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Fluctuation Theorem for Arbitrary Open Quantum Systems

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Based on the observation that the thermodynamic equilibrium free energy of an open quantum system in contact with a thermal environment is the difference between the free energy of the total system and that of the bare environment, the validity of the Crooks theorem and of the Jarzynski equality is extended to open quantum systems. No restrictions on the nature of the environment or on the strength of the coupling between system and environment need to be imposed. This free energy entering the Crooks theorem and the Jarzynski equality is closely related to the Hamiltonian of mean force that generalizes the classical statistical mechanical concept of the potential of mean force.

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Since its formulation in 1997, the classical nonequilibrium work relation by Jarzynski [1] (now commonly referred to as the Jarzynski equality)

$$\langle e^{-\beta w} \rangle = e^{-\beta \Delta F} \quad (1)$$

has continued to raise questions and concerns on its range of validity and applicability. Here, w denotes the work performed on a system when some parameters of this system are changed according to a prescribed protocol. This work is given by the difference of the energies contained in the system at the end and at the beginning of the protocol. Initially, the system is supposed to be prepared in a thermal equilibrium state at the inverse temperature β . The brackets $\langle \cdot \rangle$ denote a nonequilibrium average over many repetitions of this process, running under the same protocol. According to the Jarzynski equality, the average of the exponentiated negative work is independent of the details of the protocol and solely determined by the thermal equilibrium free energy difference ΔF between the initial equilibrium state and a hypothetical equilibrium state at the initial temperature and those parameter values that are reached at the end of the protocol. In the mentioned Letter [1], the validity of this equality was demonstrated within a classical statistical approach for isolated systems which initially are in the required equilibrium state at inverse temperature β and also for classical systems that stay in weak contact with a thermal bath during the protocol.

Considerable effort has been devoted to the development of the quantum version of Eq. (1), and more generally of the Crooks fluctuation theorem [2] that underlies it; i.e.,

$$\frac{p_{t_f, t_0}(+w)}{p_{t_0, t_f}(-w)} = e^{\beta(w - \Delta F)}, \quad (2)$$

where $p_{t_f, t_0}(w)$ denotes the probability density function (PDF) of work performed by the parameter changes according to a protocol running between the initial time t_0 and final time t_f . The PDF of work for the reversed protocol is denoted by $p_{t_0, t_f}(w)$. All these attempts refer to

quantum isolated or weakly coupled systems with Hamiltonian or Markovian dynamics, respectively [3–9]. The proof of the validity of Eqs. (1) and (2) in the quantum case with weak coupling, allowing for an otherwise general non-Markovian dynamics of the open quantum dynamics and arbitrary force protocols, was provided only recently in Ref. [10].

The applicability of Eqs. (1) and (2) to the case of weak coupling is consistent with the construction of quantum and classical statistical mechanics which relies on that assumption. In striking contrast, extending the methods of statistical mechanics to cases that involve a non-negligible system-environment interaction presents a major challenge [11,12]. Addressing this question is by now becoming more and more pressing, as the advancement of technology poses us in the position to investigate experimentally the thermodynamic behavior of nanosystems operating in the quantum regime, whose reduced sizes make the system-environment coupling an important issue.

A satisfactory generalization of the applicability of Eq. (1) for the classical strong coupling regime was put forward by Chris Jarzynski himself [13]; it should be stressed, however, that the objective of the corresponding quantum treatment has not been achieved yet. The key tool used in Ref. [13] to overcome the difficulties posed by the presence of strong coupling is the Hamiltonian of mean force $H^*(\Gamma_S, t)$, where Γ_S denotes a point in the phase space of the subsystem of interest. This Hamiltonian of mean force is defined as the effective Hamiltonian that describes the Boltzmann-Gibbs equilibrium of the marginal probability density of the subsystem of interest; it reads

$$H^*(\Gamma_S; t) = H_S(\Gamma_S, t) - \frac{1}{\beta} \times \ln \frac{\int d\Gamma_B \exp[-\beta(H_B(\Gamma_B) + H_{SB}(\Gamma_S, \Gamma_B))]}{\int d\Gamma_B \exp(-\beta H_B(\Gamma_B))}, \quad (3)$$

where Γ_B denotes a point in the phase space of the bath.

The total Hamiltonian of system plus environment is given by

$$H(\Gamma_S, \Gamma_B, t) = H_S(\Gamma_S, t) + H_B(\Gamma_B) + H_{SB}(\Gamma_S, \Gamma_B), \quad (4)$$

which is composed of the Hamiltonian of the isolated system of interest, $H_S(\Gamma_S, t)$ (time-dependent), the bath Hamiltonian $H_B(\Gamma_B)$, and the interaction Hamiltonian $H_{SB}(\Gamma_S, \Gamma_B)$. This Hamiltonian of mean force generalizes the concept of the potential of mean force, see Eq. (14) below, that is commonly employed, for example, in reaction rate theory [14] and in the study of implicit solvent models in terms of biomolecular simulations [15].

