Superstatistical generalization of the work fluctuation theorem

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Abstract

We derive a generalized version of the work fluctuation theorem for nonequilibrium systems with spatio-temporal temperature fluctuations. For χ^2-distributed inverse temperature we obtain a generalized fluctuation theorem based on q-exponentials, whereas for other temperature distributions more complicated formulae arise. Since q-exponentials have a power law decay, the decay rate in this generalized fluctuation theorem is much slower than the conventional exponential decay. This implies that work fluctuations can be of relevance for the design of micro or nano structures, since the work done on the system is relatively much larger than in the conventional fluctuation theorem.

1 Introduction

In this paper two recent developments are being combined: Fluctuation theorems [1] — [13] and Tsallis statistics (and further generalized statistics) in non-equilibrium stationary states [14] — [26].

The conventional fluctuation theorems give the ratio of the probability $P(W_\tau)$ to find a fluctuation of, e.g., the work W_τ done on a system over a time interval τ to the probability $P(-W_\tau)$ of an equal amount of work $-W_\tau$ done by the system. This ratio is given by an exponential function of W_τ, i.e. one has $P(W_\tau)/P(-W_\tau) = \exp(\beta W_\tau)$, where β is the inverse temperature. On the other hand, the 'superstatistical' generalization, derived here, can yield for this ratio (for example) a power law instead of exponential behavior.

Superstatistics is a 'statistics of a statistics' relevant for driven nonequilibrium systems with a stationary state [23] — [26]. One assumes that the system has spatio-temporal temperature fluctuations on a relatively large scale, due to external forces acting on the system. One statistics is then given by ordinary Boltzmann factors (in space-time cells where the temperature is sufficiently constant), and the other one by the probability distribution of β in the various cells. It has been shown that these types of models generate Tsallis statistics if β is χ^2-distributed [16,17]. But many other generalized statistics are possible as well [22,23,27].

We will present a superstatistical generalization of the fluctuation theorem. Our result could have important consequences for the work fluctuations in micro or nano systems, because the ratio $P(-W_\tau)/P(W_\tau)$ of the above mentioned probabilities is much larger for the superstatistical case. In fact, this implies that for large fluctuations a micro or nano structure will be subjected relatively to much more work than in the conventional case. This could, in particular, be of relevance if micro or nano systems are placed into a fluctuating or turbulent environment, with *externally* produced temperature fluctuations due to constantly acting external driving forces. Moreover, besides the work fluctuation theorem, there is also a heat fluctuation theorem [12]. For small systems the heat fluctuations allowed by the heat fluctuation theorem can also lead to *internal* fluctuations of the temperature. All this illustrates the need to consider fluctuation theorems for systems where the temperature is not constant but fluctuates.

The Fluctuation Theorem can be visualized by considering a very long trajectory in the phase space of the system in a non-equilibrium stationary state, then partitioning this trajectory in segments, on all of which the system spends an equal time τ. A histogram is then made of W_τ and $W_{-\tau}$ for all segments, which will allow an (approximate) determination of the probabilities $P(W_\tau)$ and $P(-W_\tau)$ and their ratio.

The main difference between the conventional and the superstatistical Fluctuation Theorem is that e.g. in the case of a Brownian particle, as considered here, the friction and the noise strength in the Langevin equation are constants, while in the case of superstatistics these quantities can fluctuate in space and time. A concrete physical interpretation of the Langevin equation with constant coefficients in terms of electric circuits has been proposed in [13]. In this approach, the velocity of the Brownian particle corresponds to the time-dependent current measured in the circuit. Applying this physical interpretation to our Langevin equation with fluctuating coefficients, our superstatistical fluctation theorem describes the work fluctuations in a small circuit system whose surrounding temperature fluctuates on a relatively large time scale.

In this paper we will only be concerned with fluctuations of the work done on or by a system in a non-equilibrium stationary state in the large time t limit. The fluctuations of the heat are much more complicated and will not be considered here [12]. There are very many other similar fluctuation theorems for work and heat e.g. for transient states and for finite times, all of which could be generalized to superstatistical fluctuation theorems. As said, we will restrict ourselves here to the simple case, in order to elucidate the principle of the superstatistical generalization of the conventional fluctuation theorems on the above described model: the replacement of an exponential by e.g. a power law.

