)^2 - v^2\right]$ from where the first and second cumulants of the work $A(E)$ and $B(E)$ can be calculated as:

$$\begin{aligned} \langle\omega\rangle &= A(E) = \left\langle (F(x))^2 \right\rangle \Delta t^2 && (3.42) \\ \left\langle\omega^2\right\rangle_c &= B(E) = \frac{2}{\beta}\left\langle (F(x))^2 \right\rangle \Delta t^2 && (3.43) \end{aligned}$$

The above two verify the fluctuation-dissipation relation Eq.(3.18). Since we are essentially dealing with a quasi-static process we can describe the evolution of the energy by a Fokker-Planck equation Eq.(3.14) that for a system satisfying fluctuation-dissipation relation Eq.(3.18) takes the form Eq.(3.23) as discussed earlier.

Now by taking $\beta \propto E^{-\alpha}$ and $F(x) \propto x^r$ we find using Eq.(3.42)

$$A(E) \propto \langle x^{2r} \rangle \propto \varepsilon^r \propto E^{\alpha r} \tag{3.44}$$

Using Eq.(3.25) we have $s = \alpha r$; then Eq.(3.28) implies that

$$\eta = 2\alpha r - 1 - \alpha \tag{3.45}$$

Now different values of η can be obtained using different impulse forces and systems.

For example, for a system with $\alpha = 1/2$, such as fermi liquid or a one-dimensional harmonic system

- with $r = 1$; we obtain $\eta = -1/2$ leading to the Gibbs-like regime Eq.(??) with

$$\frac{\sigma^2}{\sigma^2_{eq}} \rightarrow 2$$

- with $r = 3/2$; we obtain $\eta = 0$ we are at critical point Eq.(3.34).
- with $r = 2$; we obtain $\eta = 1/2$ leading to the run-away regime Eq.(3.32) with

$$\frac{\sigma^2}{\sigma^2_{eq}} \sim E^{1/2} \tag{3.46}$$

3.4 General derivation via Quantum Crooks equality

3.4.1 Extended Crooks Relation for repeated cycles

In order to show the validity of Crooks fluctuation theorem [6] for isolated driven system we simply follow D. Cohen and Y. Imry's approach [11]. In this paper they have derived Crook's equality for a system that is almost equivalent to our sytem. They took a system that was initially prepared in thermal equilibrium at temperature T. This could be done easily by connecting the system to a reservoir of that temperature for a long time. The system starts equilibrating with the bath untill its temperature becomes equal to that of the bath. After that the system is subjected to a work process. During this an agent changes the value of X from X_0 to X_1. Here X is a variable that is coupled linearly to an observable of the system. Let

$H(X(t))$ denotes the Hamiltonian of the system and is described by a time dependent control parameter X. At $t = t_0$ the system is . During the work process dissipation of some heat Q into the bath is always possible. But here we consider the simplest scenario that the system is isolated, and heat flow is not involved. At the end of the work process the system is in non-equilibrium state.

Let at $t = t_0$ the system is in an eigenstate $n^{(0)}$ of $H(X_0)$, but at later time $t = t_1$, when the working agent changes the value of X from X_0 to X_1, the system shifts to an eigenstate $m^{(1)}$ of $H(X_1)$. Let us take

$$\omega = E_m^{(1)} - E_{(n)}^{(0)} \tag{3.47}$$

Where $E_m^{(1)}$and $E_{(n)}^{(0)}$ are the eigenvalues corresponding to the eigenstates $m^{(1)}$ and $n^{(0)}$ respectively.

Since an isolated system is always described by a unitary evolution so the transition probability between the eigenstates $m^{(1)}$ and $n^{(0)}$ could be expressed in the following way

$$P_{0\rightsquigarrow 1}(m|n) = \left|\left\langle m^{(1)} \left|U_{0\rightsquigarrow 1}\right| n^{(0)}\right\rangle\right|^2 \tag{3.48}$$

Where

U = time-evolution operator

The power spectrum of the fluctuations of an observable A is given by the following spectral decomposition

$$\widetilde{S}(\omega) = \sum_{n,m} p_n \left|\langle m\left|A\right| n\rangle\right|^2 \delta\left(\omega - (E_m - E_n)\right) \tag{3.49}$$

For a canonical preparation we take

$$p_n = \frac{1}{Z} e^{-\frac{E_n}{T}} = \exp\left[-\frac{E_n - F(X_0)}{T}\right] \tag{3.50}$$

Where

Z = partition function

$F(X)$ = Helmholtz free energy at temperature T

In Eq.(3.49) and Eq.(3.50) we have assumed a stationary preparation that can be taken as a mixture of eigenstates with weights p_n. Here we have taken a time independent Hamiltonian and calculated p_n for the fixed value of the control parameter X. In complete analogy with Eq.(3.49) we define the spectral kernel for our time dependent Hamiltonian $H(X(t))$ as follows:

$$P_{o \rightsquigarrow 1}(\omega) = \sum_{n,m} p_n^{(0)} P(m|n)\, \delta\left(\omega - \left(E_m^{(1)} - E_n^{(0)}\right)\right) \tag{3.51}$$

Here the superscript indicates whether we refer to the initial Hamiltonian $H(X_0)$ or to the final Hamiltonian $H(X_1)$. For the reversed process we write

$$P_{1 \rightsquigarrow 0}(\omega) = \sum_{n,m} p_m^{(1)} P_{1 \rightsquigarrow 0}(n|m)\, \delta\left(\omega - \left(E_n^{(1)} - E_m^{(0)}\right)\right) \tag{3.52}$$

In analogy with the usual detailed balance condition, taking the ratio of the spectral functions $P_{o \rightsquigarrow 1}(\omega)$ and $P_{1 \rightsquigarrow 0}(\omega)$:

$$\frac{P_{o \rightsquigarrow 1}(\omega)}{P_{1 \rightsquigarrow 0}(\omega)} = \frac{\sum_{n,m} p_n^{(0)} P_{o \rightsquigarrow 1}(m|n)\, \delta\left(\omega - \left(E_m^{(1)} - E_n^{(0)}\right)\right)}{\sum_{n,m} p_m^{(1)} P_{1 \rightsquigarrow 0}(n|m)\, \delta\left(\omega - \left(E_n^{(1)} - E_m^{(0)}\right)\right)} \tag{3.53}$$

Using the condition of microreversibility of dynamics which requires

$$P_{o \rightsquigarrow 1}(m|n) = P_{1 \rightsquigarrow 0}(n|m) \tag{3.54}$$

So Eq.(3.53) becomes

$$\frac{P_{o \rightsquigarrow 1}(\omega)}{P_{1 \rightsquigarrow 0}(\omega)} = \frac{p_n^{(0)}}{p_m^{(1)}} \tag{3.55}$$

The initial probabilities $p_n^{(0)}$ and $p_m^{(1)}$ are given by Eq.(3.50) as

$$p_n^{(0)} = \exp\left[-\frac{E_n - F(X_0)}{T}\right] \tag{3.56}$$

and

$$p_m^{(1)} = \exp\left[-\frac{E_m - F(X_1)}{T}\right] \tag{3.57}$$

Hence Eq.(3.55) leads to

$$\frac{P_{o\rightsquigarrow 1}(\omega)}{P_{1\rightsquigarrow 0}(-\omega)} = \exp\left\{\frac{\omega - [F(X_1) - F(X_0)]}{T}\right\} \tag{3.58}$$

Where both $F(X_1)$ and $F(X_0)$ refer to the same preparation temperature T.

