Experimental Test of the Fluctuation Theorem for a Driven Two-Level System with Time-Dependent Rates

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A single defect center in diamond periodically excited by a laser is shown to provide a simple realization for a system obeying a fluctuation theorem for nonthermal noise. The distribution of these fluctuations is distinctly non-Gaussian, which has also been verified by numerical calculation. For driving protocols symmetric under time reversal a more restricted form of the theorem holds, which is also known from entropy fluctuations caused by thermal noise.

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Introduction.—Fluctuation theorems constitute a class of exact results for nonequilibrium systems driven externally beyond the validity of linear-response regimes. Their discovery during the last decade within quite different approaches, the emerging classification, and the attempts at experimental verification contribute to an exciting period in nonequilibrium statistical mechanics. For a rough classification, one should distinguish *steady states* from *time-dependent* driving. For steady states, a fluctuation relation first showed up in computer simulations of sheared liquids as a surprisingly simple relation between the probability to observe a certain entropy production to that of observing the corresponding entropy "consumption" [1]. This fluctuation theorem has later been derived for chaotic and contracting deterministic dynamics [2,3], for driven diffusive systems [4,5], for nonequilibrium chemical reactions [6], and for a single enzyme or molecular motor [7]. For an experimental verification, a colloidal particle has been dragged through a viscous fluid by a laser trap moving with constant velocity [8,9].

For time-dependent driving, Jarzynski's relation [10–12] constrains a nonlinear average of the dissipated work spent while driving a system from one equilibrium state to another in a surrounding heat bath. Since this relation allows us to extract free energy differences from nonequilibrium data on the work, it has found widespread applications [13], in particular, in the analysis of mechanical single molecule experiments and for corresponding simulations [14–16]. For time-dependent transitions between different steady states, Hatano and Sasa [17] have derived a related expression for the dissipated heat involved in such a transition which has been verified experimentally recently by using again a colloidal particle in an optical tweezer [18].

So far, the time-dependent relations refer typically to transitions in thermal systems, where temperature and exchanged heat are still reasonable concepts despite the fact that the small system (biopolymer or colloidal particle) is transiently in distinct nonequilibrium. A heat bath with a well-defined temperature providing thermal noise, however, is not crucial for this class of theorems. They essentially derive from the behavior of the system under time reversal [19] which can be defined for other dynamics as well. In fact, for a stochastic dynamics using a master equation with time-dependent rates, the corresponding fluctuation theorem has recently been proven [20].

The purpose of this Letter is to test experimentally this type of nonthermal fluctuation theorem in a strongly driven system for the paradigmatic case of a two-level system with time-dependent transition rates. Moreover, by choosing a periodic driving function (or "protocol"), the more detailed fluctuation theorem for entropy fluctuations valid for steady states is recovered for those specific discrete values for the length of the trajectories where the periodic protocol becomes invariant with respect to time reversal. This observation shows that between steady states and time-dependent transitions, an intermediate class is emerging for such *symmetric protocols*.

Fluctuation theorem for time-dependent rates.—Let a transition between discrete states m and n occur with a rate $w_{mn}(\lambda)$, which depends on an externally controlled time-dependent parameter $\lambda(\tau)$. The master equation for the time-dependent probability $p_n(\tau)$ then reads

$$\frac{\partial p_n(\tau)}{\partial \tau} = \sum_{m\neq n} [w_{mn}(\lambda) p_m(\tau) - w_{nm}(\lambda) p_n(\tau)]. \tag{1}$$

For any fixed λ, there is a steady state $p_n^s(\lambda)$. If the system is driven externally from $\lambda(0)$ to $\lambda(t)$ according to a protocol $\lambda(\tau)$, with $0 \leqslant \tau \leqslant t$, the fluctuation theorem derived in [20] reads

$$\langle e^{-R[n(\tau)]} \rangle = 1, \tag{2}$$

where the average is taken over many realizations of length t starting in the steady state corresponding to $\lambda(0)$. The stochastic quantity $R[n(\tau)]$ is related to the probability $P[n(\tau)]$ of such a trajectory under the protocol $\lambda(\tau)$ compared to the probability $\tilde{P}[\tilde{n}(\tau)]$ for the reversed trajectory $\tilde{n}(\tau) \equiv n(t-\tau)$ to occur under the reversed protocol

