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Exact analysis of work fluctuations in two-level systems

Evžen Šubrt and Petr Chvosta

Department of Macromolecular Physics, Faculty of Mathematics and Physics, Charles University, V Holešovičkách 2, CZ-18000 Praha, Czech Republic
E-mail: subrt@kmf.troja.mff.cuni.cz and chvosta@kmf.troja.mff.cuni.cz

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Abstract. This paper presents an exact probabilistic description of the work done by an external agent on a two-level system. We first develop a general scheme which is suitable for the treatment of functionals of the time-inhomogeneous Markov processes. Subsequently, we apply the procedure to the analysis of the isothermal-work probability density and we obtain its exact analytical forms in two specific settings. In both models, the state energies change with a constant velocity. On the other hand, the two models differ in their interstate transition rates. The explicit forms of the probability density allow a detailed discussion of the mean work. Moreover, we discuss the weight of the trajectories which display a smaller value of work than the corresponding equilibrium work. The results are controlled by a single dimensionless parameter which expresses the ratio of two underlying timescales: the velocity of the energy changes and the relaxation time in the case of frozen energies. If this parameter is large, the process is a strongly irreversible one and the work probability density differs substantially from a Gaussian curve.

Keywords: exact results, nonequilibrium fluctuations in small systems

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1. Introduction

Consider a *macroscopic* system in equilibrium with a heat bath. Assume we start changing one of the system's external parameters, the schedule of the driving being arbitrary but fixed. The system responds by changing its state. During the ensuing (generally nonequilibrium) isothermal process we measure the work done on the system. If we repeat the experiment with the same driving protocol, we always detect the same single value of the work. On the other hand, varying the protocol, the work can assume different values, but it can never fall below a certain limit. As a consequence of the second law of thermodynamics the limiting value equals the difference of the Helmholtz free energies which correspond to the equilibrium states compatible with the final and with the initial values of the external parameters. The value is attained in the case of the quasistatic process, i.e. for infinitely slow changes of the external parameters.

On the other hand, consider a *small* system, such as a single RNA molecule in a solution. Then, by repeating the experiment with the fixed driving protocol, the value of the work done by the external agent varies from one realization of the experiment to another. This is because the work is significantly influenced by the thermal fluctuations and we cannot guarantee the same 'protocol' of thermal fluctuations during every repetition of the experiment. Some values of the work are even smaller than the above described difference of the Helmholtz free energies. In other words, the work is a random variable and the experiment yields its probability density.

In several recent years there was extensive theoretical and experimental research in this field [1]. Thanks to the recent progress in the micromanipulation techniques the work distributions become accessible experimentally. Let us mention just two examples of such experiments: dragging of a colloidal particle through a viscous fluid [2, 3] and the mechanical unfolding of RNA molecules using optical tweezers [4].

From the theoretical point of view the distribution of work depends on the driving schedule, but it also contains important information concerning the system itself. In order to understand this information, the exact theoretical calculation of the work probability density would be of considerable importance. But there are two difficulties related to such an exact analysis. First, the underlying evolution equation, e.g. the Fokker–Planck equation or the Pauli master equation, must reflect the time dependence of the external parameters. Typically, then, one has to solve the diffusion equation including a time-dependent potential [5]–[7], or the Pauli equation with the time-dependent transition rates [7]–[9]. But even the explicit solution of the evolution equation does not suit our purpose. Actually, the work done on the system represents a *functional* of the underlying evolution. In other words, the work done during an arbitrary but fixed time interval depends on the whole history of the system evolution during the interval. For these two reasons, the theoretical analysis of the work distribution lags behind its experimental investigation. On the other hand, the theoretical studies have already predicted several generic properties of the work distribution. For example, the work probability density must be compatible with the Jarzynski equality [10] and with the Crooks fluctuation relation [11].

In the recent literature, one can find several attempts to calculate the work probability density. Namely, Ritort presents the path integral representation of the work distribution in the large ensemble of non-interacting two-state systems [12]. Later, these results have been extended to the interacting mean-field systems beyond the two-state case [13, 14]. Moreover, the works [15]–[17] are focused on the calculation of the probability density of the work which is being exerted on the long molecule during the pulling experiments. Also the first measurements of the work (or entropy) probability density were made on the real periodically driven two-level systems [18, 19].

In the present paper, the analysis will be sharply focused on the exact calculation of the work probability density within two simple nontrivial settings. The main results are equations (24)–(27) for the first model, and equations (49)–(52) for the second one. To the best of our knowledge, these formulae are the first exact work probability densities available in the literature. We believe that they can be helpful in the interpretation of the above-mentioned experiments and also as benchmarks in testing computer simulations within more complicated settings.

2. Work as a functional of the time-inhomogeneous Markov process

Consider a N-state system in contact with a thermal reservoir. Let the individual states be characterized by their energies E_i, $i = 1, \ldots, N$. At an arbitrary fixed time t, the state of the system is specified by the occupation probabilities $p_i(t)$, $i = 1, \ldots, N$ of the individual energy levels. In many experimentally important situations, the time evolution of the system state is described as a Markov process and, consequently, the occupation probabilities are governed by the Pauli master (or rate) equation [20]. The transition rates in the equation depend on the bath temperature and on the external parameters which influence the energy levels. Frequently, one focuses on the autonomous relaxation of the system state in a given environment. Then the transition rates are time-independent. However, in the context of the present paper, the external parameters will change in time. Consequently, the energies $E_i(t)$, $i = 1, \ldots, N$, and therefore also the transition rates will be time-dependent. The underlying Markov process will be a time inhomogeneous one.

One possible probabilistic approach [21] to the analysis of a continuous time Markov process consists in its decomposition into (i) the discrete time Markov chain and (ii) the system of random points on the time axis. The transitions between the states of the Markov chain occur just at the random instants. Usually, the time intervals between the neighboring instants are taken as independent and exponentially distributed random variables. We shall demonstrate below that such a decomposition is particularly well suited for the calculation of certain functionals of the Markov process in question. Let us now describe the main points of the decomposition procedure.

Let $\{\mathsf{D}_n\}_{n=0}^{\infty}$ be the conventional *time inhomogeneous* N-state Markov chain [22]. Usually, the random variables D_n, $n = 0, 1, \ldots$, describe the state of the system at equally spaced time instants. However, in anticipating the transition towards continuous time, we assume that the nth transition occurs at the time t_n, $n = 0, 1, 2, \ldots$, and we designate the random variables which form the chain as $\{\mathsf{D}(t_n)\}_{n=0}^{\infty}$. Notice that the intervals $(t_n - t_{n-1})$, $n = 1, 2, \ldots$, are not necessarily of the same duration. We shall call the time instants t_n as the *attempt times*. If not stated otherwise, we assume $t_0 = 0$.

An arbitrary fixed random variable $\mathsf{D}(t_n)$ assumes the values from the state space $\{d_i\}_{i=1}^{N}$. The complete description of the Markov chain $\{\mathsf{D}(t_n)\}_{n=0}^{\infty}$ requires the specification of the initial condition and the prescription for the transition probabilities. As for the initial condition, we must prescribe the probabilities $p_i(0) = \langle i|p(0)\rangle = \mathrm{Prob}\{\mathsf{D}(0) = d_i\}$, $i = 1, \ldots, N$. Here and below, we use the bracket notation for the components of the probability vector. As for the transition probabilities, we must define the sequence of the matrices $\mathbb{K}(t_n)$, $n = 1, 2, \ldots$, with the matrix elements $k_{ij}(t_n) = \langle i|\,\mathbb{K}(t_n)\,|j\rangle = \mathrm{Prob}\{\mathsf{D}(t_n) = d_i|\mathsf{D}(t_{n-1}) = d_j\}$, $i, j = 1, \ldots, N$. In other words, $k_{ij}(t)$ is the probability of the transition from the jth state to the ith one, provided the transition occurs at the time t. The transition probabilities reflect the instantaneous tendency to change the state. The specific way they depend on the time variable reflects the driving scenario and it will be specified in section 3.

Having described the Markov chain, we now assume that the attempt times form a random sequence $\{\mathsf{T}_n\}_{n=0}^{\infty}$ on the time axis. More precisely, we identify the attempt times with the so-called Poisson points [23, 24]: the time intervals between the neighboring attempt times are independent and exponentially distributed random variables. We designate $\phi(t) = \nu \exp(-\nu t)$ the generic probability density for the inter-attempt times $(\mathsf{T}_n - \mathsf{T}_{n-1})$, $n = 1, 2, \ldots$. The parameter ν represents the mean frequency with which the attempt times occur, i.e. $1/\nu$ is the mean duration of the time interval between the neighboring attempt times.

As mentioned above, the process which originates from allowing the state transitions just at the random attempt times is a time inhomogeneous Markov process; we shall designate it as $\mathsf{D}(t)$. We should be able to derive the dynamical equation for the occupation probabilities $\langle i|p(t)\rangle = \mathrm{Prob}\{\mathsf{D}(t) = d_i\}$, $i = 1, \ldots, N$. More importantly for the present paper, the construction allows for a transparent probabilistic description of the individual sample paths (trajectories) of the process $\mathsf{D}(t)$. Let us make this idea quite explicit. We designate as $P(t, n; j_n, j_{n-1}, \ldots, j_1, j_0; t_n, t_{n-1}, \ldots, t_1, t_0) \prod_{k=1}^{n} \mathrm{d}t_k$ the probability of a path including exactly n attempt times within the interval $(0, t)$ which, moreover, evolves as follows. It departs with probability 1 from the state d_{j_0}. The first attempt time is localized within the time interval $(t_1, t_1 + \mathrm{d}t_1)$. Having reached it, the trajectory jumps from the state d_{j_0} into the state d_{j_1}. Similar transitions occur at the attempt times localized in the

infinitesimal intervals $(t_k, t_k + \mathrm{d}t_k)$, $k = 2, 3, \ldots n$. At the last attempt time, the state variable jumps from the state $d_{j_{n-1}}$ to the state d_{j_n}. Afterwards, the trajectory remains in the state d_{j_n} up to the time t. The trajectory just described has been decomposed into a sequence of individual events. For example, the probability that the path departs from the state d_{j_0} is $p_j(0)$. Further, the probability that the first attempt time occurs within the infinitesimal time interval $(t_1, t_1 + \mathrm{d}t)$ is $\phi(t_1)\,\mathrm{d}t_1$. The probability of the first transition $d_{j_0} \to d_{j_1}$ within the path is $k_{j_1 j_0}(t_1)$, and similarly for the other transitions. Eventually, the probability that there occurs no further attempt time between t_n and t is $f(t-t_n) = 1 - \int_0^{t-t_n} \phi(t')\,\mathrm{d}t = \exp[-\nu(t-t_n)]$. Collecting the probabilities of all individual events, the probability of the whole trajectory is

$$P(t, n; j_n, \ldots, j_0; t_n, \ldots, t_0) \prod_{k=1}^{n} \mathrm{d}t_k = f(t - t_n) \prod_{k=1}^{n} [k_{j_k j_{k-1}}(t_k) \phi(t_k - t_{k-1})\,\mathrm{d}t_k] p_{j_0}(0). \qquad (1)$$

If $n = 0$, we take the empty product as unity.

