Previously derived expressions for the characteristic function of work performed on a quantum system by a classical external force are generalized to arbitrary initial states of the considered system and to Hamiltonians with degenerate spectra. In the particular case of microcanonical initial states, explicit expressions for the characteristic function and the corresponding probability density of work are formulated. Their classical limit as well as their relations to the corresponding canonical expressions are discussed. A fluctuation theorem is derived that expresses the ratio of probabilities of work for a process and its time reversal to the ratio of densities of states of the microcanonical equilibrium systems with corresponding initial and final Hamiltonians. From this Crooks-type fluctuation theorem a relation between entropies of different systems can be derived which does not involve the time-reversed process. This entropy-from-work theorem provides an experimentally accessible way to measure entropies.

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I. INTRODUCTION

During the last decade various fluctuation and work theorems [1–4] have been formulated and discussed. They provide information about the fully nonlinear response of a system under the action of a time-dependent force [5–8], in contrast to linear response theories in which the response is expressed in terms of correlation functions of the unperturbed system [9–13]. Moreover, these theorems were used to establish the second law of thermodynamics and to sharpen its formulation [14–16]. Fluctuation and work theorems have primarily been derived, numerically tested, and experimentally confirmed for classical systems which initially or permanently are in contact with a heat bath [17–19]. The system then initially stays in a state described by a canonical (Maxwell-Boltzmann) distribution at the temperature of the heat bath. Classical isolated systems which initially are in a microcanonical state were investigated in Ref. [20]. Quantum mechanical generalizations were proposed recently [21–26], but only for canonical initial states. The equivalence of canonical and microcanonical initial states was demonstrated for classical systems in the thermodynamic limit [27]. Little emphasis has been given to the impact of general initial conditions on the work performed on a quantum system by a classical force [28].

In the present paper we investigate the work performed by an external force acting on an otherwise isolated quantum system. The characteristic function of the work is shown to always assume the form of a correlation function of the exponentiated system Hamiltonians at the initial and final times, regardless of how the system was initially prepared. This characteristic function comprises all aspects of the statistics of the work. In the special case of a microcanonical initial state, the inverse Fourier transform leads to an expression for the probability density of performed work which directly leads to a quantum generalization of the microcanonical version of the Crooks theorem. This theorem relates the probability densities of work of the processes and its time-reversed partner process to the difference of entropies of the equilibrium states that correspond to the initial and final Hamiltonians. Such relations have been confirmed for classical systems by computer experiments [20]. In real experiments an active time reversal is not feasible. We yet present an "entropy-from-work" theorem that does not contain the time-reversed process and still allows one to obtain the entropy of the equilibrium system for the system with the final Hamiltonian, provided the entropy of the system with the initial Hamiltonian is known.

Apart from its use in numerical investigations such as molecular dynamics [29,30] or microcanonical Monte Carlo simulations [31], the microcanonical ensemble is known to provide the valid description of isolated systems in equilibrium [32]. It presents the proper statistical mechanical framework for the description of isolated systems of finite size, such as clusters of atoms [33], atomic nuclei [34], or Bose Einstein condensates [35], and even allows for phase transitions in finite systems [36–38].

The paper is organized as follows. In Sec. II the characteristic function of work is expressed as a correlation function of exponentiated Hamiltonians. The density matrix that enters this expression is given by the initial density matrix of the system projected onto the diagonal elements with respect to the eigenbasis of the initial Hamiltonian. In the special case of a canonical density matrix the known form of the canonical characteristic function is recovered. In Sec. III we consider a microcanonical initial state, and derive microcanonical quantum fluctuation and work theorems. Moreover, the probability densities and characteristic functions for canonical initial states are shown to be related to the corresponding microcanonical quantities by properly weighted Laplace transforms. Conclusions are presented in the final section.