$\tilde{\lambda}(\tau) \equiv \lambda(t-\tau)$. It can be expressed as

$$R[n(\tau)] \equiv \ln \frac{P[n(\tau)]}{\tilde{P}[\tilde{n}(\tau)]} = -\int_0^t d\tau \dot{\lambda}(\tau) \frac{\partial \ln p^{s}_{n(\tau)}}{\partial \lambda}. \quad (3)$$

The physical meaning of R becomes more transparent if one considers the case of a system with energy levels $E_n(\lambda)$ and free energy $F(\lambda)$ driven in contact with a heat bath at inverse temperature β. By choosing $p^s_n(\lambda) = \exp\{-\beta[E_n(\lambda) - F(\lambda)]\}$, R becomes the dissipated work βW_d spent in the process. Therefore, Eq. (2) generalizes the Jarzynski relation [10] to nonthermal systems.

Two-level system.—For an experimental demonstration of the fluctuation theorem in a nonthermal system with time-dependent rates we have chosen a single defect center in natural IIa-type diamond (Drukker) excited by a red and a green laser simultaneously. The defect is defined by its optical properties (see Fig. 1), indicating that we are dealing with a nickel-related center [21]. As explained in the caption of Fig. 1, it is sufficient to consider the defect center as an effective two-level system

$$0(\text{dark}) \underset{b}{\overset{a}{\rightleftharpoons}} 1(\text{bright}) \quad (4)$$

with rates $a \equiv w_{01}$ and $b \equiv w_{10}$.

This system is driven out of the initial equilibrium by modulating the intensity of the green laser with a sinusoidal protocol $\lambda(\tau)$ with modulation period $t_{\rm m}$. This leads to the time-dependent rate

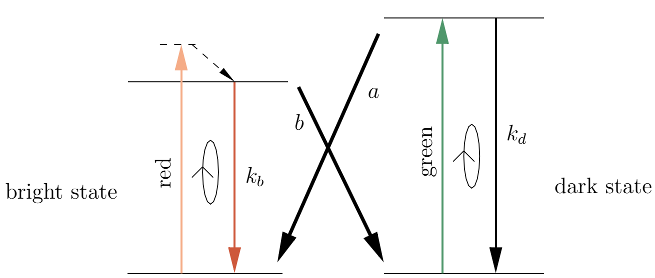

FIG. 1 (color online). This simple energy level scheme describes the observed optical properties of the defect center in diamond as two coupled two-level systems (TLS). In the first TLS, the center can be excited with a red light of wavelength 680 nm, responding with a Stokes shifted fluorescence of rate $k_b^{-1} = 5.5$ ns. The second TLS is excited with a green light of wavelength 514 nm and decays nonradiatively with rate k_d. Since these nanosecond transitions are not resolved, the first TLS appears as bright whereas the second TLS is dark. Depending on the intensity of the red excitation light, the bright TLS decays with another rate b into the dark TLS, from which it can be pumped back with rate a using the green laser. The transition rates a and b between the two TLSs are several orders of magnitude smaller than k_b and k_d and depend linearly on the intensities of the green (rate a) and red (rate b) laser, respectively, (data not shown). Hence, it is sufficient to consider the whole system as one effective TLS with a dark and a bright state.

$$a(\tau) = a_0[1 + \gamma\lambda(\tau)] \quad (5)$$

with

$$\lambda(\tau) \equiv \sin(2\pi\tau/t_{\rm m}), \quad (6)$$

where $0 < \gamma < 1$ is the strength of the modulation. The intensity of the red laser is constant and therefore $b = b_0$. For fixed λ, the system relaxes to the steady state

$$p^s_0(\lambda) = 1 - p^s_1(\lambda) = b_0/[a(\lambda) + b_0], \quad (7)$$

which, for a two-level system, is necessarily an equilibrium state.

