Fluctuation theorems and atypical trajectories

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Abstract

In this work, we have studied simple models that can be solved analytically to illustrate various fluctuation theorems. These fluctuation theorems provide symmetries individually to the distributions of physical quantities such as the classical work ($W_c$), thermodynamic work ($W$), total entropy ($\Delta s_{\text{tot}}$) and dissipated heat ($Q$), when the system is driven arbitrarily out of equilibrium. All these quantities can be defined for individual trajectories. We have studied the number of trajectories which exhibit behaviour unexpected at the macroscopic level. As the time of observation increases, the fraction of such atypical trajectories decreases, as expected at the macroscale. The distributions for the thermodynamic work and entropy production in nonlinear models may exhibit a peak (most probable value) in the atypical regime without violating the expected average behaviour. However, dissipated heat and classical work exhibit a peak in the regime of typical behaviour only.

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(Some figures in this article are in colour only in the electronic version)

1. Introduction

The last two decades have observed a crescendo of research activity in the field of nonequilibrium statistical mechanics [1]. One of the major breakthroughs has been the emergence of the so-called fluctuation theorems [1–22]. These are one of the few relations that are valid even when one is far away from equilibrium, a region that is beyond the scope of the well-established linear response theory. They provide a quantitative measure of the probability of a phase space trajectory to dissipate heat, work, or entropy as compared to the probability of its time-reversed trajectory to absorb the same. In other words, it quantifies
the probability of violating the average trend which is dictated by the second law. The general relation can be written in the form

\[ \frac{P_f(x)}{P_r(-x)} = e^{\alpha x}, \]

where \( \alpha \) is a constant with inverse dimension of that of \( x \), \( P_f(x) \), and \( P_r(x) \) are the probability densities of \( x \) along the forward and the backward processes, respectively. As a specific example, let us consider Crooks’ fluctuation theorem (CFT) for the dissipated work \( W_d \) \[14, 23\]. \( W_d \) is related to the thermodynamic work \( W \) and free energy difference \( \Delta F \) between terminal states as \( W_d = W - \Delta F \). Suppose that a Brownian particle is initially in thermal equilibrium with a heat bath and it is driven into a nonequilibrium state by an external protocol \( \lambda(t) \). The dissipated work depends on the microstate of the initial equilibrium state and on the stochastic path of the trajectory as well as on \( \lambda(t) \). Hence, repeated measurements yield different values for \( W_d \), the probability of which obeys

\[ \frac{P_f(W_d)}{P_r(-W_d)} = e^{\beta W_d}, \]

(1)

\( \beta \) being the inverse temperature of the bath.

The theorem says that the frequency of observing a forward trajectory holds a ratio of \( e^{\beta W_d} \) with that of observing a time-reversed one. In a macroscopic regime, since dissipated work increases with the system size, the above statement implies that there is only small probability for an observer to detect a reverse trajectory. This is consistent with the emergence of macroscopic irreversibility (an outcome of the second law).

The CFT was an example of what are collectively called the transient fluctuation theorems, for which the system must begin in a state of thermal equilibrium with the bath and is thereafter allowed to evolve under the given protocol. Using the CFT, the Jarzynski Equality follows \[10, 23\], namely

\[ \langle e^{-\beta W} \rangle = e^{-\beta \Delta F}, \]

(2)

where \( \langle \cdots \rangle \) denotes ensemble average over all trajectories for a system being prepared in an initial equilibrium state and subjected to the same protocol. It may be noted that the LHS of (2) contains nonequilibrium properties whereas the RHS contains equilibrium free-energy difference between the two terminal states. This identity has gained importance due to its ability to calculate the free-energy difference from nonequilibrium measurements. If instead of thermodynamic work, we consider the classical work defined below, then the Bochkov–Kuzovlev identity follows \[20–22\], i.e.

\[ \langle e^{-\beta W_c} \rangle = 1, \]

(3)

If the total potential including external protocol is given by \( U(x, t) \) (inclusive approach), then the thermodynamic work equals \( W = \int_0^\tau \frac{\partial U(x, t)}{\partial t} \, dt \). If the potential is decomposed as an unperturbed potential \( U_0(x) \) and perturbing potential \( U_p(x) \) (exclusive approach), then the classical work \( W_c \) defined over a time interval \( \tau \) is given by \( W_c = -\int_0^\tau \frac{\partial U_p(x, t)}{\partial x} \dot{x} \, dt \). Seifert has generalized \[15, 16\] the concept of entropy to a stochastic trajectory. He has proved the integral fluctuation theorem, namely,

\[ \langle e^{-\Delta S_{\text{tot}}} \rangle = 1. \]