Let us now consider all possible trajectories which depart with probability 1 from the state d_j and which, at time t, are found in the state d_i. The sum of the probabilities of all such paths is simply the conditional probability $\mathrm{Prob}\{\mathsf{D}(t) = d_i | \mathsf{D}(0) = d_j\}$. We abbreviate this expression as $r_{ij}(t)$ and we introduce the $(N \times N)$ matrix with the matrix elements $r_{ij}(t) = \langle i | \, \mathbb{R}(t) \, | j \rangle$. In other words, $\mathbb{R}(t)$ is the time-evolution operator for the state probabilities in the sense that the state vector $|p(t)\rangle$ can be calculated by the simple multiplication $\mathbb{R}(t)\,|p(0)\rangle$. Considering simultaneously all N^2 pairs of the initial and the final states and summing up the probabilities of the paths, the evolution operator emerges in the form

$$\mathbb{R}(t) = f(t)\mathbb{I} + \sum_{n=1}^{\infty} \int_0^t \mathrm{d}t_n \ldots \int_0^{t_2} \mathrm{d}t_1\, f(t - t_n) \mathbb{K}(t_n) \phi(t_n - t_{n-1}) \times \mathbb{K}(t_{n-1}) \ldots \phi(t_2 - t_1) \mathbb{K}(t_1). \qquad (2)$$

The summation takes into account all possible numbers of attempt points within the path. For an arbitrary fixed number n, the multiple integration incorporates all possible localizations of the attempt times. Finally, the matrix multiplication after the integration signs expresses the summation of all possible sequences of the transitions which occur along the trajectories. The direct evaluation of the right-hand side in equation (2) would be very difficult. However, if we first carry out its time derivative we get immediately the Pauli master equation

$$\frac{\mathrm{d}}{\mathrm{d}t} \mathbb{R}(t) = -\nu \mathbb{L}(t) \mathbb{R}(t), \qquad \mathbb{R}(0) = \mathbb{I}, \qquad (3)$$

where $\mathbb{L}(t) = \mathbb{I} - \mathbb{K}(t)$. Summarizing the derivation up to this point, we have started with the time inhomogeneous Markov chain, as described by the transition probabilities matrix $\mathbb{K}(t)$, and with the system of Poisson points, as defined by the inter-point probability density $\phi(t) = \nu \exp(-\nu t)$. After combining these two ingredients, we have arrived at the Pauli master equation with the transition rates given by the elements of the matrix $\nu \mathbb{L}(t)$.

We now concentrate on the work done by an external agent along the above described trajectory. In between the attempt times, the changes of the system state are, by their very construction, excluded. The work is done on the system by changing its energy

levels while the occupation of the states remains fixed [11]. For example, if the system resides during the time interval (t_1, t_2) in the ith state, the work done on it during this time interval is $E_i(t_2) - E_i(t_1)$. Similarly, if the state evolves along the above described trajectory, the work done on the system during the time interval (t_0, t) is

$$W(t, n; j_n, \ldots, j_0; t_n, \ldots, t_0) = [E_{j_n}(t) - E_{j_n}(t_n)] + \sum_{k=1}^{n} [E_{j_{k-1}}(t_k) - E_{j_{k-1}}(t_{k-1})]. \tag{4}$$

For an arbitrary fixed trajectory, equation (1) describes its probability and equation (4) expresses the work attributed to this trajectory. These two expressions are needed to perform an averaging over the trajectories. Symbolically, and more generally, if $\mathsf{Z}(t)$ is any trajectory-dependent random variable, its mean value can be written as

$$\langle \mathsf{Z}(t) \rangle = \sum_{\text{all trajectories}} \begin{pmatrix} \text{probability for} \\ \text{a fixed trajectory} \end{pmatrix} \times \begin{pmatrix} \text{the value of the variable} \\ \mathsf{Z}(t) \text{ for this trajectory} \end{pmatrix}. \tag{5}$$

For example, if we want to calculate the mean work $\langle \mathsf{W}(t) \rangle$, we insert into the first bracket on the right-hand side the expression (1) and into the second bracket the expression (4). But our main goal is the probability density for the work $\rho(w, t) = \langle \delta(\mathsf{W}(t) - w) \rangle$. We should therefore identify the random variable $\mathsf{Z}(t)$ in the above prescription with the random variable $\delta(\mathsf{W}(t) - w)$. However, due to computational reasons, instead of the direct calculation of the probability density $\rho(w, t)$, we will first calculate its Laplace transformation with respect to the variable w. In other words, we shall first focus on the mean value $\rho(u, t) = \langle \exp[-u\mathsf{W}(t)] \rangle$ and the starting point of its calculation assumes the form

$$\begin{aligned} \rho(u, t) &= \langle \exp[-u\mathsf{W}(t)] \rangle \\ &= \sum_{n=0}^{\infty} \int_0^t \mathrm{d}t_n \ldots \int_0^{t_2} \mathrm{d}t_1 \sum_{j_n=1}^{N} \ldots \sum_{j_0=1}^{N} \exp[-uW(t, n; j_n, \ldots, j_0; t_n, \ldots, t_0)] \\ &\quad \times P(t, n; j_n, \ldots, j_0; t_n, \ldots, t_0). \end{aligned} \tag{6}$$

By pinning down the initial state and the final state, we can again treat separately N^2 subgroups of the trajectories. We arrange the marginal averages over these subgroups into the matrix $\mathbb{G}(u, t)$ with the matrix elements

$$g_{ij}(u, t) = \langle i | \, \mathbb{G}(u, t) \, | j \rangle = \langle \exp[-u\mathsf{W}(t)] \rangle_{(ij)}. \tag{7}$$

The subscript (ij) in the last expression denotes the marginal average over all those trajectories which depart from the state d_j and which, at the time t, reside in the state d_i.

We now insert the specific expression for the trajectory probabilities (cf the right-hand side of equation (1)) and for the trajectory-dependent work (cf the right-hand side of equation (4)) into equation (6). After a rather extensive rearrangement, we arrive at the expression

$$\begin{aligned} \mathbb{G}(u, t) = \mathbb{E}(u, t) \Bigg[f(t) + \sum_{n=1}^{\infty} \int_0^t \mathrm{d}t_n \ldots \int_0^{t_2} \mathrm{d}t_1 \, f(t - t_n) \mathbb{M}(u, t_n) \\ \times \phi(t_n - t_{n-1}) \ldots \mathbb{M}(u, t_1) \phi(t_1) \Bigg] \mathbb{E}^{-1}(u, 0). \end{aligned} \tag{8}$$

Here we have introduced the diagonal matrices $\mathbb{E}(u,t) = \exp[-u\mathbb{H}(t)]$ and $\mathbb{H}(t) = \mathrm{diag}\{E_1(t), E_2(t), \ldots, E_N(t)\}$. Further, the matrix $\mathbb{M}(u,t)$ denotes the product $\mathbb{E}^{-1}(u,t)\mathbb{K}(t)\mathbb{E}(u,t)$. Similarly to equation (2), the individual terms in the summation on the right-hand side of the last formula are the conditional averages, the condition being a fixed number n of attempt times. The multiple integration takes into account all possible localizations of the attempt times, and the matrix multiplication in the integrated expression incorporates the summation over all possible sequences of the states.

In the next step, we perform the time derivation of the expression on the right-hand side of equation (8). Choosing a suitable matrix norm, the sum on the right-hand side converges and it can be derived term by term. Collecting all terms arising, the resulting dynamical equation for the matrix $\mathbb{G}(u,t)$ is

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbb{G}(u,t) = -\left[u\dot{\mathbb{H}}(t) + \nu\mathbb{L}(t)\right]\mathbb{G}(u,t), \qquad \mathbb{G}(u,0) = \mathbb{I}. \tag{9}$$

The dot in the expression $\dot{\mathbb{H}}(t)$ denotes the time derivation. The first term in the square brackets represents the *driving scenario*, its form being dictated by the specific time dependence of the state energies $E_i(t)$, $i = 1, \ldots, N$. The second term in the square brackets expresses the *transition scenario* in the sense that it contains the instantaneous values of the transition rates. In section 3, the two scenarios will be fully specified. Due to the detailed balance condition, the transition scenario is coupled with the driving one.

The *formal* solution of equation (9) is obviously

$$\mathbb{G}(u,t) = \exp_{\leftarrow}\left\{-u\left[\mathbb{H}(t) - \mathbb{H}(0)\right] - \nu\int_0^t \mathbb{L}(t')\,\mathrm{d}t'\right\}, \tag{10}$$

with $\exp_{\leftarrow}$ designating the time-ordered exponential [25]. On the other hand, the *explicit* solution of the system (9) represents a nontrivial mathematical problem and we discuss it in section 3. Assuming we have the solution, the inverse Laplace transformation of the matrix elements $g_{ij}(u,t) = \langle i|\,\mathbb{G}(u,t)\,|j\rangle$ with respect to the variable u yields the probability density for the random variable $\mathsf{W}(t)$. Actually, the density $\rho(w,t)$ is connected with the matrix $\mathbb{G}(w,t)$ through the simple formula

$$\rho(w,t) = \sum_{i,j=1}^{N} \langle i|\,\mathbb{G}(w,t)\,|j\rangle\,\langle j|\,p(0)\rangle. \tag{11}$$

Let us now turn our attention to another quantity which characterizes the time inhomogeneous Markov process in question. Namely, we focus on the so-called *occupation times* for the individual states. Let us fix a state, say the kth one, and consider the random variable

$$\mathsf{T}^{(k)}(t) = \int_0^t \Xi(\mathsf{D}(t') - d_k)\,\mathrm{d}t'. \tag{12}$$

Here the indicator function $\Xi(x)$ equals unity for $x = 0$ and vanishes for $x \neq 0$. Hence $\mathsf{T}^{(k)}(t)$ is the time the system resides in the kth state during the time interval $(0,t)$. The occupation times $\mathsf{T}^{(k)}(t)$, $k = 1, 2, \ldots, N$, are random variables and we are interested in their probability densities $\psi^{(k)}(s,t) = \langle\delta(\mathsf{T}^{(k)}(t) - s)\rangle$. Within our scheme, their calculation proceeds along similar lines, as above.

