Exactly solvable model illustrating far-from-equilibrium predictions

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Abstract

We describe an exactly solvable model which illustrates the \textit{fluctuation theorem} and other predictions for systems evolving far from equilibrium. Our model describes a particle dragged by a spring through a thermal environment. The rate at which the spring is pulled is arbitrary.

Keywords: \textit{fluctuation theorem}, \textit{irreversible processes}

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INTRODUCTION

In recent years, a number of theoretical results pertaining to systems evolving far from thermal equilibrium have been derived; see, for instance, Refs. [1–6]. While not identical, these results bear a similar structure, and the term fluctuation theorem has come to refer to them collectively. Our purpose in this paper is to illustrate these and other [7,8] results, with a highly idealized but exactly solvable model of a system far from equilibrium.

The paper is organized as follows. In Section I we briefly review the four theoretical predictions which we will illustrate with our model. These are: the steady-state and transient fluctuation theorems, a detailed fluctuation theorem, and a nonequilibrium work relation for free energy differences. In Section II we introduce and solve our model, representing a particle dragged through a thermal environment by a uniformly translating harmonic force. In Section III we use this solution to show that our model indeed satisfies the above-mentioned nonequilibrium results.

I. BACKGROUND

Statements of the fluctuation theorem (FT) which have appeared in the literature can be expressed by the following equation:

\[
\lim_{\tau \to \infty} \frac{1}{\tau} \ln \frac{p_\tau(\sigma^+)}{p_\tau(\sigma^-)} = \sigma.
\] (1)

Here, \( \sigma \) is the average rate at which entropy is generated during a given time interval – or segment – of duration \( \tau \), for a system away from thermal equilibrium; \( p_\tau(\sigma) \) is the distribution of values of \( \sigma \) over a statistical ensemble of such segments; and Boltzmann’s constant \( k_B = 1 \). (Note that the words “average rate” denote the time average over a given segment, not an average over the ensemble of segments.) Following the literature, we will distinguish between two versions of the FT, steady-state and transient, which differ in the statistical ensemble of segments considered. In the steady-state case [2], we imagine observing the system in a nonequilibrium steady state for an “infinite” length of time, which we chop up into infinitely many segments of duration \( \tau \), and we compute the average entropy generation rate, \( \bar{\sigma} \), for each segment; \( p_\tau(\sigma) \) is then the distribution of values of \( \sigma \) over this ensemble of segments. In the transient case [4], by contrast, we imagine that the system of interest begins in an equilibrium state, but is then driven away from equilibrium, for instance by the sudden application of an external force. We observe the response of the system for a time \( \tau \), starting from the moment the external perturbation is applied. Then \( p_\tau(\sigma) \) is the distribution of values of average entropy generation rate over infinitely many repetitions of this process. The transient FT is valid for any duration \( \tau \), whereas the steady-state FT becomes valid as \( \tau \to \infty \); hence the parenthetical appearance of that limit in Eq. 1.

In the examples considered in the literature, the physical origin of entropy generation is the exchange of heat between the system and some infinite reservoir. To model the evolution of a system in contact with a reservoir, a variety of schemes are available, and in each case one must define what is meant by the “entropy generated”. The FT has been derived or illustrated numerically for a number of such schemes, involving both deterministic and
stochastic equations of motion. Of particular relevance for the present paper is the work of Kurchan \[3\], who showed that the FT is valid for Langevin processes.

Apart from the usual (steady-state and transient) statements of the FT, a detailed fluctuation theorem (DFT) was derived in Ref. \[7\]. This result pertains to a finite time interval $\tau$, and has a structure similar to that of the usual FT, but in addition exhibits a dependence on the initial and final microstates of the system. Specifically, consider a process $\Pi^+$ during which a system of interest evolves in contact with a heat reservoir, while – possibly – some work parameter $\lambda$ (e.g. an applied field) is being manipulated externally. Let $\lambda^+(t)$ be the externally imposed time-dependence of this parameter, from $t = 0$ to $t = \tau$, and let $\Delta s$ denote the entropy produced during a particular realization of this process. Now consider the “reverse” process, $\Pi^-$, defined exactly as $\Pi^+$, but with the time-dependence of the work parameter reversed: $\lambda^-(t) = \lambda^+(\tau - t)$. For the forward process $\Pi^+$, let $P_+(z_f, \Delta s | z_i)$ denote the joint probability that the entropy produced over the interval of observation will be $\Delta s$, and the final microstate of the system will be $z_f$, given an initial microstate $z_i$; and let $P_-(z_f, \Delta s | z_i)$ denote the same for the reverse process, $\Pi^-$. Then the DFT states that these joint, conditional probability distributions satisfy the following relation:

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

where the asterisk (*) denotes a reversal of momenta: $(q, p)^* = (q, -p)$.

