Fluctuation symmetries for work and heat

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We consider a particle dragged through a medium at constant temperature as described by a Langevin equation with a time-dependent potential. The time dependence is specified by an external protocol. We give conditions on potential and protocol under which the fluctuations of the dissipative work satisfy an exact symmetry for all times. We also present counterexamples to that fluctuation theorem when our conditions are not satisfied. Finally, we consider the dissipated heat, which differs from the work by a temporal boundary term. We explain why there is a correction to the standard fluctuation theorem due to the unboundedness of that temporal boundary. However, the corrected fluctuation relation has again a general validity.

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I. INTRODUCTION

Recent years have seen an explosion of results and discussions on a particular symmetry in the fluctuations of various dissipation functions. While started in the context of smooth dynamical systems and of thermostating algorithms and simulations [1–3], soon the symmetry was judged relevant in the construction of nonequilibrium statistical mechanics. Shortly thereafter, these results were recovered for finite systems undergoing a Langevin dynamics [4], and for finite-dimensional Markov processes [5]. Moreover, a unifying scheme was developed under which the various fluctuation theorems were found to be the result of a common feature [6]. The basic idea there is that a dissipation function for a physical model can be identified with the source of time-symmetry breaking in the statistical distribution of system histories, see, e.g., [6–8] for more details. That dissipation function is mostly related to the variable entropy production but, depending on the particular realization, can also refer to heat dissipation or to dissipative work. For a given effective model, one of course always needs to check again that basic relation between time reversal and dissipation.

In the present paper, we look at a particle's position x_t that undergoes a Langevin evolution for a time-dependent potential U_t. Because of that time dependence, which is externally monitored, work W is done on the particle, changing its energy. At the same time, some of it flows as heat Q to the surrounding medium, checking the conservation of energy $\Delta U = U_\tau(x_\tau) - U_0(x_0) = W - Q$ for the evolution during a time interval $0 \leqslant t \leqslant \tau$. Both W and Q are fluctuating quantities and they are path-dependent. Our main result concerns a symmetry in the fluctuations of W. We give conditions on the potential and on its time dependence U_t under which a well-known fluctuation symmetry for W is exactly verified, i.e., that for all times τ, without further approximation,

$$\frac{\text{Prob}_{\rho_0}(W^{\text{dis}} = w)}{\text{Prob}_{\rho_0}(W^{\text{dis}} = -w)} = \exp(\beta w). \tag{1}$$

Here, the particle's position is initially distributed with $\rho_0 \sim \exp(-\beta U_0)$ according to thermal equilibrium at inverse temperature β. The notation W^{dis} refers to the dissipated work which equals the work W up to a difference in free energies, see also later in Eq. (10). If the evolution would be reversible, then $W^{\text{dis}}=0$. In general, and confirming the second law, we have $\langle W^{\text{dis}}\rangle \geqslant 0$ but Eq. (1) also takes into account the trajectories where $W^{\text{dis}}<0$. The exact fluctuation theorem (1) tells us that such "negative dissipative work" trajectories are exponentially damped.

Since the heat Q differs from the dissipated work only by a temporal boundary term Δ, $Q = W^{\text{dis}} - \Delta$, where $\Delta = \Delta(\tau; x_0, x_\tau)$ is nonextensive in time τ, one could perhaps expect that Q satisfies the standard fluctuation theorem, i.e., that the same as in Eq. (1) is true after taking the logarithm and letting $\tau \uparrow +\infty$. Interestingly, that is not what always happens, see [9],

$$\lim_{\tau\uparrow+\infty} \frac{1}{\tau} \log \frac{\text{Prob}_{\rho_0}(Q = q\tau)}{\text{Prob}_{\rho_0}(Q = -q\tau)} \neq \beta q \tag{2}$$

for q the heat per unit time. We will explain how the unboundedness of the potential U_τ can correct the relation (2). For small enough q (basically, for $0 \leqslant q\tau \leqslant \langle W^{\text{dis}}\rangle$), the equality in relation (2) remains intact while the left-hand side of Eq. (2) saturates and is constant for all large enough q.

In what follows, we discuss the fluctuation theorems (1) and (2) in mathematical detail. In particular, we give near to optimal conditions on potential and protocol for which Eq. (1) holds. Before, that was shown only via an explicit calculation for the case of a harmonic potential where the minimum of the potential is moved with a fixed speed [9]. There the modification to Eq. (2) was explicitly calculated. Here we will argue for more general protocols and potentials to give estimates about the range of validity of (2). The main point is to understand when and how terms, nonextensive in the time τ, can still contribute to the large deviations of the heat Q. The point is indeed that the delivered work can be stored in excessive amounts in the particle's potential energy.

II. MODEL AND RESULTS

In the present paper, we apply the general scheme and algorithm of [7,8] to a model that has previously and recently been considered by a number of groups [9–12]. We find optimal conditions on potential and protocol under which the

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dissipated work satisfies an exact fluctuation theorem, i.e., one that is valid for all times. The heat differs from that dissipated work via a temporal boundary term and also satisfies some general fluctuation relation asymptotically in time. Because the potential is unbounded, that last theorem is not the same as in the standard steady-state fluctuation theorem. Below we give more details.

A. Model

We consider a family of one-dimensional potentials $U_t, t \in [0,\tau]$, as parametrized via a deterministic protocol γ_t: $U_t(x)=U(x,\gamma_t)$, with $x,\gamma_t \in \mathbb{R}$. The corresponding equilibria at inverse temperature β are

$$\rho_t(x) \equiv \frac{e^{-\beta U_t(x)}}{Z_t},$$

$$Z_t \equiv \exp[-\beta F_t] \equiv \int_{-\infty}^{+\infty} dx e^{-\beta U_t(x)} \tag{3}$$

with Helmholtz free energy F_t. The time dependence in γ_t is supposed to be given and can be quite arbitrary; of course, the partition function Z_t must be finite. The dynamics is now specified by a Langevin-Itô-type equation

$$dx_t = -\frac{\partial U_t}{\partial x}(x_t)dt + \sqrt{\frac{2}{\beta}}db_t, \tag{4}$$

where db_t is standard white noise. Such dynamics have been considered before in a wide variety of contexts, but for fluctuation theorems the emphasis has been on the Gaussian case. An experimental realization [12] of that dynamics was theoretically investigated by [9], who started from Eq. (4) with

$$U_t(x) = \frac{(x-vt)^2}{2}. \tag{5}$$

A more general analysis for driven harmonic diffusive systems was given in [13]. Quite recently in [10] further experiments were considered for more general potentials and protocols.