Namely, for an arbitrary fixed path as described before equation (1), we first write the path-dependent occupation time of the kth state in the form

$$T^{(k)}(t,n;j_n,\ldots,j_0;t_n,\ldots,t_0)=(t-t_n)\,\delta_{j_n,k}+\sum_{m=1}^{n}(t_m-t_{m-1})\,\delta_{j_{m-1},k}. \tag{13}$$

The probability of the individual trajectory is still given by equation (1). We have now both ingredients required in the averaging prescription (5). Instead of the direct calculation of the density $\psi^{(k)}(s,t)$, we focus on its Laplace transformation with respect to the variable v. The transformed function will be designated as $\psi^{(k)}(v,t)$. Therefore, the role of the random variable $\mathsf{Z}(t)$ in equation (5) is presently played by the random variable $\exp[-v\mathsf{T}^{(k)}(t)]$. We again build up the matrix $\mathbb{F}^{(k)}(v,t)$ with the matrix elements given as the marginal averages over the subgroups of trajectories with the pinned down initial and final states. Repeating the step before equation (9), the final dynamical equation for the matrix $\mathbb{F}^{(k)}(v,t)$ is

$$\frac{\mathrm{d}}{\mathrm{d}\tau}\mathbb{F}^{(k)}(v,t)=-\left[v\mathbb{Q}^{(k)}+\nu\mathbb{L}(t)\right]\mathbb{F}^{(k)}(v,t),\qquad \mathbb{F}^{(k)}(v,0)=\mathbb{I}. \tag{14}$$

Here $\mathbb{Q}^{(k)}=|k\rangle\langle k|$, i.e. $\langle i|\,\mathbb{Q}^{(k)}\,|j\rangle=\delta_{ik}\delta_{jk}$, $i,j=1,2,\ldots,N$. Finally, assuming we can solve this matrix equation, the inverse Laplace transformation of the matrix $\mathbb{F}^{(k)}(v,t)$ with respect to the variable v leads to the probability density $\psi^{(k)}(s,t)=\langle\delta(\mathsf{T}^{(k)}(t)-s)\rangle$. In this step, we use the formula

$$\psi^{(k)}(s,t)=\sum_{i,j=1}^{N}\langle i|\,\mathbb{F}^{(k)}(s,t)\,|j\rangle\,\langle j|\,p(0)\rangle. \tag{15}$$

Before closing this section we wish to add some comments concerning the Jarzynski equality [1, 10, 11, 26]. It is usually stated in the form $\langle\exp[-\beta\mathsf{W}(t)]\,\rangle=\exp\{-\beta[F(t)-F(0)]\}$, where $F(t)$ and $F(0)$ are the Helmholtz free energies which correspond to the final and initial equilibrium states. The fixed energies which define the properties of the final and the initial equilibrium states are equal to the driven energies $E_i(t)$, $i=1,\ldots,N$, at the initial time $t=0$ (for the initial equilibrium state), and at the final time t (for the final equilibrium state). The initial state for the non-equilibrium evolution is the Gibbs equilibrium state defined by the initial values $E_i(0)$. Within our scheme, after explicit calculation of the free energies required, Jarzynski's relation assumes the form

$$\langle+|\mathbb{G}(\beta,t)|\pi(0)\rangle=\frac{\sum_{i=1}^{N}\exp[-\beta E_i(t)]}{\sum_{i=1}^{N}\exp[-\beta E_i(0)]}=\frac{Z(t)}{Z(0)}. \tag{16}$$

Here $|+\rangle$ represents the vector with all elements equal to unity and $Z(t)=\sum_{i=1}^{N}\exp[-\beta E_i(t)]$ denotes the partition function corresponding to the actual energies at the time instant t. The vector $|\pi(0)\rangle$ represents the initial equilibrium state. We can write it in the form $|\pi(0)\rangle=\mathbb{E}(\beta,0)|+\rangle/Z(0)$. On the whole, we are to prove the relation $\langle+|\,\mathbb{G}(\beta,t)\mathbb{E}(\beta,0)|+\rangle=\langle+|\mathbb{E}(\beta,t)|+\rangle$.

Starting the proof, we first notice that every summand in the n expansion of the operator $\mathbb{G}(\beta,t)$ in equation (8) ends with the matrix $\mathbb{E}^{-1}(\beta,0)$. Hence we should focus on the column vector $\mathbb{M}(\beta,t)|+\rangle$. After a short analysis, the vector exhibits an important

property

$$\mathbb{M}(\beta,t)|+\rangle = |+\rangle \Longleftrightarrow k_{ij}(t)\exp[-\beta E_j(t)] = k_{ji}(t)\exp[-\beta E_i(t)], \quad i,j=1,\ldots,N. \tag{17}$$

The condition on the right-hand side of the equivalence is the (time local) detailed-balance condition. The equivalence is valid for an arbitrary driving scenario, i.e. for arbitrary forms of the state energies $E_i(t)$, $i = 1,\ldots,N$. Therefore, assuming the detailed-balance condition holds, we can write

$$\mathbb{G}(\beta,t)\mathbb{E}(\beta,0)|+\rangle = \mathbb{E}(\beta,t)|+\rangle\left\{f(t) + \int_0^t \mathrm{d}t_1\, f(t-t_1)\phi(t_1) + \int_0^t \mathrm{d}t_2 \int_0^{t_2} \mathrm{d}t_1\, f(t-t_2)\phi(t_2-t_1)\phi(t_1) + \cdots\right\}. \tag{18}$$

Using the Laplace transformation, we can sum up the series in the curly brackets. The sum equals unity. This concludes the proof of Jarzynski's equality within our N-level setting.

The assertion that the curly bracketed expression in equation (18) is equal to 1 holds true not only for the Poisson renewal process. In fact, it is valid for any renewal [21]. Similarly, the n expansion of the operator $\mathbb{G}(u,t)$, which has been used in the proof, is valid for an arbitrary renewal. Notice, however, that if the renewal process in question differs from the Poisson process, the resulting process $\mathsf{D}(t)$ is not a Markovian one. In this case, our proof provides an example of a non-Markovian time-nonhomogeneous dynamics for which Jarzynski's equality still keeps its validity.

Summing up the section, we have derived the dynamical equation for the Laplace transformation of the probability density of two physically important quantities. The solution of equation (9) yields, through the inverse Laplace transformation with respect to the variable u, the probability density $\rho(w,t)$ for the work done on the system by the external agent. Similarly, the solution of equation (14) leads, through its inverse Laplace transformation with respect to the variable v, to the probability density $\psi^{(k)}(s,t)$ for the occupation time of the kth state.

3. The explicit solution for two transition scenarios

One of the principal motivations behind the present paper has been a comparison of the exact work probability density in two fairly analogous models. First, in both models, we consider only two states, i.e. $N = 2$. Second, the driving scenarios for both models coincide. Namely, we assume the linear driving regime with the state energies $E_1(t) = \varepsilon\omega t$ and $E_2(t) = -\varepsilon\omega t$. Hence the energies coincide at $t_0 = 0$ and then their difference increases linearly with time, the velocity of the increase being measured by the parameter $\varepsilon\omega$. The energy difference reaches the value 2ε at the time $1/\omega$. Thus $1/\omega$ settles one of the two principal timescales, the other being the mean time interval between the attempt times $1/\nu$. Third, in both models, we assume that the system departs from the Gibbs equilibrium. Hence the initial occupation probabilities of the two states are equal, $p_i(0) = \frac{1}{2}$, $i = 1,2$.

On the other hand, the two models in question differ in their transition scenarios. In order to make this point explicit, let us return to the Pauli master equation (3). In the present context, it assumes the form

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbb{R}(t) = -\nu \begin{pmatrix} l_1(t) & -l_2(t) \\ -l_1(t) & l_2(t) \end{pmatrix} \mathbb{R}(t), \qquad \mathbb{R}(0) = \mathbb{I}, \tag{19}$$

where the functions $l_1(t)$ and $l_2(t)$ are given by the *transition probabilities* for the Markov chain, $l_i(t) = 1 - k_{ii}(t)$, $i = 1, 2$. We shall specify them below. Differently speaking, the two time-dependent *transition rates* in the Pauli master equation are $\lambda_i(t) = \nu l_i(t)$.

Due to our assumption of having only two levels, the Pauli master equation can be solved for arbitrary functions $l_1(t)$ and $l_2(t)$, i.e. for arbitrary transition rates $\lambda_1(t)$ and $\lambda_2(t)$. The solution is [8]

$$\begin{aligned} \mathbb{R}(t) = \mathbb{I} - \tfrac{1}{2} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \left\{ 1 - \exp\left[- \int_0^t \mathrm{d}t' \, \gamma_+(t') \right] \right\} \\ + \tfrac{1}{2} \begin{pmatrix} -1 & -1 \\ 1 & 1 \end{pmatrix} \int_0^t \mathrm{d}t' \exp\left[- \int_{t'}^t \mathrm{d}t'' \gamma_+(t'') \right] \gamma_-(t'), \end{aligned} \tag{20}$$

where $\gamma_\pm(t) = \lambda_1(t) \pm \lambda_2(t)$.

Imagine that the state energies are suddenly frozen at their instantaneous values. The system is in contact with the thermal environment and hence the following relaxation process must bring the system towards the equilibrium state. Moreover, the ensuing equilibrium must be compatible with the fixed values of the energies. This requirement can be translated into the (time local) detailed balance condition [11, 15]. Namely, the two transition rates $\lambda_1(t)$ and $\lambda_2(t)$ are no longer independent. They must comply with the relation $\lambda_1(t) \exp[-\beta E_1(t)] = \lambda_2(t) \exp[-\beta E_2(t)]$, where $\beta = 1/(k_\mathrm{B} T)$ and T is the absolute temperature of the thermal environment. Therefore, what remains to be fixed is just one of the two functions $l_1(t)$, $l_2(t)$.

Let us now incorporate the assumptions made up to this point into the dynamical equation (9). We can write it as

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}\mathbb{G}(u,t) = -\left[u\varepsilon\omega \begin{pmatrix} +1 & 0 \\ 0 & -1 \end{pmatrix} + \nu l_1(t) \begin{pmatrix} +1 & -\mathrm{e}^{-2\beta\varepsilon\omega t} \\ -1 & +\mathrm{e}^{-2\beta\varepsilon\omega t} \end{pmatrix} \right] \mathbb{G}(u,t), \\ \mathbb{G}(u,0) = \mathbb{I}. \end{aligned} \tag{21}$$

This form motivates a convenient dimensionless variable to be used in the following calculation. First of all, we introduce the dimensionless time $\tau = 2\beta\varepsilon\omega t$. Further, instead of the variable u in the direct Laplace transformation $\mathbb{G}(u,t)$, we shall use the variable $s = u/(2\beta)$. This means that the dimensionless work variable will be $\eta = 2\beta w$. If we divide equation (21) by the expression $2\beta\varepsilon\omega$ we get the matrix equation for the reduced matrix $\widetilde{\mathbb{G}}(s,\tau) = \mathbb{G}(u/(2\beta), 2\beta\varepsilon\omega t)$. The inverse Laplace transformation of the matrix $\widetilde{\mathbb{G}}(s,\tau)$ with respect to the variable s will be designated as $\widetilde{\mathbb{G}}(\eta,\tau)$. The original matrix $\mathbb{G}(w,t)$ is then related to the reduced one $\widetilde{\mathbb{G}}(\eta,\tau)$ through the formula $\mathbb{G}(w,t) = 2\beta\widetilde{\mathbb{G}}(2\beta w, 2\beta\varepsilon\omega t)$. During the reduction procedure, there occurs an important combination of the model parameters $a = \nu/(2\beta\varepsilon\omega)$. This dimensionless parameter will play a crucial role in the following calculation. It measures the temperature reduced ratio of the two timescales mentioned above. From a different perspective, the single parameter a will control the

degree of irreversibility of the resulting isothermal process. If it is small, the ensuing process departs substantially from the equilibrium one. We shall return to this point in the last section.

3.1. Metropolis scenario: $l_1(\tau) = 1$

As mentioned above, our construction must be completed by the explicit form of the transition probabilities $l_1(\tau)$, $l_2(\tau)$, or, equivalently, by the explicit prescription for the transition rates $\lambda_1(\tau)$ and $\lambda_2(\tau)$ in the Pauli master equation (21). Our first choice is inspired by the idea that is widely used in the Monte Carlo simulations. Namely, we adopt the well-known *Metropolis* algorithm. While residing in the state with the higher energy, the system jumps with probability 1 to the state with the lower energy, whenever there occurs a possibility to do so. Translated into our construction, we simply take $l_1(\tau) = 1$ for all τ. This assumption, together with the detailed balance condition, already dictates the transition probability for the transition from the energetically lower state to the higher one. Namely, we have $l_2(\tau) = \mathrm{e}^{-\tau}$. In words, the probability to leave the lower state exponentially decreases with the increasing energy difference. This specific choice of the transition probabilities will be henceforward referred to as the *Metropolis scenario*.