Finally, in Ref. \[8\] the following nonequilibrium work relation for free energy differences was established:

$$\langle e^{-\beta W} \rangle = e^{-\beta \Delta F}.$$  \(\text{(3)}\)

(See also Ref. \[9\] for an elegant derivation of Eq.\(3\) specific to stochastic processes.) This result applies to a situation in which a system of interest, in contact – and initially in equilibrium – with a heat reservoir at temperature $\beta^{-1}$, evolves in time as an external parameter $\lambda$ is switched at a finite rate from and initial to a final value, say, from 0 to 1. The finite-rate switching of $\lambda$ drives the system out of equilibrium. $W$ is the work performed during one realization of this process. The precise value of $W$ will depend on the microscopic initial conditions of both the system of interest and the reservoir; by repeating the process infinitely many times (sampling initial conditions from equilibrium ensembles), we obtain a statistical ensemble of microscopic realizations of the process. The angular brackets then denote an average over this ensemble of realizations, and $\Delta F$ is the free energy difference between the equilibrium states (at temperature $\beta^{-1}$) corresponding to the values $\lambda = 0$ and $\lambda = 1$.

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1 In fact, the formulation of Ref. \[6\] is somewhat more general than that described here: the system is allowed to be in contact with numerous reservoirs, at various temperatures; furthermore, contact between the system and any of the assorted reservoirs can be externally established and broken during the course of the process.

2 The validity of Eq.\(3\) does not require that the system end in the equilibrium state corresponding to $\lambda = 1$, only that such an equilibrium state exists, and that the final value of the external parameter is 1.
is valid regardless of how slowly or quickly \( \lambda \) is switched from 0 to 1, hence applies even if the system is driven far from equilibrium by a violent variation of the external parameter.

Eqs. 1, 2, and 3 represent general theoretical predictions applicable to systems far from thermal equilibrium. We now introduce and solve a simple model which illustrates these results.

II. THE MODEL

In this section we introduce our (one-dimensional) model of a particle dragged through a thermal medium, and then we solve it exactly: given the particle’s initial location, we compute the joint probability distribution of the final location and the net external work performed on the particle, after an arbitrary time of evolution. In the following section we use this result to confirm both the steady-state and transient fluctuation theorems, as well as the detailed fluctuation theorem and the nonequilibrium work relation for free energy differences.

In our model, the particle under consideration obeys Langevin dynamics. This model can therefore by viewed (with qualifications, see Section II A) as a special case of the situation considered by Kurchan 3, who showed that the FT is satisfied for this class of stochastic dynamics. In essence, we are illustrating Kurchan’s results with a specific model. However, the definition of entropy generated which we choose differs from that of Ref. 3, and so we are obliged to express the steady-state and transient FT’s differently, in terms of power delivered rather than entropy generation rate. We stress that this difference (between the formulation of the FT given below, and that in Kurchan’s work) is only one of terminology, not substance.

Consider the following situation. A particle, in contact with a thermal medium at temperature \( \beta^{-1} \), is pulled through that medium by a time-dependent external harmonic force. Assuming a single degree of freedom, let \( x \) denote the location of the particle, and let

\[
U(x, t) = \frac{k}{2}(x - ut)^2
\]

be the moving potential well which drags the particle. We can picture the particle as being attached to a spring, the other end of which moves with a constant speed \( u \). Assume furthermore that the thermal forces can be modeled as the sum of linear friction and white noise, and that the motion of the particle is overdamped. Then the equation of motion for the position of the particle is:

\[
\dot{x} = -\frac{k}{\gamma}(x - ut) + \tilde{v},
\]

where \( \dot{x} \equiv dx/dt \), \( \gamma \) is the coefficient of friction, and \( \tilde{v}(t) \) represents delta-correlated white noise with variance \( 2/\beta\gamma \) (as mandated by the fluctuation-dissipation relation):

\[
\langle \tilde{v}(t_1)\tilde{v}(t_2) \rangle = \frac{2}{\beta\gamma} \cdot \delta(t_2 - t_1).
\]

Imagine that we observe the evolution of such a particle over a time interval from \( t = 0 \) to \( t = \tau \), and from the observed trajectory we compute the total work \( W \) performed by the
external potential over this interval. Then the central result of this section will be an answer to the following question. **Given an initial location** \( x_0 \), **what is the joint probability distribution for the final location and value of work performed** \( (x, W) \)?

To answer this question, we first introduce a “work accumulated” function, \( w(t) \), which gives the work performed on the particle up to time \( t \); hence, \( W = w(\tau) \). This function satisfies

\[
\dot{w}(t) = \frac{\partial U}{\partial t}(x(t), t) = -uk(x(t) - ut),
\]

along with the initial condition \( w(0) = 0 \).