In the present paper we work with the general (3) but we sometimes restrict ourselves to the physically relevant case of

$$U_t(x) = U(x-\gamma_t) \tag{6}$$

for a given protocol $\gamma=(\gamma_t, t\in[0,\tau])$ that marks the shift in a potential U as time goes on. In that case, F_t does not depend on time and the associated difference in free energies,

$$\Delta F = -\frac{1}{\beta}\ln\left(\frac{Z_\tau}{Z_0}\right), \tag{7}$$

is zero.

The model (4) defines a Markov diffusion process. We write

$$\omega = (x_t, t\in[0,\tau])$$

for the (random) positions of the particle. If the initial distribution of the position x_0 is given via a density ρ, then $\mathrm{Prob}_\rho(\omega|\gamma)$ denotes the probability density of observing a trajectory ω under the influence of the protocol γ, with respect to the thermal noise $\sqrt{2/\beta}db_t$. Given a path ω and a protocol γ, we also consider their time-reversed versions,

$$\Theta\omega_i \equiv \omega_{\tau-i} = x_{\tau-i},$$

$$\Theta\gamma_i \equiv \gamma_{\tau-i}. \tag{8}$$

B. Problem

The observables of interest are the work and the heat.

The work W_γ is associated to the external agent, in changing the potential via the protocol γ,

$$W_\gamma(\omega) \equiv \int_0^\tau dt\dot{\gamma}_t \frac{\partial U_t}{\partial \gamma_t}(x_t). \tag{9}$$

The dissipative work can then be identified with

$$W_\gamma^{\mathrm{dis}}(\omega) = W_\gamma(\omega) - \Delta F. \tag{10}$$

One has to remember here that for a reversible and isothermal evolution the change in free energy precisely equals the work W_γ done on the system. Furthermore, in the situation (6) one has $\Delta F=0$ so that $W_\gamma = W_\gamma^{\mathrm{dis}}$.

The heat Q_γ is most easily defined via the first law of thermodynamics, see also [14],

$$\Delta U = U_\tau(x_\tau) - U_0(x_0) = W_\gamma(\omega) - Q_\gamma(\omega),$$

$$Q_\gamma(\omega) \equiv -\int_0^\tau dx_t \circ \frac{\partial U_t}{\partial x}(x_t) = -\int_0^\tau dt\dot{x}_t \frac{\partial U_t}{\partial x}(x_t). \tag{11}$$

The integral (with the "$\circ$") should be understood in the sense of Stratonovich; it coincides better with the usual intuition of integrals and it does not suffer from the lack of time symmetry in the Itô integral, which will be important for us; see also [15].

In the present paper we ask the following.

(i) Under what conditions does the work (9) or (10) satisfy an exact fluctuation theorem (EFT) (1)?

(ii) What are the possible corrections to the standard fluctuation theorem (2) for the fluctuations of the heat (11)?

So far, these questions have been theoretically investigated via explicit computation for the special case of a linearly dragged particle in the harmonic potential (5), in [9]; question (ii) has been generally addressed in [16] in the context of dynamical systems. Experimental and numerical work (in agreement with the results below) was done in [10–12,17].

C. Results

We start with the exact fluctuation theorem for the work (9). First we consider the harmonic case $U(x)=x^2/2$ with a general protocol γ_t as in Eq. (6). Then we give a general condition under which the work satisfies an EFT, and we give instances under which that condition is satisfied. Counterexamples (for which the work does not satisfy an EFT) will show why these conditions are close to optimal. We end with a discussion on the relevance of temporal boundary terms in the large deviations of the heat (11). For the proofs we refer to Sec. IV.

1. Work

First look at quadratic potentials, e.g., for

$$U_t(x) = \frac{(x-\gamma_t)^2}{2}, \tag{12}$$

which coincides with the potential (5) if $\gamma_t = vt$. For that class of quadratic potentials, as in Eq. (12), one has a Gaussian distribution of the work (9) for all protocols γ_t.

In what follows, the probability density for the (dissipated) work is denoted by $\mathrm{Prob}_{\rho_0}[W_\gamma^{(\mathrm{dis})}(\omega)=w]$ as a function of $w \in \mathbb{R}$. This (dissipated) work $W_\gamma^{(\mathrm{dis})}$ depends on the time τ, see Eqs. (9) and (10).

Proposition II.1 (Harmonic case). If the distribution of the work W_γ is Gaussian, then for a general protocol γ_t in Eq. (6),

$$\frac{\mathrm{Prob}_{\rho_0}[W_\gamma^{\mathrm{dis}}(\omega)=w]}{\mathrm{Prob}_{\rho_0}[W_\gamma^{\mathrm{dis}}(\omega)=-w]} = \exp(\beta w) \tag{13}$$

for all times τ. ■

That fluctuation theorem is easily checked to hold also for quadratic potentials that are more general than Eq. (12). One could argue that any Gaussian distributed observable can be made to satisfy a fluctuation theorem by rescaling the mean and the variance. However, that is not what happens here: no scaling at all is required for the work W_γ to satisfy the exact fluctuation theorem.

For more general potentials, we start by specifying the following general condition:

Assumption. We assume that there exists an involution s on path space, $s^2=\mathbb{1}$, with $s\Theta=\Theta s$ and such that

$$\mathrm{Prob}_{\rho_\tau}(\omega|\Theta\gamma) = \mathrm{Prob}_{\rho_0}(s\omega|\gamma). \tag{14}$$

■

The involution s relates trajectories under the protocol γ and its time-reversed protocol $\Theta\gamma$. The next theorem stipulates that the existence of s implies an exact fluctuation relation for the work. We illustrate that assumption below by enumerating the cases in which the assumption is certainly verified; see also Sec. III.

Theorem II.2 (EFT work). Under the assumption (14) above, the dissipative work (10) satisfies an EFT: for all $\tau>0$ and for all w,

$$\frac{\mathrm{Prob}_{\rho_0}[W_\gamma^{\mathrm{dis}}(\omega)=w]}{\mathrm{Prob}_{\rho_0}[W_\gamma^{\mathrm{dis}}(\omega)=-w]} = \exp(\beta w). \tag{15}$$

■

The assumption (14) can be split in two subassumptions, as we now state.

