A quantum version of free energy - irreversible work relations

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Abstract: We give a quantum version of the Jarzynski relation between the distribution of work done over a certain time-interval on a system and the difference of equilibrium free energies. The main new ingredient is the identification of work depending on the quantum history of the system and the proper definition of various quantum ensembles over which the averages should be made. We also discuss a number of different regimes that have been considered by other authors and which are unified in the present set-up. In all cases, and quantum or classical, it is a general relation between heat and time-reversal that makes the Jarzynski relation so universally valid.

KEY WORDS: irreversible work, nonequilibrium processes, entropy production.

1. Introduction

Thermodynamic potentials such as the Helmholtz free energy are crucial in applications of thermodynamics. They give insight in what processes are *a priori* workable, with what effects and under what circumstances. Basically one is interested in two types of information. One is the expression of these potentials as a function of system-parameters. That determines the thermodynamic landscape and it yields the thermodynamic forces. A second type of information concerns the mutual relation between these potentials and the link with available work and entropy-energy transformations. For example, for a system that can extract heat from an environment at constant temperature T, the energy that is available to do work is exactly the free energy $F \equiv V - TS$, that is its energy V minus the heat term TS where S is the entropy of the system. Furthermore, to study its equilibrium properties we should maximize the total entropy (of system and reservoir) for a given energy contents but that again is equivalent with minimizing the free energy at fixed temperature.

If, as often happens, no very reliable computation of the free energy landscape can be made, the above provides immediate rescue. It suffices to measure the work done under isothermal conditions in changing

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the parameters of the system and it will be equal to the free energy difference. That however is only valid if the thermodynamic process involved is quasi-static. In other words, the changes must be done very slowly, a situation that cannot be hoped for in many cases. It was therefore very useful that an extended relation between free energy and work was proposed and exploited in a series of papers since the pioneering work of Jarzynski in 1997, [4]. That relation looks as follows:

$$e^{-\beta\Delta F} = \langle e^{-\beta W}\rangle \tag{1.1}$$

In the left-hand side ΔF is what we want to know, the difference in free energies between two equilibria with parameter values κ_f and κ_i. The right-hand side is an average over all possible paths that take the system in equilibrium for a certain parameter value κ_i in its initial Hamiltonian to a state where that parameter is changed into κ_f. The work done W depends on the path if the process is not adiabatic (i.e. without heat transfer) or if it is not quasi-static. The protocol, i.e. the sequence of forcing in the time-dependent Hamiltonian, is always kept fixed.

Derivations of the Jarzynski relation (1.1) have been made in various ways and in various approximations, see [3, 4, 5, 6, 7, 8, 14, 13]. From such a relation free energy differences can be measured even in situations where the process of changing the parameters is not so well-controlled. That has already been experimentally realized in e.g. molecular systems [9, 11, 16].

A natural extension of (1.1) concerns the quantum regime. That appears possibly important and relevant when the system in question should be treated with the methods of quantum mechanics. In nanodevices the interplay between nanomechanics and thermodynamics becomes all important. Yet, a more fundamental reason to be interested in a quantum version of (1.1) is the question that it poses on the quantum nature of path-dependence. We enter here the domain of quantum mechanics on histories. It is *a priori* not clear how to define quantum mechanical work that depends on a path that the system has followed. In the present paper we derive a quantum extension of (1.1) where we explicitly deal with that path-dependence and where we start from a time-dependent unitary evolution on the level of the system plus environment.

2. Previous results

Various proposals for quantum extensions of the Jarzynski relation have appeared in the literature. We briefly bring up some aspects of such studies.

