

Fluctuation theorems in driven open quantum systems

Peter Talkner, Michele Campisi and Peter Hänggi

Institute of Physics, University of Augsburg, D-86135 Augsburg, Germany

E-mail: peter.talkner@physik.uni-augsburg.de,

Michele.Campisi@physik.uni-augsburg.de and hanggi@physik.uni-augsburg.de

Abstract. The characteristic function for the joint measurement of the changes of two or more commuting observables upon an external forcing of a quantum system is derived. In particular, the statistics of the internal energy, the exchanged heat and the work of a quantum system that *weakly* couples to its environment are determined in terms of the energy changes of the system and the environment due to the action of a classical, external force on the system. If the system and the environment initially are in a canonical equilibrium, the work performed on the system is shown to satisfy the Tasaki–Crooks theorem and the Jarzynski equality.

Keywords: dissipative systems (theory), mesoscopic systems (theory), dynamical processes (theory), fluctuations (theory)

Contents

1. Introduction	2
2. Characteristic functions of work, heat and internal energy	4
3. The fluctuation theorem for work and heat	7
3.1. Non-equilibrium free energy/work relations	8
3.2. Non-equilibrium relations for conditional and marginal probabilities	9
3.3. Non-equilibrium equalities for exponentiated internal energy and heat	10
4. Conclusions	10
Acknowledgments	11
References	11

1. Introduction

About one decade ago Jarzynski proved a quite remarkable equality that relates free energy differences to average exponentiated work done on a thermally insulated system that is acted upon by external time dependent forces varying according to a specified protocol. This equation, now commonly referred to as the Jarzynski equality, reads [1]

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

with w the work, ΔF the free energy difference between a reference equilibrium state of the system at the initial temperature β with the force values reached at the end of the force protocol and the truly thermal initial state. Note that the Jarzynski equality holds irrespectively of whether the system ever reaches this reference equilibrium state.

Crooks [2] later showed that equation (1) results from the following work fluctuation theorem:

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

that relates the probability density function (pdf) of work $p_{t_f, t_0}(w)$ in the real forward process proceeding from the time t_0 until t_f to the pdf of negative work $p_{t_0, t_f}(-w)$ of the mirror image process where the time ideally runs backward.

An important question that naturally arises is that of whether equations (1) and (2) keep holding in the more realistic situation where the system remains in thermal contact with its environment while the forcing protocol is in action. In regard to equation (1) a positive answer to this question was already given in [1] on the basis of classical arguments.

Moreover, quantum extensions of equations (1) and (2) were developed, too: first the quantum version of the Jarzynski equality for cyclic processes [3], and shortly after the Crooks theorem were demonstrated to hold also for closed quantum systems [4]. A specification of the full statistics in terms of the characteristic function, i.e. the Fourier transform of the probability density function (pdf) of the work, was obtained in [5],

and a proof of the Crooks relation on the basis of this characteristic function was given in [6]. A generalization to arbitrary initial states such as the microcanonical state was obtained in [7]. In the latter case a microcanonical Crooks theorem was proved by means of which the change of the thermodynamic entropy can be inferred from the statistics of the work [7, 8]. Illustrative examples for differently driven quantum harmonic oscillators were discussed in [9, 10]. An experimental test was proposed in [11].

Quantum generalizations of the Jarzynski equality and the Crooks theorem for open quantum systems have almost exclusively been studied for systems with Markovian dynamics [12]–[15]. Therefore, so far, only systems with weak coupling to their environments have been considered, as weak coupling is implicit in the Markovian assumption [16]–[19]¹.

In the present paper we too restrict ourselves to the case of weak interaction between the system and its environment. We do so because to the best of our knowledge currently an unambiguous definition of work and heat of a small open quantum system is only known in this very case of weak coupling [24, 25]. However, neither the dynamics of the system nor that of the bath is restricted otherwise. In this way we allow for *general non-Markovian dynamics* imposed by the bath and arbitrary force protocols which are neither constrained to be fast nor constrained to be slow.

Here we employ the characteristic function approach of [5, 7] to address the question regarding the validity of the equations (1) and (2) for quantum systems in weak contact with their environment. Hence the focus of this study is on the characteristic function of the *joint* statistics of simultaneous measurements of system and environmental energies, which are commuting observables. Under the assumption of weak coupling the changes of these two energies imposed by the action of an external force can immediately be related to the changes of internal energy and the heat exchanged with the environment, or, equivalently, to the work and heat. Our central result is the derivation of a fluctuation theorem of the Tasaki–Crooks type, for the joint pdfs of either internal energy and heat, or heat and work (see equation (32) below). As a corollary of this theorem, we recover the Jarzynski equation (1) and the Crooks theorem (2) for the marginal pdf of work. This formally proves that the validity of these relations keeps holding for quantum systems weakly interacting with an environment.