Upon the direct substitution of the transition rates into equation (20) we obtain the explicit form of the occupation probabilities. Actually, the solution of the Pauli master equation is

$$\mathbb{R}(\tau) = \mathbb{I} - \tfrac{1}{2}\begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}[1 - \mathrm{e}^{-a(1+\tau-\mathrm{e}^{-\tau})}] + \frac{a}{2}\begin{pmatrix} -1 & -1 \\ 1 & 1 \end{pmatrix}\int_0^\tau \mathrm{d}\tau' \mathrm{e}^{-a(\tau-\tau'-\mathrm{e}^{-\tau}+\mathrm{e}^{-\tau'})}(1-\mathrm{e}^{-\tau'}). \tag{22}$$

Here the definite integral cannot be written in a closed form, but, if needed, it can be evaluated numerically. Intuitively, the upper state gradually becomes depleted and the occupation probability of the lower one approaches unity.

Let us now focus on the dynamical equation (21). Incorporating the present form of the transition probabilities, it assume the form

$$\frac{\mathrm{d}}{\mathrm{d}\tau}\widetilde{\mathbb{G}}(s,\tau) = -\left[s\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + a\begin{pmatrix} 1 & -\mathrm{e}^{-\tau} \\ -1 & \mathrm{e}^{-\tau} \end{pmatrix}\right]\widetilde{\mathbb{G}}(s,\tau), \qquad \widetilde{\mathbb{G}}(s,0) = \mathbb{I}. \tag{23}$$

Hence we are faced with two independent systems of two coupled equations for the individual matrix elements. The solution of the two systems and the subsequent inverse Laplace transformation with respect to the variable s represent an interesting mathematical problem. Reference [27] describes its solution in full detail. Therefore we confine ourselves just to the translations of the results as obtained in [27] into our present setting. The explicit form of the individual matrix elements of the matrix $\widetilde{\mathbb{G}}(\eta,\tau)$ is

$$\widetilde{g}_{11}(\eta,\tau) = \delta(\tau-\eta)\mathrm{e}^{-a\tau} + \frac{a^2}{2}\Theta(\tau+\eta)\Theta(\tau-\eta) \times \mathrm{e}^{-ax_-}(1-x_+)^a\, x_+(1-x_-)\ {}_1\mathrm{F}_1(a+1;2;\varphi(\eta,\tau)), \tag{24}$$

$$\widetilde{g}_{21}(\eta,\tau) = \frac{a}{2}\Theta(\tau+\eta)\Theta(\tau-\eta)\,\mathrm{e}^{-ax_-}(1-x_+)^a\ {}_1\mathrm{F}_1(a+1;1;\varphi(\eta,\tau)), \tag{25}$$

$$\widetilde{g}_{12}(\eta,\tau)=\frac{a}{2}\Theta(\tau+\eta)\Theta(\tau-\eta)\,\mathrm{e}^{-ax_-}(1-x_+)^a\,(1-x_-)\;{}_1\mathrm{F}_1(a;1;\varphi(\eta,\tau)), \tag{26}$$

$$\widetilde{g}_{22}(\eta,\tau)=\delta(\tau+\eta)\exp\left[-a\left(1-\mathrm{e}^{-\tau}\right)\right] + \frac{a^2}{2}\Theta(\tau+\eta)\Theta(\tau-\eta)\,\mathrm{e}^{-ax_-}(1-x_+)^a\,x_-\;{}_1\mathrm{F}_1(a+1;2;\varphi(\eta,\tau))\,. \tag{27}$$

Here ${}_1\mathrm{F}_1(\alpha,\beta;z)$ denotes the Kummer function [31] of the variable z with the parameters α, and β. Further, $x_\pm$ are two functions of two variables defined as $x_\pm = x_\pm(\eta,\tau) = 1-\exp(-(\tau\pm\eta)/2)$. Finally, in the formulae (24)–(27), the variable of the Kummer function is another function of two variables, namely

$$\varphi(\eta,\tau)=a\,x_+x_-=a(1-\mathrm{e}^{-(\tau+\eta)/2})(1-\mathrm{e}^{-(\tau-\eta)/2}). \tag{28}$$

Using the formulae (24)–(27) in equation (11), we get the explicit expression for the reduced work probability density. Provided a equals a positive integer, the Kummer functions reduces to the product of a polynomial and the exponential function. In this case, the formulae (24)–(27) assume a considerably simpler form. For example, if $a=1$, the reduced probability density is

$$\widetilde{\rho}(\eta,\tau)=\tfrac{1}{4}\delta(\tau+\eta)\exp\left[-(1-\mathrm{e}^{-\tau})\right]+\tfrac{1}{4}\delta(\tau-\eta)\,\mathrm{e}^{-\tau}+\tfrac{1}{4}\Theta(\tau+\eta)\Theta(\tau-\eta) \times\;\exp\left[\mathrm{e}^{-\tau}-\mathrm{e}^{-(\tau+\eta)/2}\right]\mathrm{e}^{-(\tau+\eta)/2}\left(3-\mathrm{e}^{-(\tau+\eta)/2}\right). \tag{29}$$

In fact, this function equals one-half of the sum of the matrix elements (24)–(27). We postpone further discussion of the Metropolis scenario to the last section.

3.2. Heat-bath scenario: $l_1(\tau)=[1+\exp(-\tau)]^{-1}$

While doing Monte Carlo simulations on, for example, spin systems [30], one frequently adopts the so-called *heat-bath* algorithm. This algorithm has motivated our second choice for the transition probabilities. Namely, in this subsection, we assume $l_1(\tau)=[1+\exp(-\tau)]^{-1}$ and, as follows from the detailed balance condition, $l_2(t)=\exp(-\tau)[1+\exp(-\tau)]^{-1}$. Therefore the jumps out of the energetically upper state are no longer a certain event. However, the probability to leave it increases with the increasing energy difference between both states. Adopting these forms of the transition probabilities, we shall speak about the *heat-bath* scenario. Within the scenario, our setting is equivalent to that of [28] where the authors have carried out an extensive series of computer simulations. In a sense, our present work constitutes a rigorous basis for the results in [28].

We start with inserting the present heat-bath transition probabilities into equation (20). Hence, at present, the solution of the Pauli master equation is

$$\mathbb{R}(\tau)=\mathbb{I}-\frac{1}{2}\begin{pmatrix}1&-1\\-1&1\end{pmatrix}\left[1-\mathrm{e}^{-a\tau}\right]+\frac{a}{2}\begin{pmatrix}-1&-1\\1&1\end{pmatrix}\int_0^\tau \mathrm{d}\tau'\mathrm{e}^{-a(\tau-\tau')}\,\tanh\left(\frac{\tau'}{2}\right). \tag{30}$$

As for the time asymptotic behavior of the occupation probabilities, we again observe the complete evacuation of the energetically upper state. However, the *dynamics* of the depletion process differs from that in the preceding subsection.

Further, in the present context, the dynamical equation (21) assumes the form

$$\frac{\mathrm{d}}{\mathrm{d}\tau}\widetilde{\mathbb{G}}(s,\tau) = -\left[s\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} + \frac{a}{1+\mathrm{e}^{-\tau}}\begin{pmatrix}1 & -\mathrm{e}^{-\tau}\\ -1 & \mathrm{e}^{-\tau}\end{pmatrix}\right]\widetilde{\mathbb{G}}(s,\tau), \qquad \widetilde{\mathbb{G}}(s,0) = \mathbb{I}. \tag{31}$$

Again, we are to solve the underlying system of equations for the individual matrix elements *and* carry out their inverse Laplace transformation with respect to the variable s. The rest of this subsection is devoted to these two tasks.

We commence with the substitution $\widetilde{\mathbb{F}}(2s,\tau) = \mathrm{e}^{-s\tau}\widetilde{\mathbb{G}}(s,\tau)$ which yields the dynamical equation

$$\frac{\mathrm{d}}{\mathrm{d}\tau}\widetilde{\mathbb{F}}(s,\tau) = -\left[s\begin{pmatrix}1 & 0\\ 0 & 0\end{pmatrix} + \frac{a}{1+\mathrm{e}^{-\tau}}\begin{pmatrix}1 & -\mathrm{e}^{-\tau}\\ -1 & \mathrm{e}^{-\tau}\end{pmatrix}\right]\widetilde{\mathbb{F}}(s,\tau), \qquad \widetilde{\mathbb{F}}(s,0) = \mathbb{I} \tag{32}$$

for the unknown matrix $\widetilde{\mathbb{F}}(s,\tau)$. Again, the matrix equation splits into two independent systems of two coupled ordinary differential equations. Let us first consider the second pair, i.e.

$$\frac{\mathrm{d}}{\mathrm{d}\tau}\widetilde{f}_{12}(s,\tau) = -a\frac{1}{1+\mathrm{e}^{-\tau}}\widetilde{f}_{12}(s,\tau) + a\frac{\mathrm{e}^{-\tau}}{1+\mathrm{e}^{-\tau}}\widetilde{f}_{22}(s,\tau) - s\widetilde{f}_{12}(s,\tau),$$

$$\widetilde{f}_{12}(s,\tau)\Big|_{\tau=0} = 0, \tag{33}$$

$$\frac{\mathrm{d}}{\mathrm{d}\tau}\widetilde{f}_{22}(s,\tau) = a\frac{1}{1+\mathrm{e}^{-\tau}}\widetilde{f}_{12}(s,\tau) - a\frac{\mathrm{e}^{-\tau}}{1+\mathrm{e}^{-\tau}}\widetilde{f}_{22}(s,\tau),$$

$$\widetilde{f}_{22}(s,\tau)\Big|_{\tau=0} = 1. \tag{34}$$

Let us now carry out the three following steps. First, we multiply equation (33) by the expression $(1+\mathrm{e}^{-\tau})$ and we carry out the *direct* Laplace transformation in the variable τ on both sides of the resulting equation. The Laplace variable conjugated to τ will be denoted as z. During this step, the product $\mathrm{e}^{-\tau}\widetilde{f}_{22}(s,\tau)$ is transformed into $\widetilde{f}_{22}(s,z+1)$. Similarly, the product $\mathrm{e}^{-\tau}\widetilde{f}_{12}(s,\tau)$ transforms into $\widetilde{f}_{12}(s,z+1)$. Secondly, we want to eliminate the unknown function $\widetilde{f}_{22}(s,z)$. For this purpose, one could use the Laplace transformation of equation (34). Instead of that, and perhaps more conveniently, one can first sum the original equations (33), (34) and carry out the direct Laplace transformation of the emerging sum. In this way, we get the relation $(z+s)\widetilde{f}_{12}(s,z) + z\widetilde{f}_{22}(s,z) = 1$. Finally, in the third step, we use the last relation to eliminate the function $\widetilde{f}_{22}(s,z)$ from the equation obtained in the first step. On the whole, we arrive at the single *difference* equation for the function $\widetilde{f}_{12}(s,z)$. It is

$$\widetilde{f}_{12}(s,z) + \frac{(z+a+1)(z+s+1)}{(z+1)(z+s+a)}\widetilde{f}_{12}(s,z+1) = \frac{a}{(z+1)(z+s+a)}. \tag{35}$$

Similar equations emerge if we replace on both sides of this equation the variable z with $z+n$, $n = 1,2,3,\ldots$. Hence we arrive at an infinite system of linear algebraic equations for the functions $\widetilde{f}_{12}(s,z+n)$, $n = 0,1,\ldots$. The system can be rewritten in the matrix form, the matrix of the coefficients having the nonzero matrix elements just on the main diagonal and above it. Using standard algebraic methods, we solve the infinite system

and the functions $\widetilde{f}_{12}(s,z)$ emerge in the form

$$\widetilde{f}_{12}(s,z) = a\sum_{n=0}^{\infty}(-1)^n \frac{(s+z+1)_n}{(s+z+a)_{n+1}}\,\frac{(z+a+1)_n}{(z+1)_{n+1}}. \tag{36}$$

Here and below, $(z)_n = z(z+1)(z+2)\ldots(z+n-1)$ is the Pochhammer symbol [31]. We have to find the double inverse Laplace transformation of this function.