Definition of work: The main difficulty in the quantum formulation of the non-equilibrium fluctuation theorems concerns the definition of work.

- Considering an isolated system, naively we can define $W = \omega$ i.e., the work is the change in the energy of the system. But in the quantum reality this means that we have to do a measurement of the initial stage, hence the state of the system collapses and it is no longer canonical.
- By a second approach we may consider a multi-stage process that extends over two time intervals $t_0 \rightarrow t_1 \rightarrow t_2$. Here the work done is the sum $W_{0\rightsquigarrow 1} + W_{1\rightsquigarrow 2}$. With the above definition we have to perform a measurement at the time t_1. But in the quantum mechanical reality we might not have the time for that.

In the present context there is a simple way out of these subtleties. Instead of coupling $X(t)$ with any observable of the system, we take it as a dynamical variable of the working agent. Then the total Hamiltonian can be written as

$$H_{total} = H(r; X) + H_{agent}(X) \tag{3.59}$$

Where r denotes the system dynamical variables, and X is that of the agent. Then the work W is simply defined as the change in the energy of the agent

$$W = E^{(0)}_{agent} - H_{agent} \tag{3.60}$$

Where $E^{(0)}_{agent}$ is the initial energy of the agent and it is assumed that upto some small uncertainty this energy is well known. Long ago it was discussed by Y. Aharonov and D. Bohm [12] that by treating the agent as a dynamical variable we could bypass the energy-time uncertainty fallacy. It says that there is no theoretical limitation on the accuracy of the measurement of energy, once it is shifted to the agent, irrespective of the time of measurement issue. By assuming this we have taken control over the strength of the interaction between the system and the agent so that we can switch ON or OFF the coupling between system and agent in two possible ways:

1. within a restricted region in (r,X) space
2. within a restricted time duration

Once the notion of work is justified it follows automatically that for an isolated system $W = \omega$ is always valid up to the extent that the unavoidable quantum uncertainities can be ignored. Now the Crooks relation follows from Eq.(3.58)

$$\frac{P_{o\rightsquigarrow 1}(W)}{P_{1\rightsquigarrow 0}(-W)} = \exp\left\{\frac{W - [F(X_1) - F(X_0)]}{T}\right\} \tag{3.61}$$

It is usefull to rewrite the Crooks relation in terms of entropy, as was originally proposed by Crooks [6]. The difference $F = F(X_1) - F(X_0)$ is the minimum work required in a reversible quasi-static process such that the difference $W - F$ can be regarded as the dissipated work in a realistic process. Dividing by T we get S_ω that is the entropy produced in the realistic process. Here Boltzmann constant is taken as unity. Consequently the fluctuation theorem Eq.(3.61) can be restated as:

$$\frac{P_{o\rightsquigarrow 1}(S_\omega)}{P_{1\rightsquigarrow 0}(S_{-\omega})} = \exp\{\Delta S_\omega\} \tag{3.62}$$

We can explain above relation between dissipated work and entropy by allowing it to relax at the end of the driving process such that it ends up in a thermodynamic equilibrium state. Since thermodynamic functions are defined only for equilibrium states, under the above consideration we can associate well defined values of entropy with the initial and final states. The difference of these values can be expressed using thermodynamic functions:

$$\Delta S = \frac{\Delta E - \Delta F}{T} \tag{3.63}$$

Where by the first law of thermodynamics the change in the energy of the system is

$$E = W - Q \tag{3.64}$$

The total entropy change of the universe is the sum of the system entropy change, and that of the bath

$$\mathcal{S} = \Delta S + \frac{Q}{T} \tag{3.65}$$

$\Rightarrow$

$$\mathcal{S} = \frac{W - \Delta F}{T} \tag{3.66}$$

It follows that the Crooks relation Eq.(3.61) can be written as

$$\frac{P_{o\rightsquigarrow 1}(\mathcal{S})}{P_{1\rightsquigarrow 0}(-\mathcal{S})} = \exp\{\mathcal{S}\} \tag{3.67}$$

Jarzynski Inequality: It is well known that the Jarzynski equality [5] is an immediate consequence that follows from the Crooks relation Eq.(3.61). For completeness we repeat this derivation here.

Multiplying both sides of the Crooks relation Eq.(3.61) by $P_{1\rightsquigarrow 0}(-W)$ and integrating over W, we obtain

$$\int dW P_{o\rightsquigarrow 1}(W) = \int dW \exp\left\{\frac{W - [F(X_1) - F(X_0)]}{T}\right\} P_{1\rightsquigarrow 0}(-W)$$

Taking into account the normalization of $P(W)$

$$\exp\left(-\frac{F(X_1) - F(X_0)}{T}\right) \int dW \exp\left[\frac{W}{T}\right] P_{1\rightsquigarrow 0}(-W) = 1$$

$\Rightarrow$

$$\left\langle \exp\left[-\frac{W}{T}\right] \right\rangle = \exp\left[-\frac{F(X_1) - F(X_0)}{T}\right] \tag{3.68}$$

Which is the Jarzynski relation. It implies that

$$\langle W \rangle > F(X_1) - F(X_0) \tag{3.69}$$

This variation of the second law of thermodynamics is known as the maximum work principle, because it sets an upper bound on the work $W = -W$ that can be extracted from a work process. Optionally it can be regarded as the minimum work W needed from the agent to do the process. Since we have taken X as a dynamical variable that is associated with the agent therefore our sign conventions for W and Q are opposite to those that are used in actual. Similarly in case of Eq.(3.67), we deduce

$$\langle \exp\left[-\mathcal{S}\right] \rangle = 1 \tag{3.70}$$

or

$$\langle \mathcal{S} \rangle > 0 \tag{3.71}$$

i.e., in accordance with the second law of thermodynamics. Note that it is only the average $\langle \mathcal{S} \rangle$ that is positive. In a finite system $\mathcal{S}$ is negative for a fraction of the processes, with vanishing manifestation in the thermodynamic limit.

Experimental Verification of Crooks Fluctuation Theorem (CFT):

Optical tweezers and atomic force microscopes are widely used to probe the mechanical properties of single molecules as well as the interactions between them. In these techniques mechanical forces are exerted on the molecules which induce transitions e.g., dissociation, unfolding etc. These transitions are associated with hysteresis effects and also system undergoes in non-equilibrium state. These features prohibit one to extract equilibrium information from the experimental data. But fluctuation theorems allow one to extract equilibrium information from the non-equilibrium processes. D. Collin and F. Ritort [13] showed that the CFT can be used to determine folding free energies for folding and unfolding processes occurring in weak as well as strong nonequilibrium regimes. Hence they provided a test of the validity of Crooks Fluctuation ralation under such conditions.