In [17] and following [10] one introduces the probabilities

$$p_{\alpha,\alpha'} \equiv \frac{e^{-\beta V_\alpha}}{Z(\beta)}\, |\langle\varphi'_{\alpha'}|U|\varphi_\alpha\rangle|^2 \tag{2.1}$$

that the system is found in the $\alpha-$th eigenstate φ_α of the Hamiltonian H at an initial time (when the system in in thermal equilibrium at inverse temperature β) and then is found in the $\alpha'-$th eigenstate $\varphi'_{\alpha'}$ of the Hamiltonian H' at a later time. The operator U in (2.1) is the unitary operator for the time inhomogeneous evolution during the whole period. It is then an easy computation, done in [17], that

$$\sum p_{\alpha,\alpha'} \exp[\beta V_\alpha - \beta V'_{\alpha'}] = \frac{Z'(\beta)}{Z(\beta)} \tag{2.2}$$

That resembles (1.1) except for the important fact that the left-hand side averages over an exponential of a total (in time) energy difference. In particular there is no concept here of a path-dependent work. One interpretation is that the system in question is here really the total system (subsystem + heat bath) and one should follow the change in energy over the whole system. We think however that it is more useful to have a representation of work in terms of the coordinates (and history) of the subsystem only. After all, that is what free energies are all about thermodynamically. A second interpretation is that one thinks of the unitary evolution as working entirely on the subsystem itself and the heat bath is completely absent except for the inverse temperature β. That can be called the adiabatic regime and we return to it in Section 4.3.1.

The presentation in [15] contains analogies both with what was described in [3] and with the adiabatic treatment of [17]. In [3] a derivation of (1.1) was given based on a time-inhomogeneous Markov process which satisfies, at each time, the detailed balance relation for some energy function. That can be lifted to the quantum regime when the Markov process is seen as an effective description of a quantum system in contact with a heat bath. For example, the quantum weak coupling limit exactly reproduces the *classical* Markov process as dynamics for the system when in the energy basis for the system Hamiltonian. In that precise sense, [3] was the first quantum extension of the Jarzynski relation. Here one deals with an effective dynamics of the subsystem and we turn to in in Section 4.1.

Finally, in [18] the question of path-dependence of the work is analyzed in an operator-setting and it is pointed out that various ambiguities remain in the ordering of the operators. These ambiguities only seem to disappear in a quasi-static limit which unfortunately, is exactly the regime we are less interested in. While it is in principle possible to define a work-operator for the total system, the question in that setting remains whether its projection on the subsystem remains useful and its spectrum measurable.

In the present paper we deal with a unitary evolution over the total system, subsystem plus reservoir, and we deal explicitly with a path-dependent work. That is new but the reason that the Jarzynski relation (1.1) is so universally valid remains the same as for classical systems. The basic observation is that the entropy production can be identified with the source of time-reversal breaking in the action governing the distribution of system histories, see [1, 12, 13]. We briefly state that point here in a formal way to refer to it later when things become more explicit.

We take the dynamics time-dependent through which work W is done on the system over a time-period while in contact with a heat bath at constant inverse temperature β. The time-dependent dynamics starts with an energy function V_i and at time n the energy function is given by V_f. Let $q(\omega, \rho_i)$ denote the probability of a history $(\omega_t)_0^n$ (on a certain level of description) of the system started in the state ρ_i at time zero. We choose $\rho_i = \exp[-\beta V_i]/Z_i$. We now reverse the protocol (the sequence of forcing) and let $\tilde{q}(\omega, \rho_f))$ denote the probability of the history ω when started in ρ_f at time zero. We choose $\rho_f = \exp[-\beta V_f]/Z_f$ for the same temperature but with a different energy function. For the probability of the time-reversed trajectory $\Theta\omega \equiv (\omega_{n-t})_0^n$, we then write $\tilde{q}(\Theta\omega, \rho_f)$. Introducing the action $\mathcal{L}$, we have

$$q(\omega, \rho) = \rho(\omega_0) e^{-\mathcal{L}(\omega)}, \quad \frac{\tilde{q}(\Theta\omega, \rho_f)}{q(\omega, \rho_i)} = e^{-R(\omega)} \tag{2.3}$$

with

$$R(\omega) \equiv \ln \rho_i(\omega_0) - \ln \rho_f(\omega_n) + \tilde{\mathcal{L}}(\Theta\omega) - \mathcal{L}(\omega)$$