We are though aware of the difficulties that the experimental realization of the two energy difference measurements may pose. In particular, the change of the environmental energy may be rather small compared to the actual energy content of the environment and therefore be prone to a large error. A related problem afflicts the determination of the specific heat of an open quantum system [26].

Previous investigations of the Jarzynski equality for open Markovian quantum systems [13, 15] are based on the limit of infinitely many repeated measurements of the environment’s energy. In contrast, the present approach relies on energy measurements of the system and the environment at the beginning and the end of the protocol. We note that other fluctuation theorems are known in the literature for the heat exchange between two systems which couple either directly to each other [27], or through an intermediate system giving rise to a heat flow [28]. In contrast, here we consider systems which initially

¹ In the strong coupling limit the dynamics of a particle’s position is described by a classical Smoluchowski equation [20]–[23] but this equation does not provide information about the dynamics of the momentum.

are in thermal equilibrium with their environment and are then driven out of equilibrium by a classical external force.

The paper is organized as follows. In section 2 we define and obtain the general expression for the joint pdf of the internal energy and heat. In section 3 the joint pdf is further evaluated for the initial canonical state of the *total* system and a fluctuation theorem for work and heat is obtained. Conclusions are drawn in section 4.

2. Characteristic functions of work, heat and internal energy

We consider a system S that is in weak contact with its environment B . Accordingly, the Hamiltonian $H(t)$ of the total system consists of a system and an environmental part $H^S(t)$ and H^B , respectively, and the interaction Hamiltonian H^{SB} , i.e.

$$H(t) = H^S(t) + H^{SB} + H^B, \quad (3)$$

where the interaction is small compared to both the system and the environmental Hamiltonians. We assume that the gauge is fixed in such a way that the Hamiltonian $H^S(t)$ coincides with the system energy despite its time dependence [29]. This time dependence is caused by an external change of system parameters according to a prescribed protocol. Since the system and the environmental Hamiltonians commute with each other, the energies of the system and of the bath can be measured simultaneously with possible results $e_i^S(t)$ and e_α^B which are the eigenvalues of the operators $H^S(t)$ and H^B , respectively. The corresponding projection operators onto the common eigenspaces of these operators are denoted by $P_{i,\alpha}(t)$. Hence, the eigenvalues and eigenprojection operators are determined by the following equations:

$$H_S(t)P_{i,\alpha}(t) = e_i^S(t)P_{i,\alpha}(t), \quad H_B P_{i,\alpha}(t) = e_\alpha^B P_{i,\alpha}(t). \quad (4)$$

The projection operators onto the common eigenspaces of two commuting Hermitian operators are Hermitian:

$$P_{i,\alpha}^\dagger(t) = P_{i,\alpha}(t), \quad (5)$$

idempotent and mutually orthogonal:

$$P_{i,\alpha}(t)P_{i',\alpha'}(t) = \delta_{i,i'}\delta_{\alpha,\alpha'}P_{i,\alpha}(t), \quad (6)$$

and complete:

$$\sum_{i,\alpha} P_{i,\alpha}(t) = \mathbb{I}, \quad (7)$$

where \mathbb{I} denotes the unit operator on the total Hilbert space of system and environment. The first measurement is performed at the time t_0 at which the protocol starts to act. At this very time the state of the total system is assumed to be given by the density matrix $\rho(t_0)$ which we will specify later. The joint probability for measuring the respective system and environmental energies $e_i^S(t_0)$ and e_α^B in this state is given by

$$p_{i,\alpha} = \text{Tr} P_{i,\alpha}(t_0)\rho(t_0), \quad (8)$$

where Tr denotes the trace over the total Hilbert space of the system and the environment. After a measurement with the outcome $e_i^S(t_0)$, e_α^B the system is found in the initial state

projected onto the corresponding subspace. This state is given by

$$\rho_{i,\alpha} = p_{i,\alpha}^{-1} P_{i,\alpha}(t_0) \rho(t_0) P_{i,\alpha}(t_0). \quad (9)$$

