Probability distribution of work done on a two-level system during a nonequilibrium isothermal process

Petr Chvosta*
Department of Macromolecular Physics, Faculty of Mathematics and Physics, Charles University, V Holešovičkách 2, CZ-180 00 Praha, Czech Republic

Peter Reineker and Michael Schulz
Abteilung Theoretische Physik, Universität Ulm, Albert-Einstein-Allee 11, 89069 Ulm, Germany
(Received 5 October 2006; revised manuscript received 20 March 2007; published 30 April 2007)

We present an exact calculation of the probability density for the work done by an external agent on a two-level system. Due to the external drive, both the transition rates between the two states and their energies depend on time. Within this setting we calculate the probability of every possible sample path of the system evolution and also the work done along any such path. The general procedure yields an evolution equation for the characteristic function of the work. Assuming that the energies change with constant rates, the properties of the work distribution are controlled by a single parameter representing the ratio of the time scales of the driving protocol, and of the internal dynamics, respectively. We calculate the mean work and characterize those sample paths which are not in agreement with the second law. In the slow driving limit, the probability density for the work collapses to a delta function localized at the reversible work. In the strongly nonequilibrium regime, the most probable work is smaller and the mean work is bigger than the reversible work.

DOI: 10.1103/PhysRevE.75.041124 PACS number(s): 02.50.Ey

I. INTRODUCTION

The work needed to change the state of a small system, such as a single RNA molecule, fluctuates. By repeating many times measurement of the work accomplished during, e.g., the forced unfolding of an RNA molecule [1,2], one arrives at a definite histogram, or distribution. The distribution depends on how the system is driven, but it contains important information concerning the system itself. In order to understand this information, the exact theoretical calculation of the work distribution would be of considerable importance [3].

From a formal point of view, there are two difficulties in carrying out such an exact analysis. The first is that the evolution equations have to reflect the prescribed driving protocol. Differently speaking, one has to cope with, e.g., the diffusion equation with a time-dependent potential [4–6], or the rate equation with time-dependent rates [7,8]. Time-dependent potentials play a central role in the phenomenon of stochastic resonance [9], and in the physics of Brownian motors [10]. Due to an active research within these two domains, both the exact solutions of the underlying dynamical equations and the emerging effects are fairly well understood. But even the exact knowledge of the one-time characteristics of the dynamics is insufficient to analyze the work distribution. Actually, the second difficulty arises from the observation that the work is a *functional* of the underlying evolution process. The work done on the system during a time interval, say $[t_0,t]$, depends on the whole history of the system evolution within this interval.

The present paper concentrates on the two problems above in the simplest possible model, when the system being driven is a two-state system. The external agent does the work on the system by changing the energies of the two states. The driving protocol is specified by prescribing the detailed time dependence of the energy levels. Given the driving protocol, our primary objective is the explicit formula for the probability density $\rho(w,t)$ defined as

$$\rho(w,t)dw = \mathrm{Prob}\{W(t) \in (w,w+dw)\}. \tag{1}$$

Here $W(t)$ is the fluctuating work done on the system during the time interval $[t_0,t]$ (its precise definition will be given at the beginning of Sec. III). Notice that the knowledge of the probability density provides complete information about the random variable $W(t)$. In particular, the mean work $\langle W(t)\rangle$ can be calculated by a single integration. A similar single integration yields also the mean value $\langle \exp[-\beta W(t)]\rangle$, where $\beta=1/(k_BT)$. In 1997 Jarzynski discovered an identity [11,12] which relates the last average and the Helmholtz free energy of the system. More precisely, the Jarzynski identity enables one to specify the free energy difference between two equilibrium states by fixing the driving protocol, repeating a real time (i.e., nonequilibrium) experiment, and measuring the work done during each repetition. The identity has been recently experimentally tested [2].

But besides providing various mean values, the density (1) answers also the following question. What is the common weight of those experiments, during which the measured work does not exceed the reversible work? Finally, from a somewhat different viewpoint, the exact density for the work represents a missing benchmark for the simulation approaches [13,14], and approximative treatments [15].

II. INTERNAL DYNAMICS WITH TIME-DEPENDENT RATES

A conventional two-state Markov *chain* [16] is defined as a special sequence of the random variables $\{D(n)\}_{n=0}^{\infty}$. Each

*Electronic address: chvosta@kmf.troja.mff.cuni.cz

of them can only assume two fixed values, say $d_1=1$ and $d_2=-1$. A Markov chain is fully described by the following two ingredients. First, one has to define the "initial condition," i.e., the probabilities $p_j(0)=\mathrm{Prob}\{D(0)=d_j\}$, $j=1,2$. It will be convenient to arrange this distribution in a two-dimensional column vector $|p(0)\rangle$. Here and below, we use the bracket notation to make the algebraic operations more transparent. For example, we write $p_j(0)=\langle j|p(0)\rangle$. Secondly, we have to prescribe the one-step transition probabilities, i.e., the conditional probabilities that the random variable $D(n)$ assumes the value d_i provided that the "previous" random variable $D(n-1)$ has assumed the value d_j,

$$k_{ij}(n)=\mathrm{Prob}\{D(n)=d_i|D(n-1)=d_j\}, \tag{2}$$

$$i,j=1,2, \quad n=1,2,\ldots .$$

We again arrange them into the square matrix $\mathcal{K}(n)$, i.e., $k_{ij}(n)=\langle i|\mathcal{K}(n)|j\rangle$. Our designation emphasizes a point which will be very important in the following. Namely, the transition probabilities will generally vary with the discrete-time variable n. The specific form of this dependence will reflect the externally controlled time-dependent conditions, i.e., the "driving protocol" of the process. Otherwise, as usual, the matrix elements in a column of a given matrix $\mathcal{K}(n)$ are nonnegative real numbers and they add to unity. Therefore the most general form of the matrix $\mathcal{K}(n)$ will be specified by the two numbers $a(n)=k_{21}(n)$, $b(n)=k_{12}(n)$ from the interval $[0,1]$. Due to the Markov property of the chain, the distribution of the nth variable $D(n)$ can be calculated by the simple matrix multiplication

$$\mathrm{Prob}\{D(n)=d_i|D(0)=d_j\}=\langle i|\mathcal{K}(n)\mathcal{K}(n-1)\cdots\mathcal{K}(2)\mathcal{K}(1)|j\rangle. \tag{3}$$

A continuous-time Markov *process* emerges if we generate the Markov-chain transitions at the so-called Poisson points [17,18]. We shall call them *attempt times*. More precisely, the possibility of a jump between two Markov-chain states arises just at the random times $0\leqslant t_1<t_2<\cdots$, where the intervals between the neighboring attempt times (t_n-t_{n-1}), $n=1,2,\ldots$, are independent and identically distributed random variables, their generic probability density being $\phi(t)=\nu\exp(-\nu t)$. Here the parameter $1/\nu$ measures the mean time between two neighboring attempt times. Assume the first attempt time occurs at the time s. At this instant, the transitions are controlled by the transition probabilities (2), which, however, now will be designated $k_{ij}(s)$. Differently speaking, if a Poisson point occurs at a time s, the transitions are controlled by the matrix

$$\mathcal{K}(s)=\mathcal{I}-\begin{pmatrix} a(s) & -b(s) \\ -a(s) & b(s) \end{pmatrix}. \tag{4}$$

Here $\mathcal{I}$ is the unity matrix. The functions $a(s)=k_{21}(s)$ and $b(s)=k_{12}(t)$ together with the attempt frequency ν provide the complete specification of the arising time-continuous Markov process; we designate it simply as $D(t)$. If the functions $a(t)$, $b(t)$ are time independent, we end up with the standard (asymmetric) dichotomous process [19]. On the other hand, their time variation introduces a subtle interplay between a typical interattempt time, as measured by the mean frequency ν, and the time scale (scales) which controls (control) the external driving.