Proposition II.3. Suppose either (i) that the protocol is symmetric under time reversal $\gamma_t=\gamma_{\tau-t}\equiv\Theta\gamma_t$, or (ii) that the protocol is antisymmetric $\gamma_t-\gamma_0=\gamma_\tau-\gamma_{\tau-t}\equiv-\Theta(\gamma_t-\gamma_0)$ and that the potential U obeys Eq. (6) and is symmetric, $U(x)=U(-x)$. Then assumption (14) and hence the EFT (15) are verified. ■

The EFT for the harmonic case $U(x)=x^2/2$ with constant velocity $\gamma_t=vt$ as in Eq. (5), see [9,12], is treated by Proposition II.1 but is of course also a special case of Proposition II.3.

We will see further in Sec. III A how our conditions are in fact optimal. We can, however, already observe here how some symmetry of the protocol must enter when dealing with an arbitrary potential. Consider indeed, if only formally, $U(x)=x, x>0$ with a wall $U(x)=+\infty$ for $x\leqslant 0$ in Eq. (9). We can then safely assume that the trajectory satisfies $x_t-\gamma_t>0$ and Eq. (9) gives that the work $W_\gamma=W_\gamma^{\mathrm{dis}}=\gamma_\tau-\gamma_0$. Obviously this (constant) expression never satisfies an EFT unless (and then trivially) $\gamma_\tau=\gamma_0$.

The fluctuations of the work done by the white noise on the particle were studied in [18]. It was found that those fluctuations *do not* satisfy the exact fluctuation theorem and are in fact insensitive to a pinning potential.

2. Heat

The heat Q_γ defined in Eq. (11) equals the dissipative work W_γ^{dis} up to some temporal boundary term,

$$Q_\gamma = W_\gamma^{\mathrm{dis}} + \Delta(F-U).$$

The temporal boundary $\Delta(F-U)$ is, modulo the factor β, the change of equilibrium entropy in going from the equilibrium described by ρ_0 to that given by ρ_τ. For the fluctuations of the heat, we start from a situation in which we already have the EFT (15) for the (dissipative) work.

We are concerned here with the situation in which the potential in Eq. (6) is unbounded [since otherwise, Eq. (3) is not normalizable] and we assume that for some $\varepsilon, v>0$,

$$U(x) \geqslant |x|^{1+\varepsilon}, \quad \gamma_t = vt \tag{16}$$

at least for $|x|$ and t sufficiently large. For the average work, we write

$$\lim_{\tau\to+\infty} \frac{\langle W_\gamma \rangle}{\tau} \equiv \bar{w}.$$

We further continue to assume the well-defined dynamics (4) with the EFT (15) for the (dissipative) work. The latter can be summarized by introducing the rate function $I(w)$ which, in a logarithmic sense and asymptotically as $\tau\uparrow+\infty$, governs

$$\mathrm{Prob}(W_\gamma^{\mathrm{dis}} = w\tau) = \exp[-\tau I(w)].$$

We assume that $I(w)\geqslant 0$ is strictly convex with a minimum at $\bar{w}$, $I(\bar{w})=0$ and which, from the EFT (15), satisfies $I(-w)-I(w)=\beta w$. Let $w^\star$ be the solution of $I'(w)=\beta$. In case the rate function $I(w)$ is symmetric around $w=\bar{w}$, then $w^\star=3\bar{w}$.

Under these assumptions, we will argue in Sec. IV D that the following holds true in general:

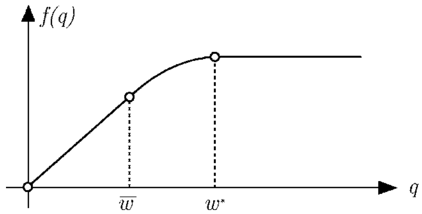

FIG. 1. Extension of the standard fluctuation theorem for the heat per unit time q. The function $f(q)$ is defined in Eq. (17). For small values of q, $f(q)$ is linear so the standard fluctuation theorem is recovered. Between $\bar{w}$ and $w^\star$, the behavior is determined by the large deviation rate function $I(q)$ of the work. The function $f(q)$ saturates for large q.

Consider, as in Eq. (2), for $q \geqslant 0$,

$$f(q) \equiv \lim_{\tau \to +\infty} \frac{1}{\tau} \log \frac{\mathrm{Prob}(Q_\gamma = \tau q)}{\mathrm{Prob}(Q_\gamma = -\tau q)}. \tag{17}$$

Then,

$$f(q) = \begin{cases} \beta q & \text{for } 0 \leqslant q \leqslant \bar{w} \\ \beta q - I(q) & \text{for } \bar{w} \leqslant q \leqslant w^\star \\ \beta w^\star - I(w^\star) & \text{for } q \geqslant w^\star, \end{cases}$$

(see Fig. 1). The antisymmetry of $f(q) = -f(-q)$ fixes the behavior for $q < 0$.

As an example, take $I(w) = \beta(w - \bar{w})^2 / 4\bar{w}$ as is the case for Eq. (5), see [9]. Then $w^\star = 3\bar{w}$ and we have three regimes: a first linear regime where we see the usual fluctuation theorem (15) for $0 < q \leqslant \bar{w}$, then a quadratic regime for $\bar{w} < q \leqslant 3\bar{w}$, which saturates to a fixed value for $q \geqslant 3\bar{w}$. Under our assumptions, we have now a general expression for the corrections of the heat fluctuation theorem, extending the results in [9] quite beyond the harmonic case (5).

A more probabilistic interpretation and a toy calculation are presented in Appendix B.

III. EXPERIMENTS AND NUMERICAL WORK

A. Simulations

In the previous sections, we have given conditions on the protocol and on the potential for the work to follow an EFT (15). We now argue via numerical examples that our sufficient conditions are also close to being necessary. To that aim, we have simulated the Langevin motion of the particle by means of an Euler-Maruyama scheme. The time interval $[0, \tau]$ is divided into n parts $dt = \tau / n$, and the evolution of the system takes place via discrete states x_i $(i = 0, 1, 2, \ldots, n)$ connected by finite dt steps,

$$x_{i+1} = x_i - \frac{\partial U(x_i, \gamma_i)}{\partial x} dt + \sqrt{2dt} B_i,$$

where B_i is a random number drawn from a normal distribution, and we have set $\beta = 1$. The work (9) is calculated through

$$W = - \sum_{i=0}^{n-1} U'(x_i - \gamma_i)(\gamma_{i+1} - \gamma_i).$$

We consider the potential, for $\alpha_+, \alpha_- > 0$,

$$U_t(x) = U(x - \gamma_t) = \begin{cases} \dfrac{|x - \gamma_t|^{\alpha_+}}{\alpha_+} & \text{for } x \geqslant \gamma_t \\ \dfrac{|x - \gamma_t|^{\alpha_-}}{\alpha_-} & \text{for } x < \gamma_t. \end{cases} \tag{18}$$