In the context of quantum rate theory, potentials of mean force have been determined for the reaction coordinate from path integral expressions of the partition function of a composed system with the reaction coordinate confined to a ‘‘centroid’’ [14,16]. A direct application of this very approach to obtain quantum fluctuation theorems for open systems though is not obvious. Jarzynski, in fact, did emphasize that his treatment is restricted to the classical case [13]. Addressing this problem thus requires a careful analysis of what one should consider as the system partition function from which the thermodynamics of the system can be inferred. One could naively take for this partition function the bare partition function of the isolated system of interest: This procedure would, however, neglect the prominent fact that the interaction with the bath alters the system properties. Such a choice, therefore, is generally physically not correct. Instead of the partition function of the isolated system one has to choose a properly defined partition function, which embraces the influence of the bath on the open quantum system.

As we will show in this Letter, the introduction of a proper partition function for an open system allows one to prove that both the Tasaki-Crooks fluctuation theorem and the Jarzynski equality in fact hold true for general open quantum systems, independent of coupling strength. Moreover, from this partition function a quantum Hamiltonian of mean force can be inferred which takes over the role of the Hamiltonian of mean force in classical statistical mechanics.

The argument.—Consider the Hamiltonian operator $\hat{H}(t)$ of a quantum system composed of the interacting system and the bath which we write as

$$\hat{H}(t) = \hat{H}_S(t) + \hat{H}_{SB} + \hat{H}_B, \quad (5)$$

where the system Hamiltonian $\hat{H}_S(t)$ is time dependent in a way that results from a prespecified protocol of system parameter changes. The interaction Hamiltonian \hat{H}_{SB} and the bath Hamiltonian \hat{H}_B are supposed to be independent of time. The change of the system’s parameters can be interpreted as a time-dependent external forcing that is able to perform work on the system.

The total system is isolated; it therefore obeys the quantum Tasaki-Crooks fluctuation theorem [3,17]:

$$\frac{p_{t_f, t_0}(+w)}{p_{t_0, t_f}(-w)} = \frac{Y(t_f)}{Y(t_0)} e^{\beta w}, \quad (6)$$

with $Y(t)$ being the total partition function, i.e.,

$$Y(t) = \text{Tr} e^{-\beta(\hat{H}_S(t) + \hat{H}_{SB} + \hat{H}_B)}, \quad (7)$$

where Tr denotes the trace over the total system Hilbert space, and the symbols $p_{t_f, t_0}(w)$ and $p_{t_0, t_f}(w)$ denote the probability densities of doing the work w when the protocol is run in the forward and backward directions, respectively. It is important to note that, due to the fact that the forces solely act on the system S , the work performed on the open quantum system coincides with the total work w .

In order to obtain the thermodynamic partition function of the open quantum system S staying in thermal equilibrium with a bath, we appeal to thermodynamic reasoning. As pointed out in Ref. [18], the thermodynamic free energy of the open system of interest is the difference between the total system free energy and the bare bath free energy:

$$F_S(t) = F(t) - F_B. \quad (8)$$

Here t merely specifies the values of the external parameters as they occur in the course of the protocol at the time t . Using the statistical mechanical relation $\beta F = -\ln Z$ between equilibrium free energy and the thermodynamic partition function, one finds from Eq. (8) for the thermodynamic partition function of an open quantum system the result that is well known to those working on strong quantum dissipation [12,18–29], namely:

$$Z_S(t) = \frac{\text{Tr} e^{-\beta(\hat{H}_S(t) + \hat{H}_{SB} + \hat{H}_B)}}{\text{Tr}_B e^{-\beta \hat{H}_B}} = \frac{Y(t)}{Z_B}, \quad (9)$$

where Tr_B is the trace over the bath Hilbert space, and Z_B is the bare bath partition function, i.e., $Z_B = \text{Tr}_B e^{-\beta \hat{H}_B}$, which is independent of time. Note that the thermodynamics that follows from the partition function $Z_S(t)$ comprises the equilibrium properties of the open quantum system in a consistent manner including the influence of environment and coupling [11,12,18–21]: In particular, the thermodynamic functions that follow from this thermodynamic partition function do not violate any known thermodynamic law.