The above construction allows for a transparent description of all possible sample paths (trajectories) of the process $D(t)$. We designate by

$$\mathcal{P}(t,n;j_n,j_{n-1},\ldots,j_0;t_n,t_{n-1},\ldots,t_1)\prod_{k=1}^{n}dt_k, \tag{5}$$

the probability of a fixed n-attempt sample path defined in the interval $[0;t]$ which runs as follows. It starts at time $t_0=0$ in the state d_{j_0}. The first attempt time occurs in the time interval (t_1,t_1+dt_1). At this time, there occurs the transition to the state d_{j_1} (if $j_1=j_0$, there is no jump and the sample path remains in the state d_{j_0}). A similar description holds for the attempts which are generated in the infinitesimal vicinity of the times $t_2,\ldots,t_n$. Finally, after the time t_n, the sample path resides in the state d_{j_n} up to the time t. The probability for the specific sample path just described reads

$$\mathcal{P}(t,n;j_n,\ldots,j_0;t_n,\ldots,t_1)\prod_{k=1}^{n}dt_k$$
$$=f(t-t_n)\prod_{k=1}^{n}[k_{j_kj_{k-1}}(t_k)\phi(t_k-t_{k-1})dt_k]p_{j_0}(0). \tag{6}$$

The function $f(t-t_n)=1-\int_0^{t-t_n}\phi(t')dt'$ accounts for the probability of there being no further attempt after the last attempt time t_n and before the final time t. In the case of $n=0$ the products are empty and $\mathcal{P}(t,0;j_0)=f(t)p_{j_0}(0)$. The last factor $p_{j_0}(0)$ takes into account the probability of the initial state d_{j_0}.

The probabilities (6) of the sample paths add up to one provided we carry out the three following steps. First, we fix the number of the attempt points n and we sum over all possible successions of $(n+1)$ states $d_0,\ldots,d_n$. Second, we integrate over any possible position of the n attempt times. Finally, we sum over any possible number of attempt times. We now show how these three operations yield also the dynamical law for the occupation probabilities. We start by introducing the evolution operator $\mathcal{R}(t)$ with the matrix elements

$$\langle i|\mathcal{R}(t)|j\rangle=\mathrm{Prob}\{D(t)=d_i|D(0)=d_j\}. \tag{7}$$

Let us now fix the final state d_i and the initial state d_j: In order to calculate the matrix element (7), we must sum the probabilities of all paths which connect the state d_j at the time $t_0=0$ with the state d_i at the time t. Hence we need to evaluate the expression

$$\langle i|\mathcal{R}(t)|j\rangle = \sum_{n=0}^{\infty} \int_0^t dt_n \cdots \int_0^{t_2} dt_1 \sum_{j_{n-1}=1}^{2} \times \cdots \sum_{j_1=1}^{2} \mathcal{P}(t,n;i,j_{n-1},\ldots,j_1,j;t_n,\ldots,t_1), \quad (8)$$

with $p_j(0)=1$. We insert here the explicit form of the sample-paths probabilities (6). The summation over the intermediate states $d_{j_1},\ldots,d_{j_{n-1}}$ can be included in the multiplication of the matrices (4). Of course, this reasoning is valid for any fixed pair of the initial and final states. Hence we focus directly on the whole evolution operator $\mathcal{R}(t)$. Invoking the matrix multiplication mentioned, we get the expression

$$\mathcal{R}(t) = f(t)\mathcal{I} + \sum_{n=1}^{\infty} \int_0^t dt_n \cdots \int_0^{t_2} dt_1 f(t-t_n)\mathcal{K}(t_n) \times \phi(t_n - t_{n-1})\mathcal{K}(t_{n-1}) \cdots \phi(t_2 - t_1)\mathcal{K}(t_1)\phi(t_1), \quad (9)$$

where again $t_0=0$. Before we proceed, one important remark is in order. Up to this point, our reasoning was valid for an arbitrary density $\phi(t)$ which describes the random interval between the two neighboring attempt times. The underlying random-point process could have been a general renewal process [16,17]. However, the resulting noise $D(t)$ will be Markovian *if and only if* the density $\phi(t)$ is exponential [17]. If not stated otherwise, we shall always keep this choice, and hence we always take $\phi(t)=\nu\exp(-\nu t)$, and therefore $f(t)=\exp(-\nu t)$.

We introduce these specific functions into Eq. (9) and we carry out the time derivative. Note that the final time t is in the upper limit of the outermost integrals, but via $f(t-t_n)$ it is also present in the expressions being integrated. Collecting the arising terms, we obtain the dynamical equation

$$\frac{d}{dt}\mathcal{R}(t) = -\begin{pmatrix} \alpha(t) & -\beta(t) \\ -\alpha(t) & \beta(t) \end{pmatrix}\mathcal{R}(t), \quad (10)$$

with the transition rates $\alpha(t)=\nu a(t)$, $\beta(t)=\nu b(t)$, and with the initial condition $\mathcal{R}(0)=\mathcal{I}$. Differently speaking, the two functions $a(t),b(t)$, which have entered our construction as the *transition probabilities* for the Markov chain, cf. Eq. (4), now control the time-dependent *transition rates* for the resulting time-inhomogeneous Markov process. The solution of the master equation above reads [8]

$$\mathcal{R}(t) = \mathcal{I} - \frac{1}{2}\begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}\left\{1 - \exp\left[-\int_0^t dt'\,\gamma_+(t')\right]\right\} + \frac{1}{2}\begin{pmatrix} -1 & -1 \\ 1 & 1 \end{pmatrix}\int_0^t dt' \exp\left[-\int_{t'}^t dt''\,\gamma_+(t'')\right]\gamma_-(t'), \quad (11)$$

where $\gamma_\pm(t)=\alpha(t)\pm\beta(t)$. The fulfillment of the initial condition $\mathcal{R}(0)=\mathcal{I}$ dictated by Eq. (9), is obvious. The validity of the Chapmann-Kolmogorov equation can be checked by direct matrix multiplication.

Turning around the reasoning used in the present section, any Markov process with time-dependent rates can be *decomposed* into a Markov chain, which controls the transitions between the Markov-chain states, and Poisson process, which controls the localization of the instants at which the transitions can occur. It is just this reversed view which enables us to calculate certain functionals of the process $D(t)$.

