Generalization of the detailed fluctuation theorem for Non-Hamiltonian Dynamics

K. Gururaj, G. Raghavan and M.C. Valsakumar

Theoretical Studies Section, Material Physics Division,
IGCAR, Kalpakkam-603102, INDIA

Abstract

Detailed fluctuation theorem, a microscopic version of the steady state fluctuation theorem, has been proposed by Jarzynski and demonstrated in the case of Hamiltonian systems weakly coupled with reservoirs. We show that an identical theorem for phase space compressibility rate can be derived for systems evolving under non-Hamiltonian extended system dynamics, without certain limiting assumptions made in the original work. Our derivation is based on the non-Hamiltonian phase space formulation of statistical mechanics and does not rely on any assumptions of thermodynamic nature. This version of the detailed fluctuation theorem is shown to be generic enough to be applicable to several thermostatting schemes. It is shown that in equilibrium, this detailed fluctuation theorem boils down to the detailed balance equation and it is further shown to reproduce the Jarzynski’s work theorem for driven systems.

*Electronic address: gururaj@igcar.gov.in
I. INTRODUCTION

A family of remarkable results in non-equilibrium statistical mechanics, collectively called *Fluctuation theorems*, has been obtained in recent years. These theorems address the issue of how macroscopic irreversibility arises from microscopic time reversible dynamics, and in a sense quantify the probability of observing Second law violating events. These fluctuation theorems are valid for systems arbitrarily far from thermodynamic equilibrium and have been demonstrated for both deterministic and stochastic evolution. It is this sweeping generality that make these results quite extraordinary. One version of the fluctuation theorem was first discovered by Evans and Searles in the context of molecular dynamics simulation of a steady state system subject to a Gaussian isokinetic thermostat. The system under consideration was a steady state system subjected to external forcing. Under such circumstances, stationarity can be attained only under constant dissipation of energy. In a dynamical system, this dissipation manifests itself as a contraction of the phase space volume. Considering a set of phase points centered around \( \Gamma_0(p_0, q_0) \) at time \( t=0 \), under the dynamics, we have the mapping \( d\Gamma_0 \rightarrow d\Gamma_t \) with:

\[
\left| \frac{d\Gamma_0}{d\Gamma_t} \right| = exp(- \int_0^t \Lambda(\Gamma_s)ds)
\]

(1)

where

\[
\Lambda(\Gamma_s) = -\frac{\partial}{\partial \Gamma_s} \dot{\Gamma}_t
\]

(2)

then the heat exchange rate with the thermostat, at temperature \( T \), is

\[
\dot{Q}(\Gamma, t) = -T\Lambda(\Gamma, t)
\]

(3)

which provides the link between phase space compression and entropy production rate. Evans and Searles then define a dissipation function :

\[
\Omega_t(\Gamma_0) = \ln \left[ \frac{f(\Gamma_0, 0)}{f(\Gamma_t, 0)} \right] - \int_0^t \Lambda(\Gamma_s, s)ds
\]

(4)

where \( f(\Gamma_s, s) \) is the phase space probability density.

For a dissipative system,

\[
\langle \Omega_t \rangle \geq 0
\]

(5)
When the initial probability density $f(\Gamma_0, 0)$ is drawn from an equilibrium distribution and the system is driven away from it by external forcing, the statement of the Evans-Searles (transient) fluctuation theorem takes the form:

$$\frac{P(\Omega_t = A)}{P(\Omega_t = -A)} = exp(At)$$  (6)

In the case where the initial phase space points are drawn from a steady state distribution, Evans and Searles derived a rearranged form of the above equation called the steady state fluctuation theorem valid for the long time limit, given by the expression:

$$\lim_{t \to \infty} \frac{1}{t} \ln \frac{P(\Omega = A)}{P(\Omega = -A)} = A$$  (7)

Independent of this work, Galavotti and Cohen derived the steady state fluctuation theorem using average compression as:

$$\lim_{t \to \infty} \frac{1}{t} \ln \frac{P(-\bar{\Lambda} = A)}{P(-\bar{\Lambda} = -A)} = A$$  (8)

These fluctuation theorem are valid in the non-linear, nonequilibrium regime where very general results are available. Fluctuation relation have been derived under a variety of conditions [8] and have been demonstrated experimentally in small systems.

**II. JARZYNSKI’S DETAILED FLUCTUATION THEOREM**

In an interesting development, Jarzynski [1, 2] derived a hybrid fluctuation theorem, which is also a statement of detailed balance. This detailed fluctuation theorem shows that under a nonequilibrium process, the ratio of the probability of observing specific trajectory - anti-trajectory pairs goes as an exponential of the entropy produced. For a trajectory that starts in a microstate $z_A$ and evolves into $z_B$ in a duration $\tau$, resulting in the production of entropy $\Delta S$, its anti-trajectory is the one that starts from $z_B^*$ and evolves into $z_A^*$ causing an entropy consumption of $\Delta S$. Here $(q, p)^*$ stands for reversal of momenta $(q, -p)$. The detailed fluctuation theorem, like all fluctuation theorems, shows that it is more likely that entropy is generated rather than consumed in a non-equilibrium process. This theorem is however distinct from the other forms of fluctuation theorems in that it makes specific reference to the initial and final microstates.
Jarzynski has derived this result for a Hamiltonian system weakly coupled to a set of Hamiltonian reservoirs. The system is manipulated by an external protocol which involves making or breaking contact with external forces and heat reservoirs in a specified sequence. In this scheme, the application of the external protocol in the reversed order amounts to the realization of the time-reversed trajectories. A process $\Pi^+$ is defined to be the execution of a given protocol for a time interval $\tau$ and correspondingly, the process $\Pi^-$ is the same protocol executed in the reverse order. The detailed fluctuation theorem then assumes the form

$$\frac{P_+(z_B, \Delta S | z_A)}{P_-(z_A, -\Delta S | z_B)} = e^{\Delta S/k_B}$$

(9)

where the numerator (denominator) in LHS is the joint conditional probability that, under the process $\Pi^+(\Pi^-)$, that the system starts from $z_A$ ($z^*_B$) and ends at $z_B$ ($z^*_A$), producing (consuming) an entropy $\Delta S$. The derivation of the theorem follows directly from the assumptions that the reservoir temperatures do not change and their degrees of freedom at both initial and final times are Maxwell-Boltzmann distributed. The entropy generated by the dynamical evolution is then assumed to be:

$$\Delta S = -\sum_{n=1}^{N} \frac{\Delta Q_n}{T_n}$$

(10)