This paper is organized as follows. In section 2 we formulate a superstatistical Langevin model for the joint process of velocity and position of a Brownian particle moving in a changing environment. In section 3 we consider the overdamped case of that model, which leads to a superstatistical Langevin equation for the position only. In section 4 we derive the superstatistical version of the work fluctuation theorem. Finally, in section 5 some concrete examples of superstatistical fluctuation theorems are written down.

2 Superstatistical Langevin model

Consider a spherical Brownian particle in three dimensions with radius R and mass m. We assume that this moves in a fluid of viscosity η in an environment that has spatio-temporal temperature fluctuations. These temperature fluctuations take place on a rather large spatio-temporal scale and are produced by external driving forces that act on the system and change the environment of the Brownian particle. A typical example could be a particle moving in a turbulent flow experiment. An effective statistical mechanics description of the test particle is given by a superstatistics [23], a 'statistics of a statistics', where one is given by a probability density associated with the Brownian particle for a locally constant temperature, while the other one is given by the distribution $f(\beta)$ of the inverse temperature β in the various spatio-temporal regions (cells) of approximately constant β. The temperature β^{-1} surrounding the Brownian particle on its way through these spatial regions of size L^3 varies on the rather large time scale τ_L (due to both, the spatial movement of the particle and also due to a possible explicit time dependendence of the temperature field). τ_L is the typical time scale the Brownian particle spends in the cell of size L^3. We assume that the relaxation time τ_r of the Brownian particle satisfies $\tau_r << \tau_L$ so that local equilibrium can be established.

To establish a fluctuation theorem, we assume that the motion of the Brownian particle is restricted by a time-dependent harmonic potential [9] . For $t \leq 0$ the minimum $\mathbf{x}_t^*$ of the harmonic potential is at the origin, $\mathbf{x}_t^* = 0$, whereas for $t > 0$ it moves with a velocity $\mathbf{v}_t^*$. This velocity $\mathbf{v}_t^*$ can, in principle, be an arbitrary function of time [11]. The equations of motion for the particle are

$$\dot{\mathbf{x}}_t = \mathbf{v}_t \tag{1a}$$
$$m\dot{\mathbf{v}}_t = -\alpha\mathbf{v}_t - k(\mathbf{x}_t - \mathbf{x}_t^*) + \zeta_t, \tag{1b}$$

where $\mathbf{x}_t$ and $\mathbf{v}_t$ are the position and velocity of the Brownian particle, respectively.

There are three different forces acting on the particle. Firstly, the damping force $-\alpha\mathbf{v}_t$, with Stokes' law yielding α as

$$\alpha = 6\pi\eta R. \tag{2}$$

Secondly, there is the harmonic force $-k(\mathbf{x}_t - \mathbf{x}_t^*)$. Finally, there is the random force ζ_t, which is taken to be Gaussian white noise:

$$\langle\zeta_t\rangle = 0; \quad \langle\zeta_t\zeta_s\rangle = 2\beta^{-1}\alpha\delta(t-s) \tag{3}$$

The important point is that β is not assumed to be constant, but varies on the rather large time scale τ_L.

The local equilibrium distribution, for some given local β, assuming that this β persists locally for a sufficiently long time interval for the Brownian particle to reach local equilibrium, is given by

$$f_{leq,\beta}(\mathbf{x},\mathbf{v}) = \left(\frac{\beta\sqrt{km}}{2\pi}\right)^3 e^{-\beta\left(\frac{1}{2}m|\mathbf{v}|^2 + \frac{1}{2}k|\mathbf{x}-\mathbf{x}_t^*|^2\right)}. \tag{4}$$