The second measurement of the system and the environmental energies is performed at the end of the protocol at time t_f . By then the density matrix of the total system has undergone a unitary time evolution in the total Hilbert space to a new state reading

$$\rho_{i,\alpha}(t_f) = U_{t_f,t_0} \rho_{i,\alpha} U_{t_f,t_0}^\dagger. \quad (10)$$

The result of the second measurement is characterized by the conditional pdf of finding energies $e_{i'}^S(t_f)$ and $e_{\alpha'}^B$ given that the results of the first measurement were $e_i^S(t_f)$ and e_α^B . This pdf is given by

$$p_{t_f,t_0}(i', \alpha' | i, \alpha) = \text{Tr } P_{i',\alpha'}(t_f) \rho_{i,\alpha}(t_f). \quad (11)$$

Consequently, the joint pdf $p_{t_f,t_0}(\Delta e^S, \Delta e^B)$ for measuring changes of the system and the environmental energies Δe^S and Δe^B , respectively, becomes

$$\begin{aligned} p_{t_f,t_0}(\Delta e^S, \Delta e^B) &= \sum_{i,i',\alpha,\alpha'} \delta(\Delta e^S - (e_{i'}^S(t_f) - e_i^S(t_0))) \\ &\times \delta(\Delta e^B - (e_{\alpha'}^B - e_\alpha^B)) p_{t_f,t_0}(i', \alpha' | i, \alpha) p_{i,\alpha}. \end{aligned} \quad (12)$$

At weak coupling between the system and the environment the random quantity Δe^S determines the change of the internal energy of the system. Then the change of the environmental energy equals the amount of energy which is exchanged as heat $Q = -\Delta e^B$ with the system. The small contribution of energy that is possibly released from or stored in the interaction Hamiltonian is negligibly small for a system weakly coupled to its environment. Hence, the joint pdf of internal energy change $E = \Delta e^S$ and heat exchange Q becomes

$$p_{t_f,t_0}(E, Q) = \sum_{i,i',\alpha,\alpha'} \delta(E - (e_{i'}^S(t_f) - e_i^S(t_0))) \delta(Q + (e_{\alpha'}^B - e_\alpha^B)) p_{t_f,t_0}(i', \alpha' | i, \alpha) p_{i,\alpha}. \quad (13)$$

The characteristic function $G_{t_f,t_0}^{E,Q}(u, v)$ provides an equivalent description of the statistics of these energy changes. It is given by the Fourier transform of this pdf, which, due to the presence of the delta functions, can readily be performed to yield

$$\begin{aligned} G_{t_f,t_0}^{E,Q}(u, v) &= \int dE \int dQ e^{i(uE+vQ)} p_{t_f,t_0}(E, Q) \\ &= \sum_{i,i',\alpha,\alpha'} e^{i(u(e_{i'}^S(t_f) - e_i^S(t_0)))} e^{-i(v(e_{\alpha'}^B - e_\alpha^B))} p(i', \alpha' | i, \alpha) p_{i,\alpha}. \end{aligned} \quad (14)$$

This expression can be further simplified by means of the equations (8), (12) and the completeness relation (7) into the form of a correlation function, reading

$$G_{t_f,t_0}^{E,Q}(u, v) = \text{Tr } e^{i(uH_H^S(t_f) - vH_H^B(t_f))} e^{-i(uH_H^S(t_0) - vH_H^B(t_0))} \bar{\rho}(t_0), \quad (15)$$

where the index H denotes the Heisenberg picture of the corresponding operators, i.e.

$$H_H^S(t_f) = U_{t_f,t_0}^\dagger H^S(t_f) U_{t_f,t_0}, \quad H_H^B(t_f) = U_{t_f,t_0}^\dagger H^B(t_f) U_{t_f,t_0}. \quad (16)$$

The density matrix $\bar{\rho}(t_0)$ describes the system immediately after the first measurement. It is given by the projection of the initial density matrix $\rho(t_0)$ onto the common eigenspaces of the measured operators. It hence assumes the form

$$\bar{\rho}(t_0) = \sum_{i,\alpha} P_{i,\alpha}(t_0)\rho(t_0)P_{i,\alpha}(t_0). \quad (17)$$

In analogy to the case of the measurement of the total energy of an isolated system the characteristic function for a joint measurement of two energies is determined by a correlation function of the exponential operator $(\exp[i(uH^S(t_f) - vH^B)])_H(t_f)$ in the Heisenberg picture at the time of the second measurement t_f and a second exponential operator $\exp[-i(uH^S(t_0) - vH^B)]$ taken at the initial time. The average is performed with respect to the initial density matrix projected onto the eigenspaces of the two operators of the first measurement.