where $\Delta Q_n$ is the change in the internal energy of the $n^{th}$ heat reservoir. These assumptions, coupled with the fact that Hamiltonian evolution is time reversible and phase-space conserving, lead directly to the detailed fluctuation theorem. Regarding the particular choice made for $\Delta S$, eq(10), Jarzynski explicitly states that it is valid only when the system is weakly coupled with the heat reservoirs possessing infinite number of degrees of freedom. Towards the end of his paper, Jarzynski suggests that it would be desirable to perform experiments to test the detailed fluctuation theorem. This requires experimental control and manipulation of the full microstates of the system which is very difficult to realize experimentally. This might explain only very few results are available on the experimental verification of the detailed fluctuation theorem in contrast to work fluctuation theorem of Jarzynski. In contrast to the experimental scenario, in molecular dynamics one has full control and information about the specific microstate and complete dynamics of the system and hence one can attempt to verify the detailed fluctuation theorem in such a setting.
In the context of molecular dynamics simulations, thermostatting is realized by appending a few extra degrees of freedom to the system, the time evolution of which is of a non-Hamiltonian character and hence cannot be understood as a simple perturbation of the original uncoupled dynamics. Hence, the question of whether these fluctuation theorems can be captured in molecular dynamics simulations has been attracting a lot of attention in recent years. For example, the work fluctuation theorem has been rederived for Nose-Hoover dynamics without the weak coupling assumption. Similarly, the validity of these fluctuation theorems for different molecular dynamics ensembles has appeared in literature. Within the context of detailed fluctuation theorem, Jarzynski, has suggested that it would be interesting to see whether the DFT manifests itself in the Nose-Hoover thermostatted dynamics. Nose-Hoover dynamics belong to a class of thermostatting schemes called Extended Phase Space Methods and we realize that in the case of such systems, there are no coupling terms in the total Hamiltonian and hence one cannot talk of a weak coupling or even delineate the system energy from the heat bath energy, as was done in the original derivation. Therefore one cannot use the canonical definition of entropy (eq 10). Further, in the extended system dynamics, temperature enters only as an external parameter and hence taking recourse to thermodynamic definition of entropy or internal energy is not viable. Given a set of autonomous equations of motion, perhaps the only quantity that can be related to entropy is the phase space compressibility. Although the absolute entropy for such systems may not be definable, one can identify, under certain assumptions, phase space compression rate with the entropy production rate. Independent of whether such an identification is to be made or not, we demonstrate that a detailed fluctuation theorem can be formulated for the phase space compressibility that takes exactly the same form as that of the original.

IV. DERIVATION OF THE DETAILED FLUCTUATION THEOREM FOR THE PHASE COMPRESSION RATE

The present derivation follows essentially the same methodology as that of the original, but differs significantly in that no use is made of the Liouville theorem since, in general,
phase space volume is not conserved under a non-Hamiltonian evolution. The notations and symbols used are identical to the ones used in the original, so as to make the similarities and distinctions between the two derivations easily observable.

We start by considering a system $\psi$ coupled to a thermostat such that, the extended system undergoes a time-reversible, non-Hamiltonian dynamics for which a constant energy functional $\mathcal{H}$, hence-forth referred to as the pseudo-Hamiltonian, can be identified. It is possible to cast many of the present day thermostats and ergostats into this form, see [4]. Let $z = (r, p)$ denote the phase space of the system $\psi$ and let the degrees of freedom of the thermostat be represented by $Y$. Let $\Gamma = (z, Y)$ denote a point in the phase space of the extended system, evolving under the deterministic non-Hamiltonian dynamics: [4]

$$\dot{\Gamma}_i = \sum_{j=1}^{2Nd} B_{ij} \frac{\partial \mathcal{H}}{\partial \Gamma_j}$$

(11)

for $i = 1, ..., 2Nd$, where $\mathcal{H}(\Gamma)$ is the generalized energy and $B$ is a $2Nd \times 2Nd$ anti-symmetric matrix. The equations are known to generate energy preserving dynamics. For instance, when $B = \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}$ where $0$ and $1$ indicate the zero and identity matrices of appropriate dimensions, these equations reduce to the usual Hamilton’s equations of motion. Any other choice of matrix $B$, so long as it is anti-symmetric, still generates a non-Hamiltonian dynamics that conserves $\mathcal{H}$:

$$\frac{d\mathcal{H}}{dt} = \sum_{i=1}^{2Nd} \sum_{j=1}^{2Nd} B_{ij} \frac{\partial \mathcal{H}}{\partial \Gamma_i} \frac{\partial \mathcal{H}}{\partial \Gamma_j} = 0$$

(12)

We further note that time reversibility of the underlying dynamics enforces the condition

$$\mathcal{H}(\Gamma) = \mathcal{H}(\Gamma^*)$$

(13)

where $\Gamma^*$ is obtained from $\Gamma$ by reversing all the momentum-like variables. The phase space contraction rate $\Lambda(\Gamma^*)$ at time $t = s$, defined earlier, may be written as

$$\Lambda(\Gamma)_{t=s} = -\sum_{i=1}^{2Nd} \frac{\partial \dot{\Gamma}_i(t)}{\partial \Gamma_i(t)} \bigg|_{t=s} - \sum_{i,j=1}^{2Nd} B_{ij} \frac{\partial \mathcal{H}}{\partial \Gamma_i \partial \Gamma_j} \bigg|_{t=s}$$

(14)
We now define entropy production in a time interval $\tau$ under a non-Hamiltonian evolution be

$$
\Delta S = k_B \int_0^\tau \Lambda(\Gamma^t)dt
$$

(15)

where $k_B$ denotes the Boltzmann constant. For a given state $\Gamma = (z, Y)$, we define a time reversed state $\Gamma^*$ to be $(z^*, Y^*)$. Let $\Gamma_+(t)$ denote the state of the extended system at time $t$ starting from an initial extended microstate $\Gamma^0$ and let $\Gamma_-(t)$ denote state of the system at time $t$ but evolving from the momentum reversed final state $\Gamma^{**}$. With this as the background, we are interested in computing the probability that the system $\psi$, at $t = 0$, starts in a particular microstate $z(0) = z_A$ and after evolving for a time $t = \tau$, reaches a state $z(\tau) = z_B$, generating an entropy $\Delta S$. Note that the evolution of $\Gamma = (z, Y)$ is deterministic, eq(11). We resort to probabilistic description when we are focusing only on the evolution of $z$. For a particular choice of the initial condition $z = z_A$, the probability distribution is over the initial conditions of heatbath variables $Y$

$$
P_+(z_B, \Delta S|z_A) = \int dY p(Y) \delta[z_B - \hat{z}^*_+(z_A, Y)].\delta[\Delta S - \hat{\Delta}S(z_A, Y)]
$$

(16)

where $z^*_+(z_A, Y)$ and $\hat{\Delta}S(z_A, Y)$ denote the final state of the system $\psi$ and the net entropy produced respectively, after $\psi$ has evolved for a time $t = \tau$ starting at $z_A$ with the reservoir starting at $Y$. Using the identity $z_A = \hat{z}^0_+(z, Y)$ we can now integrate over the full phase space vector $\Gamma = (z, Y)$:

$$
P_+(z_B, \Delta S|z_A) = \int d\Gamma p(\Gamma) \delta[z_A - \hat{z}^0_+(\Gamma)].\delta[z_B - \hat{z}^*_+(\Gamma)].\delta[\Delta S - \hat{\Delta}S(\Gamma)]
$$

(17)

if the dynamical system eq (11) possess $n_c$ independent conservation laws:

$$
\Lambda_k(\Gamma) = \lambda_k, \quad k = 1, \ldots, n_c
$$

(18)

then the probability distribution of the microstates can be written as:

$$
p(\Gamma) = \prod_{k=1}^{n_c} \delta(\Lambda_k(\Gamma) - \lambda_k)
$$

(19)

In instances where $\mathcal{H}$ is the only conserved quantity of the dynamics, the states $\Gamma$ are those drawn from the constant $\mathcal{H}$ surface

7
\[ p(\Gamma^0) = \delta(H(\Gamma^0) - E) \] 

hence, eq (17) may be rewritten as

\[ P_+(z_B, \Delta S|z_A) = \int d\Gamma^0 \delta(H(\Gamma^0) - E)\delta[z_A - \hat{z}^0(\Gamma^0)], \delta[z_B - z^r(\Gamma^0)], \delta[\Delta S - \hat{\Delta} S(\Gamma^0)] \]  

\[ P_+(z_B, \Delta S|z_A) = \int d\Gamma^0 \delta(H(\Gamma^0) - E)\delta[z_A - \hat{z}^0(\Gamma^0)], \delta[z_B - z^r(\Gamma^0)], \delta[\Delta S - \hat{\Delta} S(\Gamma^0)] \]  