III. EVOLUTION EQUATION CONTROLLING THE CHARACTERISTIC FUNCTION FOR THE WORK

We have described all possible paths of the system evolution. For an arbitrary but fixed sample path, Eq. (6) gives the probability of its realization. We now concentrate on the work done by the external agent along one path. The work is done by changing the energies of the system states while the occupation probabilities of the states remain fixed. Let as designate by $E_i(t)$, $i=1,2$ the time-dependent energies of the two-level system. Assume these two functions are known. If the system resides during the time interval $[t',t]$, $t\geqslant t'$, in the ith state, the work done by the external agent during this time interval is simply $E_i(t)-E_i(t')$. Expanding this reasoning, the work done on the system along the path described in the paragraph before Eq. (6) reads

$$\mathcal{W}(t,n;j_n,\ldots,j_0;t_n,\ldots,t_1) = [E_{j_n}(t) - E_{j_n}(t_n)] + \sum_{k=1}^{n} [E_{j_{k-1}}(t_k) - E_{j_{k-1}}(t_{k-1})]. \quad (12)$$

We are now in possession of the two ingredients needed to perform the averaging over the sample paths. Symbolically, during any such averaging procedure, we follow the standard prescription as follows:

$$\langle \Phi(\text{path})\rangle = \sum_{\text{all sample paths}} (\text{probability for a fixed sample path}) \times (\text{value of the function } \Phi, \text{ which is being averaged, for this sample path}). \quad (13)$$

In the following, the function to be averaged is the exponential $\exp[-uW(t)]$, where u is an arbitrary complex number, and $W(t)$ denotes the random work done by the external agent. With this choice, the summation over all possible sequences of the Markov-chain states can still be represented as a matrix multiplication. But more important, the inverse Laplace transform [20] of the path-averaged exponential function $\exp[-uW(t)]$ leads directly to the probability density for the random variable $W(t)$.

Guided by these remarks, we focus on the average

$$\langle \exp[-uW(t)] \rangle = \sum_{n=0}^{\infty} \int_0^t dt_n \cdots \int_0^{t_2} dt_1 \sum_{j_n=1}^{2} \cdots \sum_{j_0=1}^{2} \mathcal{P}(t,n;j_n,\ldots,j_0;t_n,\ldots,t_1) \times \exp[-u\mathcal{W}(t,n;j_n,\ldots,j_0;t_n,\ldots,t_1)], \quad (14)$$

and we insert the explicit expressions (6) for the sample-path probabilities, and Eq. (12) for the work related with the paths. Moreover, we can treat separately the four subgroups of all sample paths which arise by fixing the initial and the final state of the underlying Markov chain. An appropriate ordering of the terms in Eq. (14) brings us to the following observations. First of all, the conditional average within the subgroup (i,j) of those sample paths which start in the state d_j at the time $t_0=0$ and are found in the state d_i at the final time t can be written as the matrix element

$$\langle \exp[-uW(t)] \rangle_{(i,j)} = \langle i|\mathcal{G}(u,t)|j\rangle. \quad (15)$$

Secondly, the matrix $\mathcal{G}(u,t)$ assumes the form of an infinite series $\mathcal{G}(u,t)=\Sigma_{n=0}^{\infty}\mathcal{G}_n(u,t)$, where the individual terms in the sum represent the conditional average, the condition being the fixed number of the attempt times n. The terms are

$$\mathcal{G}_0(u,t) = \mathcal{E}(u,t)[f(t)]\mathcal{E}^{-1}(u,0),$$

$$\mathcal{G}_1(u,t) = \mathcal{E}(u,t)\left[\int_0^t dt_1 f(t-t_1)\mathcal{L}(u,t_1)\phi(t_1)\right]\mathcal{E}^{-1}(u,0),$$

$$\mathcal{G}_2(u,t) = \mathcal{E}(u,t)\left[\int_0^t dt_2 \int_0^{t_2} dt_1 f(t-t_2)\mathcal{L}(u,t_2) \times \phi(t_2-t_1)\mathcal{L}(u,t_1)\phi(t_1)\right]\mathcal{E}^{-1}(u,0),$$

$$\ldots. \quad (16)$$

Here we have introduced the matrixes

$$\mathcal{E}(u,t) = \begin{pmatrix} \exp[-uE_1(t)] & 0 \\ 0 & \exp[-uE_2(t)] \end{pmatrix}, \quad (17)$$

$$\mathcal{L}(u,t) = \mathcal{E}^{-1}(u,t)\mathcal{K}(t)\mathcal{E}(u,t).$$

A direct calculation of the matrix $\mathcal{G}(u,t)$ would be extremely cumbersome. However, we can try to derive and solve the equation of motion for this matrix. We perform the time derivative of the individual matrixes $\mathcal{G}_n(u,t)$ and collect the arising terms. Assuming again $\phi(t)=\nu\exp(-\nu t)$, $f(t)=\exp(-\nu t)$, the resulting dynamical equation reads

$$\frac{d}{dt}\mathcal{G}(u,t) = -\left\{ u\begin{pmatrix} \left[\frac{dE_1(t)}{dt}\right] & 0 \\ 0 & \left[\frac{dE_2(t)}{dt}\right] \end{pmatrix} + \nu\begin{pmatrix} a(t) & -b(t) \\ -a(t) & b(t) \end{pmatrix}\right\}\mathcal{G}(u,t), \quad (18)$$

$$\mathcal{G}(u,0) = \mathcal{I}.$$

If $|p(0)\rangle$ is an arbitrary initial condition for the process $D(t)$, then the probability density $\rho(w,t)$ for the random variable $W(t)$ will be given by the inverse Laplace transformation (with respect to the variable u) of the function $\rho(u,t)=\langle +|\mathcal{G}(u,t)|p(0)\rangle$. Here the left multiplication by the row vector $\langle +|=\langle 1|+\langle 2|$ mediates the summation over both final states of the paths.

Let us briefly comment on the convergence properties of the above expansion $\mathcal{G}(u,t)=\Sigma_{n=0}^{\infty}\mathcal{G}_n(u,t)$. Formally, the solution of Eq. (18) can be written as a time-ordered exponential. As a matter of fact, the above steps are nothing but a probabilistic construction of a special Dyson expansion of this time-ordered exponential. Using an operator norm, e.g., the norm $\|\mathcal{A}\|=\Sigma_{i=1}^{2}\Sigma_{j=1}^{2}|a_{ij}|$, the operator in the curly brackets on the right-hand side of Eq. (18) is bounded for any finite t and any finite $|u|$. This guarantees the convergence of the series $\Sigma_{n=0}^{\infty}\mathcal{G}_n(u,t)$ in the norm. Therefore its sum $\mathcal{G}(u,t)$ exists and it can be derived term by term.

The system of equations (18) has been already noted in the literature [14,21,22]. In these papers, the authors first characterize the possible changes of the joint probability densities $g_{ij}(w,t)=\langle i|\mathcal{G}(w,t)|j\rangle$ for the infinitesimal increments of the variables w and t. The derivation is then straightforward and concise. On the other hand, as noted above, our procedure rests on the explicit construction of all possible sample paths of the system evolution and on the evaluation of the work done along any such path. As such it indicates, at least in principle, which families of the trajectories are decisive in yielding, e.g., the tails of the resulting probability density $\rho(w,t)$.