It will furthermore prove convenient to specify the location of the particle by a variable \( y = x - ut \) (i.e. in the reference frame of the moving well), rather than \( x \). Under this change of variables, Eqs.\ref{eq:7} and \ref{eq:7} become:

\[
\begin{align*}
\dot{y} &= -\frac{k}{\gamma} y - u + \tilde{v} \quad \text{(8a)} \\
\dot{w} &= -uky. \quad \text{(8b)}
\end{align*}
\]

Now imagine a statistical ensemble of such particles, represented by an evolving probability distribution \( f(y, w, t) \). Eq.\ref{eq:9} then translates into the Fokker-Planck equation

\[
\frac{\partial f}{\partial t} = \frac{k}{\gamma} \frac{\partial}{\partial y}(yf) + uf \frac{\partial f}{\partial y} + uky \frac{\partial f}{\partial w} + \frac{1}{\beta \gamma} \frac{\partial^2 f}{\partial y^2}. \quad \text{(9)}
\]

What we now want is an expression for \( f(y, w, t|y_0) \), by which we mean the solution to Eq.\ref{eq:9} satisfying the initial conditions

\[
f(y, w, 0|y_0) = \delta(y - y_0)\delta(w). \quad \text{(10)}
\]

The function \( f(y, w, t|y_0) \) is the joint probability distribution for achieving a location \( y \) and a value of work accumulated \( w \), at time \( t \), given \( y_0 \) at time 0. By evaluating this solution at \( t = \tau \), and making the change of variables from \( y \) back to \( x \), we have the answer to the question posed earlier in boldface.

To solve for \( f(y, w, t|y_0) \), we first note that Eq.\ref{eq:9} has the following property: if at one instant in time the distribution happens to be Gaussian, then it will remain Gaussian for all subsequent times. This follows from the fact that the drift and diffusion coefficients in Eq.\ref{eq:9} are either constant or linear in \( y \) and \( w \). Now, a normalized Gaussian distribution \( f^G(y, w) \) is uniquely defined by the values of the following moments:

\[
\begin{align*}
\tilde{y} &\equiv \int f^G(y, w) y \\
\tilde{w} &\equiv \int f^G(y, w) w \\
\sigma_y^2 &\equiv \int f^G(y, w) (y^2 - \tilde{y}^2) \\
\sigma_w^2 &\equiv \int f^G(y, w) (w^2 - \tilde{w}^2) \\
c_{yw} &\equiv \int f^G(y, w) (yw - \tilde{y}\tilde{w}),
\end{align*}
\]

\[
\text{(11a)  \quad (11b)  \quad (11c)  \quad (11d)  \quad (11e)}
\]
where the integrals are over \((y, w)\)-space. An explicit expression for \(f^G(y, w)\) in terms of these moments is:

\[
f^G(y, w) = \frac{\sqrt{C}}{2\pi} \exp(-z^T C z / 2),
\]

where

\[
z = \begin{pmatrix} y - \hat{y} \\ w - \hat{w} \end{pmatrix}, \quad C = \begin{pmatrix} C\sigma_y^2 & -C_{yw} \\ -C_{yw} & C\sigma_w^2 \end{pmatrix}, \tag{12b}
\]

\(C = (\sigma_y^2 \sigma_w^2 - c_{yw}^2)^{-1} = \det C\), and \(z^T\) denotes the transpose of \(z\).

The evolution of a time-dependent Gaussian distribution \(f^G(y, w, t)\) is thus uniquely specified by the evolution of the moments \(\hat{y}, \ldots, c_{yw}\). Given a distribution evolving under Eq. 9, we get from Eq. 11 the following set of coupled equations of motion for these moments:

\[
\frac{d}{dt} \hat{y} = -\frac{k}{\gamma} \hat{y} - u, \quad \frac{d}{dt} \hat{w} = -uk\hat{y}, \tag{13a}
\]

\[
\frac{d}{dt} \sigma_y^2 = -\frac{2k}{\gamma} (\sigma_y^2 - \frac{1}{\beta k}), \quad \frac{d}{dt} c_{yw} = -\frac{k}{\gamma} (c_{yw} + u\gamma \sigma_y^2), \quad \frac{d}{dt} \sigma_w^2 = -2ukc_{yw}. \tag{13b}
\]