II. CHARACTERISTIC FUNCTIONS OF WORK

The response of a quantum system to a perturbation by a classical, external force can be characterized by the change
of energy contained in the total system. The energy of the total system is determined by its Hamiltonian $H(t)$. It includes the external, time-varying force and therefore depends on time. We will consider the dynamics of the system only within a finite window of time $[t_0, t_f]$ during which the force is acting in a prescribed way, resulting in a protocol of Hamiltonians, which we denote by $\{H(t)\}_{t_0}^{t_f}$. A measurement of the Hamiltonian $H(t)$ at a time $t$ will result in an energy which is an eigenvalue $e_k(t)$ of the Hamiltonian, i.e.,

$$H(t)\varphi_{k,l}(t) = e_k(t)\varphi_{k,l}(t),$$

where $\lambda$ is a quantum number that labels a possible degeneracy of the eigenvalue $e_k(t)$. The eigenfunctions $\varphi_{k,l}(t)$ can be chosen as normalized and pairwise orthogonal. They span the eigenspace of $H(t)$ belonging to $e_k(t)$. The projection operator on this eigenspace becomes

$$P_k(t) = \sum_l |\varphi_{k,l}(t)\rangle\langle\varphi_{k,l}(t)|.$$  

Measuring the Hamiltonian at the times of measurement $t_0$ and $t_f$, one obtains as results eigenvalues $e_n(t_0)$ and $e_m(t_f)$ of the Hamiltonian $H(t)$. The work $w$ performed on the system is given by the difference of the measured energies, i.e., by

$$w = e_m(t_f) - e_n(t_0).$$

The energy values $e_n$ and $e_m$ arising from the measurements are random quantities. Consequently, the observed value of work, $w$, too is a random quantity. The probability $p_n$ with which the particular eigenvalue $e_n(t_0)$ is observed in the first measurement depends on the density matrix $\rho(t_0)$ that describes the state of the total system at time $t_0$. According to the laws of quantum mechanics, this probability is given by the expectation value of the projection operator $P_n(t_0)$ onto the subspace of eigenstates of the Hamiltonian $H(t_0)$ with energy $e_n(t_0)$, i.e., by

$$p_n = \text{Tr} P_n(t_0)\rho(t_0).$$

Immediately after this measurement the system is found in the corresponding state with properly normalized density matrix

$$\rho_n = \frac{P_n(t_0)\rho(t_0)P_n(t_0)}{p_n}$$

and then evolves in time according to

$$\rho_n(t) = U_{t_f,t_0}\rho_n U_{t_f,t_0}^\dagger,$$

where the unitary time evolution operator $U_{t_f,t_0}$ obeys the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} U_{t_f,t_0} = H(t) U_{t_f,t_0}, \quad U_{t_f,t_0} = 1.$$  

Note that in general the time-evolved states $\psi_{k,l}(t) = U_{t_f,t_0}\varphi_{k,l}(t)$ are not eigenfunctions of $H(t)$. Exceptions are quasistatic changes of the Hamiltonian for which the adiabatic theorem holds [39]. The second measurement, at time $t_f$, produces an eigenvalue $e_m(t_f)$ of $H(t_f)$ which occurs with probability

$$p(m|n) = \text{Tr} P_m(t_f)\rho_n(t_f) = \text{Tr} P_m(t_f)U_{t_f,t_0}\rho_n U_{t_f,t_0}^\dagger.$$  

The probability density of work, $p_{t_f}(w)$, can then be expressed as

$$p_{t_f}(w) = \sum_{m,n} \delta(w - [e_m(t_f) - e_n(t_0)])p(m|n)p_n.$$  

For the characteristic function of the work, we find

$$G_{t_f}(u) = \int dw \ e^{iuw} p_{t_f}(w),$$

which is the Fourier transform of the probability density of work (see, e.g., [13,40]),

$$G_{t_f}(u) = \sum_{m,n} e^{iuw_{m,n}} e^{iuw_{t_0}} \text{Tr} P_m(t_f)U_{t_f,t_0}^\dagger P_n U_{t_f,t_0}^\dagger \rho_n.$$  

