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Research Article

Dissipation and Relative Entropy

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Abstract. It is shown that the total dissipative work is exactly given by the sum of two contributions. First by the relative entropy of probability of forward path and its time reversed path and second by the relative entropy of non equilibrium and equilibrium probability distribution at that time. The conclusion is supported using a simple model.

Keywords. Fluctuation theorem, Non equilibrium and irreversible thermodynamic, Random process

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1. Introduction

Second law of thermodynamic asserts that for a macroscopic closed system entropy will never decrease. A somewhat alternative version of second law for macroscopic thermodynamic is $W \ge \Delta F^{eq}$, where W is the work done in changing the state of the system in contact with a constant temperature heat reservoir and ΔF^{eq} is the free energy difference of final and initial equilibrium states. Work done is controlled by an external time dependent parameter $\lambda(t)$. The control parameters represent the parameters which the experimentalist can control, to apply the external perturbation. For example, it may represent, the strength of an external field, or the volume of space within which the system is confined. If control parameter is varied from initial to final value infinity slowly, above inequality become equality and for finite switching rate inequality follows. As the system size gets small, work done in different realization will be different, in other words fluctuation starts playing significant role. In such case for finite switching rate, in second law of thermodynamic, work W is replaced by its average value $\langle W \rangle$ i.e. $\langle W \rangle \ge \Delta F^{eq}$ [6, 16–18]. Only for reversible process (the system remains at equilibrium all along the process) equality is valid, for irreversible we have inequality.

The main difference between a reversible and irreversible thermodynamic processes is dissipation. Average dissipative work is defined as $\langle W \rangle_{dissp} = \langle W \rangle - \Delta F^{eq}$. The second law of thermodynamics can also be stated that average dissipative work is always greater or equal to zero. It is zero only for reversible process. Dissipation is important. In past few years there are some very interesting results related to dissipation:

- (i) Dissipation quantitatively signifies the time reversal asymmetry between forward and reverse process [19].
- (ii) Dissipation also gives quantitative measure of the loss of the equilibrium or lag of equilibrium with respect to initial equilibrium state during an irreversible process [30].

Dissipation can directly be related to a quantity called relative entropy (also called Kullback-Leibler distance). Relative entropy is a positive definite quantity and it measures lower bound on dissipative work in the sense that dissipative work done in a process is greater or equal to relative entropy. For example, as in [19].

$$\beta \langle W \rangle_{dissp} \ge D[\rho_F \| \rho_R], \tag{1.1}$$

where ρ_F and ρ_R are the probability distribution of phase space at some fix time for forward process and reverse process. $D[\rho_F \| \rho_R]$ is the relative entropy. In reference [30]

$$\beta \langle W \rangle_{dissp} \ge D[\rho \| \rho^{eq}], \tag{1.2}$$

where ρ is the non equilibrium distribution at some time t along the froward process and ρ^{eq} is the corresponding equilibrium distribution at same time t. $D[\rho \| \rho^{eq}]$ is the relative entropy. In both equations equality establishes if dynamics is hamiltonian, for stochastic system (for example system remains in thermal contact with a heat reservoir all along the process) inequality remains. This indicates, as rightly pointed out in [11, 15] that if we do not know about the exact trajectory of the system than our lack of information reflects in lack of complete measurement of dissipative work by the relative entropy. Key feature of reference [11] is the fact that instead of working in phase space if one works in trajectory space than this shortcoming of relative entropy can be avoided:

$$\beta \langle W \rangle_{dissp} = D[P(path) \| P(path)]. \tag{1.3}$$

Here P(path) and P(path) are the probability of forward and reverse path. Eq. (1.3) is true for both hamiltonian and stochastic evolution. Eq. (1.1) can be thought as a special case of eq. (1.3) since if we project from path space onto phase space, e.g. $P(path) \rightarrow \rho_F$ then the relative entropy decreases, and we obtain the inequality as in eq. (1.1). This is referred as coarse-graining in time in reference [11]. Relative entropy decreases on coarse graining.

The goal of the present paper is to point out that equality in eq. (1.3) is strictly true only if final state is an equilibrium state, if final state is in general a non equilibrium state than there will exist a strict inequality in eq. (1.3) even without coarse graining. An equality can be derived between dissipative work and relative entropy for stochastic evolution, it is proved that in that case the two definitions (points (i) and (ii)) of dissipative work can be written in a single equation. Result is also verified using a simple model.