As the dynamics is time reversal invariant, and \( \mathcal{H} \) is conserved and we have:

\[ \Delta \hat{S}(\Gamma^*) = -\hat{\Delta} S(\Gamma^0) \]  

\[ \mathcal{H}(\Gamma^0) = \mathcal{H}(\Gamma^*) \]  

\[ \hat{z}^0(\Gamma^0) = [z^r(\Gamma^*)]^* \]  

With these expressions at hand, we may now recast the above integral as:

\[ P_+(z_B, \Delta S|z_A) = \int d\Gamma^0 \delta(H(\Gamma^*) - E)\delta[\hat{z}_A^* - \hat{z}^r(\Gamma^*)], \delta[z_B - \hat{z}^0(\Gamma^*)], \delta[\Delta S + \hat{\Delta} S(\Gamma^*)] \]

where we have cast all the variables in the r.h.s of the above integral with the time reversed counterparts of the final states, except for the integration volume element \( d\Gamma^0 \). In general, as the phase space volume is not conserved in a non-Hamiltonian evolution, \( d\Gamma^0 \) is not an invariant volume under eq(11) and hence \( d\Gamma^0 \) cannot be directly replaced by \( d\Gamma^* \). The Jacobian of transformation from the initial to the final time reversed phase space coordinates \( J(\Gamma^*; \Gamma^0) \) is not unity and we have

\[ d\Gamma^* = J(\Gamma^*; \Gamma^0)d\Gamma^0 = J(\Gamma^*; \Gamma^r)J(\Gamma^r; \Gamma^0)d\Gamma^0 \]

As the dynamical system eq(11) is assumed to be time reversal invariant,

\[ J(\Gamma^*; \Gamma^r) = 1 \]

therefore,

\[ J(\Gamma^*; \Gamma^0) = J(\Gamma^r; \Gamma^0) \]
The time evolution of Jacobian of transformation is:

\[
\frac{dJ}{dt} = J \sum_{l=1}^{2N_d} \frac{\partial \dot{\Gamma}_l(t)}{\partial \Gamma_l(t)}
\]

The sum on the right is nothing but the negative of the phase space compressibility rate \( \Lambda(\Gamma^t) \), hence:

\[
J(\Gamma^\tau; \Gamma^0) = e^{-\int_0^\tau \Lambda(\Gamma^t) dt} = e^{-\frac{\Delta S(\Gamma^0)}{k_B}}
\]

From eq.(22), we know that \( \Delta \hat{S}(\Gamma^{\tau^*}) = -\hat{\Delta}S(\Gamma^0) \) and we have,

\[
d\Gamma^{\tau^*} = e^{\frac{\Delta S(\Gamma^{\tau^*})}{k_B}} d\Gamma^0
\]

We may now replace \( d\Gamma^0 \) in eq.(25) with \( e^{\frac{\Delta S(\Gamma^{\tau^*})}{k_B}} d\Gamma^{\tau^*} \) and we have:

\[
P_+(z_B, \Delta S|z_A) = \int e^{\frac{\Delta S(\Gamma^{\tau^*})}{k_B}} d\Gamma^{\tau^*} \delta(\mathcal{H}(\Gamma^{\tau^*}) - E) \delta[z_A - \hat{z}^0(\Gamma^{\tau^*})] \delta[z_B - z^{\tau^*}(\Gamma^{\tau^*})] \delta[\Delta S + \hat{\Delta}S(\Gamma^{\tau^*})],
\]

We can pull out the factor \( e^{\frac{\Delta S}{k_B}} \) out of the integration due to the presence of the delta function \( \delta[\Delta S + \hat{\Delta}S(\Gamma^{\tau^*})] \).

\[
P_+(z_B, \Delta S|z_A) = e^{\frac{\Delta S}{k_B}} \int d\Gamma^{\tau^*} \delta(\mathcal{H}(\Gamma^{\tau^*}) - E) \delta[z_A - \hat{z}^0(\Gamma^{\tau^*})] \delta[z_B - z^{\tau^*}(\Gamma^{\tau^*})] \delta[\Delta S + \hat{\Delta}S(\Gamma^{\tau^*})],
\]

The right hand side of the above equation is nothing but \( e^{\frac{\Delta S}{k_B}} \) times the probability distribution \( P(z_B^*, -\Delta S|z_A^*) \). Thus we have the final result of the Detailed Fluctuation theorem:

\[
P(z_B, \Delta S|z_A) = e^{\frac{\Delta S}{k_B}} P(z_B^*, -\Delta S|z_A^*),
\]

In summary, from the ingredients of the above derivation we list all the requirements that a dynamical system has to satisfy for the present derivation to go through:

1. The phase space of the extended system is of even number of dimensions.
2. The evolution is deterministic and equations of motion are time reversal invariant.
3. The phase space compressibility of the system is non-zero.
4. A constant of motion, usually a “psuedo-Hamiltonian” can be identified for the system that is time reversal invariant.

From the above points, it can be see that no assumptions have been made about the specific type of interactions present in the system and there are no restrictions on system size and time scale $\tau$ over which these fluctuations are realized. It should also be appreciated that this detailed fluctuation theorem is valid arbitrarily far from equilibrium, as no assumptions of thermodynamic nature has been made in the derivation. Further, unlike in the original derivation, there is no requirement for the system to be driven out of equilibrium through a given protocol. As there are fluctuations in the phase space compressibility even at equilibrium, one can capture the detailed fluctuation theorem even in an equilibrium simulation. This result is in contrast to many other fluctuation theorems which are valid far from equilibrium and at equilibrium they boil down to trivial identities as there is no average entropy production or consumption at equilibrium.

Another issue is the choice of the microcanonical ensemble for the extended system. This is in contrast with Jarzynski’s suggestion, which is to sample the reservoir degree of freedom from a Gaussian distribution. Instead, the present derivation treats all the degrees of freedom on equal footing and hence is more appealing, where the only assumptions made are the usual ones of ergodicity and equal apriori probabilities \[3, 9\].

V. ILLUSTRATION OF DETAILED FLUCTUATION THEOREM IN DIFFERENT ENSEMBLES

For a better appreciation of our results, we shall study the detailed fluctuation theorem in the context of a few popular extended phase space methods. All the examples mentioned below have the non-Hamiltonian evolution such that the system of interest evolves consistent with the appropriate ensemble the equations are supposed to mimic. The statistical mechanical properties of these systems are very extensively studied in the earlier papers \[3, 14, 15\] and hence our interest here will be limited to examining them in the light of the applicability of the detailed fluctuation theorem.
A. NOSE HOOVER DYNAMICS

In the Nose-Hoover thermostating scheme, an N particle system in \(d\) spatial dimensions with Cartesian positions \(\mathbf{r} \equiv \{ \mathbf{r}_1, \ldots, \mathbf{r}_N \}\) and momenta \(\mathbf{p} \equiv \{ \mathbf{p}_1, \ldots, \mathbf{p}_N \}\) interacting through \(N\) particle potential \(\Phi(\mathbf{r}_1, \ldots, \mathbf{r}_N)\) is augmented with 2 heat bath variables \(\mathbf{Y} = (\eta, p_\eta)\) such that the \(2dN + 2\) dimensional extended phase space vector \(\mathbf{\Gamma} = (\mathbf{r}, \mathbf{p}, \eta, p_\eta)\) evolves as follows:

\[
\begin{align*}
\dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m} \\
\dot{\mathbf{p}}_i &= -\frac{\partial \Phi(\mathbf{r}_1)}{\partial \mathbf{r}_1} - \frac{p_\eta}{Q} \mathbf{p}_i \\
\dot{\eta} &= \frac{p_\eta}{Q} \\
\dot{p}_\eta &= \left[ \sum_{i=1}^N \frac{\mathbf{p}_i^2}{m} - dNk_B T \right] \\
\end{align*}
\]