The stochastic trajectory $n(\tau)$ of the state occupied by the system at time τ consists of N consecutive jumps at times τ_i between state 0 and state 1, where $\tau_0 = 0$ and $\tau_{N+1} = t$. In the ith interval $\tau_i \leqslant \tau \leqslant \tau_{i+1}$, the state is denoted by n_i. Inserting the steady state (7) into Eq. (3), the functional along $n(\tau)$ then becomes

$$R[n(\tau)] = -\sum_{i=0}^{N} n_i \ln\frac{a(\tau_{i+1})}{a(\tau_i)} + \ln\frac{a(t) + b_0}{a_0 + b_0}. \quad (8)$$

The second term vanishes if we start and end the driving at the same laser intensity.

Data acquisition and processing.—Single centers have been addressed with a home-built confocal microscope [22]. To illuminate the sample with red and green light at the same time, we superimposed the stabilized beam of a DCM dye laser (Coherent CR-699) operating at 680 nm and the 514 nm line of an argon ion laser (Coherent Innova 300). The time-dependent sinusoidal protocol was realized using a function generator controlled acousto-optical

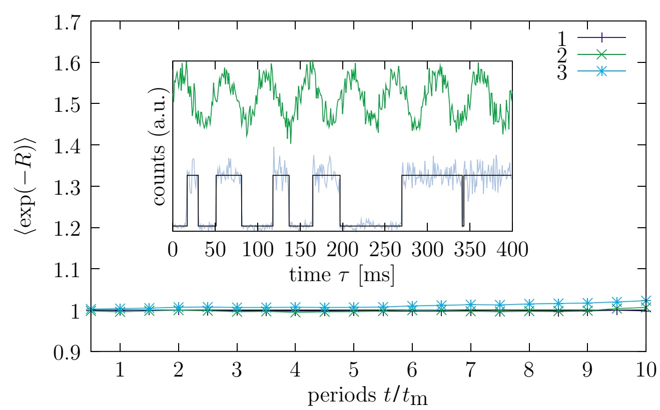

FIG. 2 (color online). Experimental test of the fluctuation theorem (2). The main frame shows mean $\langle\exp(-R)\rangle$ for trajectories of length t, for three different parameter values: (1) $a_0^{-1} = 26$ ms, $b_0^{-1} = 31$ ms, $t_{\rm m} = 50$ ms, $\gamma = 0.07$ for 1000 traces; (2) $a_0^{-1} = 27$ ms, $b_0^{-1} = 31$ ms, $t_{\rm m} = 50$ ms, $\gamma = 0.14$ for 1100 traces; (3) $a_0^{-1} = 64$ ms, $b_0^{-1} = 30$ ms, $t_{\rm m} = 20$ ms, $\gamma = 0.23$ for 4000 traces. The inset shows both the modulated intensity of the green laser and the fluorescence signal with the filtered trajectory $n(\tau)$ of an example trace of experiment (2).

modulator. The fluorescence signal as well as the modulated intensity of the green laser were detected with two avalanche photodiodes. To carry out the actual experiment, the data of the two detectors were acquired simultaneously after starting the sinusoidal protocol. Following a certain number of periods, the system was given 800 ms of relaxation time forming the unmodulated tail. The combination of recorded modulation and subsequent relaxation will be referred to as a fluorescence trace. Part of a trace is shown in the inset of Fig. 2. The three experiments presented in this Letter cover 1000, 1100, and 4000 of such traces.

In order to calculate R, one has to determine the rates. The rate b_0 has been obtained from a histogram of the lifetime of the bright state, which is unaffected by the modulation. The offset of the transition rate a_0 in Eq. (5) has been obtained from the lifetime of the dark state using the unmodulated tail, ignoring the first 300 ms while the system is still relaxing. The modulation strength γ has been calculated by fitting the green laser's raw intensity to a sine function. The calculation of R is now straightforward. By filtering the fluorescence signal we obtain a binary trajectory $n(\tau)$ for each trace, representing either the dark or the bright state. The actual value of R is calculated by inserting this trajectory $n(\tau)$ and the rate $a(\tau)$ from Eq. (5) into Eq. (8).