In the paper we have used the stochastic thermodynamic on the trajectory level [23, 27]. Stochastic thermodynamics systematically provides a framework for extending the notions of classical thermodynamics like work, heat and entropy production to the level of individual trajectories. First law and second law of thermodynamic on the trajectory level was first discussed by Sekimoto [28, 29]. Subsequently, it was Seifert [25, 26], who introduced the concept of entropy on trajectory level and hence established the trajectory dependent second law of

thermodynamics. Seifert work is particularly important because entropy always thought as an ensemble property and hence should not be related to a single trajectory. On the other hand, fluctuation theorem [8,9,14,20,22] quite generally relates the probability of entropy generating trajectories to those of entropy annihilating ones which requires a definition of entropy even for a single trajectory.

2. Preliminary

Let us consider a small system in thermal contact with an ideal heat reservoir. Ideal heat reservoir is macroscopically big as compare to system and assumed to be remained always at equilibrium. Let also consider that initially system is in thermal equilibrium with the heat reservoir. Consider a process in which system moves from some initial equilibrium state at temperature T (heat reservoir's temperature) to some non-equilibrium state by varying an external control parameter $\lambda(t)$. during this whole process system remain in contact with heat reservoir hence the dynamics of the system will be stochastic in nature. During one such realization over a time interval $0 \le t \le \tau$, system will traverse a trajectory in face space. For simplicity lets divide the time into n equal intervals $\Delta t = \frac{t_n - t_i}{n}$ where $t_i = 0$ and $t_n = \tau$. System will jump from one state to another. Since a trajectory or a path is a causal chain, one such path is represented by a series of discrete states labeled by time parameter. $(i, t_i; j, t_1; k, t_2 \dots r, t_{n-1}; f, t_n)$, where $t_i < t_1 < t_2 < \dots < t_{n-1} < t_n$. System is in thermal equilibrium only at initial time (hence the state i is sampled from canonical distribution) and subsequently system starts moving away from equilibrium.

Probability that system takes a trajectory or path is given by:

$$P(Path) = P(i, t_i; j, t_1; k, t_2 \dots r, t_{n-1}; f, t_n),$$
(2.1)

which represent the probability that system takes a state *i* at time t = 0 then a state *j* at later time t_1 and so on till system finally reached to a state *f* at time $t = \tau$. Under Markhov assumption and assumption that jump from one state to other only depends on elapsed time, we can write eq. (2.1) as:

$$P(Path) = P(i)P(j,\Delta t|i)P(k,\Delta t|j)\dots P(f,\Delta t|r),$$

$$(2.2)$$

where $P(m, \Delta t|l)$ is the transition probability from state *l* to state *m*. States *l* and *m* stand for above mentioned series of states.

If Δt is very small we can write every transition probabilities as $P(m, \Delta t|l) = P(l \rightarrow m)\Delta t$, where $P(l \rightarrow m)$ is the transition probability per unit time or transition rate from some state lto state m. Under above assumptions the probability of a path or trajectory is:

$$P(Path) = P(i)P(i \to j)P(j \to k) \dots P(r \to f)\Delta t^{n}.$$
(2.3)

One can also assume a time reversed path where system starts from state f and then subsequently traces its states exactly in backward direction. For a time reverse path the probability will be

$$P(\widetilde{Path}) = P(f)P(f \to r) \dots P(k \to j)P(j \to i)\Delta t^{n}.$$
(2.4)

Taking logarithm of eqs. (2.3) and (2.4) and subtracting will give:

$$\ln \frac{P(Path)}{P(\widetilde{Path})} = \ln \frac{P(i)P(i \to j)P(j \to k)\dots P(r \to f)}{P(f)P(f \to r)\dots P(k \to j)P(j \to i)}.$$
(2.5)

A system in contact with a big ideal heat reservoir will always satisfy a kind of microscopic detailed balance condition even if system is not at equilibrium with the reservoir [24]. For two microscopic states l and m of the system, probability of going from l to m is not same as going

from m to l.

$$\frac{p(l \to m)}{p(m \to l)} = \exp[-\beta dq_{l \to m}], \tag{2.6}$$

where β is the inverse temperature of the ideal heat reservoir. In this paper Boltzmann constant k_B is assumed one. The factor $-\beta dq_{l \to m}$ can be interpreted as the entropy decrease of the reservoir, $ds_r^{l \to m} = -\frac{dq_{l \to m}}{T}$, during the process when system jumps from state l to state m. For a system in equilibrium with the reservoir, the net amount of heat exchanged with the heat reservoir is zero and for such a reversible process right hand side of the eq. (2.6) will be one.