In passing, we note that analogously to the internal energy and the exchanged heat being represented by the Hamiltonians of the system and environment, respectively, the characteristic function of the changes x_i of any mutually commuting set of N observables $X^i(t)$ can be represented as a correlation function:

$$G_{t_f,t_0}^{\{x_i\}}(u_1, u_2, \dots, u_N) = \text{Tr} e^{i\sum_{i=1}^N u_i X_H^i(t_f)} e^{-i\sum_{i=1}^N u_i X^i(t_0)} \bar{\rho}_0, \quad (18)$$

where u_i denotes the Fourier variable conjugate to x_i , $X_H^i(t_f)$ denotes the observable $X^i(t)$ in the Heisenberg picture and the density matrix $\bar{\rho}_0$ is given by the projection of the initial density matrix ρ_0 onto the common eigenspaces of the observables $X_i(t_0)$, $i = 1, \dots, N$, as in equation (17). We close this short digression by noting that both the central result of this paper, equation (14), and its generalization, (18), are valid independently of the dimensionality of the common eigenspaces of the sets of commuting observables $H^S(t)$, H^B in the first and $\{X_i(t)\}$ in the second case. In other words there is no restriction regarding a possible degeneracy of the energy eigenvalues of the uncoupled system and environment, or of the observables $X_i(t)$.

Once the statistical properties of internal energy changes and the exchange of heat are known, the marginal distributions of these quantities can equivalently be characterized in terms of their respective characteristic functions $G_{t_f,t_0}^E(u)$ and $G_{t_f,t_0}^Q(v)$; i.e.,

$$\begin{aligned} G_{t_f,t_0}^E(u) &= G_{t_f,t_0}^{E,Q}(u, 0), \\ G_{t_f,t_0}^Q(v) &= G_{t_f,t_0}^{E,Q}(0, v). \end{aligned} \quad (19)$$

Moreover, the internal energy change and the heat exchange determine the work

$$w = E - Q \quad (20)$$

performed on the system according to the First Law. Correspondingly, the joint characteristic function of heat and work, $G_{t_f,t_0}^{Q,w}(x, y)$, is related to that of internal energy and heat by

$$G_{t_f,t_0}^{Q,w}(x, y) = G_{t_f,t_0}^{E,Q}(y, x - y). \quad (21)$$

Then, the marginal characteristic function of work performed on the system becomes

$$G_{t_f,t_0}^w(z) = G_{t_f,t_0}^{E,Q}(z, -z). \quad (22)$$

So far we have not yet specified the initial density matrix $\rho(t_0)$. In section 3 we consider the particularly relevant case of a canonical state of the total system at a given temperature.

3. The fluctuation theorem for work and heat

We now assume that the total system consisting of the system considered and its environment is initially, i.e. at $t = t_0$, in a thermodynamical equilibrium at inverse temperature β and is consequently described by the Gibbs state

$$\rho_\beta(t_0) = Z^{-1}(t_0) e^{-\beta(H^S(t_0)+H^B+H^{SB})}, \quad (23)$$

where

$$Z(t_0) = \text{Tr} e^{-\beta(H^S(t_0)+H^B+H^{SB})} \quad (24)$$

denotes the partition function. In the particular case of weak coupling between the system and its environment a perturbation expansion of the density matrix with respect to the interaction Hamiltonian yields up to first order

$$\rho_\beta(t_0) \approx \rho^0(t_0) - Z_S^{-1}(t_0)Z_B^{-1} \int_0^\beta d\beta' e^{-(\beta-\beta')(H^S(t_0)+H^B)} \delta H^{SB} e^{-\beta'(H^S(t_0)+H^B)}, \quad (25)$$

where

$$Z^S(t_0) = \text{Tr}_S e^{-\beta H^S(t_0)}, \quad (26)$$

$$Z^B = \text{Tr}_B e^{-\beta H^S}. \quad (27)$$

Here Tr_S and Tr_B denote the traces over the system and the environmental Hilbert spaces, respectively. The operator $\delta H^{SB} = H^{SB} - \langle H^{SB} \rangle_0$ specifies the deviation of the interaction from its expectation value with respect to the factorizing state