Let $P_U(W)$ denotes the probability distribution of the work performed on the molecule along the unfolding (U) process, and analogously $P_R(W)$ taken for the reverse (R) process. The condition of time-reversal symmetry must be full filled in order to apply CFT. In above experiment this could be achieved by moving the optical trap at the same speeds during unfolding and refolding processes. Moreover, the molecular transitions should always start from an equilibrium state that is folded in the unfolding process and unfolded in the refolding process and must reach a well-defined final state. Then according to CFT $P_U(W)$ and $P_R(-W)$ can be written as:

$$\frac{P_U(W)}{P_R(-W)} = \exp\left(\frac{W - \Delta F}{T}\right) \tag{3.72}$$

Where

ΔF = free-energy change between the final and the initial states

This free energy change is equal to the reversible work associated with this process. Here in our setup equilibration occurs without change of the control parameter and therefore contributes no work. So W is given by the known force-extension integral:

$$W = \sum_{i=1}^{N_s} f_i \Delta x_i \tag{3.73}$$

Where

x_i = distance between the ends of the molecule

N_s = number of intervals used in the sum

Eq.(3.72) shows that:

- The work values larger than ΔF occur along the unfolding path while values smaller than ΔF occur more often along the refolding path quantatively explaining the hysterisis effects.

- Although $P_U(W)$, $P_R(-W)$ depend on the pulling protocol, their ratio depends only on the value of ΔF. Thus once the two distributions are known we can easily determine the value of ΔF. The two distributions cross at $W = \Delta F$ regardless of the pulling speed which implies that

$$P_U(W) = P_R(-W) \Rightarrow W = \Delta F \tag{3.74}$$

Validity test of CFT near equilibrium: In order to test the validity of CFT near equilibrium a short interfering (si) RNA hairpin is used as optical tweezers that targets the

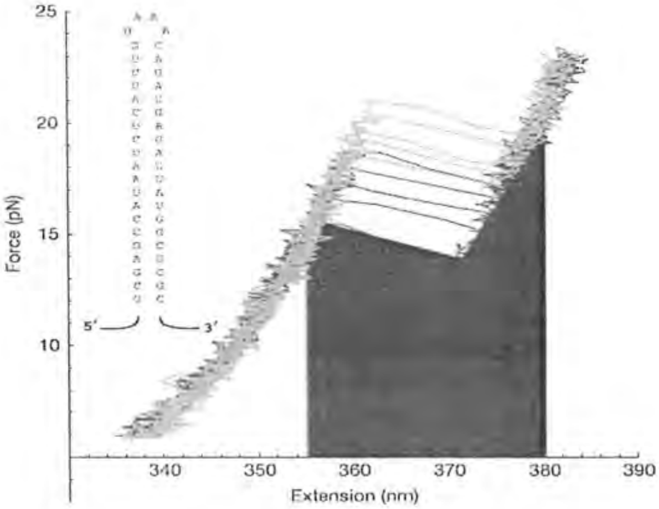

Figure 3-6: Force-extension curves;Five unfolding (orange) and refolding (blue) force-extension curves for the RNA hairpin are shown (loading rate of $7.5pNs^{-1}$). The blue area under the curve represents the work returned to the machine as the molecule switches from the unfolded to the folded state. The RNA sequence is shown as an inset.

messenger RNA of the CD4 receptor of HIV (human immunodeficiency virus). At pulling speeds for which dissipated work values less than 6k$_B$T it unfolds irreversibly but not too far from equilibrium. Under these conditions, the unfolding and refolding work distributions overlap over a sufficiently large range of work values. The work done on the molecules during either pulling or relaxation is given by the areas below the corresponding force–extension curves (see fig. 3-5)

Unfolding and refolding work distributions at three different pulling speeds are shown in Figure (see fig. 3-6). It is shown in the graph that:

- Irreversibility increases with the pulling speed and unfolding-refolding work distributions become progressively more separated.
- Unfolding and the refolding distributions cross at a value of the work $\Delta F = 110.3 \pm 0.5 k_B T$ that does not depend on the pulling speed, as already discussed in context of Eq.(3.74).
- The work distributions satisfy the CFT given in Eq.(3.72).

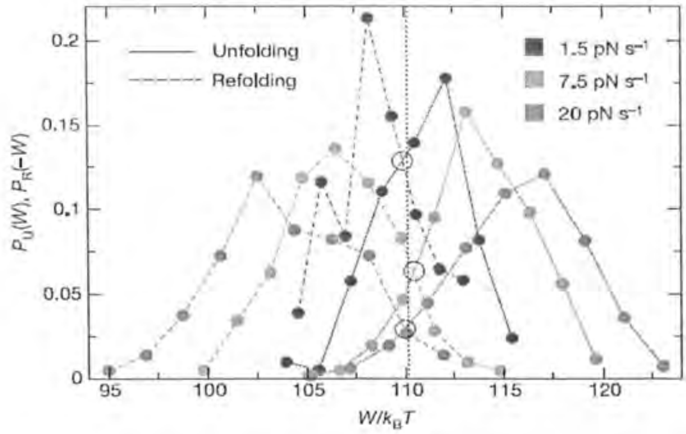

Figure 3-7: Test of CFT near equilibrium.Work distributions for RNA unfolding (continuous lines) and refolding (dashed lines)

- Work distributions are compatible with the gaussian distributions.

Validity test of CFT very-far-from-equilibrium regime To extend the experimental test of the validity of the CFT to the very far from equilibrium regime where the work distributions are no longer gaussian, CFT is applied to determine the difference in folding free energy between an RNA molecule and a mutant that differs only by one base-pair. Experiments were carried out on the wild-type and mutant S15 three-helix junction. The unfolding and refolding work distributions for the wild-type and mutant molecules (work values were binded into about 10–20 equally spaced intervals) are depicted in the figure (see fig. 3-7)

For both molecules, the distributions display a very narrow overlapping region. In contrast with the hairpin distribution, the average dissipated work for the unfolding pathway is now much larger—in the range 20-40k_BT—and the unfolding work distribution shows a large tail and strong deviations from gaussian behaviour. Thus, these molecules are ideal to test the validity of Eq.(3.72) in the far-from-equilibrium regime. As shown in the inset of above graph (see fig. 3-7) the plot of the log ratio of the unfolding to the refolding probabilities versus total work done on the molecule can be fitted to a straight line with a slope of 1.06, thus establishing the validity of the CFT (see Eq.(3.72)) under far from equilibrium conditions. Our measurements