(4)

Here the average is over the ensemble of finite time trajectories. For this theorem to hold, the initial state of the system need not be in equilibrium. There are also steady-state fluctuation theorems where the system begins and thereafter remains throughout in some
given (nonequilibrium) steady state. One such theorem is that provided by Seifert [15, 16] for the total entropy:
\[
\frac{P(\Delta s_{\text{tot}})}{P(-\Delta s_{\text{tot}})} = e^{\Delta s_{\text{tot}}},
\]
where \(\Delta s_{\text{tot}}\) is the total change in entropy of the system and the bath. Similar steady-state fluctuation theorems can also be derived for work and heat. Once again, the connection with the second law is obvious. It can be shown from the above theorems, using Jensen’s inequality, that on average, we will retrieve the statements of the second law: \(\langle W \rangle \geq \Delta F\) or \(\langle \Delta s_{\text{tot}} \rangle \geq 0\). Similarly, we also obtain \(\langle W_c \rangle \geq 0\), as expected for macroscopic systems.

By separate analysis, one can show that the average heat \(\langle Q \rangle\) dissipated into the bath follows \(\langle Q \rangle \geq 0\). Here too, given a stochastic trajectory, of a system, one can evaluate the dissipated heat \(Q\) using the framework of stochastic thermodynamics [24]. There are several trajectories which do not obey the properties dictated by the second law, i.e. some trajectories exhibit excursions away from the typical behaviour, \(W_c < 0, W < \Delta F, Q < 0\) and \(\Delta s_{\text{tot}} < 0\) [25]. It turns out that these trajectories are necessary for the satisfaction of the fluctuation theorems.

Now one might ask: what is the rate of decay of the number of these atypical trajectories as we make the size of the system larger or observe it over a longer period of time [30]? We shall show here analytically that if the probability distribution of the observable is Gaussian, then the number decays according as the complementary error function. Further, if the various observables, namely the thermodynamic work \((W)\), classical work \((W_c)\) and the dissipated heat \((Q)\), are measured for each trajectory, then the realizations along which \(W < \Delta F\) need not be the same as those along which \(W_c < 0, Q < 0\) or \(\Delta s_{\text{tot}} < 0\). In other words, the atypical trajectories corresponding to one observable may be typical with respect to the others. We have also analysed the nature of distributions \(P(W), P(W_c), P(Q)\) and \(P(\Delta s_{\text{tot}})\). Surprisingly, the distributions for thermodynamic work and the entropy production in nonlinear models may exhibit most probable value in the atypical regime without violating the expected average behaviour. However, the dissipated heat and the classical work exhibit peak in the regime of typical behaviour only. For simplicity, throughout our analysis, the system is driven out of equilibrium by the same sinusoidal force only.

2. The system

Our system consists of a Brownian particle in a potential \(V(x)\), in contact with a heat bath at temperature \(T\), and subjected to an external drive \(f(t)\). It follows the overdamped equation of motion:
\[
\gamma \dot{x} = -\frac{\partial V(x)}{\partial x} + f(t) + \xi(t),
\]
where the noise \(\xi(t)\) is white and Gaussian, so that \(\langle \xi(t) \rangle = 0\) and \(\langle \xi(t)\xi(t') \rangle = 2\gamma T \delta(t-t')\). According to the concept of stochastic thermodynamics [24], we have the following definitions for thermodynamic work \((W)\), classical work \((W_c)\), change in internal energy \((\Delta U)\) and dissipated heat \((Q)\):
\[
W(\tau) = -\int_0^\tau dt x(t) \frac{df(t)}{dt};
\]
\[
W_c = \int_0^\tau f(t)x dt = W - f(\tau)x(\tau) + f(0)x(0);
\]
\[
\Delta U(\tau) = V(x, \tau) - V(x_0);
\]
\[ Q(\tau) = \int_0^\tau \left( -\frac{\partial V(x)}{\partial x} + f(t) \right) \dot{x}(t) = W(\tau) - \Delta U(\tau). \quad (7d) \]