where

$$H(t_f) = U_{t_f,t_0}^\dagger H(t_f) U_{t_f,t_0}$$

denotes the Hamiltonian in the Heisenberg picture. Further, we used the completeness relation $\sum_n P_n(t_f) = 1$ and introduced the density matrix

$$\bar{\rho}(t_0) = \sum_n p_n \rho_n = \sum_n P_n(t_0)\rho(t_0) P_n$$

with respect to which the average of the correlation function $(e^{i\text{d}H(t_f)}e^{-i\text{d}H(t_0)})_{t_0}$ is performed. This density matrix describes the state of the system projected onto the eigenbasis of the Hamiltonian at time $t = t_0$. It coincides with the initial density matrix $\rho(t_0)$ only if $\rho(t_0)$ commutes with the Hamiltonian $H(t_0)$, i.e.,

$$\bar{\rho}(t_0) = \rho(t_0) \Leftrightarrow [\rho(t_0), H(t_0)] = 0.$$  

In particular, if the system is initially in a canonical state the known form of the canonical characteristic function results [25]. From this very result the Tasaki-Crooks fluctuation theorem and the Jarzynski work theorem follow readily [25,26]. Notably, the characteristic function (11) assumes the form of a two-point quantum correlation as is the case in linear response theory, despite the fact that it embraces the full nonlinear response to the perturbation by the applied force.

III. FLUCTUATION THEOREMS FOR MICROCANONICAL INITIAL STATES

A microcanonical initial state is characterized by an ensemble that consists of all eigenstates of $H(t_0)$ with eigenval-
ues in a narrow band around an energy $E$. All contributing states have equal weights. In the ideal case of an arbitrarily narrow energy range around $E$, the state of the system is given by the following density matrix:

$$p_{E}(t_{0}) = \omega_{E}^{-1}(t_{0}) \delta(H(t_{0}) - E) = \omega_{E}^{-1}(t_{0}) \sum_{k} \delta(e_{k}(t_{0}) - E) P_{k}(t_{0}),$$

(15)

where

$$\omega_{E}(t_{0}) = \text{Tr} \, \delta(H(t_{0}) - E) = \sum_{k} g_{k} \delta(e_{k}(t_{0}) - E)$$

(16)
denotes the density of states of the system described by the Hamiltonian $H(t_{0})$, and $g_{k} = \text{Tr} \, P_{k}(t_{0})$ the degeneracy of the energy $e_{k}(t_{0})$. Equation (15) presents a rather formal expression for the density matrix. It can be regularized in the standard way by replacing the $\delta$ function by any smooth function $\tilde{\delta}(H(t_{0}) - E)$ which approaches the $\delta$ function in the limit $\epsilon \rightarrow 0$. The value of $\epsilon$ may be chosen such that the width of $\tilde{\delta}(H(t_{0}) - E)$ is of the order of the accepted uncertainty in the energy. It is also convenient to take an approximating $\delta$ function with infinite support such as a Gaussian function in order to have a well-defined density matrix for all energies $E$, even if $E$ falls in a gap of the spectrum. Since the width $\epsilon$ is always assumed to be much smaller than all other relevant energies in all following expressions, the formal manipulations with $\delta$ functions also correspond to the corresponding expressions containing the regularized $\delta$ functions. Combining Eqs. (11) and (15), we find the following expression for the characteristic function of work:

$$G_{t_0,tf}(E,u) = \omega_{E}^{-1}(t_{0}) \text{Tr} \, e^{iH(t_{0})} e^{-iuH(t_{0})} \delta(E - H(t_{0})) = \omega_{E}^{-1}(t_{0}) \text{Tr} \, e^{iH(t_{0}) - E} \delta(H(t_{0}) - E).$$

(17)

The inverse Fourier transform is readily performed to yield the probability density of work,

$$p_{E}(t_{0},w) = \int \frac{du}{2\pi} e^{-iuw} G_{t_{0},tf}(E,u) = \omega_{E}^{-1}(t_{0}) \text{Tr} \, \delta(H(t_{f}) - E - w) \delta(H(t_{0}) - E).$$

(18)