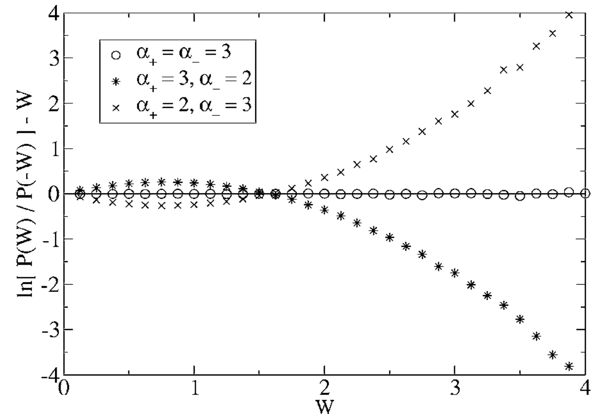

FIG. 2. Plot of the deviations from the EFT (15), for several values of the exponents α_+ and α_- in (18). A potential that is dragged with constant velocity $v = 1$ is considered: the EFT is verified for the symmetric potential (here we chose $\alpha_+ = \alpha_- = 3$), while it is not observed for asymmetric potentials. Parameters are $\tau = 1$ and $dt = 10^{-3}$.

The first case examined is where the potential above is moved with a linear protocol $\gamma_t = t$ for $t > 0$. At $t = 0$, we generate equilibrated configurations, sampled with a usual Markov chain and a METROPOLIS criterion. First we choose a generic (nonharmonic) symmetric potential, with $\alpha_+ = \alpha_- = 3$, for which we expect the EFT (15) to hold. That is confirmed in Fig. 2, in which we plot the difference

$$\ln\left[\frac{P(W = w)}{P(W = -w)}\right] - w$$

between the left-hand side and the right-hand side in Eq. (15). Indeed, there are no noticeable deviations from zero for the case of a symmetric potential. On the other hand, in the same figure, the results found for asymmetric potentials are not in agreement with the EFT. In that case, the conditions of Proposition II.3 are not verified. Note that the symmetric deviations from the origin found for the choices $(\alpha_+ = 3, \alpha_- = 2)$ and $(\alpha_+ = 2, \alpha_- = 3)$ represent an indirect verification of the Crooks relation, see further in Sec. IV A. Using that Crooks relation, one can show that the free-energy difference ΔF between the equilibria corresponding to the initial and final state can be read off where these two curves intersect. Here, with a potential of the form (6), we recover that $\Delta F = 0$.

In Fig. 3, one sees again how our conditions in Proposition II.3 are necessary. This time we take a protocol that lacks the suitable temporal symmetries, like $\gamma_t = t + t^4$.

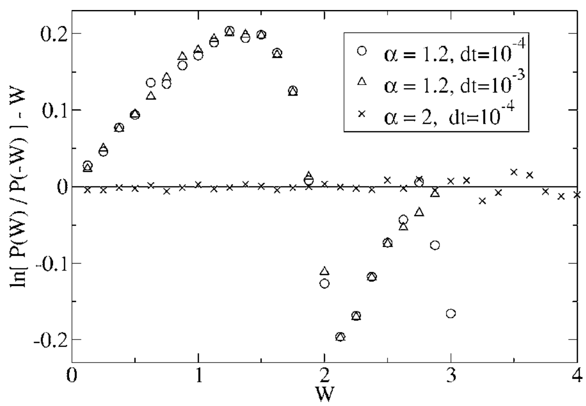

FIG. 3. Plot of the deviations from the EFT (15), for symmetric potentials [$\alpha_+=\alpha_-\equiv\alpha$ in Eq. (18)] and spatially translated with protocol $\gamma_t=t+t^4$. We chose $\tau=1$ and $dt=10^{-4}$. The fluctuation theorem is verified for the harmonic potential, while it is not valid for a symmetric potential with exponent $\alpha_+=\alpha_-=1.2$. For the latter potential, a simulation with $dt=10^{-3}$ shows that the numerical approximation is negligible.

The EFT is then not verified even for a symmetric potential as in Eq. (18) with $\alpha_+=\alpha_-(\neq 2)$. However, as expected, the simulation of the special case of the harmonic potential $\alpha_+=\alpha_-=2$ obeys the conclusion of Proposition II.1. Similar conclusions are drawn from Fig. 4.

B. Experiments

Previous experiments to test fluctuation relations for nonequilibrium systems included a particle dragged in water. In [12], Wang *et al.* consider a particle equilibrated in an optical trap and then dragged by the trap at constant speed relative to the surrounding water. The particle is micrometer-sized, the force is of order of a pico-Newton, and about 500 particle trajectories were recorded for times up to 2 s after initiation. The protocol specifies the time-dependent position of the trap, approximated as the position of the minimum in a harmonic potential with spring constant κ. The external force exerted on the particle is thus $F_t(q)=-\kappa(q-\gamma_t)$. The motion of $\gamma_t=vt$ is about rectilinear. In a second experiment [11], the shape of the confining potential was changed. However, both are examples of harmonic potentials, which we have shown to be a very special class.

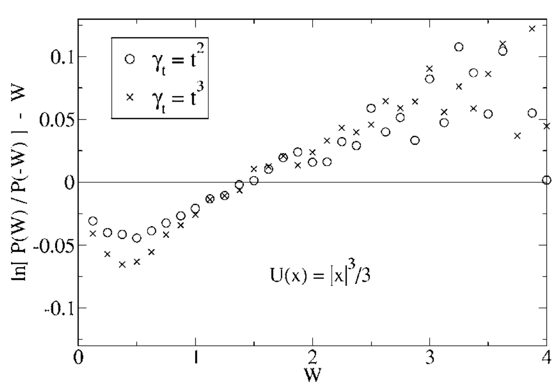

FIG. 4. Plot of the deviations from the EFT (15), for the symmetric potential $U(x)=|x|^3/3$ [$\alpha_+=\alpha_-=3$ in Eq. (18)] and spatially translated with protocol $\gamma_t=t^2$ and $\gamma_t=t^3$. We chose $\tau=1$ and $dt=10^{-4}$. Since both protocols are neither symmetric or antisymmetric, the EFT is indeed not expected to hold.