In the long-term, the particle moves through spatial regions which have different inverse temperatures β. Denoting the probability density of β by $f(\beta)$, one asymptotically obtains a convolution of the various equilibrium distributions for different β. The observed long-term distribution (the marginal distribution where β is not fixed anymore), relevant for $t >> \tau_L$, is obtained by integrating over all β:

$$p(\mathbf{x},\mathbf{v}) = \int_0^\infty f(\beta) f_{leq,\beta}(\mathbf{x},\mathbf{v})d\beta. \tag{5}$$

Let us consider an important example, namely a χ^2-distributed β [28,16,17,23]. This means the probability density of β is given by

$$f(\beta) = \frac{1}{\Gamma\left(\frac{n}{2}\right)}\left\{\frac{n}{2\beta_0}\right\}^{\frac{n}{2}} \beta^{\frac{n}{2}-1}\exp\left\{-\frac{n\beta}{2\beta_0}\right\}. \tag{6}$$

n denotes the number of independent Gaussians X_i contributing to the χ^2-distribution of $\beta = \sum_{i=1}^n X_i^2$. The mean of the inverse temperature is given by

$$\langle \beta \rangle = \int_0^\infty \beta f(\beta) d\beta = \beta_0 \tag{7}$$

and the variance by

$$\langle \beta^2 \rangle - \beta_0^2 = \frac{2}{n}\beta_0^2. \tag{8}$$

Let us define the energy of the Brownian particle as

$$E = \frac{1}{2}m|\mathbf{v}|^2 + \frac{1}{2}k|\mathbf{x} - \mathbf{x}_t^*|^2. \tag{9}$$

The integration in Eq. (5) can be performed explicitly, and one obtains [17] the generalized canonical distributions of nonextensive statistical mechanics [14,15,19,20]

$$p(\mathbf{x}, \mathbf{v}) \sim \frac{1}{\left(1 + \tilde{\beta}(q-1)E\right)^{\frac{1}{q-1}}} \tag{10}$$

with the following identifications

$$q = 1 + \frac{2}{n+6} \tag{11}$$

and

$$\tilde{\beta} = \frac{\beta_0}{1 - 3(q-1)}. \tag{12}$$

The marginal distribution (10) describing the long-term distribution of position and momentum of the particle becomes a so-called q-exponential [15,20]. For other distributions $f(\beta)$, one obtains other superstatistics, which all reduce to Tsallis statistics for sharply peaked temperature distributions, as shown in [23].

3 Simplification for the overdamped case

To proceed to a simpler stochastic model, we may proceed in the usual way [29] and consider the system in the overdamped case

$$mk \ll \alpha^2. \tag{13}$$

In that limit one obtains a Langevin equation for the position only,

$$\dot{\mathbf{x}}_t = -\tau_r^{-1}(\mathbf{x}_t - \mathbf{x}_t^*) + \alpha^{-1}\zeta_t, \tag{14}$$

with relaxation time

$$\tau_r = \frac{\alpha}{k}. \tag{15}$$

The local equilibrium distribution reduces to

$$p_{eq,\beta}(\mathbf{x}) = \int d\mathbf{v}\, f_{eq}(\mathbf{x},\mathbf{v}) = (k\beta/2\pi)^{3/2} e^{-\beta\frac{k}{2}|\mathbf{x}-\mathbf{x}_t^*|^2}, \tag{16}$$

and again the marginal distribution is given by

$$p(\mathbf{x}) = \int_0^\infty f(\beta) p_{eq,\beta}(\mathbf{x}) d\beta. \tag{17}$$

For the example of a χ^2-distributed inverse temperature, we obtain

$$p(\mathbf{x}) \sim \frac{1}{\left(1 + \frac{1}{2}k\tilde{\beta}(q-1)|\mathbf{x}-\mathbf{x}_t^*|^2\right)^{\frac{1}{q-1}}} \tag{18}$$

with

$$q = 1 + \frac{2}{n+3} \tag{19}$$

and

$$\tilde{\beta} = \frac{\beta_0}{1 - \frac{3}{2}(q-1)}. \tag{20}$$

4 Generalized work fluctuation theorem

In this section we follow reference [11] with appropriate modifications to solve our superstatistical model.