The distribution \(f(y, w, t|y_0)\) will thus be a Gaussian whose moments evolve according to Eq. 13 and satisfy the initial conditions: \(\hat{y} = y_0, \hat{w} = \sigma_y^2 = c_{yw} = \sigma_w^2 = 0\). The solution, as easily verified by substitution, is:

\[
\begin{align*}
\hat{y}(t|y_0) &= -l + (y_0 + l)e^{-kt/\gamma} \tag{14a} \\
\hat{w}(t|y_0) &= uklt + u\gamma(y_0 + l)(e^{-kt/\gamma} - 1) \tag{14b} \\
\sigma_y^2(t|y_0) &= \frac{1}{\beta k}(1 - e^{-2kt/\gamma}) \tag{14c} \\
c_{yw}(t|y_0) &= -\frac{u\gamma}{\beta k}(e^{-kt/\gamma} - 1)^2 \tag{14d} \\
\sigma_w^2(t|y_0) &= \frac{u^2\gamma^2}{\beta k} \left( \frac{2kt}{\gamma} - e^{-2kt/\gamma} + 4e^{-kt/\gamma} - 3 \right), \tag{14e}
\end{align*}
\]

where

\[
l = \frac{\gamma u}{k}. \tag{15}
\]

The combination of Eqs. 14 and 12 gives the solution for \(f(y, w, t|y_0)\) for all times \(t \geq 0\) (and for all values of \(y, w, \) and \(y_0\)). The explicit expression given in the Appendix. Note that, by projecting out either of the two independent variables \(y\) and \(w\), we can obtain the marginal probability distributions for the other:

\[
\rho(y, t|y_0) \equiv \int dw f(y, w, t|y_0) = \frac{1}{\sqrt{2\pi \sigma_y^2}} \exp\left[-(y - \hat{y})^2/2\sigma_y^2\right] \tag{16a}
\]

\[
\eta(w, t|y_0) \equiv \int dy f(y, w, t|y_0) = \frac{1}{\sqrt{2\pi \sigma_w^2}} \exp\left[-(w - \hat{w})^2/2\sigma_w^2\right]. \tag{16b}
\]
It is instructive to consider the limit of asymptotically long times, \( kt/\gamma \gg 1 \). In this limit,

\[
\begin{align*}
\dot{y}(t|y_0) &\to -l \\
\dot{w}(t|y_0) &\to ukl t + O(1) \\
\sigma_y^2(t|y_0) &\to 1/\beta k \\
c_{yy}(t|y_0) &\to -w\gamma/\beta k \\
\sigma_w^2(t|y_0) &\to 2u^2\gamma t/\beta + O(1),
\end{align*}
\]

where the “order unity” corrections to \( \dot{w}(t|y_0) \) and \( \sigma_w^2(t|y_0) \) represent terms which converge to a constant as \( t \to \infty \). We see that, for any \( y_0 \), the distribution of positions settles into a steady-state Gaussian of variance \( 1/\beta k \), centered at a displacement \(-l\) from the minimum of the confining potential \( U \) (Eqs.17a, 17c). Note that a canonical (equilibrium) distribution of positions would have the same variance, but centered at the minimum. Hence, \( l \) represents the extent to which the steady-state distribution of positions “lags behind” the instantaneous equilibrium distribution. This lag could have been predicted with an educated guess, by ignoring fluctuations and simply balancing the frictional and harmonic forces, \(-\gamma u\) and \(-k y\). One can similarly understand the leading behavior of \( \dot{w}(t) \): if the position of the particle is (on average) a distance \( l \) behind the instantaneous minimum of the well, then the harmonic spring is pulling the particle with a force \(+kl\), at a velocity \( u \), hence delivering a power \( ukl \).

A. Energy conservation and entropy generation

In our model, energy conservation translates into the following balance equation between the external work \( W \) performed on the particle, the heat \( Q \) absorbed from the thermal surroundings, and the net change in the internal energy of the particle [10]:

\[
W + Q = \Delta U,
\]

where \( \Delta U = U(x(\tau), \tau) - U(x(0), 0) \), \( W = w(\tau) \), and

\[
Q = \int_0^\tau \dot{x}(t) \frac{\partial U}{\partial x}(x(t), t) \, dt.
\]

In addition to these quantities (\( W, Q, \) and \( \Delta U \)), we need a microscopic definition of the entropy generated over one realization of the process. There is necessarily some arbitrariness in such a definition, but we will use the following one:

\[
\Delta S \equiv -\beta Q.
\]

Thus, we identify the entropy generated with the amount of heat dumped into the environment \((-Q)\), divided by the temperature. This definition – motivated by macroscopic thermodynamics (see e.g. Ref. [3]) – differs from that of Kurchan [3], who identifies the entropy production rate with the external power delivered to the system, divided by the reservoir temperature. Both definitions seem to be reasonable, but we will use Eq.20.
Quite apart from the definition of entropy generation, our set-up differs from Kurchan’s in the way in which external work is defined; see Section 2.2 of Ref. [3]. Nevertheless, the general analytical approach taken by Kurchan applies to our set-up as well. Hence, any results derived in Ref. [3] regarding average power delivery (external work performed, divided by the duration of the time interval), extend to our situation.