From this expression one may formally obtain the corresponding classical result by replacing the Hamilton operators by the corresponding Hamilton functions and the trace by an integral over all possible initial states. Thereby, the Hamiltonian at the final time, $H_{tf}(t_{f})$, must be replaced by the Hamilton function depending on the initial phase space variables $z_{0}$ via the solutions $z(z_{0},t)$ of Hamilton’s equations of motion at the final time. This results in the expression

$$p_{E}(t_{0},w) = \omega_{E}^{-1}(t_{0}) \int dz_{0} \delta(H(z_{0},t_{f}) - E - w) \times \delta(H(z_{0},t_{0}) - E),$$

(19)

which agrees with the result obtained on the basis of classical statistical mechanics in Ref. [20]. In the classical formulation it is of course correct to replace the energy $E$ in the first $\delta$ function by the Hamilton function at the initial time as dictated by the second $\delta$ function. This transformation is not possible in the quantum expression, confirming the recent observation that work is not a quantum mechanical observable [25].

A. Microcanonical quantum Crooks theorem

The dependence on the work $w$ can be shifted in Eq. (18) from the first to the second $\delta$ function by introducing the final energy $E_{f} = E + w$. For the product of the density of states $\omega_{E}(t_{0})$ and the probability density $p_{E}(E,w)$, one obtains

$$\omega_{E}(t_{0}) p_{E}(E,w) = \text{Tr} \, \delta(H_{tf}(t_{f}) - E_{f}) \delta(H(t_{0}) - E_{f} + w)$$

$$= \text{Tr} \, \delta(H(t_{f}) - E_{f}) \delta(H_{tf}(t_{f}) - E_{f} + w)$$

$$= \omega_{E_{f}}(t_{f}) p_{E}(E + w, -w),$$

(20)

where, in going to the second equality, we used the cyclic invariance of the trace and the unitarity of the time evolution in order to transfer the time dependence from the first to the second $\delta$ function. Here the operator $H_{tf}(t_{f})$ denotes the Hamiltonian in the Heisenberg picture for the time evolution running in reversed order with a backward protocol from the final to the initial time, i.e.,

$$H_{tf}(t_{f}) = U_{tf}^{\dagger} H(t_{f}) U_{tf}.$$

(21)

In the third equality of Eq. (20) the result was again written in terms of the probability density of work as a function of the initial energy $E_{f}$. This relation can be formulated as the microcanonical quantum version of Crooks’ theorem [4,20,26] saying that

$$\frac{p_{E}(E,w)}{p_{E}(E + w, -w)} = e^{S_{\Delta}(E,w,t) - S_{\Delta}(E_{f},t)} k_{B}.$$  

(22)

It relates the ratio between the probability densities of work for a process and for the corresponding time-reversed process to the difference of the entropies that belong to microcanonical equilibrium systems with Hamiltonians $H(t_{0})$ and $H(t_{f})$. The entropies are defined in terms of the corresponding densities of states via the standard statistical mechanical relation

$$S_{\Delta}(E,t) = k_{B} \ln \omega_{E}(t),$$

(23)

where $k_{B}$ denotes the Boltzmann constant. Note that the similar looking canonical Crooks’ theorem [4] contains a non-equilibrium entropy production $\omega_{\text{Crooks}}$ which is given by $T \omega_{\text{Crooks}} = -T S_{\text{Crooks}} + Q = w - \Delta F$ where $S_{\text{Crooks}}$ denotes the non-equilibrium entropy, $Q$ the eq.-heat, $\Delta F$ the thermodynamic free energy, and $w$ the nonequilibrium work. This entropy production is distinctly different from the statistical mechanical expression (23) for the microcanonical entropy entering Eq. (22).