In order to accomplish the goal, we introduce an important auxiliary function

$$H(a;s,z) = \sum_{n=0}^{\infty}(-1)^n \frac{(s+b)_n}{(s)_{n+1}}\,\frac{(z+a)_n}{(z)_{n+1}}, \tag{37}$$

where $b = 1-a$ (i.e. the function possesses just *one* independent parameter). Its fundamental role stems from the following two observations. First, we have succeeded in calculating the double inverse Laplace transformation of the function (37). This calculation is presented in the appendix, the result being

$$H(a;\eta,\tau) = \Theta(\eta)\Theta(\tau)\frac{1}{(1+\mathrm{e}^{-\eta})^a}\frac{1}{(1+\mathrm{e}^{-\tau})^{1-a}}\;{}_2\mathrm{F}_1\!\left(a,1-a;1;-\frac{1-\mathrm{e}^{-\eta}}{1+\mathrm{e}^{-\eta}}\,\frac{1-\mathrm{e}^{-\tau}}{1+\mathrm{e}^{-\tau}}\right). \tag{38}$$

Here $\Theta(\eta)$ is the unit step function, and ${}_2\mathrm{F}_1(\alpha,\beta;\gamma;z)$ denotes the Gauss hypergeometric function [33] of the variable z and with the parameters α, β and γ. Second, as follows from the comparison of equations (36) and (37), we have that

$$\widetilde{f}_{12}(s,z) = aH(a;s+z-b+1,z+1), \tag{39}$$

and hence also the double inverse Laplace transformation of the function $\widetilde{f}_{12}(s,z)$ must be related to the double inverse Laplace transformation of the function $H(a;s,z)$. Let us particularize their relation. We first carry out the inverse Laplace transformation of the function $H(a;s+z-b+1,z+1)$ with respect to the variable s. The result is $\exp[-\eta(z-b+1)]\,H(a;\eta,z+1)$. Thereupon, we perform the inverse Laplace transformation with respect to the variable z. In this step, the function $H(a;\eta,z+1)$ will be inverted into $\exp(-\tau)H(a;\eta,\tau)$ and the exponential factor $\exp(-\eta z)$ induces the shift in the original variable τ. Summing up, the functions $\widetilde{f}_{12}(\eta,\tau)$ and $H(a;\eta,\tau)$ are related through the formula

$$\widetilde{f}_{12}(\eta,\tau) = a\mathrm{e}^{-(a-1)\eta}\mathrm{e}^{-\tau}H(a;\eta,\tau-\eta). \tag{40}$$

Eventually, making use of the explicit form (38), we have that

$$\widetilde{f}_{12}(\eta,\tau) = \Theta(\eta)\Theta(\tau-\eta)\frac{a\,\mathrm{e}^{-a\eta}\mathrm{e}^{-(\tau-\eta)}}{(1+\mathrm{e}^{-\eta})^a(1+\mathrm{e}^{-(\tau-\eta)})^{1-a}}\;{}_2\mathrm{F}_1(a,1-a;1;\psi(\eta,\tau)). \tag{41}$$

Here we have introduced the abbreviation $\psi(\eta,\tau) = -(1-\mathrm{e}^{-\eta})(1-\mathrm{e}^{-(\tau-\eta)})[(1+\mathrm{e}^{-\eta})(1+\mathrm{e}^{-(\tau-\eta)})]^{-1}$.

Let us now turn our attention to the matrix element $\widetilde{f}_{22}(\eta,\tau)$. It is coupled with the matrix element $\widetilde{f}_{12}(\eta,\tau)$ through the system of equations (33) and (34). We now use the standard rules [32] of the operational calculus and carry out the inverse Laplace transformation with respect to the variable s on both sides of equation (33). After this

step, we obtain

$$\widetilde{f}_{22}(\eta,\tau)=\frac{1+\mathrm{e}^{-\tau}}{a\,\mathrm{e}^{-\tau}}\left[\frac{\partial}{\partial\tau}\widetilde{f}_{12}(\eta,\tau)+\frac{\partial}{\partial\eta}\widetilde{f}_{12}(\eta,\tau)\right]+\mathrm{e}^{\tau}\widetilde{f}_{12}(\eta,\tau). \tag{42}$$

In the next step, it suffices to insert the above explicit form (41) and carry out the partial derivatives required. Notice that the partial derivative of the unit step function produces a term proportional to the Dirac δ-function, cf the first term on the right-hand side of equation (43) below. After a rather extensive algebraic manipulation, the result assumes the form

$$\begin{aligned}\widetilde{f}_{22}(\eta,\tau)=\delta(\eta)\left(\frac{1+\mathrm{e}^{-\tau}}{2}\right)^{a}&+\Theta(\eta)\Theta(\tau-\eta)\frac{a\,\mathrm{e}^{-a\eta}(1-\mathrm{e}^{-(\tau-\eta)})}{(1+\mathrm{e}^{-\eta})^{a+1}(1+\mathrm{e}^{-(\tau-\eta)})^{1-a}}\\&\times\left[{}_2\mathrm{F}_1(a,1-a;1;\psi(\eta,\tau))-\frac{2(1-a)(1+\mathrm{e}^{-\tau})}{(1+\mathrm{e}^{-\eta})(1+\mathrm{e}^{-(\tau-\eta)})}\right.\\&\times\left.{}_2\mathrm{F}_1(1+a,2-a;2;\psi(\eta,\tau))\right].\end{aligned} \tag{43}$$

Now we focus on the second pair of coupled equations that emerge from equation (32), namely

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}\tau}\widetilde{f}_{11}(s,\tau)&=-a\frac{1}{1+\mathrm{e}^{-\tau}}\widetilde{f}_{11}(s,\tau)+a\frac{\mathrm{e}^{-\tau}}{1+\mathrm{e}^{-\tau}}\widetilde{f}_{21}(s,\tau)-s\widetilde{f}_{11}(s,\tau),\\&\widetilde{f}_{11}(s,\tau)\Big|_{\tau=0}=1,\end{aligned} \tag{44}$$

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}\tau}\widetilde{f}_{21}(s,\tau)&=a\frac{1}{1+\mathrm{e}^{-\tau}}\widetilde{f}_{11}(s,\tau)-a\frac{\mathrm{e}^{-\tau}}{1+\mathrm{e}^{-\tau}}\widetilde{f}_{21}(s,\tau),\\&\widetilde{f}_{21}(s,\tau)\Big|_{\tau=0}=0.\end{aligned} \tag{45}$$

Except for the initial conditions, this system is identical to the system (33) and (34). Hence its solution will proceed along the same steps as above and we restrict ourselves to the main results. We carry out the direct Laplace transformation with respect to the variable τ and eliminate the unknown function $\widetilde{f}_{11}(s,z)$. Further, we compose the infinite system of algebraic equations for $\widetilde{f}_{21}(s,z+n)$, $n=0,1,\ldots$, its solution yielding

$$\widetilde{f}_{21}(s,z)=a\sum_{n=0}^{\infty}(-1)^n\frac{(s+z)_n}{(s+z+a)_{n+1}}\frac{(z+a+1)_n}{(z)_{n+1}}=aH(a+1;s+z+a,z). \tag{46}$$

Next, we perform the double inverse Laplace transformation of the expression (46) and we arrive at the relation $\widetilde{f}_{21}(\eta,\tau)=a\mathrm{e}^{-a\eta}H(a+1;\eta,\tau-\eta)$, with the auxiliary function $H(a;\eta,\tau)$ being given in equation (38). The final result of the whole procedure is

$$\widetilde{f}_{21}(\eta,\tau)=\Theta(\eta)\Theta(\tau-\eta)\frac{a\,\mathrm{e}^{-a\eta}}{(1+\mathrm{e}^{-\eta})^{a+1}(1+\mathrm{e}^{-(\tau-\eta)})^{-a}}\,{}_2\mathrm{F}_1(1+a,-a;1;\psi(\eta,\tau)). \tag{47}$$

Finally, consider the remaining matrix element $\widetilde{f}_{11}(\eta,\tau)$. We start with equation (45) and we carry out the inverse Laplace transformation with respect to the variable s. We obtain

a relation which interconnects the functions $\widetilde{f}_{11}(\eta,\tau)$ and $\widetilde{f}_{21}(\eta,\tau)$. Using the relation and the explicit form (47), we finally obtain

$$\widetilde{f}_{11}(\eta,\tau)=\delta(\tau-\eta)\left(\frac{2\mathrm{e}^{-\tau}}{1+\mathrm{e}^{-\tau}}\right)^{a}+\Theta(\eta)\Theta(\tau-\eta)\frac{a\,\mathrm{e}^{-a\eta}\mathrm{e}^{-(\tau-\eta)}(\mathrm{e}^{-\eta}-1)}{(1+\mathrm{e}^{-\eta})^{a+1}(1+\mathrm{e}^{-(\tau-\eta)})^{1-a}}$$
$$\times\left[{}_2\mathrm{F}_1(a+1,-a;1;\psi(\eta,\tau))-\frac{2(a+1)(1+\mathrm{e}^{-\tau})}{(1+\mathrm{e}^{-\eta})(1+\mathrm{e}^{-(\tau-\eta)})}\right.$$
$$\left.\times\ {}_2\mathrm{F}_1(a+2,1-a;2;\psi(\eta,\tau))\right]. \tag{48}$$