III. ILLUSTRATION OF FAR-FROM-EQUILIBRIUM PREDICTIONS

We now use the results of the previous section to show that Eqs. 1-3 are obeyed by our model.

A. Transient and steady-state fluctuation theorems

We begin with the transient and the steady-state fluctuation theorems. Ordinarily the FT is expressed in terms of the average entropy production rate (Eq.1). By contrast, the relations which we will show to be satisfied by our model (Eq.22) are expressed in terms of the average power delivered to our particle as it is dragged through its thermal environment. This difference – as mentioned earlier – is a consequence of our choice of definition of average entropy generation rate, \( \sigma = \frac{\Delta S}{\tau} = -\frac{\beta Q}{\tau} \). (Kurchan, by contrast, defines entropy generation in terms of power delivered, \( \sigma_{\text{Kurchan}} = \frac{\beta W}{\tau} \). [3]) In the calculations to follow, the reader should bear in mind that the transient and steady-state relations which we establish are essentially those of Kurchan; only our definition of entropy production prevents us from presenting them as such.

(It might be interesting to investigate whether or not Eq.1 remains valid under our definition of entropy production, \( \sigma = -\frac{\beta Q}{\tau} \). This would be easy to check with numerical simulations, but in the “exactly solvable” spirit of restricting ourselves to analytical results, we have not pursued this question.)

For a time interval of duration \( \tau \), let

\[ X = \frac{W}{\tau} \quad (21) \]

denote the time-averaged rate at which work is performed on the particle – i.e. the average power delivered – by the moving harmonic potential. Now imagine that we observe the particle for an “infinitely” long time as it evolves in the steady state; we divide this time of observation into infinitely many segments of duration \( \tau \); we compute the average power delivered, \( X \), over each segment; and we construct the statistical distribution of these values, \( p_{S\tau}(X) \). We will obtain an explicit expression for \( p_{S\tau}(X) \) for our model, and will show that it satisfies the following steady-state FT:

\[ \lim_{\tau \to \infty} \frac{1}{\tau} \ln \frac{p_{S\tau}(+X)}{p_{S\tau}(-X)} = \beta X. \quad (22a) \]

Now imagine instead that we begin with the particle in thermal equilibrium, and then we drag it for a time \( \tau \) with the harmonic confining potential. (That is, for \( t < 0 \) the potential is stationary, with the particle in equilibrium; then, between \( t = 0 \) and \( t = \tau \) the potential
is moved rightward with velocity \( u \). Again defining \( X \) to be the average power delivered over the interval \( 0 \leq t \leq \tau \), let \( p^C_\tau(X) \) denote the statistical distribution of values of \( X \), over infinitely many repetitions of this process, always starting from equilibrium. We will solve for \( p^C_\tau(X) \) and show that it obeys the following transient FT:

\[
\frac{1}{\tau} \ln \frac{p^C_\tau(+X)}{p^C_\tau(-X)} = \beta X,
\]

(22b)

whose validity does not require the limit \( \tau \to \infty \).

We begin by considering the steady-state case. Since the right sides of Eqs. 17a and 17c are independent of \( y_0 \), an arbitrary initial distribution of particle positions \( \rho(y,0) \) will settle into a Gaussian:

\[
\lim_{t \to \infty} \rho(y,t) = \sqrt{\frac{\beta k}{2\pi}} \exp\left[-\frac{\beta k(y + l)^2}{2}\right] \equiv \rho^S(y),
\]

(23)

which defines the instantaneous distribution of particle positions in the steady state. Then \( p^S_\tau(X) \) – the distribution of values of average power delivered, \( X = W/\tau \), over time intervals of duration \( \tau \) sampled during the steady state – can be constructed by folding together \( \rho^S(y_0) \) and \( \eta(w,\tau|y_0) \) (Eq.16b):

\[
p^S_\tau(X) = \int dw \delta(X - w/\tau) \int dy_0 \rho^S(y_0) \eta(w,\tau|y_0).
\]

(24)