$$\rho^0(t_0) = Z_S^{-1}(t_0)Z_B^{-1} e^{-\beta(H^S(t_0)+H^B)}. \quad (28)$$

In order to determine the density matrix $\bar{\rho}(t_0)$, equation (17), $\rho_\beta(t_0)$ has to be projected onto the common eigenspaces of $H^S(t_0)$ and H^B . This projection leaves the unperturbed part $\rho^0(t_0)$ of the initial density matrix (25) unchanged. The first-order correction on the right-hand side of equation (25) vanishes in all cases when the interaction between system and environment contains only off-diagonal terms with respect to the unperturbed energy basis as is the case e.g. for the spin-boson model [30], or the Caldeira–Leggett model [31]². In all of these cases the corrections to the factorizing density matrix $\rho^0(t_0)$ are at least of second order in the system–environment interaction. Therefore they can safely be neglected in the limit of weak coupling such that the diagonal projection of $\rho_\beta(t_0)$ leads to the factorizing state $\rho^0(t)$, i.e.

$$\bar{\rho}_\beta(t_0) = \rho^0(t_0) \equiv Z_S^{-1}(t_0)Z_B^{-1} e^{-\beta(H^S(t_0)+H^B)}. \quad (29)$$

We emphasize that this holds under the conditions of weak interaction between the system and its environment.

² If the interaction contains diagonal terms, these can safely be added to the system Hamiltonian, which then would be redefined accordingly. This actually leads to a redefinition of the system which will introduce only a minor change in the case of weak coupling. For strong coupling we refer to the comment at the end of section 4.

With this initial state the characteristic function for the statistics of internal energy and heat becomes

$$G_{t_f, t_0}^{E, Q}(u, v) = Z_S^{-1}(t_0) Z_B^{-1} \text{Tr} e^{i(uH_H^S(t_f) - vH_H^B(t_f))} e^{-i(uH^S(t_0) - vH^B)} e^{-\beta(H^S(t_0) + H^B)}. \quad (30)$$

Analogously to the characteristic function of work performed on a closed system initially in a canonical state [6], this expression can be continued to an analytic function of the variables u and v in the interior of the stripes $\mathcal{S}_u = \{u = u' + iu'' | u' \in \mathbb{R}, 0 \leq u'' \leq \beta\}$ and $\mathcal{S}_v = \{v = v' + iv'' | v' \in \mathbb{R}, -\beta \leq v'' \leq 0\}$ of the complex plane. At the boundaries the characteristic function is a continuous function of u and v . The proof is based on the fact that the operator under the trace on the right-hand side of equation (30) is an element of the trace class [32] for all $u \in \mathcal{S}_u$ and $v \in \mathcal{S}_v$ and that this operator is an analytic function in the interior and a continuous function at the boundaries of these stripes [33]. Setting $u = \bar{u} + i\beta$ and $v = \bar{v} + i\beta$ one finds

$$\begin{aligned} Z^S(t_0) G_{t_f, t_0}^{E, Q}(u, v) &= Z^S(t_f) G_{t_0, t_f}^{E, Q}(-\bar{u}, -\bar{v}) \\ &= Z^S(t_f) G_{t_0, t_f}^{E, Q}(-u + i\beta, -v - i\beta), \end{aligned} \quad (31)$$

where $G_{t_0, t_f}^{E, Q}(u, v)$ is the characteristic function of the internal energy change and heat transfer for a fictitious process that runs under the action of the time reversed process backward in time. The proof is analogous to that for the case of a closed system initially in a canonical state [6]. Applying the inverse Fourier transform with respect to both variables u and v one obtains a Tasaki–Crooks type of expression [2, 4]. It establishes a connection between the joint pdf of internal energy change and exchanged heat for the original process and the corresponding quantity for the time reversed process. This fluctuation theorem reads accordingly

$$\frac{p_{t_f, t_0}(E, Q)}{p_{t_0, t_f}(-E, -Q)} = \frac{Z^S(t_f)}{Z^S(t_0)} e^{\beta(E-Q)} = e^{-\beta(\Delta F - E + Q)}, \quad (32)$$

where $\Delta F = -\beta^{-1} \ln[Z^S(t_f)/Z^S(t_0)]$ denotes the free energy difference between the system in the canonical state with the parameter values at t_f and in the initial state at t_0 .