The work W_τ done on the system during a time interval τ is given by

$$W_\tau = \int_0^\tau dt\, \mathbf{v}_t^* \cdot [-k(\mathbf{x}_t - \mathbf{x}_t^*)]. \tag{21}$$

The conventional fluctuation theorem for stationary states with a given constant inverse temperature β reads for sufficiently large τ:

$$\frac{P(-W_\tau)}{P(W_\tau)} = e^{-\beta W_\tau}. \tag{22}$$

In [11] the fluctuation theorem was derived from a Langevin model with constant temperature. We now extend this approach to nonequilibrium systems with spatio-temporally fluctuating temperatures.

Let us first restrict to spatial regions (cells) where the temperature can be taken to be locally constant. Within these cells, all relevant random variables are Gaussians provided $\tau < \tau_L$. In Eq. (21), W_τ is a linear function of

$\mathbf{x}_t$. Combined with the Gaussian nature both of the Green's function of the Ornstein-Uhlenbeck process and of the initial distribution, this implies that the distribution P of W_τ in a given cell for a given time interval τ is Gaussian as well:

$$P(W_\tau) = \frac{1}{\sqrt{2\pi V_\tau}} \exp\left\{-\frac{(W_\tau - M_\tau)^2}{2V_\tau}\right\} \tag{23}$$

Here M_τ denotes the mean of W_τ and V_τ the variance of W_τ.

Following section C in [11], we obtain straightforwardly for sufficiently large τ

$$M_\tau = k \int_0^\tau dt'_2 \int_0^{t'_2} dt'_1 \, e^{-(t'_2-t'_1)/\tau_r} \mathbf{v}^*_{t'_2} \cdot \mathbf{v}^*_{t'_1} \tag{24}$$

and

$$V_\tau = 2\beta^{-1} M_\tau. \tag{25}$$

This relation proves a *local* fluctuation theorem in the cells with constant β. Combining Eq. (23) and Eq. (25), we may write

$$P(W_\tau) = \sqrt{\frac{\beta}{4\pi M_\tau}} \exp\left\{-\frac{\beta}{4M_\tau}(W_\tau - M_\tau)^2\right\} \tag{26}$$

and

$$P(-W_\tau) = \sqrt{\frac{\beta}{4\pi M_\tau}} \exp\left\{-\frac{\beta}{4M_\tau}(W_\tau + M_\tau)^2\right\}, \tag{27}$$

which immediately leads to

$$\frac{P(-W_\tau)}{P(W_\tau)} = e^{-\beta W_\tau}. \tag{28}$$

Let us now take into account the temperature fluctuations. We have the following ordering of time scales

$$\tau_r << \tau < \tau_L << t, \tag{29}$$

where τ_r is the relaxation time to local equilibrium, τ is the time scale of a local fluctuation theorem, τ_L is the time scale the particle spends in a cell of size L^3, and t is the total time elapsed. Two different experimental setups seem possible, for which we derive two different versions of a generalized fluctuation theorem for $t \to \infty$.

Setup 1. In the experiment one measures the ratio $P(-W_\tau)/P(W_\tau)$ in local time intervals $\tau < \tau_L$, within which the temperature stays sufficiently constant. In this case one obtains in the long-term ($t >> \tau$)

$$\langle \frac{P(-W_\tau)}{P(W_\tau)} \rangle = \int_0^\infty f(\beta) e^{-\beta W_\tau} d\beta. \tag{30}$$

Here the expectation $\langle\cdots\rangle$ denotes an expectation with respect to the distribution $f(\beta)$.