More recently, more general situations have been investigated, see [10,17]. For example, a two-level system was realized experimentally with a single defect in a diamond. When the system is externally driven by a laser, the dissipation $R=\beta W^{\mathrm{dis}}$ displays non-Gaussian fluctuations. It was noticed that integrated versions of the fluctuation theorem in their experiment are observed only for particular protocols, in line with our general results about the symmetric protocols (Proposition II.3). In the more recent paper [10], the distribution of the work performed on a particle was computed for a nonharmonic potential. Again, the time-symmetric protocol has been found to yield results consistent with the EFT. Note, however, that our results show that a symmetric protocol is not necessary; also, the application of an antisymmetric (e.g., linear) protocol combined with a symmetric potential provides a verification of the EFT (see Proposition II.3 and Fig. 2).

IV. PROOFS

A. Exact identities (Crooks and Jarzynski relations)

The proofs of the results listed in Sec. II C are discussed here. The basic ingredient for approaching the fluctuations of dissipation functions via the method of time reversal was already mentioned in the Introduction. In particular, for stochastic dynamics and especially those that we study here under Eq. (4), the following relation is known as the Crooks fluctuation theorem, see [19]; remember the notation around Eq. (8).

Lemma IV.1.

$$\frac{\mathrm{Prob}_{\rho_0}(\omega|\gamma)}{\mathrm{Prob}_{\rho_\tau}(\Theta\omega|\Theta\gamma)}=\exp(\beta(W_\gamma(\omega)-\Delta F)). \tag{19}$$

Proof. Using the Girsanov formula [20], the probability density $\mathrm{Prob}_{\rho_0}(\omega|\gamma)$ on trajectories can be expressed in terms of the potential. Remember that the reference measure is associated to the $U=0$ case (pure Brownian trajectories), starting from ρ_0,

$$\mathrm{Prob}_{\rho_0}(\omega|\gamma)=\exp\left[-\frac{\beta}{2}\int_0^\tau dx_t\circ\frac{\partial U_t}{\partial x}(x_t)+ST\right]$$
$$=\exp\left[\frac{\beta Q_\gamma(\omega)}{2}+ST\right], \tag{20}$$

where

$$ST=\frac{\beta}{4}\int_0^\tau dt\left[\frac{\partial^2U_t}{\partial x^2}(x_t)-\left(\frac{\partial U_t}{\partial x}(x_t)\right)^2\right].$$

The ratio of time-forward and time-backward probabilities can then be computed by using

$$Q_{\Theta\gamma}(\Theta\omega)=-Q_\gamma(\omega),$$

$$\Theta(ST)=ST,$$

$$\frac{\mathrm{Prob}^{U=0}_{\rho_0}(\omega)}{\mathrm{Prob}^{U=0}_{\rho_\tau}(\Theta\omega)} = \frac{\rho_0(x_0)}{\rho_\tau(x_\tau)}. \tag{21}$$

That leads to

$$\frac{\mathrm{Prob}_{\rho_0}(\omega|\gamma)}{\mathrm{Prob}_{\rho_\tau}(\Theta\omega|\Theta\gamma)} = \frac{\rho_0(x_0)}{\rho_\tau(x_\tau)}\exp[\beta Q_\gamma(\omega)]$$
$$= \exp[\beta\Delta U - \beta\Delta F + \beta Q_\gamma(\omega)],$$

which is Eq. (19) since $\Delta U = -Q_\gamma + W_\gamma$. ■

From the Crooks relation (19) follows easily the so called Jarzynski relation [21]. In our context, this is the normalization of the probability distribution,

$$1 = \left\langle \frac{\mathrm{Prob}_{\rho_\tau}(\Theta\omega|\Theta\gamma)}{\mathrm{Prob}_{\rho_0}(\omega|\gamma)} \right\rangle_{\rho_0} = e^{\beta\Delta F}\langle e^{-\beta W_\gamma(\omega)}\rangle_{\rho_0},$$

where $\langle\cdot\rangle_{\rho_0}$ is the expectation starting from ρ_0. The conclusion is

$$e^{-\beta\Delta F} = \langle e^{-\beta W_\gamma(\omega)}\rangle_{\rho_0}. \tag{22}$$

A more microscopic and physically inspired derivation of the Jarzynski relation follows in Appendix A.

B. The harmonic potential with a general protocol

For the harmonic potential (12), all protocols γ lead to an exact fluctuation theorem for the work. The proof can easily be generalized to other quadratic forms of the potential where, for example, the protocol works multiplicatively [e.g., $U_t(x) = U(\gamma_t x)$].

From the definition of work (9), it is easy to see that the distribution of the work is Gaussian in the case of a harmonic potential.

Proposition II.1. The free-energy difference (7) is $\Delta F = 0$. If the distribution of the work is Gaussian with mean $\bar{w}$ and variance σ^2, the expectation value in Eq. (22) can be computed explicitly,

$$1 = \langle e^{-\beta W_\gamma(\omega)}\rangle = \exp\left[\frac{1}{2\sigma^2}(-2\bar{w}\sigma^2\beta + \sigma^4\beta^2)\right].$$

Thus, necessarily, $\bar{w} = \frac{1}{2}\sigma^2\beta$.

Finally, it is easy to check that a Gaussian random variable whose mean $\bar{w}$ and variance σ^2 are related by $\bar{w} = \frac{1}{2}\sigma^2\beta$ satisfies Eq. (13). ■

C. Work EFT

By applying property (14) of the involution s to the numerator and denominator of the Crooks relation (19), we find

$$\exp\{\beta[W_\gamma(\omega) - \Delta F]\} = \frac{\mathrm{Prob}_{\rho_0}(\omega|\gamma)}{\mathrm{Prob}_{\rho_\tau}(\Theta\omega|\Theta\gamma)} = \frac{\mathrm{Prob}_{\rho_\tau}(s\omega|\Theta\gamma)}{\mathrm{Prob}_{\rho_0}(\Theta s\omega|\gamma)}$$
$$= \exp\{-\beta[W_\gamma(s\Theta\omega) + \Delta F]\}.$$

Hence,

$$W_\gamma(s\Theta\omega) = -W_\gamma(\omega) + 2\Delta F. \tag{23}$$

From the first law combined with Eq. (21), one also concludes that $W_{\Theta\gamma}(\Theta\omega) = -W_\gamma(\omega)$.