3.1. Non-equilibrium free energy/work relations

Replacing the internal energy by the work performed on the system we obtain

$$Z^S(t_0) G_{t_f, t_0}^{Q, w}(x, y) = Z^S(t_f) G_{t_0, t_f}^{Q, w}(-x - y, -y + i\beta), \quad (33)$$

or equivalently

$$\frac{p_{t_f, t_0}^{Q, w}(Q, w)}{p_{t_0, t_f}^{Q, w}(-Q, -w)} = e^{-\beta(\Delta F - w)}. \quad (34)$$

Here $p_{t_f, t_0}^{Q, w}(Q, w) = p_{t_f, t_0}(Q + w, Q)$ denotes the joint pdf of heat and work corresponding to the characteristic function $G_{t_f, t_0}^{Q, w}(x, y)$ defined in equation (21). Integrating over all possible values of the exchanged heat one obtains the Tasaki–Crooks theorem for an open system which couples weakly to its environment. It reads

$$\frac{p_{t_f, t_0}^w(w)}{p_{t_0, t_f}^w(-w)} = e^{-\beta(\Delta F - w)}, \quad (35)$$

where $p_{t_f, t_0}^w(w) = \int dQ p_{t_f, t_0}^{Q, w}(Q, w)$ denotes the marginal pdf of work. From the Tasaki-Crooks theorem Jarzynski's work theorem follows immediately, saying that the mean value of the exponentiated negative work performed on an open system in weak contact with its environment coincides with the exponentiated negative free energy difference [1], i.e.,

$$\langle e^{-\beta w} \rangle = e^{-\beta \Delta F}. \quad (36)$$

3.2. Non-equilibrium relations for conditional and marginal probabilities

From equation (32) one can obtain non-equilibrium relations for the marginal distribution of heat

$$p_{t_f, t_0}^Q(Q) = \int dw p_{t_f, t_0}^{Q, w}(Q, w), \quad (37)$$

for the pdf of work w under the condition that the heat Q is measured, i.e.,

$$p_{t_f, t_0}(w|Q) = \frac{p_{t_f, t_0}^{Q, w}(Q, w)}{p_{t_f, t_0}^Q(Q)}, \quad (38)$$

and for the pdf of heat Q under the condition that the work w is measured, i.e.,

$$p_{t_f, t_0}(Q|w) = \frac{p_{t_f, t_0}^{Q, w}(Q, w)}{p_{t_f, t_0}^w(w)}. \quad (39)$$

A straightforward calculation yields

$$\frac{p_{t_0, t_f}^Q(-Q)}{p_{t_f, t_0}^Q(Q)} = e^{\beta \Delta F} \langle e^{-\beta w} | Q \rangle, \quad (40)$$

where the symbol $\langle \cdot | Q \rangle$ denotes the average over $p_{t_f, t_0}(w|Q)$.

On the other hand one finds the following relation:

$$\frac{p_{t_f, t_0}(Q|w)}{p_{t_0, t_f}(-Q| -w)} = 1, \quad (41)$$

for the conditional pdfs of heat Q given the work w , in the forward and backward processes. For the forward and backward conditional pdfs of work given the heat, one obtains the less symmetric relation

$$\frac{p_{t_f, t_0}(w|Q)}{p_{t_0, t_f}(-w| -Q)} = e^{\beta w} \langle e^{-\beta w} | Q \rangle. \quad (42)$$

The relations (40)–(42) continue to hold true also in the classical limit. To the best of our knowledge, they have been unknown both in the classical and in the quantum context.

3.3. Non-equilibrium equalities for exponentiated internal energy and heat

By noting that

$$\langle e^{\beta Q} \rangle_Q = \int dQ p_{t_f, t_0}^Q(Q) e^{\beta Q} = G_{t_f, t_0}^Q(-i\beta) \quad (43)$$

and

$$\langle e^{-\beta E} \rangle_E = \int dE p_{t_f, t_0}^E(E) e^{-\beta E} = G_{t_f, t_0}^E(i\beta), \quad (44)$$

and using equations (19) and (30) one finds two non-equilibrium equalities for heat and internal energy:

$$\langle e^{\beta Q} \rangle_Q = \frac{\text{Tr} e^{-\beta H^S(t_0)} e^{-\beta H_H^B(t_f)}}{Z_S(t_0) Z_B}, \quad (45)$$

$$\langle e^{-\beta E} \rangle_E = \frac{\text{Tr} e^{-\beta H_H^S(t_f)} e^{-\beta H^B}}{Z_S(t_0) Z_B}. \quad (46)$$

In clear contrast to the Jarzynski equality, the average of the exponentiated heat as well as that of the exponentiated negative energy do depend on the details of the protocol, i.e. these relations do not depend only on equilibrium properties of the system.