Actually, a yet different statistical mechanical entropy can be defined. It is proportional to the logarithm of the number of states below the energy $E$ rather than that of the density of
states at the energy $E$ \cite{41}. This entropy then takes the form

$$S_{\Omega}(E, t) = k_B \ln \Omega_\epsilon(t)$$  \hspace{1cm} (24)

where

$$\Omega_\epsilon(t) = \int_{-\infty}^{E} dE' \omega_{E'}(t)$$  \hspace{1cm} (25)

denotes the number of states below $E$. For systems with short-ranged interactions the two definitions are known to coincide in the thermodynamic limit, i.e., in the limit of infinite systems. For small systems though, $S_{\Omega}(E)$ has been proved to be more advantageous as it is an increasing function of energy by definition \cite{29, 42}.

We note that, for an ensemble of initial states with energies uniformly distributed up to the energy $E$, a fluctuation theorem of the form of Eq. (22) can be derived, in which the difference of the entropies $S_\omega$, is replaced by the corresponding difference of $S_\Omega$, i.e.,

$$\frac{p_{t_0}^{<}(E,w)}{p_{t_0}^{>}(E+w,w)} = e^{S_{\Omega}(E+w,t_0)-S_{\Omega}(E_\omega(t_0))} k_B.$$  \hspace{1cm} (26)

This follows along the same line of arguments leading to the relation (22) for the uniform initial density matrix $\rho^{<}(t_0)$, which is given by

$$\rho^{<}(t_0) = \Omega_\epsilon^{-1}(t_0) \Theta(E-H(t_0))$$  \hspace{1cm} (27)

and which was introduced by Ruelle \cite{43} in the context of the microcanonical ensemble. The probability of work $p_{t_0}^{<}(E,w)$ for this ensemble is obtained from the corresponding microcanonical probability by an integration over the energy, i.e.,

$$p_{t_0}^{<}(E,w) = \Omega_\epsilon^{-1}(t_0) \int_{-\infty}^{E} dE' \omega_{E'}(t_0)p_{t_0}^{<}(E',w).$$  \hspace{1cm} (28)

The fact that the microcanonical quantum Crooks theorem (22) depends on the time-reversed process seemingly restricts its practical usefulness. As opposed to computer experiments, it is impossible to perform an active reversal of time, i.e., to let time run backward, in real experiments.

\section*{B. Entropy-from-work theorem}

The experimentally inaccessible probability density of the time-reversed process though can be eliminated by first expressing the initial energy in terms of the final energy and the performed work, and next by integrating Eq. (20) over all possible values of the work. In this way, the density of states at the later time can be expressed by an integral of the initial density of states, weighted by $p_{t_0}^{<}(E_f-w,w)$, i.e.,

$$\int dw \omega_{E_f-w}(t_0)p_{t_0}^{<}(E_f-w,w) = \int dw \omega_{E_f}(t_f)p_{t_0}^{<}(E_f-w)$$  \hspace{1cm} (29)

With the definition (23) the following relation between the entropy of the initial system and the unknown entropy of the final system can be established:

$$\int dw e^{S_{\omega}(E_f-t_0)} p_{t_0}^{<}(E_f-w,w) = e^{S_{\omega}(E_f(t_f))}.$$  \hspace{1cm} (30)

Note that for a fixed final energy the weighting function $p_{t_0}^{<}(E_f-w,w)$ is not a probability density of the performed work. In the following we demonstrate that the left-hand side of Eq. (29) can be written in terms of a properly defined average of the exponentiated entropy conditioned on the final energy.

In general, from a single initial energy not all relevant final energies are likely to be reached; they may even be impossible to reach. Therefore, in an experiment the initial energies have to be scanned over a sufficiently large range of values. For each initial energy, a sufficient number of experiments has to be performed in order that a reliable statistics of work can be compiled for conveniently binned final energies. Based on such statistics, the probability density of initial energies $E$ conditioned on the final energy $E_f$, $p_{t_0}^{<}(E|E_f)$, can be inferred. If the initial energies $E$ are uniformly sampled in a range of energies of size $E^\text{f}$, the joint probability of initial and final energies is given by $\rho(E,E_f) = p_{t_0}^{<}(E,E_f-E)/E^\text{f}$. According to the Bayes theorem, the conditional probability density $p_{t_0}^{<}(E|E_f)$ becomes

$$p_{t_0}^{<}(E|E_f) = \frac{\rho(E,E_f)}{\int dE \rho(E,E_f)}.$$  \hspace{1cm} (31)