Then,

$$\ln \rho_0(\omega_0) - \ln \rho_n(\omega_n) = \beta[V_f(\omega_n) - V_i(\omega_0)] - \beta\Delta F, \quad \Delta F \equiv -\frac{1}{\beta} \ln \frac{Z_f}{Z_i}$$

The change in energy $V_f(\omega_n) - V_i(\omega_0)$ equals the work W minus the heat Q that flows into the bath. On the other hand, it can be argued that the source term of time-symmetry breaking $\tilde{\mathcal{L}}(\Theta\omega) - \mathcal{L}(\omega)$ equals the entropy production βQ, see [13]. Hence, we get from (2.3) that

$$\frac{\tilde{q}(\Theta\omega,\rho_n)}{q(\omega,\rho_0)} = e^{-\beta W(\omega)+\beta\Delta F}$$

But, by normalization, multiplying the above relation with $q(\omega,\rho_i)$ and summing over all ω gives one; hence (1.1) obtains.

What remains to be done is to give a quantum expression for the above quantities and that is the subject of the present paper. In other words, we want to obtain an algorithm, valid for a system subject to the laws of quantum mechanics, through which we can measure the difference in equilibrium free energies. Moreover, we want this algorithm to be formulated on the level of the subsystem. That means that we must trace out the heat bath from the equality (2.2).

3. Formulation of the problem

We model a possibly small quantum system in contact with a much larger heat reservoir kept at fixed inverse temperature β. The Hilbert space of the subsystem is denoted by $\mathcal{H}_S$ and that of the environment by $\mathcal{H}_R$; both are assumed finite dimensional. As usual the total real and self-adjoint Hamiltonian is a sum of three contributions,

$$H_t = H_t^S + H^R + \gamma H^I \tag{3.1}$$

where the system-part H_t^S is parameterized by $t = 0, 1, \ldots, n$ and acts on $\mathcal{H}_S$. The Hamiltonian of the reservoir H^R (acting on $\mathcal{H}_R$) and the coupling H^I between system and reservoir are assumed fixed. We will not need any explicit description of these terms. Setting $\gamma = 0$ decouples system and reservoir. The canonical density matrices describing equilibrium for the decoupled system are

$$\rho^t \equiv \frac{1}{Z_t} e^{-\beta H_t^S} \otimes \frac{1}{Z^R} e^{-\beta H^R} \tag{3.2}$$

We are interested in the difference of Helmholtz free energies

$$\Delta F \equiv -\frac{1}{\beta} \ln \frac{Z_n}{Z_0} \tag{3.3}$$

The dynamics for the total system is unitary and time-dependent with unitary operator

$$U_t = e^{i\lambda H_t}$$

acting on $\mathcal{H}_S \otimes \mathcal{H}_R$. The parameter λ is real and sets the energy-time scale.

While the left-hand side of (1.1) is clear and given by (3.3) the question is about the quantum version of the right-hand side: What is the averaging and what is the work? Different reduced dynamics for the subsystem can be imagined that are relevant in different types of regimes.

4. Results

4.1. **Effective regime.** Here we suppose that the dynamics for the subsystem is described via some effective dynamics. There are various candidates but one class of examples is obtained as the quantum analogue of a Markov process on $\mathcal{H}_S$. These can be rigorously obtained under various conditions and in various limiting regimes. Following [2], one can start with a time-dependent Hamiltonian H_t and take the weak coupling limit. Obviously the driving protocol has to vary on the same time scale as the dissipation processes through contact with the reservoir. What results is a time-inhomogeneous Markov process such that the instantaneous generator at time t satisfies detailed balance with respect to $H(t)$. One way to implement that is to think of a sequence $\varphi^0_{\alpha_O} \to \varphi^0_{\alpha_1} \to \varphi^1_{\alpha_1} \to \varphi^1_{\alpha_2} \to \ldots \to \varphi^{n-1}_{\alpha_{n-1}} \to \varphi^{n-1}_{\alpha_n} \to \varphi^n_{\alpha_n}$ where alternating in time, the transition is either thermal as for $\varphi^t_{\alpha_t} \to \varphi^t_{\alpha_{t+1}}$, and is modelled by a completely positive map Λ_t which satisfies the condition of detailed balance with respect to $\rho_t \equiv e^{-\beta H^S_t}/Z_t$,