Test of fluctuation theorem.—We distinguish moderate driving from strong driving by comparing the intrinsic relaxation time of the unmodulated system

$$t_r = [a_0 + b_0]^{-1} \tag{9}$$

with the modulation period t_m. For the first two experiments, $t_r = 14$ ms compared to $t_m = 50$ ms means that the system is only moderately driven into nonequilibrium. For the third run, the modulation period is reduced to $t_m = 20$ ms compared to a relaxation time $t_r = 20$ ms. In this case the modulation period and intrinsic relaxation time are approximately equal, which corresponds to a strongly driven system. Furthermore, this allows us to measure a greater number of 4000 trajectories, thereby greatly improving statistics. The experimental test of the fluctuation theorem is shown in Fig. 2, where the average $\langle e^{-R}\rangle$ is plotted as a function of the length t of the trajectories, which is in agreement with the theoretical expectation (2).

Probability distribution.—Insight into the statistical properties is gained by looking directly at the probability distribution $P(R)$ of the quantity R. For the calculation of this distribution, it is convenient to introduce the joint probability $\rho_n \equiv \rho_n(R, \tau)$, which is the probability of the system to be in state n at time τ and to have accumulated an amount R up to this time. Starting from the master equation (1), the time evolution of ρ_n is then governed by the differential Chapman-Kolmogorov equation [23–25]

$$\frac{\partial \rho_n}{\partial \tau} = \sum_{m=0}^{1} w_{mn}(\tau)\rho_m + \dot{\lambda}\frac{\partial \ln p_n^{s}}{\partial \lambda}\frac{\partial \rho_n}{\partial R}, \tag{10}$$

where $w_{01} = -w_{00} = a(\tau)$ and $w_{10} = -w_{11} = b_0$. Since we start out of a steady state, the initial condition is $\rho_n(R, 0) = p_n^{s}(0)\delta(R)$. In general, Eq. (10) must be solved numerically. The distribution $P(R, \tau)$ can then be obtained by adding the contributions of the final states, $P(R, \tau) = \rho_0(R, \tau) + \rho_1(R, \tau)$.

For sufficiently slow driving, i.e., if the relaxation time t_r is much smaller than the modulation period t_m, the distribution $P(R)$ is a Gaussian [24]. For large t, our experimental results and numerical calculations indicate that $P(R)$ again is a Gaussian (data not shown). In the intermediate regime of short trajectories and fast driving, the distribution $P(R)$ shows distinctly non-Gaussian behavior with a pronounced peak structure, as shown in Fig. 3. Here, we compare experimentally obtained histograms for two different trajectory lengths to the basically exact numerical solution.

The numerically obtained center peak and the four narrow side peaks can be resolved partially by the experimental histograms. These peaks can only be observed for short trajectories, where there are at most a few jumps. The center peak derives from trajectories which do not jump within t. The positions of the other four peaks are at $R = \pm \ln(1 \pm \gamma)$, independent of the driving frequency, which demonstrates that this is not a resonance phenomena. Rather, the explanation is as follows. Independent of the probability density $p(\tau_i)$ to jump at τ_i, the most probable value of a is either near the maximum $a = a_0(1 + \gamma)$ or the minimum $a = a_0(1 - \gamma)$, as can be seen by inverting $p(a)da = p(a(\tau_i))d\tau_i$. For a jump at those values of a, R in Eq. (8) picks up a contribution $\pm \ln(1 \pm \gamma)$ corresponding to the location of the peaks. Therefore, these peaks are a consequence of the discrete nature of the system and the shape of the protocol $\lambda(\tau)$.