Setup 2. In a different experimental setup $P(W_\tau)$ and $P(-W_\tau)$ are each measured over a very long time period that includes many different states with different temperatures. In this case one obtains in the long-term ($t >> \tau$)

$$\frac{\langle P(-W_\tau)\rangle}{\langle P(W_\tau)\rangle} = \frac{\int_0^\infty f(\beta)\exp\left\{-\frac{\beta}{4M_\tau}(W_\tau + M_\tau)^2\right\}\sqrt{\beta}d\beta}{\int_0^\infty f(\beta)\exp\left\{-\frac{\beta}{4M_\tau}(W_\tau - M_\tau)^2\right\}\sqrt{\beta}d\beta}. \tag{31}$$

5 Some examples

5.1 χ^2-distribution

The assumption of a χ^2-distributed inverse temperature β of the form (6) leads to a Tsallis-generalized fluctuation theorem. One obtains for an experimental setup of type 1 a generalized fluctuation theorem of the form

$$\langle\frac{P(-W_\tau)}{P(W_\tau)}\rangle = \int_0^\infty e^{-\beta W_\tau} f(\beta)d\beta = (1+\tilde{\beta}(q-1)W_\tau)^{-\frac{1}{q-1}}, \tag{32}$$

with

$$q = 1 + \frac{2}{n} \tag{33}$$

and

$$\tilde{\beta} = \beta_0. \tag{34}$$

This means the ordinary exponential e^x in the fluctuation theorem is replaced by a q-expontial $e_q^x := (1-(q-1)x)^{-\frac{1}{q-1}}$ [19,20]. Note that in the fluctuation theorem there is now an asymptotic power law in W_τ for large W_τ, which means that events with negative work-production, i.e. with work done on the system, are now much more likely than in the case without β fluctuations. Thus rare events are significantly enhanced by the temperature fluctuations: previously they were exponentially suppressed, now they obey a power law. This can be of potential interest for small electrical circuits [13] in a fluctuating environment [23]. Also note that the q relevant for the generalized fluctuation theorem as given by eq. (33) is different from the one for the nonextensive equilibrium distribution given in Eq. (11) or Eq. (19), due to the fact that for the superstatistical invariant distributions we integrate over β-dependent normalization factors, whereas for the fluctuation theorem (in setup 1) we do not.

For small W_τ, the result (32) can also be written as the following power expansion (cf.[23], eq. (14)):

$$\langle\frac{P(-W_\tau)}{P(W_\tau)}\rangle = e^{-\beta_0 W_\tau}(1+\frac{1}{2}(q-1)\beta_0^2W_\tau^2 - \frac{1}{3}(q-1)^2\beta_0^3W_\tau^3 + ...) \tag{35}$$

For setup 2 we obtain the formula

$$\frac{\langle P(-W_\tau)\rangle}{\langle P(W_\tau)\rangle} = \left(\frac{1+\tilde{\beta}(q-1)\frac{(W_\tau-M_\tau)^2}{4M_\tau}}{(1+\tilde{\beta}(q-1)\frac{(W_\tau+M_\tau)^2}{4M_\tau}}\right)^{\frac{1}{q-1}} \tag{36}$$

where

$$q = 1+\frac{2}{n+1} \tag{37}$$

and

$$\tilde{\beta} = \frac{\beta_0}{1-\frac{1}{2}(q-1)}. \tag{38}$$

5.2 Log-normal distribution

The log-normal distribution

$$f(\beta) = \frac{1}{\beta s\sqrt{2\pi}}\exp\left\{\frac{-(\log\frac{\beta}{m})^2}{2s^2}\right\} \tag{39}$$

yields yet another possible superstatistics. m and s are parameters. The average β_0 of the above log-normal distribution is given by $\beta_0 = m\sqrt{w}$ and the variance by $\sigma^2 = m^2w(w-1)$, where $w := e^{s^2}$ [23]. Lognormal superstatistics has applications in Lagrangian turbulence models [25,26]. Experimentally measured data of single-particle accelerations are described very well by these models. The physical meaning of the variables occurring in the turbulence models is different, for example the variable $\mathbf{x}$ in the Langevin equation is representing the acceleration of a test particle in the turbulent flow, rather than the position of a Brownian particle, while β is not related to the inverse physical temperature in the flow but to the fluctuating energy dissipation in a cascade. Nevertheless, the mathematics is the same and one obtains in experimental setup 1 a fluctuation theorem of the form (30), which for small W_τ has the power law expansion (cf.[23], eq.(16))

$$\langle\frac{P(-W_\tau)}{P(W_\tau)}\rangle = e^{-\beta_0 W_\tau}[1+\frac{1}{2}m^2w(w-1)W_\tau^2 + O(W_\tau^3)]. \tag{40}$$

One might speculate that these or similar types of fluctuation theorems describe the backward scattering in the turbulent energy cascade.