The explicit solution of Eq. (18) will be given in the next section. Before, several immediate consequences will be derived. First of all, we note that putting $u=0$ in Eq. (18) gives $\mathcal{G}(0,t)=\mathcal{R}(t)$, where the matrix $\mathcal{R}(t)$ controls the occupation probabilities for the levels, cf. its explicit form (11). This observation follows also from a comparison of Eqs. (8) and (14). Since the occupation probabilities sum to one, we have

$\rho(u=0,t)=1$. Therefore the density $\rho(w,t)$ is properly normalized. A similar reasoning holds for the direct calculation of the *mean* work. If we are able to solve Eq. (18) up to the first order in the variable u, we can use the identity

$$w_{\mathrm{mean}}(t)=\langle W(t)\rangle=-\left.\frac{\partial}{\partial u}\langle\exp[-uW(t)]\rangle\right|_{u=0}$$
$$=-\frac{\partial}{\partial u}\langle+|\mathcal{G}(u,t)|p(0)\rangle|_{u=0}, \quad (19)$$

and similarly for the higher-order moments of the random variable $W(t)$.

Let us now check the solution in simple limiting cases. First, assume the energies $E_i(t)$, $i=1,2$, are time independent. Then Eq. (18) again reduces to Eq. (10) and consequently $\rho(u,t)=1$ for any u and t. The inverse Laplace transformation with respect to the variable u gives $\rho(w,t)=\delta(w)$. For any time t, the work is zero with the probability one. Secondly, consider the limit $\nu\to 0$. If there are no attempt points at all, the work depends only on the initial conditions and on the driving schedule. It is $[E_1(t)-E_1(0)]$ with the probability $p_1(0)$, and $[E_2(t)-E_2(0)]$ with the probability $p_2(0)$. This conclusion follows directly from Eq. (18) if we insert $\nu=0$.

A less elementary consequence of Eq. (18) is the following one. The exact function $\rho(w,t)$ will always include a singular part, describing the conditional work originating from the sample paths of the process $D(t)$ without any jumps. These trajectories yield again the work $[E_1(t)-E_1(0)]$ or $[E_2(t)-E_2(0)]$, but their common weight decreases with the time. The specific form of the decrease is dictated by the driving schedule. It is obtained if we consider only the diagonal part of the matrix in the curly brackets on the right-hand side of Eq. (18). We solve the system modified in this way and perform the inverse Laplace transformation. The singular part of the density assumes the form

$$\rho_s(w,t)=p_1(0)\exp\left[-\nu\int_0^t dt' a(t')\right]\delta(w-[E_1(t)-E_1(0)])$$
$$+p_2(0)\exp\left[-\nu\int_0^t dt' b(t')\right]\delta(w-[E_2(t)-E_2(0)]). \quad (20)$$

Since the functions $a(t),b(t)$ are non-negative, the weights of the delta functions always decrease with time. In the long-time limit they either vanish or remain finite, depending on whether the integrals in the respective exponents diverge or converge to positive nonzero constants. In the latter case the transitions between the two levels are effectively eliminated by a rapid damping of the functions $a(t)$ and/or $b(t)$. Differently speaking, in the long-time regime, the model behaves as if the jumping frequency ν were zero. But before this regime is settled, some trajectories succeeded to realize one or more jumps. These trajectories contribute to the nonsingular part of the density $\rho(w,t)$. Hence they weaken the weights of the delta functions in the singular part (20).

Before closing the section we wish to add some comments concerning the Jarzynski equality [2,11,12]. It is usually stated in the form $\langle\exp[-\beta W(t)]\rangle=\exp[-\beta(F_f-F_i)]$, where $F_f(F_i)$ is the Helmholtz free energy which corresponds to the final (initial) equilibrium state. The fixed energies which define the properties of the initial and final equilibrium states are equal to the driven energies $E_i(t)$, $i=1,2$, at the initial time $t_0=0$ (for the initial equilibrium state), and at the final time t (for the final equilibrium state). The initial state for the nonequilibrium evolution is the equilibrium state defined by the initial values $E_i(t_0)$, $i=1,2$. Within our scheme, after explicitly calculating the two free energies required, the Jarzynski relation assumes the form

$$\langle+|\mathcal{G}(\beta,t)|\pi(0)\rangle=\frac{\exp[-\beta E_1(t)]+\exp[-\beta E_2(t)]}{\exp[-\beta E_1(0)]+\exp[-\beta E_2(0)]}. \quad (21)$$

In this equation, $|\pi(0)\rangle$ denotes the equilibrium state corresponding to the energies $E_i(0)$, $i=1,2$. It can be written in the form $|\pi(0)\rangle=\mathcal{E}(\beta,0)|+\rangle/Z_i$, where $Z_i=\exp[-\beta E_1(0)]+\exp[-\beta E_2(0)]$ is the partition function for the initial equilibrium state. Therefore, we have to prove the relation $\langle+|\mathcal{G}(\beta,t)\mathcal{E}(\beta,0)|+\rangle=\langle+|\mathcal{E}(\beta,t)|+\rangle$.

In the following proof, we assume an arbitrary, possibly nonexponential form of the density $\phi(t)$. We first notice that every term (16) in the n expansion of the operator $\mathcal{G}(\beta,t)$ ends with the matrix $\mathcal{E}^{-1}(\beta,0)$. Hence we should focus on the column vector $\mathcal{L}(\beta,t)|+\rangle$. A short analysis, using $\langle+|=\langle 1|+\langle 2|$ and the definitions (17), reveals that the vector $\mathcal{L}(\beta,t)|+\rangle$ reduces to $\langle+|$ if and only if the functions $a(t)$ and $b(t)$ (which were up to now arbitrary) are coupled with the driving protocol. More precisely, we arrive at the equivalence of two equations

$$\mathcal{L}(\beta,t)|+\rangle=|+\rangle\Leftrightarrow a(t)\exp[-\beta E_1(t)]=b(t)\exp[-\beta E_2(t)]. \quad (22)$$

The condition on the right-hand side of the equivalence is of course the well known detailed-balance condition. The equivalence is valid for any energy protocols $E_i(t)$, $i=1,2$. Therefore, if and only if the detailed-balance condition holds, we can write

$$\mathcal{G}(\beta,t)\mathcal{E}(\beta,0)|+\rangle=\mathcal{E}(\beta,t)|+\rangle\left\{f(t)+\int_0^t dt_1 f(t-t_1)\phi(t_1)\right.$$
$$+\int_0^t dt_2\int_0^{t_2} dt_1 f(t-t_2)\phi(t_2-t_1)\phi(t_1)$$
$$\left.+\cdots\right\}. \quad (23)$$

Finally, using the Laplace transformation, we can sum up the series in the curly brackets. The sums equal unity. This concludes the proof of Jarzynski's relation within our two-level setting.

The assertion that the curly bracketed expression in Eq. (23) is equal to one holds true not only for the Poisson renewal process. It is valid for any renewal [17]. Similarly, the n expansion of the operator $\mathcal{G}(u,t)$, which has been used in the proof, is valid for an arbitrary renewal. We thus have an interesting example of a non-Markovian time-inhomogeneous process for which Jarzynski's relation still keeps its validity.