4. Conclusions

We proved that the Tasaki–Crooks fluctuation theorem and the Jarzynski equality hold in open quantum systems that are weakly coupled to their environments. This was accomplished by introducing the characteristic function for the probability of joint measurements of system and environmental energies, which are commuting observables. This characteristic function was further evaluated for canonical initial states. Our approach rests on two basic assumptions: first, the total system made up of the system of interest and its environment is governed by Hamiltonian dynamics; and second, the coupling between the system and its environment is assumed to be weak. The first assumption leads to a unitary time evolution of the total system. The second assumption has two important consequences. First, it allows one to determine the internal energy from the Hamiltonian of the system and the heat from the Hamiltonian of the environment. The work performed on the system then follows by means of the First Law. The contribution of the interaction Hamiltonian is neglected in the definitions of these three energies. The second consequence of the weak coupling assumption is the factorization of the state of the total system immediately after the first measurements of energies into a product of the Gibbs states of the system and the environment as if they were uncoupled up to second-order corrections in the system environment interaction. In order for these corrections to be small for weak but non-zero coupling, the temperature of the initial state must not be too low. In contrast, we formally allowed for the exact time evolution such that fast as well as slow protocols can be described adequately.

By an inverse Fourier transformation the joint statistics of internal energy and heat (defined as the energy ceded to the environment) was shown to obey a Tasaki–Crooks type of fluctuation theorem. From this we derived the Tasaki–Crooks fluctuation theorem and

the Jarzynski equality, for a quantum system that weakly couples to its environment [6]. Further non-equilibrium relations for the marginal and conditional pdfs of work given the heat and heat given the work were derived.

In the present paper we restricted ourselves to the case where the external forces directly influence the system Hamiltonian but leave the interaction and the environment Hamiltonians unchanged. Our approach can be generalized to more complex situations where the forces immediately influence the system plus the environment. In this general case the Tasaki–Crooks theorem, equation (34), continues to hold in a slightly modified form: also the change of the free energy of the environment has to be taken into account, i.e. ΔF has to be replaced by $\Delta F + \Delta F_B$, where ΔF_B denotes the change in free energy of the environment due to the parameter change of the environmental Hamiltonian. In those special cases where only the system and the interaction Hamiltonians are influenced by the external forcing, the form of the Tasaki–Crooks theorem as given by equation (34) stays unchanged. As a consequence the Jarzynski equality remains valid for forces changing the system and its interaction with the environment but leaves the Hamiltonian of the environment unchanged.

For a system that strongly couples to its environment it frequently is possible to ‘dress’ the system with excitations of its environment such that the dressed system interacts only weakly with its properly redefined environment. Quasi-particles in solid state physics are typical examples of such systems. An external force acting on the original system will also be felt by the dressed system. For the work exerted on the dressed system and the heat exchanged with the properly redefined environment all conditions for the presented theory apply and therefore the Tasaki–Crooks theorem and consequently the Jarzynski equality remain valid for such dressed systems. More general systems that strongly interact with the environment will be considered elsewhere.

Acknowledgments

Financial support by the German Excellence Initiative via the *Nanosystems Initiative Munich* (NIM) and the Volkswagen Foundation (project I/80424) is gratefully acknowledged.

References

- [1] Jarzynski C, *Nonequilibrium equality for free energy differences*, 1997 *Phys. Rev. Lett.* **78** 2690
- [2] Crooks G E, *Entropy production fluctuation theorem and the nonequilibrium work relation for free energy differences*, 1999 *Phys. Rev. E* **60** 2721
- [3] Kurchan G, *A quantum fluctuation theorem*, 2000 arXiv:cond-mat/0007360
- [4] Tasaki H, *Jarzynski relations for quantum systems and some applications*, 2000 arXiv:cond-mat/0009244
- [5] Talkner P, Lutz E and Hänggi P, *Fluctuation theorems: work is not an observable*, 2007 *Phys. Rev. E* **75** 050102
- [6] Talkner P and Hänggi P, *The Tasaki–Crooks quantum fluctuation theorem*, 2007 *J. Phys. A: Math. Theor.* **40** F569
- [7] Talkner P, Hänggi P and Morillo M, *Microcanonical quantum fluctuation theorems*, 2008 *Phys. Rev. E* **77** 05113
- [8] Campisi M, *Complementary expressions for the entropy-from-work theorem*, 2008 *Phys. Rev. E* **78** 012102
- [9] Deffner S and Lutz E, *Nonequilibrium work distribution of a quantum harmonic oscillator*, 2008 *Phys. Rev. E* **77** 021128
- [10] Talkner P, Burada P S and Hänggi P, *Statistics of work performed on a forced quantum oscillator*, 2008 *Phys. Rev. E* **78** 011115