The parameter \(Q\) represents the strength of the Nose-Hoover coupling which controls the time scale over which the equilibration takes place and \(T\) is the temperature at which we wish to maintain the system of interest. A curious point that can be noted in these equations is that the variable \(\eta\) does not explicitly get connected to other degrees of freedom. Still, it is profitable to retain this variable in the dynamical equations of motion as it facilitates the casting of these equations in the desired form

\[
\begin{pmatrix}
\dot{\mathbf{r}}_i \\
\dot{\eta} \\
\dot{\mathbf{p}}_i \\
\dot{p}_\eta
\end{pmatrix}
= \begin{pmatrix}
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1 \\
-1 & 0 & 0 & -\mathbf{p}_i \\
0 & -1 & \mathbf{p}_i & 0
\end{pmatrix}
\begin{pmatrix}
\frac{\partial \Phi(\mathbf{r}_1)}{\partial \mathbf{r}_1} \\
\partial Nk_B T \\
\frac{p_\eta}{m} \\
\frac{p_\eta}{Q}
\end{pmatrix}
\]

for

\[
\mathcal{H}(\mathbf{\Gamma}) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + \Phi(\mathbf{r}) + \frac{p_\eta^2}{2Q} + dNk_B T \eta
\]

Identifying the first two terms of the above as the system Hamiltonian,

\[
H^*([\mathbf{r}], [\mathbf{p}]) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + \Phi(\mathbf{r})
\]
we have
\[
\mathcal{H}(\Gamma) = H^s(\{r\}, \{p\}) + \frac{p_\eta^2}{2Q} + dNk_B T \eta
\] (42)

Nose-Hoover dynamics is time reversal invariant and possesses a “pseudo-Hamiltonian” as a constant of motion and hence, satisfies the essential requirements needed for the present analysis. The phase space compressibility of this system is given by eq (14)

\[
\Lambda(\Gamma^s) = -\sum_{i=1}^{2n+2} \frac{\partial \dot{r}_i^s}{\partial \Gamma^i} = -\sum_i \frac{\partial p_i}{\partial \Gamma^i} = \frac{dNp_\eta}{Q} = dN\eta
\] (43)

so the total phase space compression during an evolution from \(t=0\) to \(t=\tau\) is from eq (15)

\[
\Delta S = k_B \int_0^\tau \Lambda(\Gamma^s) ds = k_B dN(\eta(\tau) - \eta(0))
\] (44)

There are several points in order. Given a time evolution of \(\Gamma^0 = (r_0^0, p_0^0, \eta^0, p_\eta^0)\) to \(\Gamma^t = (r_t^0, p_t^0, \eta^t, p_\eta^t)\), there is a phase space compression of \(k_B dN(\eta^t - \eta^0)\). Note that this quantity is path independent and depends only on the initial and final state of the position variable of the heat bath, and does not explicitly depend upon the functional form of the potential.

With this definition, one can gather all the trajectories that start at \((z_A^0, \eta, p_\eta)\) and evolve to \((z_B, \eta + \Delta S, \hat{p}_\eta)\) where \(z_A^0\) and \(z_B\) are fixed initial and final states (positions and momenta) of the system of interest and \(\eta, p_\eta\) and \(\hat{p}_\eta\) are arbitrary (subject to the requirement that the extended state vector \(\Gamma\) stays on a constant energy hypersurface). The probability of obtaining such a trajectory is \(P_+(z_B, \eta + \Delta S | z_A^0)\). To obtain the anti-trajectories, from the time reversed final states one gathers all those states that start from \((z_B^*, \eta, \hat{p}_\eta)\) and evolve into \((z_A^*, \eta - \Delta S, p_\eta)\). The probability of obtaining such a trajectory is \(P_-(z_A^*, -\Delta S | z_B^*)\). The detailed fluctuation theorem requires the ratio of these two probabilities go like \(e^{\Delta S / k_B}\).

Further, in the limit of \(Q \rightarrow \infty\), the equations of motion eq(35) and eq(36) are reduced to that of a Hamiltonian evolution and we have, from eq(37), \(\eta(\tau) = \eta(0)\) and hence, from eq (44), \(\Delta S = 0\). This means that the probabilities of forward and backward trajectories are identical:

\[
P(z_A \rightarrow z_B) = P(z_B^* \rightarrow z_A^*)
\] (45)

as can be expected for an isolated system.
Now, consider the probability that the system $\psi$ evolves from state $z_A$ to state $z_B$ in a time $\tau$. This probability, let it be denoted by $P(z_A \mapsto z_B)$, is

$$P(z_A \mapsto z_B) = \int P(z_B, \Delta S|z_A) d(\Delta S)$$  \hspace{1cm} (46)$$

Now, applying the detailed fluctuation theorem on the right hand side, we have

$$P(z_A \mapsto z_B) = \int e^{\frac{\Delta S}{k_B}} P(z'_A, -\Delta S|z'_B) d(\Delta S)$$  \hspace{1cm} (47)$$

For the Nose-Hoover thermostat, we know that $\Delta S = k_B dN (\eta(\tau) - \eta(0))$ and from eq(42) we have

$$\eta(0) = \frac{\left[ E - H^s(z_A) - p^2_0(0) \right]}{2Q}, \hspace{1cm} \eta(\tau) = \frac{\left[ E - H^s(z_B) - p^2_0(\tau) \right]}{2Q}$$  \hspace{1cm} (48)$$

where $E$ is the constant energy over which the microcanonical ensemble of the full system is defined. Hence we have,

$$\frac{\Delta S}{k_B} = dN (\eta(\tau) - \eta(0)) = \frac{H^s(z_A) - p^2_0(0) + H^s(z_B) + p^2_0(\tau)}{2Q}$$  \hspace{1cm} (49)$$

Inserting this into the right hand side of eq(47),

$$P(z_A \mapsto z_B) = \int e^{\frac{H^s(z_A) - p^2_0(0) - H^s(z_B) + p^2_0(\tau)}{2Q}} P(z'_A, -\Delta S|z'_B) d(\Delta S)$$  \hspace{1cm} (50)$$

Since the $z_A$ and $z_B$ are independent of the integration variable, they can be pulled out of the integration and we have

$$P(z_A \mapsto z_B) = e^{\frac{H^s(z_A) - H^s(z_B)}{k_B T}} \int e^{\frac{p^2_0(\tau) - p^2_0(0)}{2Qk_B T}} P(z'_A, -\Delta S|z'_B) d(\Delta S)$$  \hspace{1cm} (51)$$

Re-arranging the above,

$$e^{\frac{-H^s(z_A)}{k_B T}} P(z_A \mapsto z_B) = e^{\frac{-H^s(z_B)}{k_B T}} \int e^{\frac{p^2_0(\tau) - p^2_0(0)}{2Qk_B T}} P(z'_A, -\Delta S|z'_B) d(\Delta S)$$  \hspace{1cm} (52)$$

Assuming that the times $t = 0$ and $t = \tau$ are chosen sufficiently long time after the system has equilibrated, we can assume that the kinetic energy distribution is consistent with the equipartition theorem, and hence the total kinetic energy is equal to the $\frac{1}{2}dNk_BT$. 