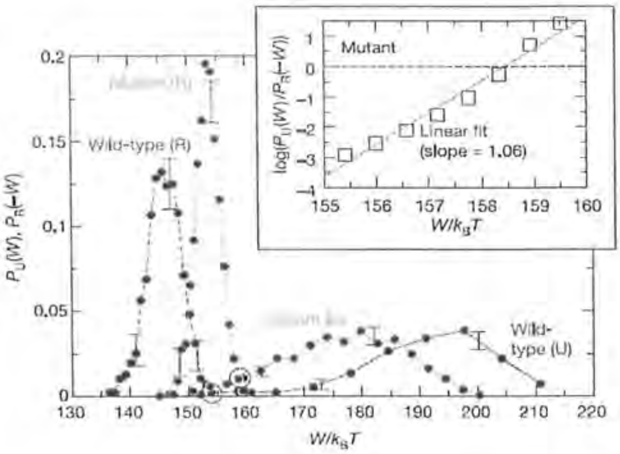

Figure 3-8: Test of CFT far from equilibrium.Non-Gaussian work distributions; unfolding (continuous lines) refolding (dashed lines)

reveal the presence of long tails in the work distribution $P_U(W)$ along the unfolding path and narrow work distributions $P_R(W)$ along the refolding path. These distributions complement each other, one being large where the other is small, thereby providing thermodynamically important information about the free energy landscape.

3.4.2 Derivation of Fluctuation-Dissipation relation 3.18 using Quantum Crooks relation

In this section Eq.(3.18) is derived on the basis of Crooks theorem as per supplementary information given in [9]. For a closed system obeying classical Hamiltonian dynamics, the Crooks theorem relies on the incompressibility of trajectories in phase space (Liouville's theorem) and microscopic time reversibility. Here the idea is extended to isolated quantum Hamiltonian systems with a discrete spectrum. This proof of the quantum Crook's relation bears some similarities with that discussed earlier [14], and is presented here for completeness. This will emphasize some important properties of the transition matrix, highlight that the Crook's relation does not rely on assumptions related to energy measurements, e.g. at intermediate steps, and extend the fluctuation-dissipation relation Eq.(3.18) to non-canonical distributions.

Let us assume that a system prepared in a stationary state, described by a diagonal density matrix in the energy basis, undergoes some process described by a unitary operator $U(t)$. According to standard quantum mechanics the density matrix evolves in time as $\rho(t) = U(t)\rho(0)U^{\dagger}(t)$. This means that the diagonal elements of the time evolved density matrix in the new energy basis are given by

$$\rho_{nn}(t) = \sum_{m} U_{nm}(t)\,\rho_{mm}(0)\,U^{\dagger}_{mn}(t) \tag{3.75}$$

But $T_{m\to n} = |U_{mn}|^2$is the transition probability, so

$$\rho_{nn}(t) = \sum_{m} T_{m\to n}\rho_{mm}(0) \tag{3.76}$$

The matrix $T_{m\to n}$ is doubly stochastic meaning that $\sum_m T_{m\to n} = \sum_n T_{n\to m} = 1$. The first equality is simply the conservation of probability the second is a direct consequence of unitarity. This equality is violated if there are losses in the system due to spontaneous emission etc.

Now let us imagine a time reversed protocol described by the inverse evolution operator U^{-1}. From the definition of the transition probabilities it is clear that

$$\widetilde{T}_{n\to m} = T_{m\to n} \tag{3.77}$$

Where $\widetilde{T}_{n\to m}$ refers to the reverse process. The transition probabilities also satisfy detailed-balance, $T_{n\to m} = T_{m\to n}$, in the following two situations:

1. If the Hamiltonian of the system is time-reversal invariant at each moment of time and the protocol is time symmetric so that $U(t) = U(T-t)$, where T is the period of the cycle.

2. If the transition probabilities during one cycle are small and can be computed within first order in an adiabatic perturbation theory.

To proceed we use energy disribution

$$P(E) = \sum_{n} \rho_{nn}\delta(E - E_n) \tag{3.78}$$

Relating transition probabilities between energy levels to the transition probabilities between energy shells:

$$T_{E\to E'} = \frac{1}{\Omega(E)} \sum_{n,m} \delta(E - E_n)\, \delta(E' - E_m)\, T_{n\to m} \tag{3.79}$$

Where $\Omega(E) = \sum_n \delta(E - E_n)$ is the many-body density of state. The factor $1/\Omega(E)$ ensures conservation of probability: $\int dE' T_{E\to E'} = 1$. The master equation (3.75) then given by

$$P(E') = \int dE T_{E\to E'} P_0(E) \tag{3.80}$$

Now multiplying both sides of Eq.(3.77) by $\delta(E - E_n)\,\delta(E' - E_m)$

$$\delta(E - E_n)\, \delta(E' - E_m)\, \widetilde{T}_{n\to m} = \delta(E - E_n)\, \delta(E' - E_m)\, T_{m\to n}$$

Summing over n,m and using Eq.(3.79) we get

$$\Omega(E)\, T_{E\to E'} = \Omega(E')\, \widetilde{T}_{E'\to E} \tag{3.81}$$

Let $E' = E + \omega$, also

$$\begin{aligned} S(E) &= k \ln \Omega(E) \\ \Omega(E) &= \exp[S(E)] \end{aligned} \tag{3.82}$$

and

$$\Omega(E') = \exp[S(E + \omega)]$$

Then Eq.(3.81) ⇒

$$\exp[S(E)]\, T_{E\to E+\omega} = \exp[S(E + \omega)]\, \widetilde{T}_{E+\omega\to E}$$

$\Rightarrow$

$$\widetilde{T}_{E+\omega\to E} = T_{E\to E+\omega}e^{-S(E+\omega)+S(E)} \tag{3.83}$$

The above expression is known as Crooks relation [6].

To prove Eq.(3.18), Eq.(3.83) is used; entropy and transition probability $T_{E\to E+\omega}$ are expanded in ω (using Taylor's expansion) giving

$$S\left(E+\omega\right) - S\left(E\right) \approx S\left(E\right) + \omega\partial_E S\left(E\right) + \frac{\omega^2}{2!}\partial_E^2 S\left(E\right)\cdots\cdots - S\left(E\right)$$

$$S\left(E+\omega\right) - S\left(E\right) \approx \omega\partial_E S\left(E\right) + \frac{\omega^2}{2!}\partial_E^2 S\left(E\right) \tag{3.84}$$

Where using Eq.(3.82)

$$\partial_E S\left(E\right) = T^{-1} \tag{3.85}$$

so

$$\begin{aligned} \partial_E^2 S\left(E\right) &= \partial_E[\partial_E S\left(E\right)] \\ &= \partial_E T^{-1} \\ &= \partial_T T^{-1}\frac{\partial T}{\partial E} \\ &= -\frac{1}{T^2}\frac{1}{C_v} \end{aligned} \tag{3.86}$$

Using values from Eq.(3.85) and Eq.(3.86) in Eq.(3.84) we get

$$S\left(E+\omega\right) - S\left(E\right) \approx \frac{\omega}{T} - \frac{\omega^2}{2T^2C_v}$$