$$\frac{\text{Tr }[P^t_{\alpha_t}\Lambda_t(P^t_{\alpha_{t-1}})]}{\text{Tr }[P^t_{\alpha_{t-1}}\Lambda_t(P^t_{\alpha_t})]} = \exp[-\beta(V^t_{\alpha_t} - V^t_{\alpha_{t-1}})] \tag{4.1}$$

or is mechanical as for $\varphi^t_{\alpha_t} \to \varphi^{t+1}_{\alpha_t}$. That last transition is imagined instantaneously performed so that we define the probability of a trajectory ω as the product

$$\begin{aligned} q^D_\beta(\omega) \equiv \text{Tr }[P^n_{\alpha_n}\Lambda_n(P^n_{\alpha_{n-1}})] \qquad & \text{Tr }[P^{n-1}_{\alpha_{n-1}}\Lambda_{n-1}(P^{n-1}_{\alpha_{n-2}})]\ldots \\ & \ldots \text{Tr }[P^1_{\alpha_1}\Lambda_1(P^1_{\alpha_0})]\frac{e^{-\beta V^0_{\alpha_0}}}{Z_0} \end{aligned} \tag{4.2}$$

Expectations will be denoted by $\langle\cdot\rangle_D$. The total change in energy is $\Delta V \equiv V^n_{\alpha_n} - V^0_{\alpha_0}$ and the total heat that flows in the heat bath in the thermal transitions (4.1) is

$$Q(\omega) \equiv -\sum_{t=1}^{n}(V^t_{\alpha_t} - V^t_{\alpha_{t-1}}) \tag{4.3}$$

The total work is therefore defined as

$$W(\omega) \equiv Q(\omega) + \Delta V = \sum_{t=0}^{n-1} (V^{t+1}_{\alpha_t} - V^t_{\alpha_t}) \tag{4.4}$$

and is done over the transitions $\varphi^t_{\alpha_t} \to \varphi^{t+1}_{\alpha_t}$. We then have

$$\langle e^{-\beta W}\rangle_D = e^{-\beta \Delta F} \tag{4.5}$$

The simplest way to prove (4.5) is to use the relation between entropy production and time-reversal as in [12, 13, 1, 3]. Let $\Theta\omega \equiv (\alpha_n, \ldots, \alpha_0)$ be the time-reversed trajectory. Similar to (4.2) we define a path-space measure starting from ρ_n:

$$\tilde{q}^D_\beta(\Theta\omega) \equiv \text{Tr }[P^1_{\alpha_0}\Lambda_1(P^1_{\alpha_1})] \ldots \text{Tr }[P^n_{\alpha_{n-1}}\Lambda_n(P^n_{\alpha_n})]\frac{e^{-\beta V^n_{\alpha_n}}}{Z_n} \tag{4.6}$$

and compute the ratio

$$\frac{q^D_\beta(\omega)}{\tilde{q}^D_\beta(\Theta\omega)} = e^{\beta(V^n_{\alpha_n} - V^0_{\alpha_0})}\frac{Z_n}{Z_0}\frac{\text{Tr }[P^n_{\alpha_n}\Lambda_n(P^n_{\alpha_{n-1}})]}{\text{Tr }[P^n_{\alpha_{n-1}}\Lambda_n(P^n_{\alpha_n})]}\cdots\frac{\text{Tr }[P^1_{\alpha_1}\Lambda_1(P^1_{\alpha_0})]}{\text{Tr }[P^1_{\alpha_0}\Lambda_1(P^1_{\alpha_1})]}$$

By using detailed balance (4.1) at every time-step and the definitions (4.3)–(4.4), one arrives at

$$\frac{q^D_\beta(\omega)}{\tilde{q}^D_\beta(\Theta\omega)} = e^{\beta\Delta V - \beta\Delta F + \beta Q} = e^{\beta W - \beta \Delta F}$$

Apply to that relation the normalization condition

$$\sum_\omega q^D_\beta(\omega)\frac{\tilde{q}^D_\beta(\Theta\omega)}{q^D_\beta(\omega)} = 1$$

to conclude (4.5). The proof above mimics exactly the scenario of (2.3). The result is the very analogue of the main identity by Crooks in [3] but where the transition rates in (4.2) have a quantum mechanical expression.