13
\[
\sum_{i=1}^{N} \frac{p_i^2}{2m} = \frac{1}{2} dN k_B T
\]  

With this assumption, and from the last of the Nose-Hoover equations eq\((53)\), we see that \(\dot{\eta}_j = 0\), and hence \(e^{\frac{p_j^2(\tau) - p_j^2(0)}{2Q k_B T}} = 1\). Substituting this in eq \((52)\), we get

\[
e^{-\frac{H_r(z^*_A)}{k_B T}} P(z_A \Rightarrow z_B) = e^{-\frac{H_r(z^*_B)}{k_B T}} \int P(z_A^*, -\Delta S | z_B^*) d(\Delta S)
\]  

The integral in right hand side of the above equation can readily be identified as the probability \(P(z_B^* \Rightarrow z_A^*)\) and since the system Hamiltonian also the time reversal invariance, this probability is also equal to \(P(z_B \Rightarrow z_A)\). So, we have:

\[
e^{-\frac{H_r(z^*_A)}{k_B T}} P(z_A \Rightarrow z_B) = e^{-\frac{H_r(z^*_B)}{k_B T}} P(z_B \Rightarrow z_A)
\]  

Which is nothing but the statement of detailed balance, which is valid for any system at equilibrium.

**B. NOSE HOOVER CHAIN DYNAMICS**

If more than one conservation laws are obeyed by the dynamical system, it is well known that the Nose-Hoover thermostatting scheme fails to generate the canonical ensemble. This happens because the accessible phase space gets restricted by the conservation and hence the system fails to access all the regions of the phase space in the course of its dynamics. This problem can be overcome by extending the number of heat bath variables. One such method is the Nose-Hoover chain thermostat. Its equations of motion are given by:

\[
\dot{r}_i = \frac{p_i}{m}
\]  

\[
\dot{p}_i = -\frac{\partial \Phi(\{r_j\})}{\partial r_i} - \frac{p_{\eta}}{Q_1} p_i
\]  

\[
\dot{\eta}_j = \frac{p_{\eta}}{Q_j}, \quad j = 1, ..., M
\]  

\[
p_{\eta} = \left[ \sum_{i=1}^{N} \frac{p_i^2}{m_i} - dN k_B T \right] - \frac{p_{\eta}}{Q_2} p_{\eta}
\]
\[ p_{\eta_j} = \left[ \frac{p_{\eta_{j-1}}^2}{Q_{j-1}} - k_B T \right] - \frac{p_{\eta_{j+1}}}{Q_{j+1}} p_{\eta_j}, \quad j = 2, ..., M - 1 \] (60)

\[ p_{\eta_M} = \left[ \frac{p_{\eta_{M-1}}^2}{Q_{M-1}} - k_B T \right] \] (61)

It can be shown that these equations of motion, preserve the psuedo-Hamiltonian:

\[ H(\Gamma) = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + \Phi(\{r\}) + \sum_{j=1}^{N} \frac{p_{\eta_j}^2}{2Q_j} + dNkT\eta_1 + k_B T \sum_{k=2}^{M} \eta_k \] (62)

The phase space compressibility for this system of equations is given by

\[ \Lambda(\Gamma^*) = (dN\dot{\eta}_1 + \dot{\eta}_2 + \dot{\eta}_3 + ... + \dot{\eta}_M) \] (63)

Again, the phase space compressibility rate for this system is also a total time derivative of the heat bath variables and the psuedo-Hamiltonian is invariant under time reversal. Hence we can derive the detailed fluctuation theorem in the context of Nose-Hoover chain thermostat.

C. MTK ISOBARIC ENSEMBLE

The Martyna, Tobias and Klein ensemble is also based on the Non-Hamiltonian phase space formulation and is known to generate the correct isobaric ensemble. The equations of motion read ([15])

\[ \dot{r}_i = \frac{p_i}{m} + \frac{P_g}{W_g} r_i \] (64)

\[ \dot{p}_i = -\frac{\partial \Phi(\{r\})}{\partial r_i} - \frac{P_g}{W_g} p_i - \frac{1}{N_f} Tr(p_g) p_i - \frac{p_{\eta_1}}{Q_1} p_i \] (65)

\[ \dot{h} = \frac{P_g h}{W_g} \] (66)

\[ \dot{p}_g = det[h] (P^{(int)} - IP) + \frac{1}{N_f} \sum \frac{p_i^2}{m} I - \frac{p_{\eta_1}}{Q_1} p_g \] (67)
\[ \dot{\eta}_j = \frac{p_{\eta_j}}{Q_j} \quad \dot{\xi}_j = \frac{p_{\xi_j}}{Q_j} \]  

(68)

\[ p_{\eta M} = G_M \]  

(69)

\[ \dot{p}_{\xi_j} = G_j - \frac{p_{\xi_{j+1}}}{Q_{j+1}} p_{\xi_j} \quad \dot{p}_{\xi M} = G_M \]  

(70)

where \( P^{(int)} \) is the internal pressure, \( I \) is the 3x3 identity matrix and \( G_j \) are the thermostat forces, given by

\[ G_1 = \sum_{i=1}^{N} \frac{p_i^2}{m_i} - d k_B T \quad G_j = \frac{p_{\eta_{j-1}}^2}{Q_{j-1}} - k_B T \]  

(71)

and

\[ \dot{G}_1 = \frac{Tr[p_g^T p_g]}{W_g} - d^2 kT \quad \dot{G}_j = \frac{p_{\xi_{j-1}}^2}{Q_{j-1}} - k_B T \]  

(72)

These equations have the pseudo-Hamiltonian as

\[ H = \sum_i \frac{p_i^2}{2m_i} + \Phi(\{r\}) + \frac{Tr(p_g^T p_g)}{2W_g} + P_{\text{det}}(\mathbf{h}) + \sum_{j=2}^{M} \left[ \frac{p_{\eta_j}^2}{2Q_j} + \frac{p_{\xi_j}^2}{2Q_j} \right] + N_j k_B T \eta_1 + d^2 k_B T \xi_1 + k_B T \sum_{k=2}^{M} (\eta_k + \xi_k) \]  

(73)

The phase space compression rate for this system of equations comes out to be

\[ \Lambda = (d-1) \frac{d}{dt} \ln[\text{det}(\mathbf{h})] + d N \dot{\eta}_1 + d^2 \dot{\xi}_1 + \sum_{k=2}^{M} [\dot{\eta}_k + \dot{\xi}_k] \]  

(74)

It is readily evident that, as with Nose-Hoover, Nose-Hoover Chain and massive thermostating schemes, the phase space compression rate is again a total time derivative of the heat bath variables alone and the pseudo-Hamiltonian is invariant under time reversal operation. Further, the phase space compressibility is a function of position-like variable of the heat bath and hence satisfies the assumption, eq(22). This implies that the MTK isobaric ensemble is capable of capturing the detailed fluctuation theorem.

Also, from eq (43), eq (63) and eq (74), we see that the phase space compression for all the extended system dynamics is dependent only on position-like variables of the heat bath and not on the system variables per se. This is evident from the extended phase space
formulation itself where there are no coupling terms between the heat bath variables and our
Hamiltonian system variables. The phase space compression for the Hamiltonian systems is
always zero, hence the contribution towards the phase space compression, eq 14 is from the
heat bath variables alone.

As is evident from the examples above, it is important to identify all the conservation
laws satisfied by a given set of dynamical equations. For instance, in many thermostatting
schemes, the psuedo-Hamiltonian, $H$ is usually not the only conserved quantity. In such
cases, the probability distribution has to be sampled from the hypersurface defined in eq
19 [3]. We note here that all conserved quantities have to be time reversal invariant for the
present proof to go through.