The change in entropy of the system, $ds_{sys}^{l \to m} = \ln \frac{p(l)}{p(m)}$, when system jumps from state l to state m in small time interval. For simplicity we have omitted the time dependence in probability. Since a trajectory or path is a collection of large number of states, the total change in entropy along a path is the sum of entropy changes in each jump. This gives us:

$$\ln \frac{P(Path)}{P(\widetilde{Path})} = \Delta s_T \,. \tag{2.7}$$

This relation implies a connection of time asymmetry to the net entropy generation, Δs_T , on a trajectory level. Although eq. (2.7) is derived here for discrete time case but its still remain valid for continuous trajectory [1, 10]. Eq. (2.7) is the starting equation for our analysis. Such relation already existed in literature, derived using stochastic as well as hamiltonian dynamics [4,5, 12]. Here P(Path) and P(Path) represent the probability of a single forward and its time reverse trajectory or path. Δs_T need not be always positive.

Using trajectory thermodynamics, not only entropy but it is possible to define the energy, heat, work along a single trajectory [5]. For a single trajectory the first law of thermodynamics is:

$$\Delta e(t) = w(t) + q(t), \tag{2.8}$$

where $\Delta e(t)$ is the change in internal energy of the system along a trajectory till time t, w(t) is the work done and q(t) is the heat absorbed by the system along that trajectory till time t. Like the ensemble average first law, for a single trajectory the work done and heat exchanged are trajectory dependent quantities. If s(t) is the entropy of system along a trajectory at time t then we can define the trajectory dependent non-equilibrium free energy at some arbitrary time t as:

$$f(t) = e(t) - Ts(t),$$
 (2.9)

where *T* is the temperature of the ideal reservoir for which the system is in thermal contact. Free energy at time t = 0 (equilibrium free energy), is:

$$f(0) = e(0) - Ts(0).$$
(2.10)

One can define the change in the free energy:

$$\Delta f = \Delta e - T \Delta s, \tag{2.11}$$

 Δs is the change in entropy of the system along the trajectory. Total change in entropy (system+reservoir) is:

$$\Delta s_T = \Delta s_{sys} + \Delta s_r, \tag{2.12}$$

with eq. (2.11) and first law of thermodynamics that implies:

$$\Delta f = w(t) + q(t) - T(\Delta s_T - \Delta s_r). \tag{2.13}$$

Since $\Delta s_r = \frac{-q(t)}{T}$ is the change in entropy of the reservoir, after rearrangement eq. (2.13) can be written as:

$$w(t) - \Delta f = T \Delta s_T. \tag{2.14}$$

$$T\ln\frac{P(Path)}{P(\widetilde{Path})} = w(t) - \Delta f.$$
(2.15)

Important quantity here is the change in free energy along a trajectory Δf . Taking average with respect to all the trajectories that can be taken by the system

$$TD(P(path)||P(path)) = \langle W(t) \rangle - \Delta F, \qquad (2.16)$$

where

$$D(P(path) \| P(\widetilde{path})) = \sum_{i,j\dots m} P(path) \ln \frac{P(path)}{P(\widetilde{path})}.$$
(2.17)

 $\Delta F = F(t) - F^{eq}(0)$ and W(t) is average work done till time t. F(t), $F^{eq}(0)$ are ensemble average non equilibrium and equilibrium free energies at time t and t = 0. Adding and subtracting $F^{eq}(t)$ (ensemble average equilibrium free energy at time t) on right hand side of free energy expression, ΔF can be written as

$$\Delta F = \Delta F(t) + \Delta F^{eq}, \qquad (2.18)$$

$$\Delta F(t) = F(t) - F^{eq}(t)$$
 and $\Delta F^{eq} = F^{eq}(t) - F^{eq}(0)$. Using this expression of ΔF in eq. (2.16)

$$TD(P(path)||P(\widetilde{path})) = \langle W(t) \rangle_{dissp} - \Delta F(t).$$
(2.19)

Here $\langle W(t) \rangle_{dissp} = \langle W(t) \rangle - \Delta F^{eq}$ is the average dissipative work done during the forward process. Since $\Delta F(t)$ is always a positive definite quantity (as proved in this paper) hence left hand side of eq. (2.19) will always be less than $\langle W \rangle_{dissp}$. Although a trajectory is discritized in time but since eq. (2.7) is in general true for continuous trajectory hence eq. (2.19) will also remain valid for a continuous trajectory.