4.2. **Repeated measurements.** We come back to the set-up of (3.1)–(3.2). Assume that each H^S_t is non-degenerate and has projections P^t_α on its eigenstates φ^t_α with eigenstates V^t_α. A trajectory or path for the subsystem is a sequence $(\alpha_0, \ldots, \alpha_n)$ where each α_t runs over the possible eigenstates of $H^S_t, t = 0, \ldots, n$. We now give a probability measure on such trajectories which is obtained by tracing out the quantum mechanical probabilities for the whole system.
Let P_E denote the projection on the energy-space in $\mathcal{H}_R$ for the reservoir Hamiltonian H^R with energy E. The probability to find the total

system initially in equilibrium for (3.2) and at later times in eigenstates $\varphi^t_{\alpha_t}$ for the system and with energies E_t for the reservoir is given by

$$\begin{aligned} & p_\beta(\alpha_0, \dots, \alpha_n; E_0, \dots, E_n) \equiv \text{Tr}\,[G\,\rho^0\,G^\star] \qquad (4.7) \\ \text{with} \qquad & G \equiv P^n_{\alpha_n} \otimes P_{E_n} U_n \dots P^1_{\alpha_1} \otimes P_{E_1} U_1 P^0_{\alpha_0} \otimes P_{E_0} \end{aligned}$$

When viewed from the subsystem, the probability for trajectory $\omega = (\alpha_0, \dots, \alpha_n)$ is thus (let $e \equiv (E_0, \dots, E_n)$)

$$q_\beta(\omega) \equiv \sum_e p_\beta(\alpha_0, \dots, \alpha_n; e) \qquad (4.8)$$

and when conditioning on ω, (4.7) gives expectations denoted as

$$\langle g \rangle(\omega) \equiv \frac{1}{q_\beta(\omega)} \sum_e g(\omega, e)\; p_\beta(\omega; e) \qquad (4.9)$$

when $q_\beta(\omega)$ is non-zero. Finally, the expectations in the path-space measure (4.8) are written as

$$\langle f \rangle \equiv \sum_\omega f(\omega)\; q_\beta(\omega) \qquad (4.10)$$

The change in energy for the subsystem corresponding to the path ω is $V^n_{\alpha_n} - V^0_{\alpha_0}$ where V^t_α is the energy of φ^t_α. We define a path-dependent work by the formula

$$W(\omega) \equiv V^n_{\alpha_n} - V^0_{\alpha_0} - \frac{1}{\beta} \ln\langle e^{-\beta(E_n - E_0)} \rangle(\omega) \qquad (4.11)$$

The interpretation follows the first law of thermodynamics. To change the parameters in the Hamiltonian H^S_t isothermally some heat must flow from the bath into the system. That is the second term in (4.11). We can expect that the heat bath is dispersionfree with respect to the subsystem in the sense that through each step $\varphi^t_{\alpha_t} \to \varphi^{t+1}_{\alpha_{t+1}}$ of the trajectory ω, the corresponding change in energies $E_{t+1} - E_t$ of the reservoir is determined:

$$-\frac{1}{\beta} \ln\langle e^{-\beta(E_n - E_0)} \rangle(\omega) \simeq \langle E_n - E_0 \rangle(\omega) \qquad (4.12)$$

That gives the heat Q flowing into the reservoir. At the same time the energy in the subsystem changes, the first term in (4.11). Combined, (4.11) gives the work performed on the subsystem.
For (4.7) – (4.11),

$$e^{-\beta \Delta F} = \langle\, e^{-\beta W}\, \rangle \qquad (4.13)$$

That means that the Jarzynski relation (1.1) is unaffected in the quantum regime when, in the averaging, the quantum mechanical probabilities are used. We will now verify (4.13).