D. GAUSSIAN ISOKINETIC ENSEMBLE

Another example where the non-Hamiltonian phase space formalism can be readily ap-
plied is the case of Gaussian isokinetic ensemble, which keeps the kinetic energy of the system
constrained to a particular value but generates a canonical distribution in the coordinate
space. The equations of motion read

$$\dot{r}_i = \frac{p_i}{m_i} \quad i = 1, \ldots, N$$  \hspace{1cm} (75)

$$\dot{p}_i = F_i - \left[ \frac{\sum_{j=1}^{N} F_j p_j / m_j}{\sum_{j=1}^{N} p_j^2 / m_j} \right] p_i \quad i = 1, \ldots, N$$  \hspace{1cm} (76)

This isokinetic ensemble method different from other non-Hamiltonian phase space
methods in that there are no extra degrees of freedom appended to the system, and also
the total energy of the system is also not conserved. But, by construction, one has the
conservation of the total kinetic energy and the unnormalized microcanonical probability
density can still be defined as:

$$p(p) = \delta\left(\sum_{i=1}^{N} \frac{p_i^2}{m} - K\right)$$  \hspace{1cm} (77)
where $K$ is an arbitrary constant. The phase space compressibility rate of this system, can be obtained as

$$
\Lambda = -\sum_{i=1}^{N} \nabla_{r_i} \dot{r}_i + \nabla_{p_i} \dot{p}_i
$$

from eq (75) and eq (76) this becomes gives

$$
\Lambda = -\frac{3N-1}{K} \frac{d\phi\{r\}}{dt}
$$

where the assumption is that there is no explicit time dependence of the potential on time, so that the partial derivative of the potential is zero.

The Compressibility for this system is given as

$$
\Delta S = -\frac{3N-1}{K} \int_{0}^{\tau} \frac{d\phi\{r\}}{dt} = -k_B \frac{3N-1}{K} [\phi(r_B) - \phi(r_A)]
$$

The above equation implies, as the system starts from $z_A \equiv (r_A, p_A)$ and evolves to $z_B \equiv (r_B, p_B)$, the entropy generated is proportional to the change in the potential energy at the end points, $\phi(r_A) - \phi(r_B)$. As the constraint, total kinetic energy, is invariant under time reversal and the phase space compressibility of the system eq(80) satisfies eq(22), the present derivation of the detailed fluctuation theorem applies for the system evolving under the Gaussian isokinetic ensemble.

The absence of external degrees of freedom in this example means that the phase space vector evolves deterministically and hence the probabilities $P(z_B, \Delta S|z_A)$ and $P(z_B^*, -\Delta S|z_A)$ are reduced to just product of delta functions as there are no heat bath variables to integrate over. The joint probability $P(z_B, \Delta S|z_A)$ is actually just a function of $z_B$ and $z_A$ alone as $\Delta S$ itself is a function of $z_B$ and $z_A$. In that case, consider the probability $P(r_A \rightarrow r_B) \equiv P(r_B|r_A)$ that the system evolves from a position $r_A$ to a position $r_B$ in a time $\tau$. This involves integrating over all momentum variables and all possible phase space compression values.

$$
P(r_A \rightarrow r_B) = \int d\mathbf{p}_A d\mathbf{p}_B \int P(\Delta S) d(\Delta S) P(z_B \equiv (r_B, p_B), \Delta S|z_A \equiv (r_A, p_A))
$$
where $P(\Delta S)$ is the probability distribution of $\Delta S$. Since the phase space compression depends only on the initial and final coordinates, eq (80), we have

$$P(\Delta S) = \delta \left[ \Delta S - \hat{\Delta} S(r_A, r_B) \right] \quad (82)$$

where

$$\hat{\Delta} S(r_A, r_B) = -k_B \frac{3N - 1}{K} \int_0^\tau \left( \frac{d\phi(r)}{dt} \right) dt \quad (83)$$

Inserting this into the above equation

$$P(r_A \leftrightarrow r_B) = \int d\mathbf{p}_A d\mathbf{p}_B d(\Delta S) \delta \left[ \Delta S - \hat{\Delta} S(r_A, r_B) \right] e^{\frac{\hat{\Delta} S}{k_B}} P(z_A^*, -\Delta S|z_B^*) \quad (84)$$

Now, $\hat{\Delta} S(r_A, r_B) = -\Delta S(r_B, r_A)$ hence

$$P(r_A \leftrightarrow r_B) = e^{\hat{\Delta} S(r_A, r_B)} \int d\mathbf{p}_A d\mathbf{p}_B \int d(\Delta S) \delta \left[ \Delta S + \hat{\Delta} S(r_B, r_A) \right] P(z_A^*, -\Delta S|z_B^*) \quad (85)$$

The RHS can be rearranged, remembering that the delta function is even in its arguments,

$$P(r_A \rightarrow r_B) = e^{\frac{\hat{\Delta} S(r_A, r_B)}{k_B}} \int d(-\mathbf{p}_A) d(-\mathbf{p}_B) \int d(-\Delta S) \delta \left[ \Delta S - \hat{\Delta} S(r_B, r_A) \right] P(z_A^*, \Delta S|z_B^*) \quad (86)$$

The integral on the right hand side can be readily identified as the probability of system evolving from $r_B$ to $r_A$ and hence

$$P(r_A \rightarrow r_B) = e^{\frac{\hat{\Delta} S(r_A, r_B)}{k_B}} P(r_B \rightarrow r_A) \quad (87)$$

Now, from eq (83)

$$\hat{\Delta} S(r_A, r_B) = -k_B \frac{3N - 1}{K} [\phi(r_B) - \phi(r_A)] \quad (88)$$

Choosing the arbitrary constant $K = (3N - 1)k_B T$, where $T$ is the desired temperature, we have

$$P(r_A \rightarrow r_B) = e^{\frac{\phi(r_A) - \phi(r_B)}{k_B T}} P(r_B \rightarrow r_A) \quad (89)$$
Rearranging the above equation, we see that the detailed fluctuation theorem just boils down to the detailed balance equation in the configuration space:

$$e^{-\frac{\phi(r_A)}{k_B T}} P(r_A \rightarrow r_B) = e^{-\frac{\phi(r_B)}{k_B T}} P(r_B \rightarrow r_A)$$  \hspace{1cm} (90)

The choice $K = (3N - 1)k_B T$ is natural from the equipartitioning theorem which says that every independent momentum degree of freedom has an average kinetic energy of $\frac{1}{2}k_B T$. The system has $(3N - 1)$ independent momentum degrees of freedom ($3N$ momentum variables and one constraint on the total kinetic energy), hence the total kinetic energy is $\frac{1}{2}(3N - 1)k_B T$. The Gaussian Isokinetic ensemble is a simple yet powerful example to appreciate that the Non-Hamiltonian characteristic alone is sufficient to bring out all the seemingly counter-intuitive features of the statistical mechanics like the entropy production and consumption anisotropy, direction of time emerging from the time reversible dynamics, anisotropy in the transition probabilities, emergence of Boltzmann distribution in the configuration space etc.

VI. DETAILED FLUCTUATION THEOREM AND CONSERVATION LAWS

Consider the Nose Hoover thermostating scheme. If the forces acting on the system are derivable from a two body potential,

$$\Phi(r_1, ..., r_N) = \frac{1}{2} \sum_{\substack{i,j=1 \atop i \neq j}}^N \phi_2(|r_i - r_j|)$$  \hspace{1cm} (91)

such that the net force acting on the system is zero, then there are $d$ additional conserved quantities that emerge in the Nose-Hoover dynamics:

$$P\epsilon^n = K$$  \hspace{1cm} (92)

where $P = \sum_{i=1}^n p_i$ is the total momentum of the system and $K$ is an arbitrary vector in $d$ dimensions. In our context, this would mean that we can no longer use eqs (20) but instead use $p(\Gamma) = \delta(H'(\Gamma) - E)\delta(P\epsilon^n - K)$ as the correct distribution function. The problems associated with the presence of additional conservation laws in the context of generating the dynamics appropriate to a desired ensemble is well studied, where it is shown that the presence of hidden conservation laws in the dynamics will lead to an ensemble different from the required canonical ensemble. It should be noted that the suggested solution of
appending an extended chain of thermostats, instead of one, though known to generate the
correct distribution in the system subspace, will not invalidate the presence of additional
conservation laws. So, the augmentation of the Nose-Hoover to Nose-Hoover chain will not
help in demonstration of the detailed fluctuation theorem. The problem arises from the fact
$P e^\eta$ is not invariant under time reversal: $(P e^\eta)^* \neq P e^\eta$ and it is because of this problem, the
present method of derivation hits a roadblock. In fact, for all systems which have conserved
quantities which do not have a definite parity or are of odd parity under time reversal would
fail to capture fluctuation theorems of the usual type, as the time reversed states are not
accessible to the system. But for systems which have conserved quantities which are of odd
parity under time reversal, say $K$, it is easy to see that the Detailed Fluctuation Theorem
takes the form:

$$ P_+(z_B, \triangle S|z_A, K) = e^{\frac{\triangle S}{k_B}} P_-(z_B^*, -\triangle S|z_A^*, K^*) $$ (93)