Jarzynski derived a relation [16]

$$\frac{p(m,t)}{p^{eq}(m,t)} = \frac{e^{-\beta\Delta F^{eq}}}{\langle e^{-\beta w(t)} \rangle_{m,t}},$$
(2.20)

p(m,t) and $p^{eq}(m,t)$ are the non-equilibrium and equilibrium probability distribution of a arbitrary state m at same time t. Equilibrium probability distribution corresponds to a fixed value of control parameter. $\langle \ldots \rangle_{m,t}$ denotes an average over all the trajectories that pass through state m at time t. Lets call $\langle e^{-\beta w(t)} \rangle_{m,t}$ as Q(m,t) and

$$g(m,t) = p(m,t)Q(m,t).$$
 (2.21)

Its obvious that if one sum over all the states for eq. (2.21) then

$$\langle e^{-\beta w(t)} \rangle = \sum_{m} g(m, t), \tag{2.22}$$

where average is with respect to all the trajectories. Following Jarzynski [16], if initial state is sampled from canonical equilibrium distribution, g(m,t) is given as

$$g(m,t) = e^{-\beta [H(t) - F^{eq}(0)]}.$$
(2.23)

H(t) is the hamiltonian of the system at some fixed value of the control parameter ' λ ' at time t. From eq. (2.20), one can get

$$\sum_{m} p(m,t) \ln \frac{p(m,t)}{p^{eq}m,t} = -\beta \Delta F^{eq}(t) - \sum_{m} p(m,t) \ln Q(m,t).$$
(2.24)

 $\Delta F^{eq}(t)$ is the difference in equilibrium free energy between time *t* and *t* = 0 hence it can come outside the summation. From eq. (2.21) we can obtain

$$\sum_{m} p(m,t) \ln Q(m,t) = \sum_{m} p(m,t) \ln g(m,t) - \sum_{m} p(m,t) \ln p(m,t),$$
(2.25)

where non equilibrium entropy S(t) is given as:

$$\sum_{m} p(m,t) \ln p(m,t) = S(t).$$
(2.26)

Using eq. (2.23) one can get:

$$\sum p(m,t) \ln g(m,t) = -\beta E(t) + \beta F^{eq}(0).$$
(2.27)

 $E(t) = \sum_{m} p(m, t)H(t)$. Eq. (2.27) is used in eq. (2.24):

$$\sum_{m} p(m,t) \ln \frac{p(m,t)}{p^{eq}(m,t)} = -\beta F^{eq}(t) + \beta (E(t) - TS(t)).$$
(2.28)

Defining E(t) - TS(t) as non equilibrium free energy F(t) at time t.

$$\sum_{m} p(m,t) \ln \frac{p(m,t)}{p^{eq}(m,t)} = \beta \Delta F(t).$$
(2.29)

Left hand side of eq. (2.29) is the relative entropy $D(p(m,t)||p^{eq}(m,t))$. Since relative entropy is a positive quantity hence $\Delta F(t)$ is always positive. This is the non equilibrium Landauer principle [2,7]. Celebrated Landauer principle [21] comes from information theory. It concerned with the entropic cost of processing the information, dissipation in irreversible computing etc. As is true for general information theory, it has deep links with the thermal and statistical physics. Eq. (2.29) implies couple of points. First, non-equilibrium free energy is greater than equilibrium free energy at some arbitrary time t. Second, the relative entropy implies a lag between evolution of two free energies.

3. Final Result

Eqs. (2.19) and (2.29) indicate that we can have a relation between two relative entropies, D(P(path) || P(path)) and $D(p(m,t) || p^{eq}(m,t))$.

$$TD(P(path)||P(path)) + TD(p(m,t)||p^{eq}(m,t)) = \langle W(t) \rangle_{dissp}.$$
(3.1)

Eq. (3.1) is the central result of this paper. Since D(P(path) || P(path)) and $D(p(m,t) || p^{eq}(m,t))$ are always ≥ 0 . It directly implies that $\langle W(t) \rangle_{dissp} \geq 0$. This also implies:

$$\langle W(t) \rangle_{dissp} \ge D(P(path) || P(path))$$
(3.2)

and

$$\langle W(t) \rangle_{dissp} \ge TD(p(m,t) \| p^{eq}(m,t)).$$
(3.3)

Eq. (3.1) is also true for a continuous phase space. Eq. (3.2) remains an inequality even for continuous path where complete information about the trajectory is available. This is different result than [11, 15] where it assured that in absence of course graining and if full information about trajectory is available, equality will come in eq. (3.2). The origin of this difference is second term in left hand side of eq. (3.1), which arises because of the fact that end state of the system is a non equilibrium state.