- [11] Huber G, Schmidt-Kaler F, Deffner S and Lutz E, *Employing trapped cold ions to verify the quantum Jarzynski equality*, 2008 *Phys. Rev. Lett.* **101** 070403
- [12] Mukamel S, *Quantum extension of the Jarzynski relation: analogy with stochastic dephasing*, 2003 *Phys. Rev. Lett.* **90** 170604
- [13] De Roeck W and Maes C, *Quantum version of free-energy/irreversible-work relations*, 2004 *Phys. Rev. E* **69** 026115
- [14] Esposito M and Mukamel S, *Fluctuation theorems for quantum master equations*, 2006 *Phys. Rev. E* **73** 046129
- [15] Crooks G E, *On the Jarzynski relation for dissipative quantum dynamics*, 2008 *J. Stat. Mech.* **P10023**
- [16] Grabert H, Weiss U and Talkner P, *Quantum theory of the damped harmonic oscillator*, 1984 *Z. Phys. B* **55** 87
- [17] Talkner P, *The failure of the quantum regression hypothesis*, 1986 *Ann. Phys., NY* **167** 390
- [18] Riseborough P, Hänggi P and Weiss U, *Exact results for a damped quantum mechanical oscillator*, 1985 *Phys. Rev. A* **31** 471
- [19] Hänggi H and Ingold G I, *Fundamental aspects of quantum Brownian motion*, 2005 *Chaos* **15** 026105
- [20] Ankerhold J, Pechukas P and Grabert H, *Strong friction limit in quantum mechanics: the quantum Smoluchowski equation*, 2001 *Phys. Rev. Lett.* **87** 086802
- [21] Machura L, Kostur M, Hänggi P, Talkner P and Luczka J, *Consistent description of quantum Brownian motors operating at strong friction*, 2004 *Phys. Rev. E* **70** 031107
- [22] Coffey W T, Kalmykov Y P, Titov S V and Mulligan B P, *Semiclassical Kramers and Smoluchowski equations for the Brownian motion of a particle in an external potential*, 2007 *J. Phys. A: Math. Theor.* **40** F91
- [23] Coffey W T, Kalmykov Y P, Titov S V and Cleary L, *Smoluchowski equation approach for quantum Brownian motion in a tilted periodic potential*, 2008 *Phys. Rev. E* **78** 031114
- [24] Allahverdyan A E and Nieuwenhuizen T M, *Fluctuations of work from quantum subensembles: the case against quantum work-fluctuation theorems*, 2005 *Phys. Rev. E* **71** 066102
- [25] Hörhammer C and Büttner H, *Information and entropy in quantum Brownian motion: thermodynamic entropy versus von Neumann entropy*, 2007 arXiv:0710.1716
- [26] Ingold G L, Talkner P and Hänggi P, *Negative specific heat from the partition function of a free damped particle*, 2008 arXiv:0811.3509
- [27] Jarzynski C and Wójcik D, *Classical and quantum fluctuation theorems for heat exchange*, 2004 *Phys. Rev. Lett.* **92** 230602
- [28] Saito K and Dhar A, *Fluctuation theorem in quantum heat conduction*, 2007 *Phys. Rev. Lett.* **99** 180601
- [29] Kobe D H, *Gauge-invariant classical Hamiltonian formulation of the electrodynamics of nonrelativistic particles*, 1981 *Am. J. Phys.* **49** 581
- [30] Leggett A J, Chakravarty S, Dorsey A T, Fisher M P A, Garg A and Zwerger W, *Dynamics of the dissipative two-state system*, 1987 *Rev. Mod. Phys.* **59** 1
- [31] Caldeira A O and Leggett A J, *Influence of dissipation on quantum tunneling in macroscopic systems*, 1981 *Phys. Rev. Lett.* **46** 211
- [32] Holevo A S, 2001 *Statistical Structure of Quantum Theory* (Berlin: Springer)
- [33] Haag R, Hugenholtz N M and Winnink M, *On the equilibrium states in quantum statistical mechanics*, 1967 *Commun. Math. Phys.* **5** 215