The matrix elements (41), (43), (47) and (48) constitute the matrix $\widetilde{\mathbb{F}}(\eta,\tau)$. We now consider the above introduced relation $\widetilde{\mathbb{F}}(2s,\tau)=\mathrm{e}^{-s\tau}\widetilde{\mathbb{G}}(s,\tau)$ and perform therein the inverse Laplace transformation with respect to the variable s. We obtain $\widetilde{\mathbb{G}}(\eta,\tau)=\frac{1}{2}\widetilde{\mathbb{F}}((\tau+\eta)/2,\tau)$. In other words, the simple substitution brings us to the final form of the matrix elements $\widetilde{g}_{ij}(\eta,\tau)$, $i,j=1,2$. Thus the closing result of the present subsection is

$$\widetilde{g}_{11}(\eta,\tau)=\delta(\tau-\eta)\left(\frac{2\mathrm{e}^{-\tau}}{1+\mathrm{e}^{-\tau}}\right)^{a}+\frac{1}{2}\Theta(\tau+\eta)\Theta(\tau-\eta)$$
$$\times\frac{a\,\mathrm{e}^{-a(\tau+\eta)/2}\mathrm{e}^{-(\tau-\eta)/2}(\mathrm{e}^{-(\tau+\eta)/2}-1)}{(1+\mathrm{e}^{-(\tau+\eta)/2})^{a+1}(1+\mathrm{e}^{-(\tau-\eta)/2})^{1-a}}\left[{}_2\mathrm{F}_1(a+1,-a;1;\phi(\eta,\tau))\right.$$
$$\left.-\frac{2(1+a)(1+\mathrm{e}^{-\tau})}{(1+\mathrm{e}^{-(\tau+\eta)/2})(1+\mathrm{e}^{-(\tau-\eta)/2})}\ {}_2\mathrm{F}_1(a+2,1-a;2;\phi(\eta,\tau))\right], \tag{49}$$

$$\widetilde{g}_{21}(\eta,\tau)=\frac{1}{2}\Theta(\tau+\eta)\Theta(\tau-\eta)\frac{a\,\mathrm{e}^{-a(\tau+\eta)/2}}{(1+\mathrm{e}^{-(\tau+\eta)/2})^{a+1}(1+\mathrm{e}^{-(\tau-\eta)/2})^{-a}}$$
$$\times\ {}_2\mathrm{F}_1(a+1,-a;1;\phi(\eta,\tau)), \tag{50}$$

$$\widetilde{g}_{12}(\eta,\tau)=\frac{1}{2}\Theta(\tau+\eta)\Theta(\tau-\eta)\frac{a\,\mathrm{e}^{-a(\tau+\eta)/2}\mathrm{e}^{-(\tau-\eta)/2}}{(1+\mathrm{e}^{-(\tau+\eta)/2})^{a}(1+\mathrm{e}^{-(\tau-\eta)/2})^{1-a}}$$
$$\times\ {}_2\mathrm{F}_1(a,1-a;1;\phi(\eta,\tau)), \tag{51}$$

$$\widetilde{g}_{22}(\eta,\tau)=\delta(\tau+\eta)\left(\frac{1+\mathrm{e}^{-\tau}}{2}\right)^{a}+\frac{1}{2}\Theta(\tau+\eta)\Theta(\tau-\eta)$$
$$\times\frac{a\,\mathrm{e}^{-a(\tau+\eta)/2}(1-\mathrm{e}^{-(\tau-\eta)/2})}{(1+\mathrm{e}^{-(\tau+\eta)/2})^{a+1}(1+\mathrm{e}^{-(\tau-\eta)/2})^{1-a}}\times\left[{}_2\mathrm{F}_1(a,1-a;1;\phi(\eta,\tau))\right.$$
$$\left.-\frac{2(1-a)(1+\mathrm{e}^{-\tau})}{(1+\mathrm{e}^{-(\tau+\eta)/2})(1+\mathrm{e}^{-(\tau-\eta)/2})}\ {}_2\mathrm{F}_1(a+1,2-a;2;\phi(\eta,\tau))\right]. \tag{52}$$

Here we used the abbreviation

$$\phi(\eta,\tau)=-\frac{1-\mathrm{e}^{-(\tau+\eta)/2}}{1+\mathrm{e}^{-(\tau+\eta)/2}}\,\frac{1-\mathrm{e}^{-(\tau-\eta)/2}}{1+\mathrm{e}^{-(\tau-\eta)/2}}. \tag{53}$$

Again, for a being an integer, the hypergeometric function reduces to a polynomial and

the above formulae simplify. For example, if $a = 1$, the reduced probability density is

$$\widetilde{\rho}(\eta,\tau) = \delta(\tau-\eta)\frac{\mathrm{e}^{-\tau}}{(1+\mathrm{e}^{-\tau})} + \delta(\tau+\eta)\frac{1}{4(1+\mathrm{e}^{-\tau})} + \Theta(\tau+\eta)\Theta(\tau-\eta)\frac{\mathrm{e}^{-(\tau+\eta)/2}(1+\mathrm{e}^{-\tau})}{(1+\mathrm{e}^{-(\tau+\eta)/2})^3}. \tag{54}$$

Similarly to equation (29), this function equals one-half of the sum of the matrix elements (49)–(52).

4. Discussion

Figure 1 presents a representative set of various possible forms of the work probability density $\widetilde{\rho}(\eta,\tau)$. Each panel shows the exact work probability density for both scenarios as discussed in sections 3.1 and 3.2. All curves refer to the reduced time $\tau = 1$. Individual panels correspond to the four different values of the driving parameter a.

The exact expression for the work probability density yields all one-time properties of the stochastic process $\mathsf{W}(t)$. For example, all moments $\langle \mathsf{W}^n(t)\rangle$, $n = 1, 2, \ldots$, are accessible through a single integration. Specifically, in the present section, we shall look at the reduced mean value $\widetilde{w}_{\mathrm{mean}}(\tau)$ and at the reduced variance $\widetilde{\sigma}^2(\tau)$. They are defined as

$$\widetilde{w}_{\mathrm{mean}}(\tau) = \int_{-\tau}^{\tau} \eta\, \widetilde{\rho}(\eta,\tau)\, \mathrm{d}\eta, \tag{55}$$

$$\widetilde{\sigma}^2(\tau) = \int_{-\tau}^{\tau} \eta^2\, \widetilde{\rho}(\eta,\tau)\, \mathrm{d}\eta - \widetilde{w}^2_{\mathrm{mean}}(\tau). \tag{56}$$

As pointed out at the beginning of section 3, there is just one dimensionless parameter which controls all features of the dimensionless probability density. It is the driving parameter $a = \nu/(2\beta\varepsilon\omega)$. It represents the ratio of two characteristic timescales. The first timescale $1/\nu$ plays the role of the system's relaxation time in case the energy levels would have been frozen. The second timescale $1/(\varepsilon\omega)$ represents the velocity with which the external agent changes the energies of the system. Contrary to the first scale, the second one is fully under external control. Moreover, the driving parameter is proportional to the absolute temperature of the heat bath. It turns out that the driving parameter reflects the degree of the irreversibility of the isothermal process in question.

If a is small, the process strongly departs from the equilibrium one. This can happen if one or more of the following three conditions hold. First, if ν is small, the occupation probabilities of the individual energy levels are effectively frozen during long periods of time. Therefore they lag behind the Boltzmann distribution which would correspond to the actual position of the energy levels. More precisely, the population of the energetically higher (lower) level is always, i.e. at any instant, bigger (smaller) than it would be during the corresponding reversible process. The work done on the system is then typically bigger than the equilibrium work. Second, similar consideration is valid in the case of large ω. Then the externally controlled changes of the energy levels are rapid and the populations of the energy levels again lag behind the equilibrium one. Third, the strong irreversibility occurs also in the low temperature limit. Depending on the interpretation

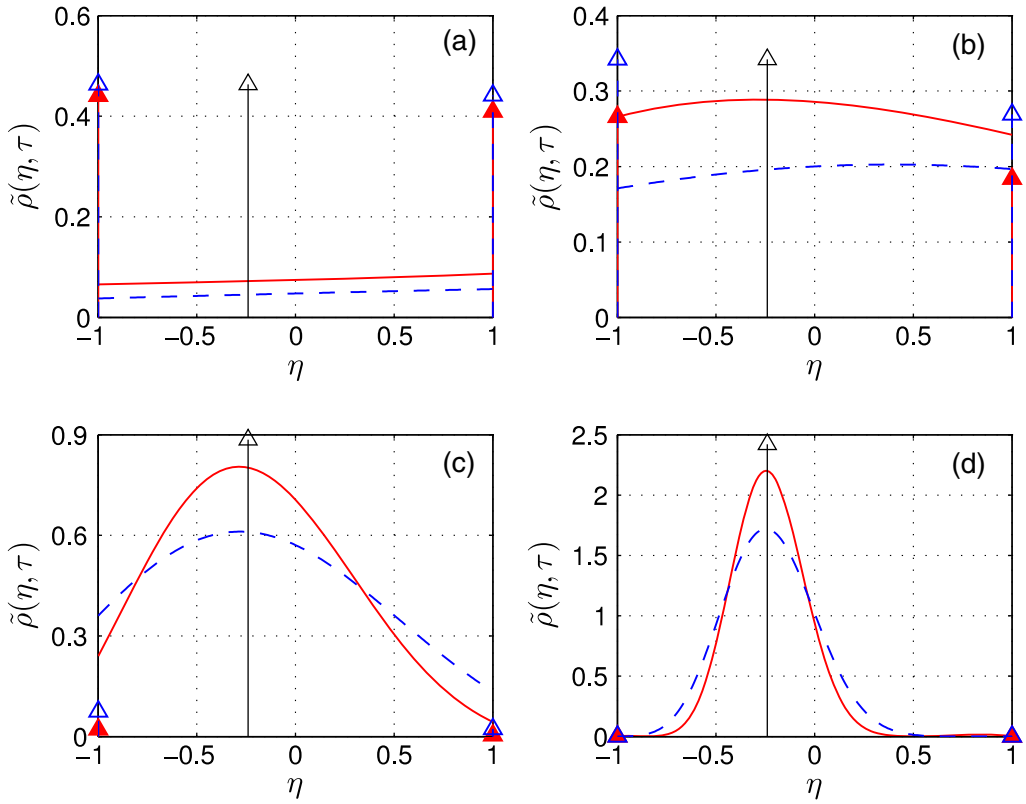

Figure 1. Comparison of the reduced probability density of work $\widetilde{\rho}(\eta,\tau)$ for the two transition scenarios. The density is illustrated as a function of the reduced work η, for the reduced time $\tau = 1$, and for four values of the driving parameter a. The full lines depict the work probability density for the Metropolis scenario, i.e. they represent one-half of the sum of the individual elements (24)–(27). Similarly, the broken lines depict the results of section 3.2, i.e. they represent one-half of the sum of the elements (49)–(52). The weights of the δ functions on the borders of the support, i.e. at the points $\eta = -\tau$ and τ, are depicted by the arrows. The heights of these arrows show the weights of the corresponding δ functions. The full heads belong to the Metropolis scenario, while the empty heads are related to the heat-bath scenario. In all panels, the arrow inside the support of the probability density marks the value of the reversible work $\widetilde{w}_{\mathrm{rev}}(\tau)$ (the height of this arrow has no meaning). The values of the driving parameter used in the individual panels are (a) $a = 0.2$, (b) $a = 1.0$, (c) $a = 5.0$ and (d) $a = 35.0$.

of the parameter a, the decreasing temperature either increases the effective relaxation time, or increases the effective velocity of the driving.

If a is large, the process is close to the reversible one. The occupation probabilities of the individual energy levels are always, i.e. at any instant, close to the equilibrium values which would correspond to the actual positions of the energies. Correspondingly, the mean work is close to the equilibrium work. It has been shown in [29] that, if the general process approaches its equilibrium limit, the work probability density assumes the Gaussian shape. The statement has been fully confirmed here. If $a \gg 1$, the reduced

work probability density approaches the form

$$\widetilde{\rho}(\eta,\tau)=\frac{1}{\sqrt{2\pi\widetilde{\sigma}^2(\tau)}}\exp\left\{-\frac{[\eta-\widetilde{w}_{\mathrm{mean}}(\tau)]^2}{2\widetilde{\sigma}^2(\tau)}\right\}, \tag{57}$$

where the functions $\widetilde{w}_{\mathrm{mean}}(\tau)$ and $\widetilde{\sigma}^2(\tau)$ are given by the expressions (55) and (56), respectively. We were not able to derive the form (57) analytically, i.e. using a suitable asymptotic expansion of our exact results. Instead, using the numerical quadrature, we have first evaluated the moments (55) and (56). Next, we have inserted the results into the right-hand side of the expression (57). Eventually, the emerging trial function has been compared with the exact probabilities for both transition scenarios. Provided a is large, the trial function coincides with the exact ones. We illustrate this feature in panel 1(d), where the driving parameter a assumes the value 35.