VII. FREE ENERGY RELATIONS FROM THE DETAILED FLUCTUATION
THEOREM

It would be worthwhile to investigate whether the free energy equality, Jarzynski’s iden-
tity, is derivable from the detailed fluctuation theorem in the non-Hamiltonian framework.
For simplicity, we shall attempt to derive the Jarzynski’s identity from the detailed fluc-
tuation theorem result for a system coupled to Nose-Hoover thermostat. The Jarzynski’s
identity [18] reads,

$$ <exp(-\beta W)> = exp(-\beta \triangle F_{AB}), \quad \beta = \frac{1}{kT} $$ (94)

where $\triangle F_{AB}$ is the equilibrium free energy difference between A and B:

$$ \triangle F_{AB} = -k_B T \ln \left( \frac{Z_A}{Z_B} \right) $$ (95)

where $Z_A$ and $Z_B$ are canonical partition functions of the systems A and B.

$$ Z_A = \int e^{-\beta H_A^{\star}(r_A, p_A)} d^3r_A d^3p_A $$ (96)

and similarly
\[ Z_B = \int e^{-\beta H_B^s(r_B, \mathbf{p}_B)} \, dr_B \, d\mathbf{p}_B \]  

(97)

where \( H_A^s \) and \( H_B^s \) are the Hamiltonian of the two systems whose free energy difference is to be computed. The Hamiltonians are superscripted to make the distinction between the Hamiltonian of the system of interest and the pseudo-Hamiltonian, which contains reservoir degrees of freedom also. We assume that there is a single time-dependent Hamiltonian, which at the time \( t = 0 \) is the Hamiltonian corresponding to the state A, \( H_A \) and at a time \( t = \tau \) transforms to the Hamiltonian corresponding to the state B, \( H_B \). This variation can be brought about by, for example, a time dependent potential \( \Phi(r_1, \ldots, r_N, t) \), such that \( \Phi(r_1, \ldots, r_N, 0) = \Phi_A(r_1, \ldots, r_N) \) and \( \Phi(r_1, \ldots, r_N, \tau) = \Phi_B(r_1, \ldots, r_N) \) where \( \Phi_A \) and \( \Phi_B \) are the potentials of states A and B respectively.

The change in the energy of the “system of interest” due to this time variation of the potential is given by [9, 11]:

\[ H_B - H_A = H^S(z_B, \tau) - H^S(z_A, 0) = \int_0^\tau dt \frac{\partial H^s(z_t, t)}{\partial z_t} \dot{z}_t + \int_0^\tau dt \frac{\partial H^s(z_t, t)}{\partial t} = Q + W \]  

(98)

The above equation can be called the mathematical formulation of the First law of Thermodynamics, where the term on the left hand side is identified with the change in the internal energy of the system, the first term of the right is identified as the heat \( Q \) transferred from the bath to the system and the second term is the work performed on the the system. Note that both, work and heat are defined in terms of the system Hamiltonian alone. The effect of thermostatting is felt only through the coupling of evolution of the system variables and heat bath variables.

From the explicit functional form for the system Hamiltonian and the Nose-Hoover equations of motion, we can calculate the first term on the right hand side of eq (98) as

\[ Q = \int_0^\tau dt \left( \frac{P_\eta(t)}{Q_1} \right) \sum_{i=1}^N \frac{p_i^2(t)}{m} \]  

(99)

Identifying the term \( \frac{P_\eta(t)}{Q_1} \) as \( \dot{\eta} \) and \( \sum_{i=1}^N \frac{p_i^2(t)}{m} \) as \( \ddot{p}_\eta + dNk_B T \) from the Nose-Hoover equations of motion eq (38) and eq (39) we get
As discussed earlier, if the times \( t = 0 \) and \( t = \tau \) are such long after the system has reached steady state such that the average kinetic energy is determined by the temperature, we have, from eq(38) and eq(53)

\[
Q(\tau) = -dNk_BT \int_0^\tau dt \dot{\eta}(t) = -dNk_BT(\eta(\tau) - \eta(0))
\]  

(101)

Identifying \( dN\dot{\eta}(t) \) as the phase space compression rate for this system, eq(43), we have

\[
Q(\tau) = k_BT \int_0^\tau \Lambda(t)dt = -T\Delta S
\]  

(102)

Thus we see that \( k_BT \) times the total phase space compression can be identified with the heat lost by the system to the thermostat. This is consistent with the assumption of eq (3).

If the term \( \Delta S \) can be identified by the change in the entropy, then the above equation boils to the Second Law of Thermodynamics. \[16, 17\]

With this identification, we are ready to take-on the Jarzynski’s work theorem in the context of Nose-Hoover thermostatted system.

\[
< e^{(-\beta W)} > = \int dz_A p(z_A) P_+(z_B, \Delta S|z_A)e^{(-\beta W(z_A,z_B,\Delta S))} d(z_B) d(\Delta S)
\]  

(103)

It is easy to understand how the above integral is constructed. The quantity \( P_+(z_B, \Delta S|z_A) \) gives the probability of system making a transition from \( z_A \) at time \( t = 0 \) to \( z_B \) at time \( t = \tau \) and in the process generates a phase space compression of \( \Delta S \). \( p(z_A) \) denotes the probability that the system is found in the state \( z_A \) at time \( t = 0 \). If the times are so chosen that the system is fully equilibrated at time \( t=0 \), this probability is actually the probability of the canonical ensemble:

\[
p(z_A) = \frac{e^{-\beta H_A^*(z_A)}}{Z_A}
\]  

(104)

where \( Z_A \) is the partition function for the system in the state A, eq (96). Substituting this and also the detailed fluctuation theorem, we have
\[ <e^{-\beta W}> = \frac{1}{Z_A} \int dz_A e^{-\beta H_A(z_A)} e^{\hat{\mathcal{S}}_B} P(z_A^*, -\Delta S|z_B^*) e^{(-\beta W(z_A, z_B, \Delta S))} d(z_B) d(\Delta S) \] (105)

Consider the terms in the exponentials, from eq(105) and eq (98) we have

\[ -\beta [H^*_A(z_A) - T \Delta S + W(z_A, z_B, \Delta S)] = -\beta (H^*_A(z_B)) \] (106)

and thus

\[ <e^{-\beta W}> = \frac{1}{Z_A} \int dz_A e^{-\beta H_B(z_B)} P(z_A^*, -\Delta S|z_B^*) d(z_B) d(\Delta S) \] (107)

But

\[ \int P(z_A^*, -\Delta S|z_B^*) d(z_B) d(\Delta S) = 1 \] (108)

And hence we have

\[ <e^{-\beta W}> = \frac{1}{Z_A} \int dz_B e^{-\beta H_B(z_B)} = \frac{Z_B}{Z_A} = \exp(-\beta \Delta F_{AB}) \] (109)

This is the Jarzynski’s Work theorem, eq(95) we set out to prove.