Consequently, the integral over the density of states can be formulated as an average over initial energies conditioned on the final energy, yielding

$$\langle \omega_{E_f}(t_0) \rangle_{E_f} = \int dE \omega_{E_f}(t_0)p_{t_0}^{<}(E|E_f)$$

$$= N(E_f)^{-1} \int dw \omega_{E_f-w}(t_0)p_{t_0}^{<}(E_f-w,w),$$  \hspace{1cm} (32)

where

$$N(E_f) = \int dE p_{t_0}^{<}(E,E_f-E).$$  \hspace{1cm} (33)

guarantees the normalization of the conditional probability. Using Eq. (29) one finds the density of states $\omega_{E_f}(t_f)$ of a microcanonical system with the Hamiltonian $H(t_f)$ represented by the average of the density of states $\omega_{E_f}(t_0)$ with respect to the conditional probability $p_{t_0}^{<}(E|E_f)$, reading

$$\omega_{E_f}(t_f) = N(E_f)\langle \omega_{E_f}(t_0) \rangle_{E_f}.$$  \hspace{1cm} (34)

Expressing the density of states in terms of the entropy (23), one obtains
denotes the characteristic function of work for a process

We call Eq. (35) the “entropy-from-work” theorem. In analogy to the Jarzynski relation, it allows one to extract equilibrium properties from nonequilibrium experiments, which are, in the case of the Jarzynski relation, the free energy and, in the present context, the entropy $S(E)$. Based on the relation (26) an entropy-from-work theorem for $S_0(E)$ follows in close analogy to the corresponding relations (34) and (35), reading

$$\Omega_{E_j}(t_f) = N^<_{E_j}(E_0)\langle \Omega_{E_j}(t_0) \rangle^{\leq}_{E_j}$$

and

$$\Omega_{E_j}(t_f) = N^<_{E_j}(E_0)\langle \Omega_{E_j}(t_0) \rangle^{\leq}_{E_j}$$

where the average $\langle \cdot \rangle_{E_j}^{\leq}$ is performed with respect to the conditional probability density

$$p_{t_f|t_0}^{\leq}(E_j|E_0) = N^<_{E_j}(E_0)^{-1}p_{t_f|t_0}^{\leq}(E_j,E_j - E)$$

and where

$$N^<_{E_j}(E) = \int dE \ p_{t_f|t_0}^{\leq}(E_j,E_j - E).$$

C. Interrelations with the characteristic function of work for canonical initial states

To establish a relation between the microcanonical and canonical work distributions we multiply the expression (17) by the product of the density of states and a Boltzmann factor $\exp(-\beta E)$ with inverse temperature $\beta$ and finally integrate over all values of the energy $E$. Performing this integration under the trace we obtain

$$\int dE \ \omega_{E}(t_0)e^{-\beta E}G_{t_f|t_0}(E,u) = \text{Tr} e^{i\beta H_{t_f}}e^{-i\beta H_{t_0}}e^{-\beta H(t_0)}$$

$$= Z(t_0)G_{t_f|t_0}^{\beta}(u),$$

where

$$G_{t_f|t_0}^{\beta}(u) = Z_{\beta}(t_0)^{-1}\text{Tr} e^{i\beta H_{t_f}}e^{-i\beta H_{t_0}}e^{-\beta H(t_0)}$$

denotes the characteristic function of work for a process starting from a canonical density matrix [25] and

$$Z_{\beta}(t_0) = \text{Tr} e^{-\beta H(t_0)}$$

the corresponding partition function. Hence, the canonical characteristic function of work is related to the microcanonical one by a Laplace transform. The reverse relation is readily obtained by the following inverse Laplace transform:

$$G_{t_f|t_0}(E,u) = \omega_{E}(t_0)^{-1} \int dE \ Z_{\beta}(t_0)e^{\beta E}G_{t_f|t_0}^{\beta}(u),$$