Theorem II.2. Let us explicitly denote the dependence of the dynamics on the protocol γ by writing $\mathrm{Prob}_{\rho_0}(W_\gamma = w|\gamma)$ for the density of the work W_γ. By Eq. (19),

$$\mathrm{Prob}_{\rho_0}[W_\gamma(\omega) = w'|\gamma] = e^{\beta(w'-\Delta F)}\mathrm{Prob}_{\rho_\tau}[W_\gamma(\Theta\omega) = w'|\Theta\gamma].$$

By Eq. (14),

$$\mathrm{Prob}_{\rho_\tau}[W_\gamma(\Theta\omega) = w'|\Theta\gamma] = \mathrm{Prob}_{\rho_0}[W_\gamma(\Theta s\omega) = w'|\gamma]$$

As a consequence, via Eq. (23),

$$\mathrm{Prob}_{\rho_0}[W_\gamma(\omega) = w'|\gamma] = e^{\beta(w'-\Delta F)}\mathrm{Prob}_{\rho_0}[W_\gamma(\omega) = 2\Delta F - w'|\gamma].$$

Substituting $w' = w + \Delta F$, we find the EFT (15) as required.

Proposition II.3. Suppose first a symmetric protocol $\Theta\gamma = \gamma$ and hence $\gamma_\tau = \gamma_0$,

$$U_0(x) = U_\tau(x) \Rightarrow \rho_0(x) = \rho_\tau(x)$$

with ρ_t the distribution (3). Choosing the identity operator as the involution $s = \mathbb{1}$, i.e., $s\omega = \omega$, we find that Eq. (14) is obviously satisfied.

For antisymmetric protocols $\gamma_{\tau-t} = X - \gamma_t$ with $X = \gamma_0 + \gamma_\tau$, we restrict ourselves to symmetric potentials of the form (6). Observe then that

$$U(X - x - \gamma_t) = U(-x + \gamma_{\tau-t}) = U(x - \gamma_{\tau-t})$$

which, for $t = 0$, implies $\rho_0(X - x) = \rho_\tau(x)$. Choose therefore the involution s in Eq. (14) as the flip $s\omega = X - \omega$, in the sense that $s(\omega)_t = X - x_t$ for $\omega = (x_t)$. Then, by simple inspection from Eq. (20), again by using that the potential U is even, we get the equality $\mathrm{Prob}_{\rho_0}(s\omega|\gamma) = \mathrm{Prob}_{\rho_\tau}(\omega|\Theta\gamma)$ of densities, as for Eq. (14). ■

D. Heat FT

We give the arguments leading to Eq. (17). Here we do not give a full proof.

For very large τ, it is appropriate for our purpose to consider $Q_\gamma/\tau = W_\gamma^{\mathrm{dis}}/\tau + \Delta(F-U)/\tau$ as the sum of two independent random variables. That asymptotic independence can be argued for on the basis of mixing properties of the Markov diffusion process (4). We thus write formally, for arbitrary q,

$$\mathrm{Prob}(Q_\gamma = q\tau) = \mathrm{Prob}[W_\gamma^{\mathrm{dis}} + \Delta(F - U) = q\tau]$$
$$= \int dw e^{-\tau[I(w)+J(q-w)]}, \tag{24}$$

where $\mathrm{Prob}(W_\gamma^{\mathrm{dis}} = w\tau) = \exp[-\tau I(w)]$, $\mathrm{Prob}[\Delta(F-U) = u\tau] = \exp[-\tau J(u)]$ in the usual sense of the theory of large deviations, as $\tau\uparrow+\infty$.

Hence, taking the logarithm of Eq. (24) and dividing by $\tau\uparrow+\infty$ takes us to

$$h(q) \equiv \lim_{\tau} \frac{1}{\tau} \log \mathrm{Prob}(Q_\gamma = q\tau) = -\inf_w [I(w) + J(q-w)] \tag{25}$$

and we want to compute $f(q)=h(q)-h(-q)$. As $I(w)$ is the rate function of the large deviations of the (dissipative) work, which we assume given and satisfying the EFT (15), the only unknown is the rate function J.

Clearly, always in the sense of large deviations,

$$J(u) = -\lim_{\tau\uparrow+\infty} \frac{1}{\tau} \log \mathrm{Prob}_{\rho_0}\left(\frac{U(x_0) - U(x_\tau - v\tau)}{\tau} = u\right).$$

Here we assume again the independence for large τ, this time between the variables $U(x_0)$ and $U(x_\tau - v\tau)$. Since $U_t(x) \geqslant 0$ if $u>0$, then, by this independence,

$$J(u) = -\lim_{\tau\uparrow+\infty} \frac{1}{\tau} \log \int_u^{+\infty} dy e^{-\beta y\tau} \mathrm{Prob}_{\rho_0}[U(x_\tau - v\tau) = (y-u)\tau]$$

$$\simeq \beta u.$$

On the other hand, if $u<0$, we have

$$J(u) = -\lim_{\tau\uparrow+\infty} \frac{1}{\tau} \log \mathrm{Prob}_{\rho_0}[U(x_\tau - v\tau) = -u\tau].$$

Now, the process $x_\tau - v\tau$ is stationary for large τ: from Eq. (4),

$$d(x_t - vt) = -U'(x_t - vt)dt - vdt + \sqrt{\frac{2}{\beta}} db_t$$

so that we can expect that for large τ, $x_\tau - v\tau$ is distributed according to the Boltzmann statistics $\exp[-\beta U(x_\tau - v\tau) - \beta v(x_\tau - v\tau)]$. As $U(x) \geqslant |x|^{1+\varepsilon}$, we have that for $u<0$, $J(u) = -\beta u$.

Summarizing, in Eq. (24) we can take $J(u)=\beta|u|$. After all, it gives the probability of finding a huge energy difference $\Delta(F-U) \simeq u\tau$ between the initial and the final state. It means that either $U_0(x_0)$ or $U_\tau(x_\tau)$ must be very large, and the energy has, in Boltzmann statistics, an exponential distribution.

Finally, to obtain the results from Sec. II C 2, one must still use that

$$-I(w) + I(-w) = \beta w, \quad I'(w) + I'(-w) = -\beta$$

so that, e.g., $I'(-\bar{w}) = -\beta$. It is then easily seen that $h(q) = -I(-\bar{w}) + \beta(\bar{w}+q)$ if $q \leqslant -\bar{w}$, $h(q) = -I(q)$ if $-\bar{w} \leqslant q \leqslant w^\star$, and $h(q) = -I(w^\star) - \beta(q - w^\star)$ if $q \geqslant w^\star$. From these one computes $f(q) = h(q) - h(-q)$.