Contrary to the above asymptotic expansion, we were able to carry out the limit $a\to\infty$, the result being

$$\lim_{a\to\infty}\widetilde{\rho}(\eta,\tau)=\delta\Big(\eta+2\log\Big(\cosh\frac{\tau}{2}\Big)\Big). \tag{58}$$

Therefore, as anticipated, the density collapses into the δ function located at the value $-2\log[\cosh(\tau/2)]$. The value is, of course, nothing but the reversible work. This can be proved by the explicit evaluation of the Helmholtz free energies corresponding to the equilibrium state compatible with the energy levels at the final time τ, and at the initial time $\tau=0$.

Let us consider another interesting feature of the work probability density $\widetilde{\rho}(\eta,\tau)$. In general, the density consists of two qualitatively different components. First, the singular component is represented by the two δ functions located at $\eta=\pm\tau$. Second, the continuous component is located in the interval $\langle-\tau,\tau\rangle$. For both transition scenarios, the weight of the δ function located at $\eta=\tau$ vanishes in the long-time limit. In fact, the weight represents the probability that the system was initially in the state 1 and remains there during the whole time interval $\langle 0,\tau\rangle$. On the other hand, the weight of the δ function located at $\eta=-\tau$ asymptotically approaches the value $\mathrm{e}^{-a}/2$ for the Metropolis scenario, and the value $2^{-(a+1)}$ for the heat-bath scenario. Similarly as above, these weights represent the probability that the system starts in the state 2 and remains there up to time τ. The weights of both δ functions for the heat-bath scenario were already reported in [28] under the assumption of a fast driving, i.e. for a being small. Our calculation verifies these results. Moreover, we show that the values are valid for an arbitrary value of the driving parameter a. Summing up, the singular component stems from encompassing the sample paths that have never jumped out of their initial state. On the other hand, the trajectories that have accomplished at least one jump before the time τ contribute to the continuous component of the probability density.

Now we turn our attention to the time-asymptotic behavior of the work probability density. In the long time limit, the energy difference between the two energy levels becomes large. Therefore $l_1(\tau)\to 1$ and the transition from the higher level to the lower one occurs at almost any attempt time. On the other hand, $l_2(\tau)\to 0$ and the transitions from the lower level to the higher one are effectively blocked. In other words, in the asymptotic regime, the system occupies practically only the energetically lower state (state 2) and consequently the work done per unit of reduced time is $-\tau$. Hence for

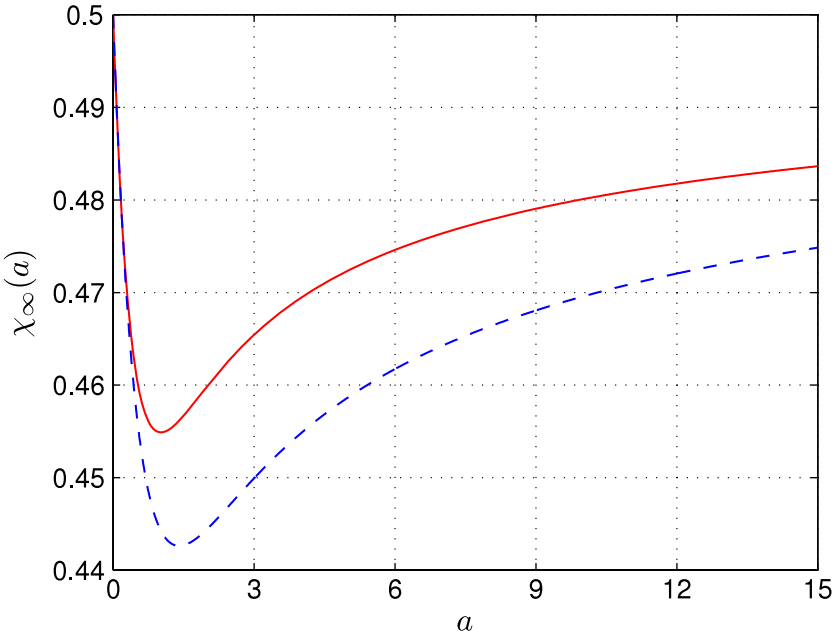

Figure 2. The violation factor $\chi_\infty(a)$ as a function of the driving parameter a. The calculation has been based on equation (59) where the integrated function $\widetilde{\rho}(\eta,\tau)$ equals one-half of the sum of the matrix elements (24)–(27) (full curve), or the matrix elements (49)–(52) (broken curve).

an arbitrary but finite reduced time τ' and for $\tau\to\infty$ we have $\widetilde{\rho}(\eta,\tau+\tau')\approx\widetilde{\rho}(\eta+\tau',\tau)$. Similar reasoning yields a time asymptotic evolution of the mean work. Specifically, $\widetilde{w}_{\rm mean}(\tau+\tau')\approx\widetilde{w}_{\rm mean}(\tau)-\tau'$.

As mentioned above, the second law of thermodynamics assesses the lower limit of the work done on the system during a general isothermal process. In our setting, the bound assumes the form $\widetilde{w}_{\rm mean}(\tau)\geq\widetilde{w}_{\rm rev}(\tau)$. The equality holds for the equilibrium isothermal process. On the other hand, in our model the work along a certain number of sample paths is *smaller* than the reversible work (see figure 1). One could ask what is the total weight of these sample paths. In other words, one considers the quantity $\chi(\tau;a)=\mathrm{Prob}\{\widetilde{\mathsf{W}}(\tau)<\widetilde{w}_{\rm rev}(\tau)\}$. Its asymptotic value $\chi_\infty(a)=\lim_{\tau\to\infty}\chi(\tau;a)$ depends solely on the driving parameter a and it will be referred to as the *violation factor*. Formally, the violation factor can be calculated as

$$\chi_\infty(a)=\lim_{\tau\to\infty}\chi(\tau;a)=\lim_{\tau\to\infty}\int_{-\tau}^{\widetilde{w}_{\rm rev}(\tau)}\widetilde{\rho}(\eta,\tau)\,\mathrm{d}\eta. \tag{59}$$

If $a=0$ there are no transitions between the energy levels and therefore all the trajectories that contribute to $\chi(\tau,a)$ or to $\chi_\infty(a)$ are those that have initially departed from the state 1. Obviously, this set of trajectories has the total probability $p_1(0)=\frac{1}{2}$, and therefore $\lim_{a\to0^+}\chi_\infty(a)=\frac{1}{2}$. On the other hand, if $a\gg1$, the probability density assumes the Gaussian shape (57) and the mean work approaches the reversible work. It follows from the symmetry of the Gaussian curve that $\lim_{a\to\infty}\chi_\infty(a)=\frac{1}{2}$. Figure 2 illustrates the violation factor $\chi_\infty(a)$ as the function of the driving parameter a. For both transition scenarios

we observe the well-pronounced minimum at a certain value of the driving parameter. However, the position of the minimum for the Metropolis scenario differs from that for the heat-bath scenario.

We have checked our analytical results against the corresponding computer simulations. Due to our specific treatment of the underlying time-inhomogeneous Markov process, our simulation procedure differs from that used in [28]. In our approach, we simply follow step by step the construction as elaborated in section 2. More precisely, we first generate an attempt time. Second, we evaluate the positions of the energy levels at that time. Third, we determine the actual transition probabilities. Finally, we generate a random number and decide whether the system changes its state or not. From its very beginning, our procedure operates with the continuous time and therefore no transition from the discrete time steps to continuous time is needed. We have carried out a rather extensive series of such computer simulations. In any particular case, our analytical results (24)–(27) and (49)–(52) have been confirmed.

Using the procedure in this paper, we have also investigated systems with more than two energy levels. For example, in the case of the three-state system, the work probability density exhibits the δ function at three different positions. Two of them are on the borders of the support, but the third one is located in between the borders. At this very point, there occurs a discontinuity of the individual matrix elements of the matrix $\mathbb{G}(w,t)$, and consequently also of the whole work probability density $\rho(w,t)$. The discontinuity is well pronounced in the strongly irreversible case. Its magnitude decreases with increasing driving parameter a.

In conclusion, we have calculated the exact probability density for the work done on the simple two-level system during the irreversible isothermal process. We have compared two different transition scenarios. The (time-local) detailed balance condition guarantees that, in the quasistatic limit, both scenarios coincide. But still, for an irreversible isothermal process, they lead to differences in the resulting work distribution.

Acknowledgments

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Appendix. The detailed calculation of the function $H(a;\eta,\tau)$

The double direct Laplace transformation of the function $H(a;\eta,\tau)$, i.e. the function $H(a;s,z)$, is given by the expression (37). The calculation of the double inverse Laplace transformation $H(a;s,z) \longrightarrow H(a;\eta,\tau)$ represents a crucial step. As a matter of fact, in section 3.2, it is the function $H(a;\eta,\tau)$ which allows for a further detailed discussion of the exact probability density $\widetilde{\rho}(\eta,\tau)$. The appendix presents details on the inversion procedure in question and equation (A.21) shows the final result.

First of all, for the reader's convenience, we repeat equation (37) from the main text:

$$H(a;s,z)=\sum_{n=0}^{\infty}(-1)^n\frac{(s+b)_n}{(s)_{n+1}}\,\frac{(z+a)_n}{(z)_{n+1}}. \tag{A.1}$$

Here and below, $b=1-a$. Let us first try to expand the rational functions $(s+b)_n/(s)_{n+1}$ and $(z+a)_n/(z)_{n+1}$ on the right-hand side into the corresponding partial fractions. We obtain the expression

$$H(a;s,z)=\sum_{n=0}^{\infty}(-1)^n\sum_{k=0}^{n}\frac{(b-k)_n}{k!(n-k)!}\,\frac{(-1)^k}{s+k}\sum_{l=0}^{n}\frac{(a-l)_n}{l!(n-l)!}\,\frac{(-1)^l}{z+l}. \tag{A.2}$$

The double inverse Laplace transformation of the above formula is quite straightforward: the simple fractions $1/(s+k)$ and $1/(z+l)$ are transformed into $\Theta(\eta)\exp(-k\eta)$ and $\Theta(\tau)\exp(-l\tau)$, respectively. Therefore the explicit form of the function $H(a;\eta,\tau)$ is

$$H(a;\eta,\tau)=\Theta(\eta)\Theta(\tau)\sum_{n=0}^{\infty}(-1)^n\sum_{k=0}^{n}\frac{(b-k)_n}{(n-k)!}\,\frac{(-\mathrm{e}^{-\eta})^k}{k!}\sum_{l=0}^{n}\frac{(a-l)_n}{(n-l)!}\,\frac{(-\mathrm{e}^{-\tau})^l}{l!}. \tag{A.3}$$

In principle, this rather complicated formula already represents an accomplishment of our goal. However, we shall show that the result can be written in a much more elegant way.

Before we proceed, we perform two preparatory steps. First, we take into account the factorization

$$H(a;\eta,\tau)=\Theta(\eta)\Theta(\tau)\widehat{H}(a;\eta,\tau), \tag{A.4}$$

and, subsequently, we focus on the calculation of the function $\widehat{H}(a;\eta,\tau)$. Second, the function $\widehat{H}(a;\eta,\tau)$ depends on its variables only through the combinations $x=\mathrm{e}^{-\eta}$, and $y=\mathrm{e}^{-\tau}$. These two abbreviations will be used below.