IV. EXPLICIT FORM OF THE PROBABILITY DENSITY FOR THE WORK

Any application of the above scheme requires two specifications. First, we must prescribe the dynamical laws $E_i(t)$, $i=1,2$, which define, through Eq. (12), the work done along a given sample path. Second, we need the explicit forms of the functions $a(t),b(t)$ in the rate equation (10). For the first requirement the simplest nontrivial choice would be a linear time dependence of the energy levels. Therefore, in this section, we take $E_1(t)=\varepsilon\omega t$, and $E_2(t)=0$. The energies are equal at the beginning and we assume that the system is initially in equilibrium, i.e., $p_1(0)=p_2(0)=\frac{1}{2}$. Afterwards, due to the external drive, the energy difference increases linearly, reaching the value ε in the time $1/\omega$. We shall call the velocity of the energy change $\varepsilon\omega$ as the driving rate. For the second requirement we assume the validity of the detailed-balance condition and hence only one of the functions $a(t),b(t)$ will be independent. We choose $a(t)=1$, i.e., $b(t)=\exp(-\beta\varepsilon\omega t)$. Differently speaking, the rate for the transitions $(1\to 2)$ is constant and equals the attempt frequency ν, whereas the rate for the opposite transitions $(2\to 1)$ decreases as $\nu\exp(-\beta\varepsilon\omega t)$. In the long time limit, the first state will be depleted and all sample paths will end up in the second state. The work can be done only before the stationary regime is established.

Our specifications suggest a natural choice for the dimensionless time variable $\tau=\beta\varepsilon\omega t$, and for the dimensionless work $\eta=\beta w$. Hence η is simply the work counted in the units k_BT. Performing the direct Laplace transformation in η, the conjugate variable will be denoted as s, i.e., $s=u/\beta$. Similarly, τ will be conjugate to z. Using the new variables, Eq. (18) assumes the form

$$\frac{d}{d\tau}\tilde{\mathcal{G}}(s,\tau)=-\begin{pmatrix} s+\alpha & -\alpha e^{-\tau} \\ -\alpha & \alpha e^{-\tau} \end{pmatrix}\tilde{\mathcal{G}}(s,\tau). \tag{24}$$

The equation includes a single control parameter, $\alpha=\nu/(\beta\varepsilon\omega)$. Therefore $1/\alpha$ is the driving rate $\varepsilon\omega$ reduced to the value of the attempt frequency multiplied by k_BT.

We now restrict ourselves to the main steps in the solution of the system (24), emphasizing the points which might be useful in dealing with more complicated settings. First we denote the unknown matrix elements as $\tilde{g}_{ij}(s,\tau)$, $i,j=1,2$, and we note that we have in fact two independent pairs of two coupled equations. The second pair represents two coupled differential equations for the functions $\tilde{g}_{22}(s,\tau)$ and $\tilde{g}_{12}(s,\tau)$, similarly for the first pair. Now instead of trying to solve the coupled systems, we first perform the *direct* Laplace transformation in the time variable τ. Hence, e.g., the product $e^{-\tau}\tilde{g}_{22}(s,\tau)$ will be transformed as $\tilde{g}_{22}(s,z+1)$. Notice that we are using the same letter for a function and for its Laplace transformation. Of course, the two functions are completely different and we distinguish them by quoting always the variables.

We thus obtain two coupled pairs of *difference* equations for the functions $\tilde{g}_{ij}(s,z)$, $i,j=1,2$ and consider only the second pair. Eliminating the function $\tilde{g}_{22}(s,z)$, the resulting difference equation for the function $\tilde{g}_{12}(s,z)$ reads

$$\tilde{g}_{12}(s,z)+\alpha\frac{1}{z+1}\frac{s+z+1}{s+z+\alpha}\tilde{g}_{12}(s,z+1)=\alpha\frac{1}{z+1}\frac{1}{s+z+\alpha}. \tag{25}$$

We now make the substitution $z\to(z+1)$ and obtain a similar equation which couples $\tilde{g}_{12}(s,z+1)$ with $\tilde{g}_{12}(s,z+2)$. Continuing in this way, we finally obtain an infinite system of linear algebraic equations for the unknown functions $\tilde{g}_{12}(s,z+n)$, $n=0,1,2,\ldots$. The matrix which describes the system has nonzero matrix elements only on the main diagonal and just above the main diagonal. The system can be solved using standard algebraic methods. The first unknown function reads

$$\frac{1}{\alpha}\tilde{g}_{12}(s,z)=\sum_{n=0}^{\infty}(-\alpha)^n e_n(z+1)r_n(s+z+\alpha;1-\alpha). \tag{26}$$

Here $e_n(z)=1/(z)_{n+1}$, $r_n(s;\gamma)=(s+\gamma)_n/(s)_{n+1}$, and $(z)_n=z(z+1)(z+2)\cdots(z+n-1)$ is Pochhammer's symbol [23]. Notice that the functions $e_n(z+1)$ contain only the Laplace variable z and the functions $r_n(s+z+\alpha;1-\alpha)$ depend only on the combination $(s+z+\alpha)$. Therefore the inverse Laplace transformation of the functions $r_n(s+z+\alpha;1-\alpha)$ with respect to the variable s will be $\exp[-\eta(z+\alpha)]r_n(\eta;1-\alpha)$. Afterwards, there remains the inverse Laplace transform of the expression $\exp(-z\eta)e_n(z+1)$ with respect to the complex variable z. The factor $\exp(-z\eta)$ induces the shift $\tau\to(\tau-\eta)$ in the τ original, i.e., we get $\exp[-(\tau-\eta)]e_n(\tau-\eta)$. Summarizing these considerations the double inverse transformation of the expression on the right-hand side of Eq. (26) yields

$$\frac{1}{\alpha}\tilde{g}_{12}(\eta,\tau)=e^{-\alpha\eta}e^{-(\tau-\eta)}\sum_{n=0}^{\infty}(-\alpha)^n e_n(\tau-\eta)r_n(\eta;1-\alpha). \tag{27}$$

In order to make this expression explicit, we must invert the functions $e_n(z)$ and $r_n(s;\gamma)$. We decompose them into partial fractions and obtain

$$e_n(\tau)=\Theta(\tau)\frac{1}{n!}(1-e^{-\tau})^n, \tag{28}$$

$$r_n(\eta;\gamma)=\Theta(\eta)\sum_{k=0}^{n}\frac{(-e^{-\eta})^k}{k!}\frac{(\gamma-k)_n}{(n-k)!}.$$

Here $\Theta(x)$ is the unit-step function; its derivative produces the Dirac functions in the final expressions (30) and (31).