Here, the integral over \( dy_0 \) produces the distribution of values of work, after time \( \tau \), given initial conditions sampled from the steady state. The integral over \( dw \) converts that distribution of values of \( w \) into one of values of \( X \). Examining Eqs. 14b, 14e, 16b, and 23, we see that, in the product \( \rho^S(y_0)\eta(w,\tau|y_0) \), the variable \( y_0 \) appears only in powers up to the quadratic inside an exponent; hence this product is a Gaussian in \( y_0 \), and the integral can be carried out explicitly. Without going through the (modestly tedious) details, we present the result:

\[
p^S_\tau(X) = \frac{1}{\sqrt{2\pi\sigma_X^2}} \exp\left[-\frac{(X - \overline{X})^2}{2\sigma_X^2}\right],
\]

(25)

where

\[
\overline{X} = ukl \quad , \quad \sigma_X^2 = \frac{2\mu\overline{X}}{\beta \tau} \quad , \quad \mu(\tau) = 1 + \frac{\gamma}{k\tau}(e^{-k\tau/\gamma} - 1).
\]

(26)

\( \overline{X} \) represents the average instantaneous power delivered to the particle, in the steady state; see the comments following Eq. 17. From this we obtain an explicit expression for the left side of Eq. 22a.

\[^3\] The superscript \( C \) indicates that the particle’s initial conditions are sampled from a canonical ensemble.
\[
\frac{1}{\tau} \ln \frac{p^S_\tau(+X)}{p^S_\tau(-X)} = \frac{1}{\tau} \cdot \frac{2\overline{X}X}{\sigma_X^2} = \frac{\beta X}{\mu}.
\] (27)

Since \(\lim_{\tau \to \infty} \mu = 1\), we conclude that the FT for power delivered in the steady state (Eq. 22a) is indeed satisfied for our model. Note, however, that the limit \(\tau \to \infty\) is necessary.

In the case of the transient FT, pertaining to a system driven away from an initial state of canonical equilibrium, we can construct \(p^C_\tau(X)\) in the same way as \(p^S_\tau(X)\), only now we fold \(\eta\) in with a canonical distribution, \(\rho^C(y) \propto \exp(-\beta ky^2/2)\), rather than the steady-state distribution:

\[
p^C_\tau(X) = \int dw \delta(X - w/\tau) \int dy_0 \rho^C(y_0) \eta(w, \tau|y_0)
\]

\[
= \frac{1}{\sqrt{2\pi \sigma_X^2}} \exp \left[ -\frac{(X - \mu X)^2}{2\sigma_X^2} \right],
\]

(28)

where \(\sigma_X^2, \overline{X}, \text{ and } \mu(\tau)\) are exactly as above. The only difference between the steady-state and the transient distribution of values of \(X\) is, we see, the factor \(\mu\) appearing inside the exponent in the latter. This small difference has the effect that the FT for power delivered in the transient case is satisfied for all positive values of \(\tau\):

\[
\frac{1}{\tau} \ln \frac{p^C_\tau(+X)}{p^C_\tau(-X)} = \frac{1}{\tau} \cdot \frac{2\mu \overline{X}X}{\sigma_X^2} = \beta X.
\]

(30)

**B. Detailed fluctuation theorem**

We now show that our model satisfies the detailed fluctuation theorem (DFT). As mentioned in Section [I], the DFT is stated in terms of two processes, \(\Pi^+\) (“forward”) and \(\Pi^-\) (“reverse”), related by time-reversal. In the present context, we take \(\Pi^+\) to be the process studied above: a particle is dragged through a thermal medium by a time-dependent potential well,

\[
U^+(x, t) = \frac{k}{2}(x - ut)^2.
\]

(31)

The reverse process, \(\Pi^-\), is then obtained by moving the well in the opposite direction:

\[
U^-(x, t) = \frac{k}{2}(x + ut - u\tau)^2.
\]

(32)

Formally, we can think of the minimum of the potential as being given by \(\lambda \Delta x\), where \(\Delta x = u\tau\) is a constant, and \(\lambda\) is an externally controlled parameter. During the process \(\Pi^+\), \(\lambda\) is changed uniformly from 0 to 1; during \(\Pi^-\), from 1 to 0.

Again taking \(y\) to be the displacement of the particle relative to the instantaneous minimum of the potential, we define \(f_+(y, w, t|y_0)\) and \(f_-(y, w, t|y_0)\) to be the joint probability distributions for attaining \((y, w)\) at time \(t\), given \(y_0\) at time 0, for the two processes. We then solve for these two distributions exactly as we solved for \(f(y, w, t|y_0)\) in Section [I]. The solutions are:
where \( f \) is just the solution obtained in Sec. I. Thus, the solution for the forward process is identical to the solution of Sec. II (as it must be, since \( \Pi^+ \) is exactly the process studied there!), whereas the solution for the reverse process is obtained from \( f \) by replacing \( u \) by \(-u\) everywhere, including in the definition of \( l \) (hence, \( l \to -l \)). This replacement is easily understood: in terms of the variable \( y \), the process \( \Pi^- \) is no different than that obtained by starting with the minimum of the potential at \( x = 0 \), and moving it with velocity \(-u\) for a time \( \tau \).

