



Fluctuation theorems for total entropy production in generalized Langevin systems



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ABSTRACT

The validity of the fluctuation theorems for total entropy production of a colloidal particle embedded in a non-Markovian heat bath driven by a time-dependent force in a harmonic potential is probed here. The dynamics of the system is modeled by the generalized Langevin equation with colored noise. The distribution function of the total entropy production is calculated and the detailed fluctuation theorem contains a renormalized temperature term which arises due to the non-Markovian characteristics of the thermal bath.

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1. Introduction

In the field of statistical mechanics, fluctuation theorems have been a topic of interest for systems driven away from thermal equilibrium by the action of an external time dependent perturbation [1–3]. These theorems have been studied both theoretically and experimentally [4,5]. A consequence of the fluctuation theorem is the Jarzynski's equality [6,7], which has been tested in many experiments such as mechanically unfolding a single RNA molecule reversibly and irreversibly between two conformations [4,5]. The fluctuation theorem (FT) states that if a system is in a state of thermal equilibrium and if it is driven away from equilibrium by an external force, then

$$\frac{P(+X)}{P(-X)} = e^X \quad (1)$$

where $P(X)$ refers to the probability densities, the + and – signs refer to the original and the time-reversed process [2]. Here X is the entropy production or any other physical quantity such as heat or work associated with it [2,8]. The Jarzynski theorem [6] and the Crooks fluctuation theorem [2] have been tested experimentally by studying the non equilibrium thermodynamics of a metallic single electron box [9,10]. The probability distributions of the dissipated energy are found to obey Jarzynski and Crooks fluctuation relations. Fluctuation theorems can be of two types, steady state [11], and transient [12]. The above equation is most commonly referred to as the detailed fluctuation theorem (DFT). Based on the principles of stochastic thermodynamics for diffusive motion, a proof of this relation was given by Kurchan [13] and Spohn et al. [14]. In all these cases, entropy production is only associated with the entropy change in the medium and the above relation holds asymptotically only in the long-time limit. If one includes the entropy change of the system, then the total entropy production has two contributions. Firstly, the heat dissipated can be associated with the change of entropy in the medium along a single trajectory and secondly there is trajectory dependent entropy of the system. The total entropy production is thus a sum of these two quantities. Later Seifert has shown that this total entropy production along a single

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trajectory for a system driven out of equilibrium by time-dependent forces follows the integral fluctuation theorem (IFT), $\langle e^{-\Delta s_{tot}} \rangle = 1$ [15,16]. The dynamics of such a system can be modeled by the over damped motion of a single colloidal particle governed by the Langevin equation. The fluctuations in the total entropy production have been studied for various systems that are initially in a state of thermal equilibrium with the heat bath [17]. It has been shown that the detailed fluctuation theorem holds well when the Brownian particle in a harmonic trap is subjected to an external time dependent force or for a particle in a dragged harmonic oscillator [18]. For all these cases, the dynamics of the particle is governed by the ordinary Langevin equation with an additive Gaussian white noise. The distribution of the entropy production has been measured experimentally for a number of systems, such as for a colloidal particle driven by a constant force along a periodic potential [19]. It has been verified that if the distribution of the total entropy production, (Δs_{tot}) is Gaussian then the IFT holds good.

In this article, we test the validity of the fluctuation theorems for the total entropy production in a system embedded in a non-Markovian heat bath. The validity of the non-equilibrium work fluctuation theorems for oscillators in non-Markovian heat baths has been tested earlier by Mai and Dhar by calculating the work distribution functions [20]. Very recently Aquino has shown that the transient work fluctuation theorem is valid for a charged Brownian harmonic oscillator embedded in a non-Markovian heat bath and under the action of crossed electric and magnetic fields [21]. Also using the concepts of stochastic thermodynamics, the Jarzynski relation was proved for non-Markovian systems with memory [22]. Fluctuation theorems for non-equilibrium quantum processes have been studied using an open system approach. It has been suggested that memory effects lead to the correlation between the single trajectories of entropy production and result in a correction of the well-known fluctuation theorem for entropy production [23]. Pekola et al. have studied the total entropy production in an environment where some of its degrees of freedom are correlated with the system [24]. Such degrees of freedom give rise to some non-equilibrium effects in the environment and one needs to include a new type of non-Markovian contribution to the total entropy production. The dynamics of a system is described in some effective temperature which is different from the equilibrium temperature of an ideal heat bath. All such Markovian and non-Markovian contributions are taken into account for deriving the fluctuation theorems for entropy production. In this study, in order to capture the effects of the non-Markovian nature of the heat bath at a constant temperature, we model the dynamics of the system by the generalized equation motion (GLE) with an associated memory kernel [25]. We find that in the presence of a non-Markovian heat bath, a renormalized temperature term is necessary to support the validity of the fluctuation theorem of total entropy production.

In Section 2, we present our theoretical model to study the dynamics of a single colloidal particle using the GLE with colored noise. We derive the Fokker–Planck (FP) equation and propose its solution. We use this solution to obtain the mean and variances of position and work and calculate the total entropy production. In Section 3, we obtain the probability distribution of total entropy production and test the validity of the fluctuation theorems. In Section 4, we conclude our results.

2. Model

The primary objective of the present study is to probe the validity of the non-equilibrium fluctuation relations for the distribution of the total entropy production along a single trajectory.

In order to model non-equilibrium fluctuations in a non-Markovian heat bath, we consider a harmonic oscillator of mass m in thermal contact with a Gaussian colored-noise heat bath and acted upon by a time-dependent force $f(t)$ [26,27]. This system serves as a model for an optically trapped colloidal particle dragged through a viscoelastic medium, and its dynamics is defined by the generalized Langevin equation [28]:

$$m\ddot{x}(t) = -kx(t) + f(t) - \zeta \int_0^t dt' K(t-t') \dot{x}(t') + \theta(t). \quad (2)$$

Here, $x(t)$ is the position of the oscillator at time t , k is the force constant of the harmonic well, ζ is the friction coefficient of the particle, and $\theta(t)$ is a Gaussian random variable with $\langle \theta(t) \rangle = 0$. The memory kernel $K(t)$ satisfies the fluctuation–dissipation relation and is given by

$$\langle \theta(t)\theta(t') \rangle = \zeta k_B T K(|t-t'|), \quad (3)$$

where T is the temperature of the reservoir and k_B is the Boltzmann's constant. If $\theta(t)$ were the white noise, and $f(t)$ a force pulling the oscillator at a constant speed u (such that $f(t)$ is equal to ku), Eq. (2) (with the inertial term neglected) would describe the model treated by Mazonka and Jarzynski [29]. As discussed in Section 1, the total entropy production involves the entropy of the system as it evolves in response to the effects of the time-dependent force and also the entropy production in the surrounding medium. According to the stochastic thermodynamic approach, the change in the internal energy ΔU and the heat dissipated Q to the bath along a stochastic trajectory $x(t)$ are related by

$$Q = w - \Delta U \quad (4)$$

where the change in internal energy $\Delta U = U(x, t) - U(x_0, 0)$. This is the first law of thermodynamics.

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