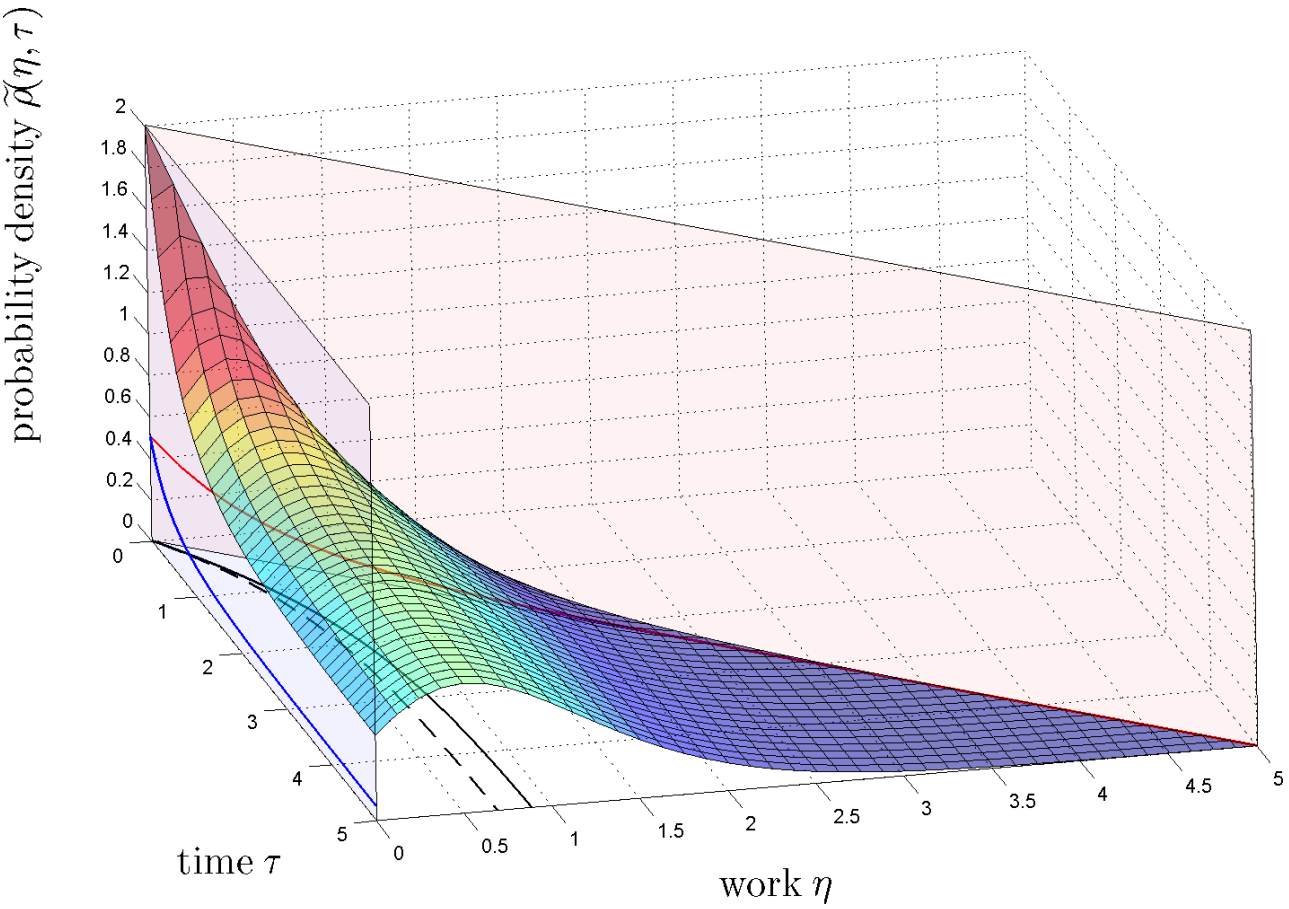

FIG. 1. (Color online) The reduced probability density for the work $\tilde{\rho}(\eta,\tau)$ as a function of the reduced work variable η and the reduced time variable τ. All three quantities are dimensionless and the relations with their physical counterparts are given in the main text. The reduced driving rate has been set to $1/\alpha=\beta\varepsilon\omega/\nu=1/2$. We have plotted one half of the sum of the functions (30)–(33). For any fixed time τ, the density vanishes outside the interval $[0,\tau]$. The curves in the planes $\eta=0$ and $\eta=\tau$, perpendicular to the base plane, depict the weights of the singular parts on the borders of the support. In the base plane, the full line represents the reduced mean work $\tilde{w}_{\mathrm{mean}}(\tau)$, and the broken curve is the reduced reversible work $\tilde{w}_{\mathrm{rev}}(\tau)$.

Hence we have succeeded in carrying out the two inverse Laplace transformations. The result is a double power series in the variables $e^{-\eta}$ and $(1-e^{-\tau})$. The very last step consists in transforming the series into a more transparent form. Here we have used Vandermonde's convolution theorem [23] and the summation theorem for Kummer's confluent hypergeometric function [24]. It turns out that the double sum can be transformed into the product of two infinite power series in more complicated variables. More specifically, we have derived the identity

$$\sum_{n=0}^{\infty}\frac{[-\alpha(1-e^{-(\tau-\eta)})]^n}{n!}\sum_{k=0}^{n}\frac{(-e^{-\eta})^k}{k!}\frac{(1-\alpha-k)_n}{(n-k)!}$$
$$=e^{-\alpha[1-e^{-(\tau-\eta)}]}{}_1F_1(\alpha;1;\alpha(1-e^{-\eta})[1-e^{-(\tau-\eta)}]). \quad (29)$$

Here ${}_1F_1(\alpha;\beta;x)$ is Kummer's confluent hypergeometric function [24]. Notice that its argument in Eq. (29) vanishes both for $\eta=0$ and for $\eta=\tau$ and hence, at these points, Kummer's function equals unity.

We have given a series of arguments which yield finally the expression (32) below. The other matrix elements can be treated in a similar manner. We skip here a considerable amount of purely computational steps and we write down the final result

$$\tilde{g}_{11}(\eta,\tau)=\delta(\tau-\eta)e^{-\alpha\tau}+\alpha^2\Theta(\eta)\Theta(\tau-\eta)e^{-\alpha\eta}$$
$$\times\exp\{-\alpha[1-e^{-(\tau-\eta)}]\}(1-e^{-\eta})e^{-(\tau-\eta)}$$
$$\times{}_1F_1(\alpha+1;2;h(\eta,\tau)), \quad (30)$$

$$\tilde{g}_{22}(\eta,\tau)=\delta(\eta)\exp[-\alpha(1-e^{-\tau})]+\alpha^2\Theta(\eta)\Theta(\tau-\eta)e^{-\alpha\eta}$$
$$\times\exp\{-\alpha[1-e^{-(\tau-\eta)}]\}[1-e^{-(\tau-\eta)}]$$
$$\times{}_1F_1(\alpha+1;2;h(\eta,\tau)), \quad (31)$$

$$\tilde{g}_{12}(\eta,\tau)=\alpha\Theta(\eta)\Theta(\tau-\eta)e^{-\alpha\eta}$$
$$\times\exp\{-\alpha[1-e^{-(\tau-\eta)}]\}e^{-(\tau-\eta)}{}_1F_1(\alpha;1;h(\eta,\tau)), \quad (32)$$

$$\tilde{g}_{21}(\eta,\tau) = \alpha\Theta(\eta)\Theta(\tau-\eta)e^{-\alpha\eta}\exp\{-\alpha[1-e^{-(\tau-\eta)}]\} \times {}_1F_1(\alpha+1;1;h(\eta,\tau)), \tag{33}$$

with $h(\eta,\tau)=\alpha(1-e^{-\eta})[1-e^{-(\tau-\eta)}]$. These formulae represent the main result of the paper. The final probability density $\tilde{\rho}(\eta,\tau)$ is simply one half of the sum of the above four functions. If needed, the transformation into the original variables is simply $\rho(w,t)=\beta\tilde{\rho}(\beta w,\beta\varepsilon\omega t)$. We have checked, both numerically, and analytically, that the density is properly normalized. If α is a positive integer then the Kummer's function can be represented as the product of an exponential function and a polynomial. For example, if $\alpha=1$ we get

$$\tilde{\rho}(\eta,\tau) = \frac{1}{2}\delta(\tau-\eta)e^{-\tau} + \frac{1}{2}\delta(\eta)\exp[-(1-e^{-\tau})] + \frac{1}{2}\Theta(\eta)\Theta(\tau-\eta)e^{-\eta}(3-e^{-\eta}) \times\exp[-(e^{-\eta}-e^{-\tau})]. \tag{34}$$