Using $\beta = T^{-1}$, and $\sigma_{eq}^2 = T^2C_v$ (for Gibbs distribution)

$$S\left(E+\omega\right) - S\left(E\right) \approx \beta\omega - \frac{\omega^2}{2\sigma_{eq}^2} \tag{3.87}$$

Similarly expanding transition probability $T_{E\to E+\omega}$ in ω , we get for cyclic process

$$\widetilde{T}_{E+\omega\to E} = \widetilde{T}_{E\to E-\omega} + \omega\partial_E \widetilde{T}_{E\to E-\omega} \tag{3.88}$$

By using entropy expansion Eq.(3.87) in Eq.(3.83) we get,

$$T_{E\to E+\omega}e^{-\beta\omega} = \widetilde{T}_{E+\omega\to E} \tag{3.89}$$

Here we have neglected $\frac{\omega^2}{2\sigma_{eq}^2}$ term.
Integrating Eq.(3.89)over $d\omega$ we get the Jarzynski like relation i.e.,

$$\int T_{E\to E+\omega}e^{-\beta\omega}d\omega = \int \widetilde{T}_{E+\omega\to E}d\omega$$

$\Rightarrow$

$$\langle \exp[-\beta\omega]\rangle = 1 \tag{3.90}$$

Cumulant expansion is given as [15]

$$\langle \exp[-\beta\omega]\rangle = \sum_{n=1} \frac{(-\beta)^n \langle \omega^n\rangle_c}{n!}$$

Now Eq.(3.90) implies

$$\exp\left[-\beta\langle\omega\rangle_c + \frac{\beta^2}{2!}\langle\omega^2\rangle_c + \cdots\cdots\right] = 1$$

Taking ln on both sides and neglecting higher order cumulants

$$\beta\langle\omega\rangle_c + \frac{\beta^2}{2!}\langle\omega^2\rangle_c \approx 0 \tag{3.91}$$

$\Rightarrow$

$$2\langle\omega\rangle_c \approx \beta\langle\omega^2\rangle_c \tag{3.92}$$

Cumulants are

$$\begin{aligned} A &= \langle \omega \rangle_c = \langle \omega \rangle \\ B &= \left\langle \omega^2 \right\rangle_c = \left\langle \omega^2 \right\rangle - \langle \omega \rangle^2 \\ C &= \left\langle \omega^3 \right\rangle_c = \left\langle \omega^3 \right\rangle - 3 \left\langle \omega^2 \right\rangle \langle \omega \rangle + 2 \langle \omega \rangle^3 \end{aligned} \tag{3.93}$$

The condition for the validity of this expression is that the third cumulant of the work is small:

$$\beta^2 \left\langle \omega^3 \right\rangle_c \ll \langle \omega \rangle \tag{3.94}$$

When the additional assumption of detailed balance holds $T = \widetilde{T}$ can be used in Eq.(3.83). Since the work per cycle is assumed to be small, it is expected that the transition probabilities are also small and can be computed perturbatively. So the assumption of $T = \widetilde{T}$ between energy shells is likely to be generic. In this case, using the expansions Eq.(3.87), Eq.(3.88) in Eq.(3.83) and integrating we get,

$$\int \widetilde{T}_{E \to E-\omega} d\omega + \partial_E \int \omega \widetilde{T}_{E \to E-\omega} d\omega = \int \exp\left(-\beta\omega + \frac{\omega^2}{2\sigma_{eq}^2}\right) T_{E \to E+\omega} d\omega$$

$$\left\langle \exp\left[-\beta\omega + \frac{\omega^2}{2\sigma_{eq}^2}\right] \right\rangle \approx 1 - \partial_E \langle \omega \rangle \tag{3.95}$$

Taking the logarithm of both sides and performing the cumulant expansion of the exponent up to order ω^2 we find

$$\ln \left\langle \exp\left[-\beta\omega + \frac{\omega^2}{2\sigma_{eq}^2}\right] \right\rangle \approx \ln(1 - \partial_E \langle \omega \rangle) \tag{3.96}$$

Using ln expansion i.e.,

$$\ln(1-x) = \sum_{n=1}^{\infty} (-1)^{2n-1} \frac{x^n}{n} \tag{3.97}$$

We get (neglecting higher order terms)

$$\ln(1 - \partial_E \langle \omega \rangle) \approx -\partial_E \langle \omega \rangle \tag{3.98}$$

Also by cumulant expansion Eq.(3.91)

$$\langle \exp\left[-\beta\omega\right]\rangle = \exp\left[-\beta\left\langle\omega\right\rangle_c + \frac{\beta^2}{2}\left(\left\langle\omega^2\right\rangle - \left\langle\omega\right\rangle^2\right) + \cdots\cdots\right]$$

We can write

$$\left\langle \exp\left[-\beta\omega + \frac{\omega^2}{2\sigma_{eq}^2}\right]\right\rangle = \exp\left[\left\langle -\beta\omega + \frac{\omega^2}{2\sigma_{eq}^2}\right\rangle + \frac{1}{2}\left(\left\langle\left(-\beta\omega + \frac{\omega^2}{2\sigma_{eq}^2}\right)^2\right\rangle - \left\langle -\beta\omega + \frac{\omega^2}{2\sigma_{eq}^2}\right\rangle^2\right) + \cdots\right]$$

By using $\delta x^2 = \left\langle x^2\right\rangle - \left\langle x\right\rangle^2$

$$\left\langle \exp\left[-\beta\omega + \frac{\omega^2}{2\sigma_{eq}^2}\right]\right\rangle = \exp\left[\left\langle -\beta\omega + \frac{\omega^2}{2\sigma_{eq}^2}\right\rangle + \frac{1}{2}\left\langle \delta\left(-\beta\omega + \frac{\omega^2}{2\sigma_{eq}^2}\right)^2\right\rangle\right]$$

Taking ln we get

$$\ln\left\langle \exp\left[-\beta\omega + \frac{\omega^2}{2\sigma_{eq}^2}\right]\right\rangle = \left\langle -\beta\omega + \frac{\omega^2}{2\sigma_{eq}^2}\right\rangle + \frac{1}{2}\left\langle \delta\left(-\beta\omega + \frac{\omega^2}{2\sigma_{eq}^2}\right)^2\right\rangle$$

Neglecting higher order terms

$$\ln\left\langle \exp\left[-\beta\omega + \frac{\omega^2}{2\sigma_{eq}^2}\right]\right\rangle \approx -\beta\left\langle\omega\right\rangle + \frac{\left\langle\omega^2\right\rangle}{2\sigma_{eq}^2} + \frac{\beta^2}{2}\left\langle\delta\omega^2\right\rangle \tag{3.99}$$

Using Eq.(3.98) and Eq.(3.99) in Eq.(3.96) we get

$$-\beta\left\langle\omega\right\rangle + \frac{\left\langle\omega^2\right\rangle}{2\sigma_{eq}^2} + \frac{\beta^2}{2}\left\langle\delta\omega^2\right\rangle \approx -\partial_E\left\langle\omega\right\rangle \tag{3.100}$$