If final state of the path is an equilibrium state than this inequality turns into equality since $\Delta F(t) = 0$. Experimentally this can be achieved by fixing the external control parameter $\lambda(t)$ at some time t and after that let the system relax with the reservoir till time $t = \tau$. There will be no extra work done but dissipative work will still be there because of extra entropy generation. Hence:

$$\langle W(\tau) \rangle_{dissp} = TD(P(path) || P(path)), \tag{3.4}$$

where trajectory is full trajectory now, from time t = 0 to τ .

Eq. (3.3) is same as the result derived by Jarzynski *et al*. [19]. It indicates that $\langle W(t) \rangle_{dissp}$ is always ≥ 0 in stochastic dynamics even if $p(t) = p^{eq}(t)$. Eq.(3.3) results into a second law kind inequality:

$$\langle W(t) \rangle_{dissp} \ge \Delta F(t).$$
 (3.5)

It asserts that not only average dissipative work $\langle W(t) \rangle_{dissp}$ is ≥ 0 for whole time all along the process but also at any time along a trajectory the average dissipative work done till that time is \geq difference in two free energies at that time.

Eq. (3.1) can be interpreted as an information-theoretic measure of dissipative work where dissipative work is completely specified by only two contributions, D(P(path) || P(path)) and $D(p(m,t) || p^{eq}(m,t))$. For a non hamiltonian system both contributed to $\langle W(t) \rangle_{dissp}$ in such a way that equality in eq. (3.1) is satisfied.

4. Simple Model

4.1 Overdamped Brownian Particle in a Moving Harmonic Potential

We can demonstrate our central result eq. (3.1) using a simple model. Lets take a particle trapped in a harmonic potential where the harmonic potential V(x,t) is moving with constant velocity u.

$$V(x,t) = \frac{k}{2}(x-ut)^2,$$
(4.1)

where *k* is the force constant. *x* represents the position of the particle at some arbitrary time *t*. x(t) is the forward trajectory taken by the particle as the control parameter $\lambda(t)$ is varied from 0 to some finite value at a finite rate. During one such realisation work is done on the particle

$$W(t) = \int_0^t \frac{\partial V}{\partial t'} dt' = -uk(x - ut), \qquad (4.2)$$

hence the average work done during many such realisations is:

$$\langle W(t)\rangle = -uk(\langle x\rangle - ut). \tag{4.3}$$

 $\langle x \rangle$ is the average position of the particle.

Assuming that initially the system is prepared in equilibrium, the initial equilibrium distribution will be gaussian:

$$p^{eq}(x,0) = \sqrt{\frac{\beta k}{2\pi}} \exp\left(\frac{-\beta k}{2}x^2\right).$$
(4.4)

For a system under consideration, initial gaussian distribution will remain gaussian for all time that means for any arbitrary time probability distribution will be:

$$p(x,t) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{(x - \langle x(t) \rangle)^2}{2\sigma^2}\right),\tag{4.5}$$

where σ is the standard deviation. Particle will obey an overdamped Langevin equation:

$$\dot{x} = -\mu \partial_x V(x,t) + \sqrt{2D}\xi(t), \tag{4.6}$$

where μ and D are the mobility and diffusion constant, related with Einstein relation $\mu = \beta D$. ξ is the gaussian random white noise satisfy $\langle \xi(t)\xi(t')\rangle = \delta(t-t')$ and $\langle \xi(t)\rangle = 0$. $\langle x(t)\rangle$ can be calculated by solving eq. (4.6) with the initial condition $\langle x(0)\rangle = 0$.

$$\langle x(t)\rangle = \frac{u}{k} \left(kt - \frac{1}{\mu} + \frac{e^{-\mu kt}}{\mu} \right). \tag{4.7}$$