Symmetric protocols.—So far, we have discussed the integral variant (2) of the fluctuation theorem which corresponds to the Jarzynski relation in this nonthermal system. For particular protocols, which obey the symmetry relation

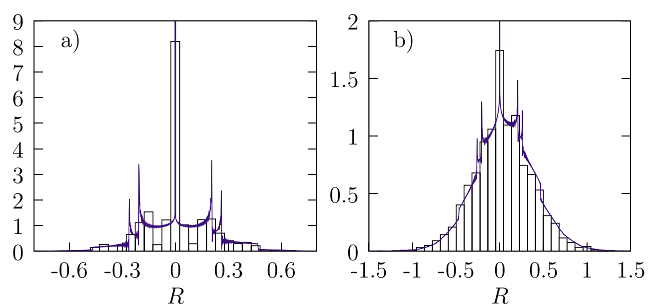

FIG. 3 (color online). Comparison of the numerically calculated probability distribution $P(R)$ with the experimentally obtained normalized histogram at times (a) $\tau = 60$ ms and (b) $\tau = 200$ ms. (In both cases: $a_0^{-1} = 64$ ms, $b_0^{-1} = 30$ ms, $t_m = 20$ ms, and $\gamma = 0.23$.)

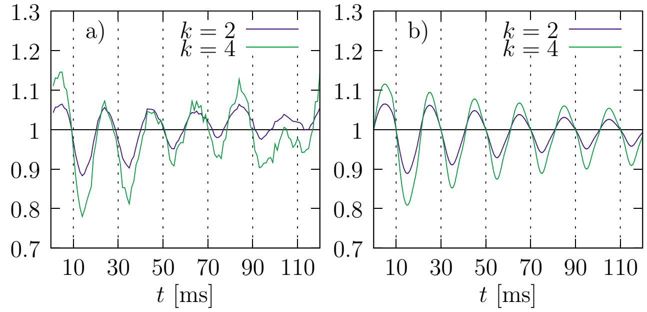

FIG. 4 (color online). Test of the moment relation (13) for the second ($k = 2$) and fourth ($k = 4$) moment. The plots show the ratio $\langle R^k e^{-R}\rangle/\langle R^k\rangle$ over trajectory length t for $t_m = 20$ ms. At the vertical dashed lines the protocol becomes symmetric; see Eq. (11). (a) Experimental data; (b) numerical data. (Parameters are as in Fig. 3.)

$$\tilde{\lambda}(\tau) \equiv \lambda(t - \tau) = \lambda(\tau), \tag{11}$$

adaptions of the arguments developed by Crooks [12] show that then the distribution $P(R)$ obeys even the stronger fluctuation theorem

$$P(-R)/P(R) = e^{-R} \tag{12}$$

also valid in steady states [1–7]. This relation implies, in particular, an intriguing condition on the kth moment

$$\langle R^k e^{-R}\rangle = (-1)^k \langle R^k\rangle. \tag{13}$$

In Fig. 4, we show the ratio between the two sides of this relation as a function of the length t of the trajectory. The theoretically calculated curves show clearly that the moment relation is valid for symmetric protocols, i.e., for $t = lt_m$ where $l = 1/2, 3/2, 5/2, \ldots$. For other values of t the relations (12) and (13) do not hold. The oscillations of the ratio are damped and hence the moment relation will become valid for all t in the limit $t \to \infty$. Even though the experimental data are somewhat noisy, they also illustrate this particular feature of a symmetric protocol which is a consequence of the fluctuation theorem (12).

Concluding perspective.—In summary, we have tested an integral fluctuation theorem (2) for time-dependent driving in a nonthermal environment by using a two-level system. The distributions $P(R)$ are distinctly non-Gaussian, which emphasizes the strong nonlinear character of this system. If the periodic protocol becomes symmetric under time reversal, besides the integral form of the fluctuation theorem the more detailed Gallavotti-Cohen symmetry relation (12) is valid as well. In this sense, symmetric protocols cover an intermediate class between steady states and time-dependent driving. We have verified this symmetry relation numerically and tested it experimentally by checking the corresponding moment relations. While a two-state system may arguably serve as paradigm for the simplest system conceivable for time-dependent driving, studying a simple three-state system will become important in the future as well. Whereas in two-state systems for constant rates detailed balance is necessarily fulfilled, a three-state system could sustain a steady state at constant driving which violates detailed balance. Ramifications of the fluctuation theorems depending on this aspect would then become accessible to experimental scrutiny.

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