Although the connection between the detailed Fluctuation theorem and the Jarzynski’s identity has been established here only for the case of Nose-Hoover thermostatting scheme, it should be evident that the Jarzynski’s work theorem can be derived in all contexts where the Detailed Fluctuation theorem is applicable.

For illustration, consider the case of Gaussian Isokinetic ensemble. As mentioned above, these equations of motion fail to generate the proper canonical sampling in the momentum space but generates a canonical distribution in the coordinate space. But from eq, we see that the Free energy differences depends on the logarithm of the ratio of the two partition functions and hence the momentum partition function cancels out in the ratio and we are left with the ratio of the configuration partition functions at the states A and B. So we can see that one can realize the Jarzynski’s identity in the Gaussian Isokinetic ensemble.

As with the Nose-Hoover thermostat example above, Consider a system given by the Hamiltonian, \( H^*(\{r\}, \{p\}, t) = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + \Phi(\{r\}, t) \) we have the Gaussian Isokinetic equations of motion of the form,

\[ \dot{r}_i = \frac{p_i}{m_i}, \quad i = 1, ..., N \] (110)
\[ \dot{p}_i = -\nabla_{r_j} \phi(\{r\}, t) + \alpha(\{r\}, \{p\}, t)p_i \quad i = 1, \ldots, N \]  

(111)

where

\[ \alpha(\{r\}, \{p\}, t) = \left[ \frac{\sum_{j=1}^{N} \nabla_{r_j} \phi(\{r\}, t)p_j/m_j}{\sum_{j=1}^{N} p_j^2/m_j} \right] \]  

(112)

and the potential \( \phi(\{r\}, t) \) is such that \( \Phi(r_1, \ldots, r_N, 0) = \Phi_A(r_1, \ldots, r_N) \) and \( \Phi(r_1, \ldots, r_N, \tau) = \Phi_B(r_1, \ldots, r_N) \) where \( \Phi_A \) and \( \Phi_B \) are the potentials of states A and B respectively. The time variation of this potential indicates that the work is done on the system.

Consider again, eq(98), we have the heat lost to the thermostat given by

\[ Q = \int_0^\tau dt \frac{\partial H^s(z_t, t)}{\partial z_t} \dot{z}_t = \int_0^\tau dt \alpha(\{r\}, \{p\}, t) \sum_{i=1}^{N} p_i^2/m_i \]  

(113)

Substituting for \( \alpha(\{r\}, \{p\}, t) \) and simplifying we have

\[ Q = \int_0^\tau dt \left[ \sum_{j=1}^{N} \nabla_{r_j} \phi(\{r\}, t)p_j/m_j \right] \]  

(114)

Identifying \( \sum_{j=1}^{N} \nabla_{r_j} \phi(\{r\}, t)p_j/m_j = \frac{K}{3N-1} \Lambda(t) \) we have \( Q = \frac{K}{3N-1} \int_0^\tau dt \Lambda(t) \)

Together with eq (44) this gives

\[ Q = -\frac{K}{3N-1} \frac{\Delta S}{k_B} \]  

(115)

Choosing the arbitrary constant \( K = (3N - 1)k_BT \) (for reasons already discussed) we have

\[ Q = -T \Delta S \]  

(116)

Again, we see that the heat lost by the system is proportional to the total phase space compression, as with the Nose-Hoover thermostat. With this identification, the procedure to calculate \( < e^{-\beta W} > \) is essentially unchanged from the Nose-Hoover case, and we have the Jarzynski’s identity in the case of a system coupled to a Gaussian Isokinetic ensemble.
VIII. CONCLUSION

Detailed Fluctuation Theorem has been extended to a class of thermostatted systems, evolving under the extended system dynamics. It is demonstrated that this theorem retains the same form as for the original DFT for entropy production when one replaces the thermodynamic entropy with phase space compressibility. This theorem is of a wider applicability than its original counterpart and can be applied even to the systems at equilibrium. It is shown that this detailed fluctuation theorem is formally equivalent to the detailed balance equation for systems at equilibrium. Rederivation of the Jarzynski’s identity through the Detailed Fluctuation theorem has been demonstrated for both Nose-Hoover thermostat and the Gaussian Isokinetic ensembles.

[1] Jarzynski C, Hamiltonian Derivation of a Detailed Fluctuation Theorem: arXiv:cond-mat/9908286v1
[2] Jarzynski C, Hamiltonian Derivation of a Detailed Fluctuation Theorem, Journal of Statistical Physics, Volume 98, Numbers 1-2 / January, 2000, DOI: 10.1023/A:1018670721277
[3] Mark E. Tuckerman, Yi Liu, Giovanni Ciccotti, and Glenn J. Martyna, Non-Hamiltonian molecular dynamics: Generalizing Hamiltonian phase space principles to non-Hamiltonian systems J. Chem. Phys. 115, 1678 (2001)
[4] Alessandro Sergi and Mauro Ferrario, Non-Hamiltonian equations of motion with a conserved energy, Phys. Rev. E 64, 056125 (2001)
[5] EGD Cohen, L. Rondoni Note on Phase Space Contraction and Entropy Production in Thermostatted Hamiltonian Systems, arXiv:cond-mat/9712213v1,
[6] Giovanni Galavotti Fluctuation relation, fluctuation theorem, thermostats and entropy creation in nonequilibrium statistical physics, C. R. Physique 8 (2007) 486-494.
[7] D. Daems, G. Nicolis Entropy production and phase space volume contraction, Phys Rev E 59, 4000 (1999)
[8] DJ Evans, DJ Searles - The fluctuation theorem-Advances in Physics, 2002, Vol. 51, No. 7, 1529-1585
[9] Michel A. Cuendet, Statistical Mechanical Derivation of Jarzynski’s Identity for Thermostatted
Non-Hamiltonian Dynamics. Phys. Rev. Lett. 96, 120602 (2006).

[10] E. Schöll-Paschinger and C. Dellago, A proof of Jarzynski’s nonequilibrium work theorem for dynamical systems that conserve the canonical distribution J. Chem. Phys 125, 054105 2006

[11] The Jarzynski identity derived from general Hamiltonian or non-Hamiltonian dynamics reproducing NVT or NPT ensembles Michel A. Cuendet, J. Chem Phys, 125, 144109 2006

[12] Riccardo Chelli, Simone Marsili, Alessandro Barducci, and Piero Procacci, Recovering the Crooks equation for dynamical systems in the isothermal-isobaric ensemble: a strategy based on the equations of motion. J. Chem. Phys 126, 044502 (2007)

[13] Riccardo Chelli, Simone Marsili, Alessandro Barducci, and Piero Procacci, Generalization of the Jarzynski and Crooks nonequilibrium work theorems in molecular dynamics simulations, Phys Rev E, 75, 050101R 2007

[14] M. E. Tuckerman, C. J. Mundy and G. J. Martyna, On the classical statistical mechanics of non-Hamiltonian systems, Euro Phys Lett, 45 (2), pp. 149-155 (1999)

[15] Statistical Mechanics: Theory and Molecular Simulation Mark. E. Tuckerman, Oxford Graduate Texts.

[16] Williams SR, Searles DJ, Evans DJ. 2004. Independence of the transient fluctuation theorem to thermostatting details. Phys. Rev. E 70 066113

[17] Bright JN, Evans DJ, Searles DJ. 2005. New observations regarding deterministic, time-reversible thermostats and Gauss’s principle of least constraint. J. Chem. Phys. 122 194106

[18] C. Jarzynski Nonequilibrium Equality for Free Energy Differences, Phys. Rev. Lett. 78, 2690–2693 (1997)