Because of the translational symmetry, the evolution of the system will not change free energy of the system i.e. $\Delta F = 0$ hence the average dissipative work done is given as:

$$\langle W(t) \rangle_{dissp} = \langle W(t) \rangle = \frac{u^2 t}{\mu} - \frac{u^2}{k\mu^2} + \frac{u^2 e^{-\mu kt}}{k\mu^2}.$$
 (4.8)

Non equilibrium probability distribution at some arbitrary time *t* is given as

$$p(x,t) = \sqrt{\frac{\beta k}{2\pi}} \exp\left(\frac{-\beta k}{2} (x - \langle x(t) \rangle)^2\right),\tag{4.9}$$

where $\sigma = \frac{1}{\sqrt{\beta k}}$ and $\langle x(t) \rangle$ is given by eq. (4.7). Corresponding equilibrium distribution is

$$p^{eq}(x,t) = \sqrt{\frac{\beta k}{2\pi}} \exp\left(\frac{-\beta k}{2}(x-ut)^2\right).$$
(4.10)

From eqs. (4.4), (4.9), (4.10) following equations can be obtained:

$$\left\langle \frac{p^{eq}x,0}{p(x,t)} \right\rangle = -\frac{\beta k}{2} \langle x(t) \rangle^2, \tag{4.11}$$

$$\left\langle \frac{p(x,t)}{p^{eq}(x,t)} \right\rangle = \frac{\beta k}{2} (\langle x(t) \rangle - ut)^2.$$
(4.12)

 $P(path) = p^{eq}(x,0)p(x|x,0)$ is probability of the forward path and for reverse path it is $P(path) = p(\tilde{x},t)p(\tilde{x}|(\tilde{x},t))$. Here p(x|x,0) and $p(\tilde{x}|(\tilde{x},t))$ are the conditional path probability for forward and reverse paths. From this one can get the relative entropy

$$\left\langle \ln \frac{P(path)}{P(\widetilde{path})} \right\rangle = \left\langle \ln \frac{p^{eq}(x,0)}{p(\tilde{x},t)} \right\rangle + \left\langle \ln \frac{p(x|x,0)}{p(\tilde{x}|(\tilde{x},t))} \right\rangle.$$
(4.13)

Eq. (4.13) will be used later on. Conditional path probability is given as [3,13]

$$p(x|x,0) = N \exp\left[-\frac{1}{2} \int_0^t dt' \xi^2(t')\right]$$
(4.14)

$$= N \exp\left[-\frac{1}{4D} \int_{0}^{t} dt'(\dot{x} + \partial_{x}V)^{2}\right],$$

$$p(\tilde{x}|(\tilde{x}, t) = N \exp\left[-\frac{1}{4D} \int_{0}^{t} dt'(\dot{x} - \partial_{x}V)^{2}\right],$$
(4.15)

N is the normalisation constant. For reverse path $\dot{x} \rightarrow -\dot{x}$. These equations give:

$$\ln \frac{p(x|x,0)}{p(\tilde{x}|(\tilde{x},t))} = -\beta \int_0^t dt' \dot{x} \partial_x V.$$
(4.16)

One can identify $\dot{x}\partial_x V(x,t') = \frac{dV}{dt'} - \frac{\partial V}{\partial t'}$. Eq. (4.16) can be written as:

$$\ln \frac{p(x|x,0)}{p(\tilde{x}|(\tilde{x},t))} = -\beta(V(x,t) - V(x,0)) + \beta \int_0^t dt' \frac{\partial V}{\partial t'}.$$
(4.17)

Taking average with respect to all the trajectories:

$$\left\langle \ln \frac{p(x|x,0)}{p(\tilde{x}|(\tilde{x},t))} \right\rangle = \frac{-\beta k}{2} (u^2 t^2 - 2ut \langle x \rangle) + \beta \langle W \rangle.$$
(4.18)

Add eqs. (4.11) and (4.18)

$$\left\langle \ln \frac{P(path)}{P(\widetilde{path})} \right\rangle = \frac{-\beta k}{2} (u^2 t^2 - 2ut \langle x \rangle) + \beta \langle W(t) \rangle - \frac{-\beta k}{2} (\langle x \rangle)^2,$$

$$\left\langle \ln \frac{P(path)}{P(\widetilde{path})} \right\rangle = \frac{-\beta k}{2} (\langle x \rangle - ut)^2 + \beta \langle W(t) \rangle_{dissp} \,. \tag{4.19}$$

Eq. 4.18 expresses the fact that if final state is non equilibrium state, relative entropy doesn't account for full dissipative work. $D(p(path)||p(path)) \leq \beta \langle W(t) \rangle_{dissp}$. First term on right hand side is precisely negative of the eq.(4.12), adding eq. 4.12 with eq. 4.19 will give full path i.e. from initial equilibrium state to final equilibrium state, relative entropy equal to $\beta \langle W(t) \rangle_{dissp}$ as it should be.