V. CONCLUSIONS

In the present paper, we have studied the probability distributions for the work done by an external agent, and the heat dissipated by the particle under influence of a Langevin dynamics. We have found a near-to-optimal condition that ensures the existence of an exact fluctuation relation (1) for the work (9). Previously, this result was only obtained in the case of specific potentials by explicit computation. For the heat fluctuation relation, we provided a general argument that shows that the corrections that were found by [9] are generic: for small values of the heat dissipation q, the familiar form of the fluctuation theorem is recovered. However, for large values, the correction saturates to a constant value determined by the large deviation rate function of the work.

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APPENDIX A: THE BASIS OF A JARZYNSKI RELATION

Let Γ be the phase space on which we have a time-dependent dynamics [24] defined in terms of invertible transformations f_t. One can think of a protocol γ that changes in discrete steps so that a phase-space point $x \in \Gamma$ flows in time t to $\varphi_{t,\gamma} x \in \Gamma$ with

$$\varphi_{t,\gamma} = f_t \cdots f_2 f_1, \quad t = 1, \ldots, \tau.$$

For the reversed protocol $\Theta\gamma$,

$$\varphi_{t,\Theta\gamma} = f_{\tau-t+1} \cdots f_{\tau-1} f_\tau.$$

We imagine a measure μ on the phase space Γ that is left invariant by $\varphi_{t,\gamma}$: $\mu(\varphi_{t,\gamma}^{-1} B) = \mu(B)$ for $B \subset \Gamma$. Furthermore, Γ is equipped with an involution π that also leaves μ invariant. We assume dynamical reversibility in the sense that for all t,

$$f_t \pi = \pi f_t^{-1}.$$

As a consequence, $\pi \varphi_{t,\Theta\gamma}^{-1} \pi = f_\tau \cdots f_{\tau-t+1}$ or $\varphi_{\tau,\gamma}^{-1} \pi \varphi_{t,\Theta\gamma}^{-1} \pi = \varphi_{\tau-t,\gamma}^{-1}$.

Let us now divide the phase space in a finite partition $\hat{\Gamma}$. It corresponds to a reduced description; each element in the partition is thought to reflect some manifest condition of the system. The entropy is defined in the manner of Boltzmann as

$$S(M) = \ln \mu(M), \quad M \in \hat{\Gamma}.$$

For example, in Hamiltonian systems one takes the Liouville measure as the invariant measure μ, and then we obtain the conventional Boltzmann definition $S = \ln|M|$. We fix probability laws $\hat{\rho}$ and $\hat{\sigma}$ on the elements of the partition and we specify the initial probability measure on Γ as

$$r_{\hat{\rho}}(A) \equiv \sum_M \frac{\mu(A \cap M)}{\mu(M)} \hat{\rho}(M).$$

This probability measures $A \subset \Gamma$ using $\hat{\rho}$ at the level of the partitions M of the reduced description and using the invariant measure μ within each partition M. The reduced trajectories of the system are sequences $\omega = (M_0, M_1, \ldots, M_\tau)$, where $M_i \in \hat{\Gamma}$, indicating subsequent moments when the phase-space point was in the set $M_i, i=0,\ldots,\tau$. The path-space measure $P_{\hat{\rho},\gamma}$ gives the probability of trajectories when starting from $r(\hat{\rho})$ and using protocol γ.

The quantity of interest that measures the irreversibility in the dynamics on the level of $\hat{\Gamma}$ is [see also Eq. (19) and (8)]

$$R = \ln \frac{P_{\hat{\rho},\gamma}(M_0, M_1, \ldots, M_\tau)}{P_{\hat{\sigma}\pi,\Theta\gamma}(\pi M_\tau, \pi M_{\tau-1}, \ldots, \pi M_0)}$$

The point is that for every probability $\hat{\rho}$ and $\hat{\sigma}$ on $\hat{\Gamma}$, and for all $M_0, \ldots, M_\tau \in \hat{\Gamma}$,

$$R = S(M_\tau) - S(M_0) - \ln \hat{\sigma}(M_\tau) + \ln \hat{\rho}(M_0). \qquad \text{(A1)}$$

To show Eq. (A1), we only have to look closer at the consequences of the dynamic reversibility. By using that $\mu(B) = \mu(\varphi^{-1}_{\tau,\gamma}\pi B)$, we have of course that

$$\mu\left[\bigcap_{t=0}^{\tau} \varphi^{-1}_{t,\Theta\gamma}\pi M_{\tau-t}\right] = \mu\left[\bigcap_{t=0}^{\tau} \varphi^{-1}_{\tau,\gamma}\pi\varphi^{-1}_{t,\Theta\gamma}\pi M_{\tau-t}\right]$$

but moreover, by reversibility, the last expression equals

$$\mu\left[\bigcap_{t=0}^{\tau} \varphi^{-1}_{\tau,\gamma}\pi \circ \varphi^{-1}_{t,\Theta\gamma}\pi M_{\tau-t}\right] = \mu\left[\bigcap_{t=0}^{\tau} \varphi^{-1}_{\tau-t,\gamma} M_{\tau-t}\right],$$

which is all that is needed.

As an immediate corollary, under the expectation $P_{\hat{\rho},\gamma}$

$$\langle e^{-S(M_\tau)+S(M_0)+\ln \hat{\sigma}(M_\tau)-\ln \hat{\rho}(M_0)} \rangle = 1. \qquad \text{(A2)}$$

A simple choice for the system and partition takes an isolated system where the reduced variables M_i refer to the energy of the system. We have still the freedom to choose $\hat{\rho}$ and $\hat{\sigma}$. Let us take $\hat{\rho}(M_0)=1$, where indeed M_0 refers to the initial energy E. As a final condition we let the system be randomly distributed on the energy shell E'. For these choices, in "suggestive" notation, Eq. (A2) becomes

$$\ln \frac{P_{E,\gamma}(E \to E')}{P_{E',\Theta\gamma}(E' \to E)} = S(E') - S(E).$$

Using that here $\Delta E = E' - E = W$ equals the work done, one thus recovers the microcanonical analogue of the Crooks relation (19), see also [22].