5.3 F-distribution

Consider a $\beta \in [0, \infty]$ distributed according to the F-distribution [28,22,23]

$$f(\beta) = \frac{\Gamma((v+w)/2)}{\Gamma(v/2)\Gamma(w/2)} \left(\frac{bv}{w}\right)^{v/2} \frac{\beta^{\frac{v}{2}-1}}{(1+\frac{vb}{w}\beta)^{(v+w)/2}}. \tag{41}$$

Here w and v are positive integers and $b > 0$ is a parameter. The average of β is given by

$$\beta_0 = w/b(w-2) \tag{42}$$

and the variance by

$$\sigma^2 = 2w^2(v+w-2)/b^2v(w-2)^2(w-4). \tag{43}$$

For small W_τ we obtain in experimental setup 1 an expansion of the form (cf.[23], eq. (20))

$$\langle \frac{P(-W_\tau)}{P(W_\tau)} \rangle = e^{-\beta_0 W_\tau}[1 + \frac{1}{2}\sigma^2 W_\tau^2 + O(W_\tau^3)]. \tag{44}$$

5.4 Sharply peaked distributions

While in general the large W_τ behavior in the various fluctuation theorems depends strongly on the superstatistics considered (i.e. on the function $f(\beta)$), the small-W_τ behavior is universal, in the sense that there is always the same quadratic correction term to the ordinary fluctuation theorem. To see this we can adopt a proof previously described in [23]. For any distribution $f(\beta)$ with average $\beta_0 := \langle \beta \rangle$ and variance $\sigma^2 := \langle \beta^2 \rangle - \beta_0^2$ we can write

$$\begin{aligned} \langle \frac{P(-W_\tau)}{P(W_\tau)} \rangle &= \langle e^{-\beta W_\tau} \rangle = e^{-\beta_0 W_\tau} e^{+\beta_0 W_\tau} \langle e^{-\beta W_\tau} \rangle \\ &= e^{-\beta_0 W_\tau} \langle e^{-(\beta-\beta_0)W_\tau} \rangle \\ &= e^{-\beta_0 W_\tau} \left(1 + \frac{1}{2}\sigma^2 W_\tau^2 + \sum_{r=3}^{\infty} \frac{(-1)^r}{r!} \langle (\beta-\beta_0)^r \rangle W_\tau^r \right). \end{aligned} \tag{45}$$

The coefficients of the powers W_τ^r are the r-th moments of the distribution $f(\beta)$ about the mean β_0. For small enough σW_τ, in setup 1 the first order correction term to the ordinary fluctuation term is always quadratic in W_τ:

$$\langle \frac{P(-W_\tau)}{P(W_\tau)} \rangle \approx e^{-\beta_0 W_\tau}(1 + \frac{1}{2}\sigma^2 W_\tau^2) \tag{46}$$

For sharply peaked distributions in β, the fluctuation theorem for experimental setup 2 also simplifies and one obtains

$$\frac{\langle P(-W_\tau)\rangle}{\langle P(W_\tau)\rangle} \approx e^{-\beta_0 W_\tau} \left(\frac{1+\frac{\sigma^2}{32}\frac{(W_\tau+M_\tau)^4}{M_\tau^2}}{1+\frac{\sigma^2}{32}\frac{(W_\tau-M_\tau)^4}{M_\tau^2}} \right) \approx e^{-\beta_0 W_\tau} \left(1 + \frac{\sigma^2}{4}\frac{W_\tau}{M_\tau}(W_\tau^2 + M_\tau^2) \right), \tag{47}$$

where β_0 and σ^2 are the mean and variance of the probability density $\tilde{f}(\beta) := C\beta^{1/2}f(\beta)$ used for mapping type-B superstatistics into type-A superstatistics [23].

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