5. Conclusion

Dissipative work gives an upper bound to the relative entropy D(P(path)||P(path)) which in turn measures the difference between forward and reverse process(i.e. direction of time). If we do not have the full information about the path taken by the system during the process, we loss the distinction between forward and reverse process. This is indicated by the inequality between relative entropy and average dissipative work.

On the other hand dissipated work, $\langle W \rangle_{dissp}$, also provides an upper bound on the value of lag between the current state of the system, p(m,t), and the instantaneous equilibrium state, $p^{eq}(m,t)$. The relative entropy $D(p(m,t)||p^{eq}(m,t))$ quantifies this relation. Eq. (3.1), expressed a relation between two types of relative entropies for stochastic dynamics, it signifies that the average dissipative work, $\langle W \rangle_{dissp}$, will always be ≥ 0 . For a non hamiltonian system both D(P(path)||P(path)) and $D(p(m,t)||p^{eq}(m,t))$, contributed to $\langle W \rangle_{dissp}$ in such a way that equality in eq. (2.27) is satisfied. If final state of the trajectory is an equilibrium sate than inequality in eq. (3.1) become equality since $D(p(m,t)||p^{eq}(m,t)) = 0$.

It is argued that even if we know about the path (in the sense that it is not coarse grained in time) and if the final state is not an equilibrium state for a process in which system starts from equilibrium state then there still exist an inequality between relative entropy and average dissipative work.

Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

All the authors contributed significantly in writing this article. The authors read and approved the final manuscript.

References

- D. Andrieux, P. Gaspard, S. Ciliberto, N. Garnier, S. Joubaud and A. Petrosyan, Entropy production and time asymmetry in nonequilibrium fluctuations, *Physical Review Letters* 98 (2007), 150601, DOI: 10.1103/PhysRevLett.98.150601.
- [2] C. Van den Broeck, Stochastic thermodynamics: A brief introduction, Proceedings of the International School of Physics "Enrico Fermi", Volume 184: Physics of Complex Colloids, pp. 155– 193, IOS Press Ebooks, DOI: 10.3254/978-1-61499-278-3-155.
- [3] V. Y. Chernyak, M. Chertkov and C. Jarzynski, Path-integral analysis of fluctuation theorems for general Langevin processes, *Journal of Statistical Mechanics: Theory and Experiment* 08 (2006), DOI: 10.1088/1742-5468/2006/08/P08001.