Figure 1 presents the three-dimensional plot of the probability density in the case of an intermediate driving rate $\alpha=2$. Notice the two lines in the base plane. The full curve in the basic plane depicts the mean (reduced) work

$$\tilde{w}_{\mathrm{mean}}(\tau) = \int_0^\tau d\eta\ \eta\tilde{\rho}(\eta,\tau) = \frac{1}{2}\sum_{i=1}^{2}\sum_{j=1}^{2}\int_0^\tau d\eta\ \eta\tilde{g}_{ij}(\eta,\tau), \tag{35}$$

the true mean work being $w_{\mathrm{mean}}(t)=\langle W(t)\rangle=\tilde{w}_{\mathrm{mean}}(\beta\varepsilon\omega t)/\beta$. Carrying out the above integration, the singular part of the function $\tilde{g}_{22}(\eta,\tau)$ does not contribute whereas the singular part of the function $\tilde{g}_{11}(\eta,\tau)$ yields the contribution $\tau\exp(-\alpha\tau)/2$. Otherwise, it does not seem possible to evaluate the required integrals analytically and we had to use the numerical integration. The dashed line in the base plane represents the reduced reversible work $\tilde{w}_{\mathrm{rev}}(\tau)=\log[2/(1+e^{-\tau})]$. The true reversible work is again $w_{\mathrm{rev}}(t)=\tilde{w}_{\mathrm{rev}}(\beta\varepsilon\omega t)/\beta$. In the rest of the paper, we always use the reduced units.

We have now the maximum possible information concerning the work fluctuations during an "experiment" which consists in driving the energy levels. We turn to extracting specific physical conclusions from the formulas (30)–(33).

V. DISCUSSION

The difference of the free energies represents the lower boundary for the work done on the system during any irreversible isothermal process. The boundary is reached if and only if the process is reversible. How is this basic law incorporated within our setting?

Figure 2 presents the probability density $\tilde{\rho}(\eta,\tau)$ for several typical cases. We already know that the density includes two delta functions on the borders of its support $[0,\tau]$, cf. the discussion of Eq. (20) in Sec. III. The weight of the delta function situated at $\eta=\tau$ equals $\exp(-\alpha\tau)/2$, i.e., it vanishes in the long time limit. The weight measures the total probability of those sample paths which have never quit the first state. Similarly, the weight of the delta function at $\eta=0$ is $\exp[-\alpha(1-e^{-\tau})]/2$ and it measures the total probability of all those paths which, up to the time τ, have made no jump out of the second state. The weight approaches a nonzero limit $e^{-\alpha}/2$ which is the weight of the sample paths which have never (i.e., within no time interval of a finite duration) left the second state. This is of course a consequence of the vanishing transfer rate out of the second state. But even if the second state no more emits any sample paths, its population increases and finally reaches unity. Notice that we have here two time scales. The time scale for locking the second state is controlled by the driving velocity whereas the scale for emitting sample paths from the first state is $1/\nu$.

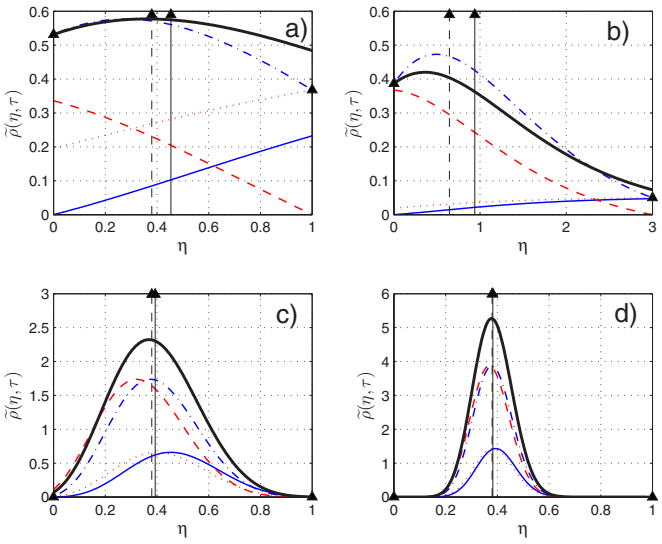

FIG. 2. (Color online) The reduced probability density for the work $\tilde{\rho}(\eta,\tau)$ as the function of the reduced work variable η for several values of the parameter α and the reduced time τ. In panel (a), we have taken $\alpha=1$, $\tau=1$; in panel (b) $\alpha=1$, $\tau=3$; in panel (c) $\alpha=10$, $\tau=1$, and in panel (d) $\alpha=50$, $\tau=1$. Using the thin lines, we illustrate the matrix elements $\tilde{g}_{ij}(\eta,\tau)$, $i,j=1,2$, as given in Eqs. (30)–(33). Specifically, $\tilde{g}_{11}(\eta,\tau)$ is illustrated by the thin full line, $\tilde{g}_{21}(\eta,\tau)$ by the thin dash-dotted line, $\tilde{g}_{12}(\eta,\tau)$ by the thin dotted line, and $\tilde{g}_{22}(\eta,\tau)$ by the thin dashed line. Notice the singular part of the matrix element $\tilde{g}_{11}(\eta,\tau)$ (the arrow situated at $\eta=\tau$), and the singular part of the matrix element $\tilde{g}_{22}(\eta,\tau)$ (the arrow situated at $\eta=0$). The heights of these two arrows show the weights of the corresponding delta functions. The reduced probability density $\tilde{\rho}(\eta,\tau)$ equals one half of the sum of the functions $\tilde{g}_{ij}(\eta,\tau)$, $i,j=1,2$. It is shown by the thick full line (its singular components at $\eta=0$ and $\eta=\tau$ are not shown in the figure). Finally, the position of the dashed black arrow indicates the reduced reversible work $\tilde{w}_{\mathrm{rev}}(\tau)$. Similarly, the position of the full black arrow marks the reduced mean work $\tilde{w}_{\mathrm{mean}}(\tau)$. The heights of these two black arrows have no meaning.

The degree of irreversibility of the emerging process is measured by the parameter α. If $1/\alpha$ is small, the attempt times are very frequent. The system has a frequent possibility to adapt the population of the states to the momentary values of their energies. The external agent does the smallest possible work; the process is close to the equilibrium one. If, on the other hand, $\alpha\ll 1$, the attempt times are very rare. The

sample paths are constrained to remain during long time intervals in their present states. Therefore although the energy of the first state increases, the sample paths do not keep up to leave it. The momentary population of the first state is bigger then the equilibrium population corresponding to the momentary energy of this state. The work done is bigger than the work during the equilibrium process.