Here, \( \tau \) is the time of observation and \( x_0 \) is the initial position of the particle. Following Seifert [15, 16], the total entropy change \( (\Delta s_{\text{tot}}) \) along a single trajectory is defined as the sum of the system entropy change \( (\Delta s \equiv -\ln P(x, \tau) + \ln P(x_0)) \) and the entropy change in the medium \( (\Delta s_m \equiv \frac{Q(\tau)}{T}) \):

\[ \Delta s_{\text{tot}} = \Delta s_m + \Delta s, \quad (8) \]

\( \Delta s_{\text{tot}} \) obeys the integral fluctuation theorem [15, 16]:

\[ \langle e^{-\Delta s_{\text{tot}}} \rangle = 1. \quad (9) \]

3. Harmonic potential

**Thermodynamic and classical work distributions.** To calculate the thermodynamic work \( (W) \) distributions, we first allow the particle to equilibrate with the bath inside a harmonic potential: \( V(x) = \frac{1}{2}kx^2 \), where \( k \) is the spring constant of the potential. At \( t = 0 \), an external drive \( f(t) = A \sin \omega t \) is switched on up to time \( t = \tau \). As has been shown in [26], it can be shown that the distribution \( P(W) \) is Gaussian (using equation \( 7a \)) and follows the fluctuation-dissipation relation:

\[ \sigma^2 \equiv \langle W^2 \rangle - \langle W \rangle^2 = 2T(\langle W \rangle - \Delta F), \quad (10) \]

where \( \Delta F \) is the change in equilibrium free energy, given by

\[ \Delta F = -\frac{A^2}{2k} \sin^2 \omega \tau. \quad (11) \]

The expression for \( \langle W \rangle \) has been given in the appendix. The classical work distributions \( (P(W_c)) \) can also similarly be shown to be Gaussian and its variance and mean to be related by \( \sigma_c^2 = 2T \langle W_c \rangle \). The value of \( \langle W_c \rangle \) has been given in the appendix.

**Total entropy distributions.** For our problem, the total entropy becomes (see equation \( 9 \))

\[ \Delta s_{\text{tot}} = \frac{W - \Delta U}{T} - \ln \frac{P(x, \tau)}{P(x_0)}. \quad (12) \]

Plugging in the expressions, we find that the total entropy also follows a Gaussian distribution (see the appendix for expression for \( \langle \Delta s_{\text{tot}} \rangle \)) and abides by the fluctuation–dissipation relation: \( \sigma^2 = 2(\Delta s_{\text{tot}}) \). Although this relation is in general valid for steady states, it holds in the transient regime only for this linear system. The details of the calculation can be obtained in [26].

**Heat distributions.** Using \( 7d \), we can find the expression for \( Q \). However, the distribution \( P(Q) \) is non-Gaussian with exponential tails, and has to be generated numerically.

3.1. Results and discussions

In figures 1(a)–(d), we have plotted the probability densities for \( W, W_c, \Delta s_{\text{tot}} \) and \( Q \), respectively for different values of time \( \tau = \tau_\omega/4, 5\tau_\omega/4 \) and \( 9\tau_\omega/4 \), as indicated in the these figures. Here \( \tau_\omega \) is the period of the external drive. We have taken all the physical quantities in dimensionless forms. All the distributions have positive means that shift towards right with increase in time of observation. \( P(W), P(W_c), \) and \( P(\Delta s_{\text{tot}}) \) are Gaussian while \( P(Q) \) is not (figure 1(d)), as expected. The finite probabilities observed for the values of
physical quantities that are atypical ($W < \Delta F$, $W_c < 0$, $\Delta s_{\text{tot}} < 0$ and $Q < 0$) are sometimes referred to as the transient second law violating trajectories. For the thermodynamic work $W$, this fraction $f_W$ is obtained by integrating $P(W)$ from $-\infty$ to $\Delta F$. Similarly, $f_{W_c}$ and $f_{\Delta s_{\text{tot}}}$ are obtained by, respectively, integrating $P(W_c)$ and $P(\Delta s_{\text{tot}})$ from $-\infty$ to $0$. The analytical results are

$$f_W = \frac{1}{2} \text{erfc} \left( \frac{1}{2} \sqrt{\frac{(W) - \Delta F}{T}} \right); \quad (13a)$$

$$f_{W_c} = \frac{1}{2} \text{erfc} \left( \frac{1}{2} \sqrt{\frac{(W_c)}{T}} \right); \quad (13b)$$

$$f_{\Delta s_{\text{tot}}} = \frac{1}{2} \text{erfc} \left( \frac{1}{2} \sqrt{\frac{(\Delta s_{\text{tot}})}{T}} \right). \quad (13c)$$

These have the general form $f = \frac{1}{\sqrt{T}} e^{-\tau}$ in the time-asymptotic limit. Further, it follows from the above equations that the fraction of violations cannot cross 0.5.