It is easy to check that up to order 1/N the equations above imply Eq.(3.18): $2A = \partial_E B + \beta B$ as long as $\frac{\left\langle\omega^2\right\rangle}{\sigma_{eq}^2}$ is negligible compared to $\beta\left\langle\omega\right\rangle$. Noting that $\left\langle\omega^2\right\rangle = \left\langle\omega^2\right\rangle_c + \left\langle\omega\right\rangle^2 = B + A^2$ this gives us a necessary condition of validity of relation Eq.(3.18):

$$A = \left\langle\omega\right\rangle \ll TC_v \tag{3.101}$$

Namely, the work per unit cycle should be small compared to the temperature multiplied by the specific heat. We note that even though we derived Eq.(3.18) to the order of 1/N, it is actually correct to all orders in 1/N. This relation is valid as long as the conditions Eq.(3.94) and Eq.(3.101) are satisfied.

Finally in order to discuss extension of the fluctuation dissipation relation Eq.(3.18) to arbitrary distributions it is weighed with an energy distribution $P(E)$ and integrated over energies. Then in the Gaussian approximation we find

$$\langle\omega\rangle \approx \frac{\beta}{2}\left\langle\omega^2\right\rangle_c + \frac{1}{2}\left(1-\frac{\sigma^2}{\sigma_{eq}^2}\right)\partial_E\left\langle\omega^2\right\rangle_c \tag{3.102}$$

Equivalence of ensembles

- For microcanonical distribution $\sigma^2 = 0$, equ $\Rightarrow$

  $$\langle\omega\rangle \approx \frac{\beta}{2}\left\langle\omega^2\right\rangle_c \tag{3.103}$$

  i.e., the conventional result obtained from the cumulant expansion of the Jarzynski relation Eq.(3.90).

- For canonical ensemble $\sigma = \sigma_{eq}$ we get the same expression as above.

  $$\langle\omega\rangle \approx \frac{\beta}{2}\left\langle\omega^2\right\rangle_c \tag{3.104}$$

3.5 Generalization

In this section we will generalize our formalism to other systems that are driven away from equilibrium by some method but are isolated otherwise e.g., driven-dissipative systems, equilibrating systems by following G. Bunin and Y. kafri [19]. This will show universality of energy fluctuations produced in isolated systems driven away from equilibrium by any of the above described way. This will also support our formalism used in above sections to describe and elaborate the physics with in such a system.

3.5.1 Generalizing to driven-dissipative systems

In this case two systems initially prepared at two different temperatures are allowed to exchange energies but are isolated otherwise. Let initially energies of the two systems are E_1

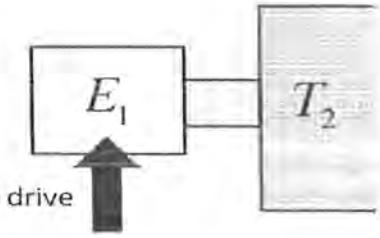

Figure 3-9: Schematic representation of driven-dissipative system

and E_2. If we take $E_1 \ll E_2$ then the second system acts as a dissipative bath. The first system is also driven by some external protocol as shown in the above figure. This is how a driven-dissipative system is described. Now as discussed in section3.2 for the assumptions of small work per cycle and taking relaxation time of subsystem less than that of driving or coupling time the time evolution of the probability distribution $P_{12}(E_1, E_2)$ is given by two dimensional Fokker-Planck equation Eq.(3.14)

$$\partial_t P_{12} = -\sum_{i=1}^{2} \partial_{E_i} (A_i P_{12}) + \frac{1}{2} \sum_{i,j=1}^{2} \partial_{E_i} \partial_{E_j} (B_{ij} P_{12}) \tag{3.105}$$

Where all $A_i's$ and $B_{ij}'s$ are given as according to Eq.(3.13)

$$A_i = \frac{\langle \Delta E_i \rangle}{\Delta t}; \quad B_{ij} = \frac{\langle \Delta E_i \Delta E_j \rangle}{\Delta t} \tag{3.106}$$

Since system 2 acts as bath its energy is insensitive to small changes as discused before Eq.(2.6) so we can drop E_2 by approximating P_{12} to $P(E_1)$ as

$$P(E_1) = \int dE_2 P_{12}(E_1, E_2) \tag{3.107}$$

so Eq.(3.105) gives

$$\partial_t P = -\partial_{E_1} (A_1 P) + \frac{1}{2} \partial_{E_1}^2 (B_{11} P) \tag{3.108}$$

The above equation is equivalent to Eq.(3.13) taken in case of isolated driven single system. Now in order to derive the fluctuation-dissipation relation for the above described system we proceed as follows according to ([19]). Let E_1,E_2 change by an amount ΔE_1,ΔE_2 in time Δt. Then ΔE_B energy exchange between system 1 and 2 ,ΔE_F i.e., energy transferred to system 1 by external protocol are defined as below

$$\begin{aligned}\Delta E_1 &= \Delta E_F - \Delta E_B \\ \Delta E_2 &= \Delta E_B\end{aligned} \tag{3.109}$$

Now implying Crooks relation to the combined isolated system as Eq.(3.83)

$$T_{E_1,E_2}\left(\Delta E_1, \Delta E_2\right) e^{S_1(E_1)+S_2(E_2)} = \widetilde{T}_{E_1+\Delta E_1,E_2+\Delta E_2}\left(-\Delta E_1, -\Delta E_2\right) e^{S_1(E_1+\Delta E_1)+S_2(E_2+\Delta E_2)} \tag{3.110}$$

where

$T_{E_1,E_2}\left(\Delta E_1, \Delta E_2\right) =$ forward transition probability from $\left(\Delta E_1, \Delta E_2\right) \rightarrow \left(E_1 + \Delta E_1, E_2 + \Delta E_2\right)$

$\widetilde{T}_{E_1+\Delta E_1,E_2+\Delta E_2}\left(-\Delta E_1, -\Delta E_2\right) =$ reversed transition probability

$S_{1,2} =$ microcanonical entropies of system 1,2 defined by $\beta_{1,2}$

Let us assume that:

- $\Delta E_1, \Delta E_2$ are very small so that $\widetilde{T}_{E_1+\Delta E_1,E_2+\Delta E_2} \rightarrow \widetilde{T}_{E_1,E_2}$
- $\Delta E_F, \Delta E_B$ are independent from each other. This means that driving protocol and interaction with bath are independent. This can be achieved when drive and interaction process occur on different parts of the subsystem at different times.