where $C$ is an inverse Laplace contour in the complex $\beta$ plane from $-i\pi + c$ to $i\pi + c$. The real constant $c$ must be chosen such that all singularities of the integrand lie to its left side. The density of states is related to the partition function by the standard relation

$$\omega_{E}(t_0) = \int \frac{dB}{2\pi} Z_{\beta}(t_0)e^{\beta E}.$$  

Accordingly, the probability densities of work for microcanonical and canonical initial states are also related by a Laplace transform, yielding

$$p_{t_f|t_0}^{\beta}(w) = Z_{\beta}(t_0)^{-1} \int dE \ \omega_{E}(t_0)e^{-\beta E}p_{t_f|t_0}^{\leq}(E,w),$$

$$p_{t_f|t_0}^{\beta}(E,w) = \omega_{E}(t_0)^{-1} \int dE \ Z_{\beta}(t_0)e^{\beta E}p_{t_f|t_0}^{\leq}(w).$$

Finally we note that the Jarzynski relation can be obtained from the microcanonical Crooks theorem. For this purpose one considers the left-hand side of the first equality and the right-hand side of the third equality of Eq. (20), multiplies both sides with $\exp[-\beta(E+w)]$, and integrates over all values of $E$ and $w$. For the left-hand side one then finds

$$\int dE \int dw \ e^{-\beta E}w \ \omega_{E}(t_0)p_{t_f|t_0}^{\leq}(E,w) = \int dw \ e^{-\beta w}Z_{\beta}(t_0)\frac{p_{t_f|t_0}^{\beta}(w)}{Z_{\beta}(t_0)},$$

while the right-hand side yields

$$\int dE \int dw \ e^{-\beta E}w \ \omega_{E}(t_0)p_{t_f|t_0}^{\leq}(E,w) = Z_{\beta}(t_0),$$

where we substituted the integration variable $E$ by $E_{t_f}=E+w$. A comparison of the last two equations immediately yields the Jarzynski relation [3,25].

IV. CONCLUSIONS

The expression for the characteristic function of work performed on an isolated quantum system by an external force was generalized for arbitrary initial states. The general structure of the characteristic function is given by a correlation function of the exponentiated system Hamiltonians at the first and second measurement times. The quantum expectation and ensemble average are jointly taken with respect to a density matrix which results from the actual initial state immediately before the first measurement by means of a state reduction with respect to the energy eigenbasis of the then measured Hamiltonian. Initial states that commute with the Hamiltonian at the initial time consequently are not modified. This form of the characteristic function holds irrespective of a possible degeneracy of the spectrum of the system’s Hamiltonian.

For a microcanonical initial state, expressions for the characteristic function of work and the corresponding probability density were established. In the classical limit, known expressions were recovered, and the validity of the microca-
nical Crooks fluctuation theorem was demonstrated for quantum systems. Moreover, we formulated an entropy-from-work theorem which allows one to infer the unknown entropy of a system from a reference system with known entropy by means of a nonequilibrium experiment. In such an experiment the initial system with known entropy is deformed into the final system within finite time according to a prescribed protocol of Hamiltonians. In this context, we want to emphasize that the entropy following from this theorem is based on either of the statistical mechanical definitions (23) or (24), which agree with each other for sufficiently large systems with short-range interactions. In contrast, the canonical Crooks theorem contains a nonequilibrium entropy production that emerges from a relation involving free energy, heat, and nonequilibrium work.

We further note that the microcanonical distribution provides the appropriate description of an isolated system if no further information about its state is available even if the energy of the considered system is a priori unknown. By registering the result of the first energy measurement, this ignorance is removed and the available information about the initial state is expressed without any bias by the microcanonical density matrix corresponding to the measured energy. However, if the unforced dynamics not only leaves invariant the energy but also other quantities such as the linear or angular total momentum, then the adequate constrained microcanonical ensemble has to be considered as the proper initial state. Finally, by means of properly weighted Laplace transforms, relations between microcanonical and canonical characteristic functions and probability densities of work were established.

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