In figures 2(a) and (b), we have plotted the fraction of transient second law violating trajectories for $W$, $W_c$, $\Delta s_{\text{tot}}$, and $Q$. The first three are plotted using our analytical results. $f_Q$
for $Q$ has been obtained from the numerical simulation. The insets show magnified portions of $f_{\Delta s_{\text{tot}}}$ and $f_{W}$. We observe that $f_{Q} > f_{\Delta s_{\text{tot}}} > f_{W} > f_{W_{c}}$. As the time of observation increases, the number of atypical trajectories decreases exponentially and goes to 0 (see figure 2(a)), thus leading to the well-defined classical thermodynamic behaviour. We would like to emphasize that given a trajectory, if it violates the relation $W \geq F$, this need not imply that the same trajectory will violate $W_{c} \geq 0$ or $\Delta s_{\text{tot}} \geq 0$ or $Q \geq 0$, since the fractional violations are in general different for different thermodynamic variables.

4. Nonlinear model

We now study the dynamics of a Brownian particle in a nonlinear system. The potential is of the form [27]

$$V(x) = e^{-\alpha x^2} + \frac{k}{q} |x|^q.$$  \hspace{1cm} (14)

Here, the first term on the right-hand side, $e^{-\alpha x^2}$ is a symmetric (about origin) concave function that exponentially decays on either side of the origin. On the other hand, the second term is also a symmetric but convex function that provides a power law increase with $x$ on either side of the origin. These two terms in conjunction lead to the double well potential. In an earlier literature it was thought that bistability is a necessary and sufficient condition to observe the phenomenon of stochastic resonance (SR). However, in recent literature [27] it has been established that bistability is a necessary but not sufficient condition for SR, using the above nonlinear model potential. It is an interesting observation. This potential is called super-harmonic if $q > 2$. In this case SR is observed. However, for sub-harmonic potential, i.e. $q < 2$, SR is completely suppressed even though the potential is bistable.

For our analysis, we have taken $\alpha = 1$, $q = 4$ and $k = 1$. All the physical quantities have been obtained numerically using Heun’s method.
4.1. Results and discussions

In figures 3(a)–(d) we have plotted distributions $P(W)$, $P(W_c)$, $P(\Delta s_{\text{tot}})$ and $P(Q)$. All the parameters are given in the figure. Initially the system is in equilibrium. In all figures we have multi-peaked distributions due to intrawell and interwell dynamics. The protocols are applied for $t = \tau \omega / 4$, $5 \tau \omega / 4$ and $9 \tau \omega / 4$. The number of peaks in the distribution increase by 2 in each successive case. This corresponds to additional crossings of the particles over the intervening potential barrier. This not only broadens the distribution but its mean shifts to the right. The peak corresponding to the initial well motions [28, 29] shrink fast. The change in the free energy $\Delta F$ of the system is the difference between the free energies at the final and the initial values of the protocol, and is calculated by using the Jarzynski equality. We get $\Delta F = -0.31$ for $A = 0.4$. We also obtain the values $\langle e^{-W} \rangle = 1.00$ and $\langle e^{-\Delta s_{\text{tot}}} \rangle = 1.07$, consistent with equations (4) and (3), respectively, within our numerical precision. Our protocol, as mentioned in the beginning, is a sinusoidal perturbation applied over different observation times as mentioned in the plots. It is clear that in all the cases, the fraction of atypical trajectories decreases as we increase the time of observation. Interestingly, $P(W)$ and $P(\Delta s_{\text{tot}})$ for $t = \tau / 4$ exhibit the most probable value in the atypical region. However, it is to be noted that $\langle W \rangle$ and $\langle \Delta s_{\text{tot}} \rangle$ are greater than $\Delta F$ and 0, respectively. That is the
typical behaviour at the macroscopic scale. In figure 4, all the distributions are plotted on the same graph for comparison. The parameters are mentioned in the figure. We clearly see that \( P(W) \) and \( P(\Delta S_{\text{tot}}) \) exhibit the peak corresponding to the most probable value in the region of atypical values. This is not a generic observation. This depends crucially on the values of the parameters, the time of observation and the protocol. However, we have verified with various protocols that the peak corresponding to the most probable value for \( W_c \) and \( Q \) always lie in the typical region. Average values of all the physical quantities increase with the time of observation as they are extensive in nature, as in the linear case. In figure 5, we have plotted the fractional violations \( f_W, f_{W_c}, f_{\Delta S_{\text{tot}}} \) and \( f_Q \) as functions of the time of observation. These fractions decrease exponentially in time and coalesce time asymptotically, as in the linear case. Again, unlike the linear model, wherein \( f_Q > f_{\Delta S_{\text{tot}}} > f_W > f_{W_c} \), this trend is not maintained. Even two curves may cross, as shown in figure 5. This is quite clear from the observations in
5. Conclusions