- [4] G. E. Crooks, Entropy production fluctuation theorem and the nonequilibrium work relation for free energy differences, *Physical Review E* **60** (1999), 2721, DOI: 10.1103/PhysRevE.60.2721.
- [5] G. E. Crooks, Nonequilibrium measurements of free energy differences for microscopically reversible Markovian systems, *Journal of Statistical Physics* **90** (1998), 1481 – 1487, DOI: 10.1023/A:1023208217925.
- [6] G. E. Crooks, Path-ensemble averages in systems driven far from equilibrium, *Physical Review E* 61 (2000), 2361, DOI: 10.1103/PhysRevE.61.2361.
- [7] M. Esposito and C. Van den Broeck, Second law and Landauer principle far from equilibrium, Europhysics Letters 95 (4) (2011), 40004, DOI: 10.1209/0295-5075/95/40004.
- [8] D. J. Evans, E. G. D. Cohen and G. P. Morriss, Probability of second law violations in shearing steady states, *Physical Review Letters* **71** (1993), 2401, DOI: 10.1103/PhysRevLett.71.2401.
- [9] G. Gallavotti and E. G. D. Cohen, Dynamical ensembles in nonequilibrium statistical mechanics, *Physical Review Letters* **74** (1995), 2694, DOI: 10.1103/PhysRevLett.74.2694.
- [10] P. Gaspard, Time-reversed dynamical entropy and irreversibility in Markovian random processes, Journal of Statistical Physics 117 (2004), 599 – 615, DOI: 10.1007/s10955-004-3455-1.
- [11] A. Gomez-Marin, J. M. R. Parrondo and C. Van den Broeck, Lower bounds on dissipation upon coarse graining, *Physical Review E* 78 (2008), 011107, DOI: 10.1103/PhysRevE.78.011107.
- [12] A. Gomez-Marin, J. M. R. Parrondo and C. Van den Broeck, The "footprints" of irreversibility, Europhysics Letters 82(5) (2008), 50002, DOI: 10.1209/0295-5075/82/50002.
- [13] M. Hattori and S. Abe, Path probability of stochastic motion: A functional approach, *Physica A:* Statistical Mechanics and its Applications 451 (2016), 198 – 204, DOI: 10.1016/j.physa.2016.01.053.
- [14] T. M. Hoang, R. Pan, J. Ahn, J. Bang, H. T. Quan and T. Li, Experimental test of the differential fluctuation theorem and a generalized Jarzynski equality for arbitrary initial states, *Physical Review Letters* 120 (2018), 080602, DOI: 10.1103/PhysRevLett.120.080602.
- [15] J. Horowitz and C. Jarzynski, Illustrative example of the relationship between dissipation and relative entropy, *Physical Review E* **79** (2009), 021106, DOI: 10.1103/PhysRevE.79.021106.
- [16] C. Jarzynski, Equilibrium free-energy differences from nonequilibrium measurements: A masterequation approach, *Physical Review E* 56 (1997), 5018, DOI: 10.1103/PhysRevE.56.5018.
- [17] C. Jarzynski, Fluctuation relations and strong inequalities for thermally isolated systems, *Physica A: Statistical Mechanics and its Applications* 552 (2020), 122077, DOI: 10.1016/j.physa.2019.122077.
- [18] C. Jarzynski, Nonequilibrium equality for free energy differences, *Physical Review Letters* 78 (1997), 2690, DOI: 10.1103/PhysRevLett.78.2690.
- [19] R. Kawai, J. M. R. Parrondo and C. Van den Broeck, Dissipation: The phase-space perspective, *Physical Review Letters* 98 (2007), 080602, DOI: 10.1103/PhysRevLett.98.080602.
- [20] J. Kurchan, Fluctuation theorem for stochastic dynamics, Journal of Physics A: Mathematical and General 31 (1998), 3719, DOI: 10.1088/0305-4470/31/16/003.
- [21] R. Landauer, Irreversibility and heat generation in the computing Process, IBM Journal of Research and Development 5 (1961), 183 – 191, DOI: 10.1147/rd.53.0183.
- [22] J. L. Lebowitz and H. Spohn, A Gallavotti-Cohen-Type symmetry in the large deviation functional for Stochastic dynamics, *Journal of Statistical Physics* 95 (1999), 333 – 365, DOI: 10.1023/A:1004589714161.

- [23] H. Qian, Mesoscopic nonequilibrium thermodynamics of single macromolecules and dynamic entropy-energy compensation, *Physical Review E* 65 (2002), 016102, DOI: 10.1103/Phys-RevE.65.016102.
- [24] F. Reif, Fundamentals of Statistical and Thermal Physics, McGraw-Hill, New York (1965).
- [25] U. Seifert, Entropy production along a Stochastic trajectory and an integral fluctuation theorem, *Physical Review Letters* 95 (2005), 040602, DOI: 10.1103/PhysRevLett.95.040602.
- [26] U. Seifert, From Stochastic thermodynamics to thermodynamic inference, Annual Review of Condensed Matter Physics 10 (2019), 171 – 192, DOI: 10.1146/annurev-conmatphys-031218-013554.
- [27] U. Seifert, Stochastic thermodynamics: Principles and perspectives, *The European Physical Journal* B 64 (2008), 423 – 431, DOI: 10.1140/epjb/e2008-00001-9.
- [28] K. Sekimoto, *Stochastic Energetics*, Lecture Notes in Physics Series, Springer-Verlag, Berlin Heidelberg (2010), DOI: 10.1007/978-3-642-05411-2.
- [29] K. Sekimoto, Langevin equation and thermodynamics, *Progress of Theoretical Physics Supplement* 130 (1998), 17 – 27, DOI: 10.1143/PTPS.130.17.
- [30] S. Vaikuntanathan and C. Jarzynski, Dissipation and lag in irreversible processes, *Europhysics Letters* 87 (2009), 60005, DOI: 10.1209/0295-5075/87/60005.