The detailed analysis of the summations on the right-hand side of (A.3) reveals the possibility to write the whole expression as a single matrix element of a certain infinite-order matrix. More precisely, we introduce the so-called shift operators $\mathbb{E}_+$ and $\mathbb{E}_-$ with the matrix elements $\langle i|\,\mathbb{E}_+\,|j\rangle=\delta_{i+1,j}$, and $\langle i|\,\mathbb{E}_-\,|j\rangle=\delta_{i,j+1}$, $i,j=0,1,\ldots$. In other words, the operator $\mathbb{E}_+$ ($\mathbb{E}_-$) has nonzero matrix elements just above (below) the main diagonal. The shift operators fulfill the obvious relations

$$\mathbb{E}_+^i\,|0\rangle=|i\rangle\qquad\text{and}\qquad\mathbb{E}_-^j\,|i\rangle=\begin{cases}|i-j\rangle & \text{for } i\geq j\\ 0 & \text{for } i<j\end{cases}\quad\text{with } i,j=0,1,2,\ldots. \tag{A.5}$$

They do not commute: $\mathbb{E}_-\mathbb{E}_+=\mathbb{I}$, and $\mathbb{E}_+\mathbb{E}_-=\mathbb{I}-|0\rangle\langle 0|$. Using the shift operators, we now depart from (A.3) and we write the function $\widehat{H}(a;x,y)$ in the form

$$\widehat{H}(a;x,y)=\langle 0|\,\frac{1}{(1-\mathbb{E}_-)^a}\,\frac{1}{(1-y\mathbb{E}_-)^b}\,\frac{1}{(1+x\mathbb{E}_+)^a}\,\frac{1}{(1+\mathbb{E}_+)^b}\,|0\rangle\,. \tag{A.6}$$

After a rather lengthy but purely algebraic rearrangement, we obtain an equivalent expression

$$\begin{aligned}\widehat{H}(a;x,y)=\frac{1}{x^a}\frac{1}{y^b}\,\langle 0|\,\frac{1}{1-\mathbb{E}_-}\,\frac{1}{\left[1-((y-1)/y)\,(1/(1-\mathbb{E}_-))\right]^b}\\ \times\,\frac{1}{\left[1-((x-1)/x)(1/(1+\mathbb{E}_+))\right]^a}\,\frac{1}{1+\mathbb{E}_+}\,|0\rangle\,.\end{aligned} \tag{A.7}$$

In the next step, we expand the second and the third operator into the corresponding power series. More precisely, we use the formal expansions

$$\frac{1}{\left[1-\left((y-1)/y\right)\left(1/(1-\mathbb{E}_-)\right)\right]^b}=\sum_{n=0}^{\infty}\frac{(b)_n}{n!}\left(\frac{y-1}{y}\right)^n\frac{1}{(1-\mathbb{E}_-)^n}\qquad\text{and}$$
$$\frac{1}{\left[1-\left((x-1)/x\right)\left(1/(1+\mathbb{E}_+)\right)\right]^a}=\sum_{m=0}^{\infty}\frac{(a)_m}{m!}\left(\frac{x-1}{x}\right)^m\frac{1}{(1+\mathbb{E}_+)^m}. \tag{A.8}$$

After substituting back into equation (A.7), we arrive at the formula

$$\widehat{H}(a;x,y)=\frac{1}{x^a}\frac{1}{y^b}\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}\frac{(b)_m\,(a)_n}{m!\,n!}\left(\frac{y-1}{y}\right)^m\left(\frac{x-1}{x}\right)^n$$
$$\times\ \langle 0|\,\frac{1}{(1-\mathbb{E}_-)^{m+1}}\,\frac{1}{(1+\mathbb{E}_+)^{n+1}}\,|0\rangle\,. \tag{A.9}$$

We are faced with the matrix elements

$$\kappa_{mn}=\langle 0|\,\frac{1}{(1-\mathbb{E}_+)^{m+1}}\,\frac{1}{(1+\mathbb{E}_-)^{n+1}}\,|0\rangle\,. \tag{A.10}$$

More generally, we consider the auxiliary functions

$$h_{mn}(u)=\langle 0|\,\frac{1}{(1-u\mathbb{E}_+)^{m+1}}\frac{1}{(1+u\mathbb{E}_-)^{n+1}}\,|0\rangle\,, \tag{A.11}$$

and, after their calculation, we aim at carrying out the limits $\kappa_{mn}=\lim_{u\to 1^-}h_{mn}(u)$. We again expand the inverse operators in equation (A.11) into the corresponding power series. After this step, we have that

$$h_{mn}(u)=\sum_{k=0}^{\infty}\sum_{l=0}^{\infty}\frac{(m+1)_k}{k!}\frac{(n+1)_l}{l!}u^k(-u)^l\,\langle 0|\,\mathbb{E}_-^k\,\mathbb{E}_+^l\,|0\rangle\,. \tag{A.12}$$

Using the property $\langle 0|\,\mathbb{E}_-^k\,\mathbb{E}_+^l\,|0\rangle=\delta_{kl}$, $k,l=0,1,\ldots$, the double summation in equation (A.12) reduces to the single one. The remaining summation can be identified with the Gauss hypergeometric series [31]. Using the standard notation, the explicit form of the auxiliary functions (A.11) is

$$h_{mn}(u)=\sum_{k=0}^{\infty}\frac{(m+1)_k}{k!}\frac{(n+1)_k}{k!}\left(-u^2\right)^k={}_2\mathrm{F}_1(m+1,n+1;1;-u^2). \tag{A.13}$$

All three parameters of the Gauss hypergeometric series are integers and the function itself reduces to a polynomial in a more complicated variable. Actually, applying first the Euler transformation [31], we get

$${}_2\mathrm{F}_1(m+1,n+1;1;-u^2)=\frac{1}{(1+u^2)^{n+1}}\,{}_2\mathrm{F}_1\left(-m,n+1;1;\frac{u^2}{1+u^2}\right)$$
$$=\frac{1}{(1+u^2)^{n+1}}\mathrm{P}_m^{(0,n-m)}\left(\frac{1-u^2}{1+u^2}\right). \tag{A.14}$$

Here $\mathrm{P}_j^{(\alpha,\beta)}(z)$ is the Jacobi polynomial of the order j, with the parameters α, β, and in the variable z [31]. In other words, the numbers κ_{mn} are

$$\kappa_{mn} = \lim_{u\to 1-} h_{mn}(u) = \frac{1}{2^{n+1}} \mathrm{P}_m^{(0,n-m)}(0). \tag{A.15}$$

Summing up these several lines, the function $\widehat{H}(a;x,y)$ assumes the form

$$\widehat{H}(a;x,y) = \frac{1}{x^a}\frac{1}{y^b} \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} \frac{1}{2^{n+1}} \frac{(b)_m\,(a)_n}{m!\,n!} \left(\frac{y-1}{y}\right)^m \left(\frac{x-1}{x}\right)^n \mathrm{P}_m^{(0,n-m)}(0). \tag{A.16}$$

At this point, using the properties of the Jacobi polynomials, we could have used the explicit formula for the numbers $\mathrm{P}_j^{(\alpha,\beta)}(0)$. However, in view of their role in the above summation, we take another route. It is known that the Jacobi polynomials can be written as integrals in the complex plane [31]. Using this observation, we have that

$$\mathrm{P}_m^{(0,n-m)}(0) = \frac{1}{2\pi\mathrm{i}} \oint \left(\frac{z^2-1}{2z}\right)^m \frac{(1+z)^{n-m}}{z}\,\mathrm{d}z. \tag{A.17}$$

Here we integrate along the positively oriented unit circle around the origin of the complex plane. We now substitute the last expression into equation (A.16). After changing the order of the summation and the integration, and after a further rearrangement, we obtain

$$\widehat{H}(a;x,y) = \frac{1}{(1+x)^a}\frac{1}{(1+y)^b}\frac{1}{2\pi\mathrm{i}} \oint \frac{1}{z} \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} \frac{(b)_m}{m!}\frac{(a)_n}{n!} \left(\frac{1}{z}\frac{1-y}{1+y}\right)^m \left(-z\,\frac{1-x}{1+x}\right)^n \mathrm{d}z. \tag{A.18}$$

We now integrate the double series term by term. Invoking the residue theorem in the form $\oint z^{n-m-1}\,\mathrm{d}z = 2\pi\mathrm{i}\delta_{mn}$, all summands with $m \neq n$ vanish and the surviving terms yield

$$\widehat{H}(a;x,y) = \frac{1}{(1+x)^a}\frac{1}{(1+y)^b} \sum_{n=0}^{\infty} \frac{(a)_n (b)_n}{n!\,n!} \left(-\frac{1-x}{1+x}\,\frac{1-y}{1+y}\right)^n. \tag{A.19}$$

On the right-hand side, we again recognize the Gauss hypergeometric series. Hence the final expression is

$$\widehat{H}(a;x,y) = \frac{1}{(1+x)^a}\frac{1}{(1+y)^b}\; {}_2\mathrm{F}_1\left(a,b;1;-\frac{1-x}{1+x}\,\frac{1-y}{1+y}\right). \tag{A.20}$$

Having attained this elegant expression, we now return to the original variables and to the original function (A.4). After these two steps, the main result of the appendix assumes the form

$$H(a;\eta,\tau) = \Theta(\eta)\Theta(\tau)\frac{1}{(1+\mathrm{e}^{-\eta})^a}\frac{1}{(1+\mathrm{e}^{-\tau})^b}\; {}_2\mathrm{F}_1\left(a,b;1;-\frac{1-\mathrm{e}^{-\eta}}{1+\mathrm{e}^{-\eta}}\,\frac{1-\mathrm{e}^{-\tau}}{1+\mathrm{e}^{-\tau}}\right). \tag{A.21}$$

This expression is used in the main text. For the reader's convenience, we repeat it in equation (38).

In closing the appendix, we would like to mention an alternative way to get the result (A.20). First, notice that the variable of the Gauss function vanishes both at $x = 1$

and at $y = 1$. In other words, our solution fulfills the boundary conditions

$$\widehat{H}(a;x,y)\Big|_{x=1} = \frac{1}{2^a}\frac{1}{(1+y)^b} \qquad \text{and} \qquad \widehat{H}(a;x,y)\Big|_{y=1} = \frac{1}{2^b}\frac{1}{(1+x)^a}. \tag{A.22}$$

The conditions are already incorporated in the system of equations (31).

On the other hand, imagine that we perform the inverse Laplace transformation with respect to the variable s directly in the original system of equations (31). Then, after some algebra, we could isolate a single hyperbolic partial differential equation for the function $\widehat{H}(a;x,y)$. Specifically, the equation is

$$\left[(1+xy)\frac{\partial}{\partial x}\frac{\partial}{\partial y} + bx\frac{\partial}{\partial x} + ay\frac{\partial}{\partial y} + ab\right]\widehat{H}(a;x,y) = 0. \tag{A.23}$$

However, presently, the equation must be explicitly supplemented by the boundary conditions (A.22). Adopting this strategy, we look for a function which solves the partial differential equation (A.23) and, at the same time, which fulfills the boundary conditions (A.22). We have verified by direct substitution that our function (A.20) actually represents the (unique) solution of the boundary problem thereby formulated.

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