Now by using definition Eq.(3.85) Eq.(3.109) and applying above assumptions Eq.(3.110) becomes

$$\begin{aligned}\widetilde{T}^F(\Delta E_F,0)\,\widetilde{T}^B(-\Delta E_B,\Delta E_B) &= T^F(\Delta E_F,0)\,T^B(-\Delta E_B,\Delta E_B)\,e^{S_1(E_1)+S_2(E_2)-S_1(E_1+\Delta E_1)-S_2(E_2+\Delta E_2)} \\ &= T^F(\Delta E_F,0)\,T^B(-\Delta E_B,\Delta E_B)\,e^{-S_1(\Delta E_1)-S_2(\Delta E_2)} \\ &= T^F(\Delta E_F,0)\,T^B(-\Delta E_B,\Delta E_B)\,e^{-S_1(\Delta E_F-\Delta E_B)-S_2(\Delta E_B)} \\ &= T^F(\Delta E_F,0)\,T^B(-\Delta E_B,\Delta E_B)\,e^{-S_1\Delta E_F-(S_2-S_1)\Delta E_B} \\ &= T^F(\Delta E_F,0)\,T^B(-\Delta E_B,\Delta E_B)\,e^{-\beta_1\Delta E_F-(\beta_2-\beta_1)\Delta E_B} \qquad (3.111)\end{aligned}$$

Integrating above equation over $\Delta E_F, \Delta E_B$ gives

$$\left\langle e^{-\beta_1\Delta E_F}\right\rangle\left\langle e^{-(\beta_2-\beta_1)\Delta E_B}\right\rangle = 1 \qquad (3.112)$$

Rearranging Eq.(3.111) and integrating over $\Delta E_F, \Delta E_B$ gives

$$\begin{aligned}T^F(\Delta E_F,0)\,T^B(-\Delta E_B,\Delta E_B)\,e^{-\beta_1\Delta E_F} &= \widetilde{T}^F(\Delta E_F,0)\,\widetilde{T}^B(-\Delta E_B,\Delta E_B)\,e^{(\beta_2-\beta_1)\Delta E_B} \\ \left\langle e^{-\beta_1\Delta E_F}\right\rangle &= \left\langle e^{-(\beta_2-\beta_1)\Delta E_B}\right\rangle \qquad (3.113)\end{aligned}$$

Eq.(3.112) and Eq.(3.113) can be combined as

$$\left\langle e^{-\beta_1\Delta E_F}\right\rangle = \left\langle e^{-(\beta_2-\beta_1)\Delta E_B}\right\rangle = 1 \qquad (3.114)$$

Expanding both to second order using Eq.(3.99) we get

$$\left\langle e^{-\beta_1\Delta E_F}\right\rangle = \exp\left[-\beta_1\langle\Delta E_F\rangle + \frac{\beta_1^2}{2}\langle\Delta E_F^2\rangle + \cdots\right] = 1$$

Taking ln of both sides

$$\begin{aligned}-\beta_1\langle\Delta E_F\rangle + \frac{\beta_1^2}{2}\langle\Delta E_F^2\rangle &= 0 \\ 2\langle\Delta E_F\rangle &= \beta_1\langle\Delta E_F^2\rangle \qquad (3.115)\end{aligned}$$

For the second term expansion is

$$\left\langle e^{-(\beta_2-\beta_1)\Delta E_B}\right\rangle = \exp\left[-(\beta_2-\beta_1)\langle\Delta E_B\rangle + \frac{(\beta_2-\beta_1)^2}{2}\langle\Delta E_B^2\rangle + \cdots\right] = 1$$

In the similar way as above we get

$$2\langle\Delta E_B\rangle = (\beta_2-\beta_1)\left\langle\Delta E_B^2\right\rangle \tag{3.116}$$

Now Eq.(3.109) gives

$$\begin{aligned}\Delta E_B^2 &= (\Delta E_F - \Delta E_1)^2\\ \Delta E_B^2 &= \Delta E_F^2 - 2\Delta E_F\Delta E_1 + \Delta E_1^2\end{aligned}$$

Taking average

$$\left\langle\Delta E_B^2\right\rangle = \left\langle\Delta E_F^2\right\rangle - 2\langle\Delta E_F\Delta E_1\rangle + \left\langle\Delta E_1^2\right\rangle$$

From independence $\langle\Delta E_F\Delta E_1\rangle \sim \left\langle\Delta E_F^2\right\rangle$ so

$$\left\langle\Delta E_B^2\right\rangle = \left\langle\Delta E_1^2\right\rangle - \left\langle\Delta E_F^2\right\rangle \tag{3.117}$$

Using Eq.(3.117), Eq.(3.109) and Eq.(3.115) in Eq.(3.116) we get

$$\begin{aligned}2\left(\langle\Delta E_F\rangle - \langle\Delta E_1\rangle\right) &= (\beta_2-\beta_1)\left(\left\langle\Delta E_!^2\right\rangle - \left\langle\Delta E_F^2\right\rangle\right)\\ &= (\beta_2-\beta_1)\left(\left\langle\Delta E_1^2\right\rangle - \frac{2}{\beta_1}\langle\Delta E_F\rangle\right)\\ &= (\beta_2-\beta_1)\left\langle\Delta E_1^2\right\rangle - \left(\frac{2\beta_2}{\beta_1}-2\right)\langle\Delta E_F\rangle\\ 2\langle\Delta E_1\rangle - \frac{2\beta_2}{\beta_1}\langle\Delta E_F\rangle &= (\beta_1-\beta_2)\left\langle\Delta E_1^2\right\rangle \end{aligned} \tag{3.118}$$

Dividing Eq.(3.118) by Δt and using Eq.(3.106) we get

$$2A_1 - \frac{2\beta_2}{\beta_1}A_F = (\beta_1-\beta_2)B_{11} \tag{3.119}$$

Where

$A_F = A_1 + A_2 = \partial_t \langle E_{total} \rangle$ = rate of energy injected by the drive

Now proceeding similar to Eq.(3.19) to Eq.(3.23) we have

$$\partial_t \langle E_1 \rangle = \langle A_1 \rangle \tag{3.120}$$

and

$$\partial_t \sigma_1^2 = \langle B_{11} \rangle + 2 \left(\langle A_1 E_1 \rangle - \langle A_1 \rangle \langle E_1 \rangle \right) \tag{3.121}$$

By combining Eq.(3.120) and Eq.(3.121) and using saddle-point approximation we get

$$\frac{\partial \sigma_1^2}{\partial \langle E_1 \rangle} = 2Z \left(\langle E_1 \rangle \right) + 2 \frac{\partial_{E_1} A_1 \left(\langle E_1 \rangle \right)}{\langle A_1 \rangle} \sigma_1^2 \left(\langle E_1 \rangle \right) \tag{3.122}$$

Where

$Z = B_{11}/2A_1$

Solving Eq.(3.122) and using Eq.(3.119) we get variance as

$$\sigma_{1,dd}^2 = \sigma_{1_0}^2 \frac{A_1^2 \left(\langle E_1 \rangle \right)}{A_1^2 \left(E_{1_0} \right)} + 2A_1^2 \left(\langle E_1 \rangle \right) \int_{E_{1_0}}^{\langle E_1 \rangle} \frac{Z \left(E' \right)}{A_1^2 \left(E' \right)} dE' \tag{3.123}$$

Where Z is given by using Eq.(3.119)

$$Z = \frac{\left[\frac{1 - \beta_2 A_F}{(\beta_1 A_1)} \right]}{(\beta_1 - \beta_2)} \tag{3.124}$$

The above expression for the variance of energy in driven-dissipative system show that energy fluctuations depend only on A_F i.e., rate of energy injected into the system and A_2 i.e., rate of energy trnsfered to the bath and is independent of the microscopic details of the system. For $\beta_2 \to 0$ the above expression becomes similar to Eq.(3.23) It means that single driven system is similar to attaching a system to a bath of infinite temperature in case of driven-dissipative system.