The mathematically trivial identity (A2) is source of all Jarzynski relations. The way in which it gets realized as, for example, an irreversible work-free energy relation depends on the specific context or example. We can also split the system from the environment. The reduced variables (M_i) can, for example, be chosen to consist of the microscopic trajectory for the system and of the sequence of energies of the environment. For a thermal environment at all times in equilibrium at inverse temperature β, we thus get $S(M_\tau) - S(M_0) = \beta Q$, where Q is the heat that flowed into the reservoir. On the other hand, we can take $\hat{\rho}$ and $\hat{\sigma}$ as equilibrium distributions, say of the weak-coupling form

$$\hat{\rho}(M) = \frac{e^{-\beta U(x,\gamma_0)}}{Z_0} h(E),$$

where $M = (x, E)$ combines the microstate x of the system and the energy E of the environment, $h(E)$ describes the reservoir distribution, and $U(x,\gamma)$ is the energy of the system with parameter γ. Similarly,

$$\hat{\sigma}(M) = \frac{e^{-\beta U(x,\gamma_\tau)}}{Z_\tau} h(E).$$

If we have that $h(E_0) \simeq h(E_\tau)$, i.e., that the energy exchanges to the environment remain small compared to the dispersion of the energy distribution in the reservoir, we get from Eq. (A2) in that context that

$$\langle e^{-\beta Q - \beta U(x_\tau,\gamma_\tau) + \beta U(x_0,\gamma_0)} \rangle_{\hat{\rho}} = \frac{Z_\tau}{Z_0},$$

which is a version of the Jarzynski relation (22).

APPENDIX B: LARGE DEVIATIONS

For the fluctuation theorem, we are interested in the large deviations of Q_γ/τ from its average as $\tau \uparrow +\infty$. Such deviations can arise from two sources. First there are the large deviations of the work W_γ, which, however, we know satisfies an EFT. Secondly, there is the possibility that ΔU also fluctuates to order τ. This second effect is responsible for the deviations from the standard fluctuation relation (2). After all, an energy is typically exponentially distributed and we can thus expect a competition with the fluctuations of the work.

In order to clearly see the influence of the unboundedness of the temporal boundary, we consider here the simplest setup in which deviations from the standard fluctuation theorem can be calculated exactly.

We consider a particle moving under the influence of a quadratic potential and a random force. For each time step $i = 1, 2, \ldots, \tau$ we take the work done on the particle y_i to be a random variable distributed according to a Gaussian of average m_i and variance v_i [25]. Let us also consider the analogue of the work (9) as the sum $W_\tau \equiv (y_1 + \cdots + y_\tau)$. By construction, the work per unit time $w_\tau \equiv W_\tau/\tau$ is again Gaussian with average $\bar{w}_\tau = (m_1 + \cdots + m_\tau)/\tau$ and variance $\sigma^2_\tau = (v_1 + \cdots + v_\tau)/\tau^2$. If $2\bar{w}_\tau = \sigma^2_\tau$, then, automatically, the probability density function $\text{Prob}(W_\tau = w\tau) = \text{Prob}(w_\tau = w)$ satisfies, for all τ,

$$\frac{\text{Prob}(w_\tau = w)}{\text{Prob}(w_\tau = -w)} = e^{w}.$$

That is the (Gaussian) analogue of the exact fluctuation theorem (15) for the work (that we here, by the previous construction, assume from the start).

We now consider a new random variable (the analogue of the heat),

$$Q_\tau(w_\tau, y_1, y_\tau) \equiv W_\tau + \eta[(y_\tau - a)^2 - (y_1 - b)^2],$$

where a, b, η are real parameters, with density $\text{Prob}(Q_\tau = q\tau)$. The aim of our toy model is to compute

$$f(q) = \lim_{\tau\to\infty} \frac{1}{\tau} \ln \frac{\text{Prob}(Q_\tau = q\tau)}{\text{Prob}(Q_\tau = -q\tau)}.$$

That can follow from $f(q) = h(q) - h(-q)$ with $h(q)$ the large deviation rate function of the heat: $\text{Prob}(Q_\tau = q\tau)$

$\simeq \exp[\tau h(q)]$. The function $h(q)$ is the Legendre transform of the generating function

$$E(t) = \lim_{\tau} \frac{1}{\tau} \ln E_{\tau}(t)$$

with

$$E_{\tau}(t) = \frac{1}{(2\pi)^{3/2} \det^{1/2} C} \int dy e^{tQ_{\tau}(y)} e^{-(1/2)(y-\bar{y})\cdot C^{-1}(y-\bar{y})}, \tag{B1}$$

where, collectively, $y=(w_{\tau}, y_1, y_{\tau})$ and $\bar{y} \equiv (\bar{w}_{\tau}, \bar{y}_1, \bar{y}_{\tau})$ represent their mean while $C=C_{\tau}$ corresponds to the covariance matrix of y. Doing the Gaussian integrals in Eq. (B1) and taking the limit $\tau \to \infty$ leads to

$$E(t) = \begin{cases} \frac{1}{2}vt^2 + t\bar{w} & \text{if } t \in [-t_\star, t_\star] \\ +\infty & \text{otherwise,} \end{cases}$$

where $t_\star = 1/2\eta$, $v = \lim_{\tau} \sigma_{\tau}^2 = 2\bar{w} = 2 \lim_{\tau} \bar{w}_{\tau}$.

We are now interested in evaluating the Legendre transform of the above, $h(q) = -\sup_t[qt - E(t)]$. The location of the supremum depends on whether $(q-\bar{w})/v$ lies within or outside the interval $[-t_\star, t_\star]$. As a result, $h(q)$ becomes a quadratic function within the interval $[-vt_\star + \bar{w}, vt_\star + \bar{w}]$ and a linear one outside. For the final result for $f(q)$, one distinguishes between the following two cases depending on the value of $\bar{w}$.

For $vt_\star < \bar{w}$,

$$f(q) = \begin{cases} 2qt_\star & \text{for } q \in [0, \bar{w} - vt_\star] \\ -\frac{1}{2v}(q-\bar{w})^2 + qt_\star - \frac{1}{2}vt_\star^2 + \bar{w}t_\star & \text{for } q \in [\bar{w} - vt_\star, \bar{w} + vt_\star] \\ 2\bar{w}t_\star & \text{for } q \in [\bar{w} + vt_\star, \infty) \end{cases} \tag{B2}$$

while for $\bar{w} < vt_\star$, one has

$$f(q) = \begin{cases} q & \text{for } q \in [0, -\bar{w} + vt_\star] \\ -\frac{1}{2v}(q-\bar{w})^2 + qt_\star - \frac{1}{2}vt_\star^2 + \bar{w}t_\star & \text{for } q \in [-\bar{w} + vt_\star, \bar{w} + vt_\star] \\ 2\bar{w}t_\star & \text{for } q \in [\bar{w} + vt_\star, \infty). \end{cases} \tag{B3}$$

The results of Sec. II C 2 and of [9], i.e., the Gaussian case in which $\beta=1$, are reproduced in Eq. (B3) by choosing $\bar{w}=1$ and $t_\star=1$ (i.e., $\eta=1/2$).

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