In our work, we have studied fluctuations in physical quantities such as thermodynamic work, classical work, total entropy and heat when the system is driven out of equilibrium. Our treatment is based on stochastic thermodynamics which gives prescription to calculate $W$, $W_c$, $\Delta s_{tot}$, $Q$, etc, for a given trajectory followed by the particle during evolution. Since we consider ensemble of trajectories, all the physical quantities become fluctuating variables, i.e. they take on random values depending on the trajectory of the particle. Unlike in thermodynamics, these physical quantities take on well-defined probability distributions which in turn satisfy the fluctuation theorems. We have analytically calculated $P(W)$, $P(W_c)$ and $P(\Delta s_{tot})$ for a sinusoidally driven linear system. The glaring differences between the linear and the nonlinear systems have been pointed out. Systematics which are present in linear systems are absent in nonlinear systems. These results are amenable to experimental verifications. We would also like to emphasize that in both the linear and in the nonlinear models, we observe that the fraction of trajectories violating typical behaviour are not greater than 50%.

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Appendix. Expressions for $\langle W \rangle$ and $\langle W_c \rangle$ for harmonic potential under sinusoidal driving

\[
\langle W \rangle = A^2 \omega^2 \tau \left[ \frac{1 - \cos 2\omega \tau}{2(k^2 + \omega^2)} \right] - \frac{A^2 k}{4(k^2 + \omega^2)} \sin 2\omega \tau - \frac{A^2 \omega^2 e^{-k \tau}}{(k^2 + \omega^2)^2} \sin \omega \tau - k \cos \omega \tau - \frac{A^2 \omega^2 k}{(k^2 + \omega^2)^2}. \quad (A.1)
\]

\[
\langle W_c \rangle = A^2 \omega^2 \tau \left[ 1 - \cos 2\omega \tau \right] - \frac{A^2 k}{4(k^2 + \omega^2)} \sin 2\omega \tau - \frac{A^2 \omega^2 e^{-k \tau}}{(k^2 + \omega^2)^2} \sin \omega \tau - \frac{A^2 \omega^2 k}{(k^2 + \omega^2)^2} + \frac{A^2 \omega^2}{2(k^2 + \omega^2)} \sin \omega \tau + \frac{A^2 \omega e^{-\omega \tau}}{k^2 + \omega^2} \sin \omega \tau. \quad (A.2)
\]

\[
\langle \Delta s_{tot} \rangle = \frac{\langle W \rangle}{T} - \frac{A^2 \omega^2 k e^{-2k \tau}}{2(k^2 + \omega^2)^2} - \frac{A^2 \omega^2}{4k} - \frac{A^2 \omega^2 k(2 + 3\omega^2)}{4(k^2 + \omega^2)^2} \cos 2\omega \tau - \frac{A^2 \omega^2}{4k \omega} \sin 2\omega \tau,
\]

\[
= \frac{A^2 \omega^2}{4k} - \frac{A^2 \omega^2 k(2 + 3\omega^2)}{4(k^2 + \omega^2)^2} \cos 2\omega \tau - \frac{A^2 \omega^2}{4k \omega} \sin 2\omega \tau.
\]
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