Let us now put these solutions to good use. The DFT, in the context of this problem, claims the following:

\[
P_+(y_B, +\Delta S|y_A) = \exp \Delta S,
\]

where \( P_\pm(y_f, \Delta s|y_i) \) denote the joint probability distributions of finding the particle at a final point \( y_f \), and a value of entropy generated \( \Delta s \), given an initial location \( y_i \), for the forward and reverse processes.\(^4\) Now consider a single realization of either process. Energy conservation, combined with our definition of entropy produced (Eqs. 18 and 20), give us the following relation between \( y_i, y_f, \Delta s, \) and the work \( w \) performed:

\[
w - \beta^{-1} \Delta s = \frac{k}{2}(y_f^2 - y_i^2) \equiv \Delta U(y_i, y_f).
\]

We can then re-express \( P_\pm \) in terms of \( f_\pm \):

\[
P_\pm(y_f, \Delta s|y_i) = \int dw f_\pm(y_f, w, \tau|y_i) \delta(\Delta s + \beta \Delta U - \beta w)
\]

\[
= \beta^{-1} f_\pm(y_f, \frac{k}{2}(y_f^2 - y_i^2) + \beta^{-1} \Delta s, \tau|y_i),
\]

from which we obtain the following explicit expressions for the numerator and denominator in Eq. 35:

\[
P_+(y_B, +\Delta S|y_A) = \beta^{-1} f_+(y_B, +\Omega, \tau|y_A)
\]

\[
P_-(y_A, -\Delta S|y_B) = \beta^{-1} f_-(y_A, -\Omega, \tau|y_B),
\]

where

\[
\Omega \equiv \frac{k}{2}(y_B^2 - y_A^2) + \beta^{-1} \Delta S.
\]

Eq. 35 is thus equivalent to the following relation:

\[
\frac{f_+(y_B, +\Omega, \tau|y_A)}{f_-(y_A, -\Omega, \tau|y_B)} = \exp[\beta \Omega - \frac{\beta k}{2}(y_B^2 - y_A^2)],
\]

where, if Eq. 35 is to be valid for all real \( \Delta S \), then Eq. 42 must hold for all real \( \Omega \). Using the expression for \( f \) given in the Appendix, one can verify that, indeed, Eq. 42 is valid for all values of \( \Omega \), hence the DFT is satisfied by our model.

---

\(^4\) Strictly speaking, these should be defined in terms of absolute locations \( x_A \) and \( x_B \), but the change of variables to relative displacements \( y_A \) and \( y_B \) is immediate.
C. Generalization

Before proceeding to the nonequilibrium work relation, we point out that our model is easily generalized to include an additional uniform, constant external force. Namely, suppose we modify the time-dependent potentials $U^\pm(x, t)$ for the forward and reverse processes, as follows:

$$U^\pm(x, t) \rightarrow U^\pm(x, t) + \alpha x, \quad \alpha > 0.$$  \hspace{1cm} (43)

This corresponds to subjecting the particle to an additional leftward-pushing force, of magnitude $\alpha$. Thus, assuming $u > 0$, the particle is dragged “up” the potential energy slope $\alpha x$ during $\Pi^+$, and “down” the slope during $\Pi^-$.

The solution in this case, for the forward process $\Pi^+$, is the same as that in the previous section, except that $l$ is everywhere replaced by

$$l_\alpha = l + \frac{\alpha}{k} = \frac{\alpha + \gamma u}{k}.$$  \hspace{1cm} (44)

Thus, in the steady state, the average position of the particle is displaced by an amount $\alpha/k$ to the left, relative to the case with no additional force (Eq.17a). This implies that additional work is performed on the particle at an average rate $u\alpha$ (Eq.17b); this is simply the average rate at which we drag the particle up the slope.

For the reverse process, the solution is obtained (as in the previous Section) by the further replacement $u \rightarrow -u$, including in the definition of $l_\alpha$.

It is straightforward to show that, with these replacements, the DFT remains valid.