From Eqs. (7) and (9), and the fact that Z_B does not depend on time t , the salient relation $Y(t_f)/Y(t_0) = Z_S(t_f)/Z_S(t_0)$ follows. This quantum result assumes a form reading just like in the classical case [13]. Therefore, Eq. (6) becomes

$$\frac{p_{t_f, t_0}(+w)}{p_{t_0, t_f}(-w)} = \frac{Z_S(t_f)}{Z_S(t_0)} e^{\beta w} = e^{\beta(w - \Delta F_S)}, \quad (10)$$

which states that the ratio of probabilities of work in the backward and forward protocols is dictated by the equilib-

rium free energy difference of the open quantum system, i.e., $\Delta F_S = F_S(t_f) - F_S(t_0)$, with $F_S(t)$ given by Eq. (8).

By multiplying Eq. (10) by $p_{t_0, t_f}(-w)e^{-\beta w}$ and integrating over w in the usual way, one obtains the very form (1) of the Jarzynski equality for open quantum systems, being valid independently of the coupling strength and the details of the bath. This is in complete analogy with Jarzynski's classical result, which, therefore, carries over to the quantum case. Hence, if a classical force acts on an open system, the average exponentiated work $e^{-\beta w}$ equals the exponentiated system equilibrium free energy difference ΔF_S , both in classical and quantum regimes.

Remarks.—The system partition function $Z_S(t)$, defined in Eq. (9), is actually the partition function associated to the quantum Hamiltonian of mean force $\hat{H}^*(t)$, defined in analogy to the classical Hamiltonian of mean force as

$$\hat{H}^*(t) := -\frac{1}{\beta} \ln \frac{\text{Tr}_B e^{-\beta(\hat{H}_S(t) + \hat{H}_{SB} + \hat{H}_B)}}{\text{Tr}_B e^{-\beta \hat{H}_B}}. \quad (11)$$

In fact, the partition function $Z_S(t)$ can be recast as

$$Z_S(t) = \text{Tr}_S e^{-\beta \hat{H}^*(t)}, \quad (12)$$

where Tr_S denotes the trace over the system Hilbert space. Using Eqs. (9) and (11), it follows that

$$Z_S^{-1}(t) e^{-\beta \hat{H}^*(t)} = Y^{-1}(t) \text{Tr}_B e^{-\beta \hat{H}(t)}, \quad (13)$$

where the right-hand side coincides with the reduced density matrix of the open system in thermal equilibrium with the heat bath. Again, t merely characterizes those parameter values that occur according to the protocol at time t . It does not indicate any dynamics. The actual time-dependent density matrix at time t does not, in general, coincide with $e^{-\beta \hat{H}^*(t)}/Z_S(t)$.

We note that the Hamiltonian of mean force $\hat{H}^*(t)$ typically is a complicated operator-valued function not only of the system's parameters but also of the system-bath coupling strength, the bath temperature and possibly of other bath parameters. In the case of weak coupling the contributions from the bath and the interaction(s) are negligible and the Hamiltonian of mean force reduces to the bare system Hamiltonian [10].

In the classical limit, the quantum Hamiltonian of mean force becomes the classical Hamiltonian of mean force in Eq. (3). This classical expression can further be simplified for a bath Hamiltonian consisting of a sum of potential, $V_B(y)$, and kinetic energy, where the latter does not depend on bath positions, y , and for an interaction, $V_{SB}(x, y)$ that is independent of the momenta. Then the mere integration over the momenta yields identical factors in the numerator and denominator of Eq. (11), which cancel each other. The remaining term under the logarithm is then only a function of the system positions, x . This leads to the renormalization of the system potential $V_S(x, t)$ —i.e., to the potential of

mean force—, mentioned before:

$$V^*(x; t) = V_S(x, t) - \frac{1}{\beta} \times \ln \frac{\int dy \exp[-\beta(V_B(y) + V_{SB}(x, y))]}{\int dy \exp(-\beta V_B(y))}, \quad (14)$$

whereas the kinetic energy of the system remains unchanged by this procedure. We note that the given conditions are sufficient but not necessary in order that the potential of mean force captures the complete effect of a bath on the equilibrium properties of the system described by the Hamiltonian $H^*(\Gamma_S, t)$. Further simplifications result, for example, for a bath consisting of a set of harmonic oscillators which linearly couple to phase space functions of the system. Then, classically, the Hamiltonian of mean force coincides with the bare Hamiltonian of the system. This is in strong contrast to the behavior of quantum systems which couple as above, i.e., linearly, to a harmonic heat bath. In this case, the Hamiltonian operator of mean force deviates from the bare system Hamiltonian with respect to the kinetic and the potential energy [20,26].

Conclusions.—Surprisingly enough, the Crooks theorem and the Jarzynski equality are valid for open quantum systems irrespective of the coupling strength to their thermal environment and of the particular nature of their environment. These theorems, hence, are valid for all types of processes in which a classical or quantum system in contact with a thermal heat bath is driven out of equilibrium by classical, generally time-dependent forces.

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