Precisely speaking, the last statement concerns the mean work $\tilde{w}_{\mathrm{mean}}(\tau)$ as defined in Eq. (35). For any fixed time τ, the mean work $\tilde{w}_{\mathrm{mean}}(\tau)$ is smaller than the value $\frac{\tau}{2}$ (which gives the mean work for the trivial case $\alpha=0$) and bigger than the reversible work $\tilde{w}_{\mathrm{rev}}(\tau)=\log[2/(1+e^{-\tau})]$. In the infinite-time limit the work density approaches the form

$$\lim_{\tau\to\infty}\tilde{\rho}(\eta,\tau)=\frac{1}{2}\delta(\eta)e^{-\alpha}+\frac{1}{2}\Theta(\eta)\alpha e^{-\alpha(1+\eta)}\times[{}_1F_1(\alpha;1;\alpha(1-e^{-\eta}))+{}_1F_1(\alpha+1;1;\alpha(1-e^{-\eta}))+(\alpha-1){}_1F_1(\alpha+1;1;\alpha(1-e^{-\eta}))]. \quad (36)$$

Consequently, the mean work approaches a definite value $\lim_{\tau\to\infty}\tilde{w}_{\mathrm{mean}}(\tau)$. The time scale for constitution of the asymptotic limit is $1/\alpha$ (i.e., $1/\omega$ in physical nonreduced units) and it is therefore under the external control.

If we increase the parameter α, then not only the mean work $\tilde{w}_{\mathrm{mean}}(\tau)$ at any fixed time τ approaches the reversible work $\tilde{w}_{\mathrm{rev}}(\tau)$ at that time, but also the density $\tilde{\rho}(\eta,\tau)$ approaches the delta function localized at $\tilde{w}_{\mathrm{rev}}(\tau)$. The relationship

$$\lim_{\alpha\to\infty}\tilde{\rho}(\eta,\tau)=\delta\left(\eta-\log\frac{2}{1+e^{-\tau}}\right) \quad (37)$$

can be proved by performing the required limit in the expression for the Laplace transformation $\tilde{\rho}(s,z)$, e.g., in Eq. (26), and then inverting the result into $\tilde{\rho}(\eta,\tau)$.

An important consequence of the work fluctuations is that the work along a certain fraction of the sample paths is smaller than the reversible work. Precisely speaking, for a fixed time, the fraction $v(\tau)$ amounts to the area below the density curve and above the interval $[0,\tilde{w}_{\mathrm{rev}}(\tau)]$ plus the weight of the delta function at $\eta=0$. The value of the reversible work is delineated by the broken-line arrow in Fig. 2. Specifically, if we take $\alpha=1$, we integrate the function (34) and obtain

$$v(\tau)=\int_0^{\tilde{w}_{\mathrm{rev}}(\tau)}d\eta\tilde{\rho}(\eta,\tau)=\frac{1}{4}(3-e^{-\tau})\exp\left[-\frac{1}{2}(1-e^{-\tau})\right], \quad (38)$$

In the long-time limit, the function approaches the value $3/(4\sqrt{e})$.

We have not exhausted the possible applications of the general method as outlined in the second section. An essential point in our construction has been the assumed renewal character for the interattempt times. Had we taken another probability density for the interattempt times than the exponential one, the underlying process $D(t)$ would be a non-Markovian one and the central evolution equation for the work characteristic function, cf. Eq. (18), would be an integrodifferential equation.

Considering a rather complicated structure of our final analytic expressions (30)–(33), we compared them with the results based on the computer simulation. Due to our specific treatment of the time-inhomogeneous Markov process $D(t)$, our numerical procedure is slightly different from that in Ref. [14]. We simply literally follow our construction, i.e., we first generate realizations of the Poisson point process [17], then evaluate the transition probabilities at the random times generated, and finally decide about the transitions between the two states. From its very formulation, our method operates with the continuous time, i.e., we do not need to control the transition from the discrete time to the continuous time [14]. In all our numerical tests, the results based on the evaluation of the expressions (30)–(33) have been confirmed.

In conclusion, we have pointed out several properties of the work fluctuation in the simple model of a nonequilibrium isothermal process. It is our belief that the present analysis can be helpful in problems which deal with more complicated driving scenarios and/or with more complicated forms of the transfer rates.

ACKNOWLEDGMENTS

We would like to thank Wolfgang Dieterich for inspiring discussions on the problem treated here. Support of this work by the Ministry of Education of the Czech Republic (Project No. MSM 0021620835), by the Grant Agency of the Czech Republic (Grant No. 202/07/0404), and by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 569) is gratefully acknowledged.

[1] J. Liphardt, S. Dumont, S. B. Smith, I. Tinoco, Jr., and C. Bustamente, Science **296**, 1832 (2002).
[2] F. Ritort, Poincaré Seminar **2**, 195 (2003).
[3] T. Speck and U. Seifert, Phys. Rev. E **70**, 066112 (2004).
[4] F. Wolf, J. Math. Phys. **29**, 305 (1988).
[5] Hu Gang, G. Nicolis, and C. Nicolis, Phys. Rev. A **42**, 2030 (1990).
[6] P. Chvosta, M. Schulz, E. Paule, and P. Reineker, New J. Phys. **7**, 190 (2005).
[7] S. A. Langer, A. T. Dorsey, and J. P. Sethna, Phys. Rev. B **40**, 345 (1989).
[8] J. J. Brey and A. Prados, Phys. Rev. B **43**, 8350 (1991).
[9] L. Gammaitoni, P. Hänggi, P. Jung, and F. Marchesoni, Rev. Mod. Phys. **70**, 223 (1998).
[10] P. Reimann, Phys. Rep. **361**, 57 (2002).
[11] C. Jarzynski, Phys. Rev. Lett. **78**, 2690 (1997).

[12] G. E. Crooks, Phys. Rev. E **61**, 2361 (2000).
[13] M. Manosas, and F. Ritort, Biophys. J. **88**, 3224 (2005).
[14] R. Marathe, and A. Dhar, Phys. Rev. E **72**, 066112 (2005).
[15] S. X. Sun, J. Chem. Phys. **118**, 5769 (2003).
[16] W. Feller, *An Introduction to Probability Theory and Its Applications*, 3rd Ed. (Wiley, New York, 1968), Vol. 1.
[17] D. L. Snyder, *Random Point Processes* (Wiley, New York, 1975).
[18] D. R. Cox, *Renewal Theory* (Wiley, New York, 1962).
[19] A. Papoulis, *Probability, Random Variables and Stochastic Processes* (McGraw-Hill, New York, 1965).
[20] G. Doetsch, *Anleitung zum praktischen Gebrauch der Laplace-Transformation und der Z-Transformation* (R. Oldenbourg, München, 1967).
[21] A. Imparato and L. Peliti, Phys. Rev. E **72**, 046114 (2005).
[22] A. Imparato and L. Peliti, Europhys. Lett. **69**, 643 (2005).
[23] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (Dover, New York, 1970).
[24] L. J. Slater, *Confluent Hypergeometric Functions* (Cambridge University Press, Cambridge, England, 1960).