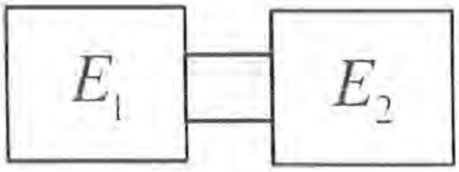

Figure 3-10: Schematic representation of equilibrating systems (similar to tea cups)

3.5.2 Generalizing to two equilibrating systems

In this case two systems initially prepared at two different temperatures are allowed to exchange energies but are isolated otherwise. Let initially energies of the two systems are E_1 and E_2. If we take $E_1 \ll E_2$ then the second system acts as a dissipative bath. Now for the same assumptions as described above that is for small coupling time the rate of probability distribution $P_{12}(E_1, E_2)$ with which the two systems are equilibrating is exactly described by the Eq.(3.105) and here we can approach to Eq.(3.108) by arguing that the total energy is fixed i.e., $E_{total} = E_1 + E_2$ so we can define E_2 in terms of E_1. Also Eq.(3.119) for no drive case i.e., $A_F = 0$ becomes

$$2A_1 = (\beta_1 - \beta_2) B_{11} \tag{3.125}$$

In this case we get Eq.(3.123) for $Z = (\beta_1 - \beta_2)$ as

$$\sigma_{1,eq}^2 = \sigma_{1_0}^2 \frac{A_1^2(\langle E_1 \rangle)}{A_1^2(E_{1_0})} + 2A_1^2(\langle E_1 \rangle) \int_{E_{1_0}}^{\langle E_1 \rangle} \frac{1}{A_1^2(E')(\beta_1 - \beta_2)} dE' \tag{3.126}$$

For $\beta_2 \rightarrow 0$ the above expression becomes similar to Eq.(3.23) It means that in single driven system the drive is equivalent to attaching system to a bath of infinite temperature. It is clear from above equation that when system 2 is a bath i.e., β_2 is constant. σ_1^2 approaches to equilibrium value $(\partial_{E_1}\beta_1)_{E_{eq}}^{-1} = k_B T^2 C_v$ from Eq.(2.20).where E_{eq} is the equilibrium value of $\langle E_1 \rangle$

Chapter 4

Summary and conclusion

4.1 Summary

In the end we present a summary of our findings as a conclusion to the dissertation. In the first chapter we reviewed a brief history how fluctuation relations developed since the time of Einstein till now. We discussed that how fluctuation relations can extract equilibrium information from the non-equilibrium phenomenon. This prevailed the importance of fluctuation relations for the non-equilibrium processes. This account was further utilized in next chapters while discussing isolated systems that are driven away from equilibrium by external agent.

In chapter 2, we discussed a thermally isolated system that is in contact with a heat bath. No external drive was applied i.e., system is simply equilibrating. We calculated energy fluctuations for this system according to conventional statistical thermodynamical approach by taking into account canonical ensemble averages. It was shown that the mean energy fluctuations are history independent and obey Gibbs like behaviour. By discussing equivalence of ensembles it was made clear that these fluctuations are universal in nature i.e., independent of microscopic details of the system. At the end we derived these results for the same system in quatum limit.

In chapter 3, we investigated a thermally isolated system subjected to a driving protocol. By considering stochastic markoff process we derived Fokker-Planck Equation describing appropriately dynamics of our system. Under the assumptions of small work per cycle and $A(E) \ll TC_v$ a Fluctuation-dissipation relation connecting work per cycle and its variance i.e., $A(E)$ and $B(E)$ was derived. Further by invoking saddle-point approximation main result giving energy fluctuation for driven isolated system is obtained.

We derived Crooks Fluctuation theorem for our system and experimentally tested its validity for systems far from equilibrium. Starting from unitarity evolution for isolated system we formulate a master equation containing transition probabilities. From here we obtained the extended crooks relation for our setup of repeated cycles. We further recovered fluctuation-dissipation relation in the limit $\langle \omega \rangle \ll TC_v$ by taking cumulant expansion of this Jarzynski relation i.e., a direct consequece of crooks relation . By using Gaussian approximation found a result for the energy fluctuations for non-canonical distributions. Further for canonical and microcanonical cases fluctuations are derived as a limiting case. In the last we generalized our approach to other systems that are some how equivalent to our main system e.g., driven-dissipative systems, equilibrating systems.

4.2 Results

In the start we put forward some questions concerning energy fluctuations in our thermally isolated driven system. Here we try to state answers of those questions as a conclusion:

- When $A\left(E\right)$ is constant the energy width depends only on $\beta\left(E\right)$, and not on the amplitude of the drive or other details of the driving protocol. Also showed that when $A\left(E\right)$ is not constant in Gibbs-like regime energy distribution is protocol independent Eq.(3.26) and in run-away depends on the driving protocol Eq.(3.27)

- When $A(E)$ is not constant, depending on the functional form of $A(E)$ and $\beta(E)$, the variance of the distribution can be larger and surprisingly, even smaller than the width of the equilibrium Gibbs distribution at the same mean energy. In fact,$\sigma^2(E)/\sigma^2_{eq}(E)$ can be made arbitrarily small by a proper choice of $A(E)$.

- When A is a function of the energy density $u = E/N$ (with a possible extensive energy independent prefactor like the total number of particles), we have $\sigma^2(E) \sim O(N)$, scaling as in equilibrium. For a single quench this result was noticed earlier by A. Silva [17]. Here it is showed that it remains valid after many quenches.

- We have showed a non-canonical expression for energy distribution in Eq.(3.102) and as

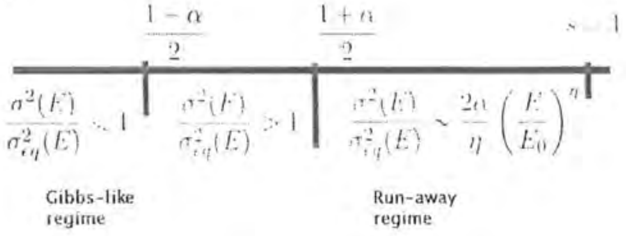

Figure 4-1: Variance of energy distribution represented on a scale line for η

limiting cases derived results for microcanonical Eq.(3.103) and canonical i.e., oven like setup.

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