D. Nonequilibrium work relation for free energy differences

Let us finally use the results derived above to show explicitly that Eq.3 is satisfied by our model. We will consider the process defined by $U^+(x, t)$ in the previous section (Eq.43). As before, let $\Delta x = u\tau$ be a fixed distance, and let $\lambda\Delta x$ define the minimum of the confining potential, so that we move that minimum from 0 to $\Delta x$ by changing $\lambda$ from 0 to 1:

$$U_\lambda(x) = \frac{k}{2}(x - \lambda\Delta x)^2 + \alpha x$$

$$U^+(x, t) = U_{\lambda(t)}(x),$$

where $\lambda(t) = t/\tau$. For any fixed value of $\lambda$ and fixed temperature $\beta^{-1}$, there exists an equilibrium state of the system, defined microscopically by a canonical distribution. The associated free energy $F_\lambda$ is then defined in terms of the logarithm of the corresponding partition function:

$$F_\lambda = -\beta^{-1} \ln \int dx \, e^{-\beta U_\lambda(x)}$$

$$= \alpha \lambda \Delta x - \frac{\alpha^2}{2k} + \frac{1}{2\beta} \ln \frac{\beta k}{2\pi}.$$  \hspace{1cm} (48)

Hence the free energy difference is simply
\[ \Delta F = F_1 - F_0 = \alpha \Delta x. \]  

(49)

Physically, this is the work required to \textit{reversibly} (i.e. infinitely slowly) change \( \lambda \) from 0 to 1, at constant temperature.

Now consider a statistical ensemble of realizations of our \textit{finite-time}, irreversible process, \( \lambda(t) = t/\tau \), with initial conditions sampled from the canonical ensemble corresponding to \( \lambda = 0 \). The associated distribution of values of work, \( W = w(\tau) \), can be written as:

\[ \eta(W) = \int dy_0 \rho^C_\alpha(y_0) \eta(W, \tau|y_0), \]  

(50)

where \( \rho^C_\alpha(y_0) \) is the canonical distribution of initial conditions (for \( \alpha \neq 0 \)), and \( \eta(W, \tau|y_0) \) is the distribution of work values at time \( \tau \), given initial condition \( y_0 \). We can use the results of Section II, with the substitutions \( l \to \tau \alpha \) and \( u = \Delta x/\tau \), to compute this integral explicitly. Once again skipping the algebra, we present the result: \( \eta(W) \) is a Gaussian distribution of mean and variance

\[ \langle W \rangle = \alpha \Delta x + \mu(\tau) \gamma(\Delta x)^2 / \tau, \]  

\[ \sigma_W^2 = 2 \mu(\tau) \gamma(\Delta x)^2 / \beta \tau, \]  

(51)  

(52)

with \( \mu(\tau) \) as defined by Eq.26. (Note that in the reversible limit – i.e. \( \tau \to \infty \) with \( \Delta x \) fixed – we get \( \langle W \rangle = \alpha \Delta x \) and \( \sigma_W^2 = 0 \), hence \( W = \Delta F \) for every realization, in agreement with the remarks following Eq.49.) Thus, for any positive value of \( \tau \), \( \eta(W) \) is a Gaussian whose mean and variance are related by

\[ \langle W \rangle = \Delta F + \beta \sigma_W^2 / 2. \]  

(53)

This implies – as can be verified by direct evaluation of \( \int dW \eta(W) \exp(-\beta W) \) – that the nonequilibrium work relation for free energy differences, Eq.3 above, is satisfied.

Eq.53 has the structure of the usual \textit{fluctuation-dissipation theorem} (FDT) for linear response, but differs from the latter in the fact that the fluctuations – represented by \( \sigma_W^2 \) – are \textit{not} obtained from the equilibrium fluctuations of the particle, but rather truly reflect behavior far from equilibrium. Indeed, the presence of \( \mu(\tau) \) in Eq.51 is evidence of non-linear response in our model: for fixed \( \Delta x \), the average dissipated work, \( \langle W \rangle - \Delta F \), is not simply inversely proportional to \( \tau \), as would be the case for linear response.

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APPENDIX

Here we give an explicit expression for the function \( f(y, w, t|y_0) \) introduced in Section II. This solution is essentially the combination of Eqs.12 and 14:

\[
f(y, w, t|y_0) = \sqrt{C} \frac{C}{2\pi} \exp(AC/2),
\]

(54)

where

\[
C = \det C = \frac{\beta^2 k^2}{2\gamma u^2 \nu_- [2\gamma \nu_- + kt \nu_+]}
\]

(55)

\[
A = (1/\beta k) \left\{ \nu_+ \nu_- (w - ktu)^2 + \gamma^2 u^2 \nu_- (y - y_0)[4\nu_- + (3\nu - 1)y_0 + (\nu - 3)y]
\right.
\]

(56)

\[
+ 2\gamma u \left( t^2 k u \nu_-^2 - t \nu_- [2w \nu_- + k tu \nu_+(y_0 - y)] - w \nu_-^2 (y_0 + y) - k tu(y - \nu y_0)^2 \right) \right\},
\]

(57)

and

\[
\nu = \exp(-kt/\gamma), \quad \nu_\pm = \nu \pm 1.
\]

(58)
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