We apply again the ideas around (2.3). We define the time-reversed path-space measure from (4.7) by reversing the order in which the time-dependent dynamics is applied and by now starting from the density matrix ρ^n of (3.2):

$$\begin{aligned} &\tilde{p}_\beta(\alpha_0,\ldots,\alpha_n;E_0,\ldots,E_n) \equiv \mathrm{Tr}\,[\tilde{G}\,\rho^n\,\tilde{G}^\star] \\ \text{with} \qquad &\tilde{G} \equiv P^n_{\alpha_n}\otimes P_{E_n}U_{1^\star}\ldots P^1_{\alpha_1}\otimes P_{E_1}U^\star_n P^0_{\alpha_0}\otimes P_{E_0} \end{aligned} \tag{4.14}$$

It follows immediately that

$$\tilde{p}_\beta(\Theta\omega;\Theta e) = p_\beta(\omega;e)e^{-\beta(V^n_{\alpha_n}-V^0_{\alpha_0}+E_n-E_0)}\frac{Z_0}{Z_n} \tag{4.15}$$

and hence

$$\begin{aligned} \langle\, e^{-\beta W}\,\rangle &= \sum_\omega q_\beta(\omega)e^{\beta(V^0_{\alpha_0}-V^{\alpha_n}_n)}\langle e^{-\beta(E_n-E_0)}\rangle(\omega) \qquad (4.16)\\ &= \sum_{\omega,e} p_\beta(\omega,e)e^{\beta(V^0_{\alpha_0}-V^n_{\alpha_n})}e^{-\beta(E_n-E_0)} \\ &= \frac{Z_n}{Z_0}\sum_{\omega,e}\tilde{p}_\beta(\Theta\omega,\Theta e) \\ &= e^{-\beta\Delta F} \end{aligned}$$

as required.

The repeated measurements introduce another aspect of randomness in the distribution of work which is absent classically. Unless one is taking an effective dynamics like in Section 4.1, one will always need to take care of that aspect to define in any useful way what is meant by work that depends on the history of the subsystem.

4.3. **Special cases.** There are a number of special cases that we treat separately.

4.3.1. *Adiabatic regime.* We consider only the subsystem that was initially brought in thermal equilibrium at inverse temperature β and that from time zero on is isolated from the environment. We take thus the same set-up as in Section 3 except that we cut the coupling with the reservoir. The initial density matrix is

$$\rho_0 \equiv \frac{1}{Z_0} e^{-\beta H_0^S}$$

and the dynamics is unitary on $\mathcal{H}_S$ and here denoted by U_t^S with $t = 0, 1, \ldots, n$ changing as time proceeds. U_t^S need not commute with H_t^S. Instead of (4.8) we now take the probability of trajectory $\omega = (\alpha_0, \ldots, \alpha_n)$ to be

$$q_\beta^S(\omega) \equiv \text{Tr}\ [P_{\alpha_n}^n U_n^S \ldots P_{\alpha_1}^1 U_1^S P_{\alpha_0}^0\, \rho_0\, (P_{\alpha_n}^n U_n^S \ldots P_{\alpha_1}^1 U_1^S P_{\alpha_0}^0)^\star] \qquad (4.17)$$

with expectations $\langle\cdot\rangle_S$. For ω the change in energy of the subsystem is $V_n - V_0$ as was the first term in (4.11). Then

$$\langle e^{\beta(V_{\alpha_0}^0 - V_{\alpha_n}^n)}\rangle_S = e^{-\beta\Delta F} \qquad (4.18)$$

That identity is the generalization of Equation 2.7 in [17]. Note that (4.18) is true for an arbitrary family of unitary operators defining the time-evolution. It can be obtained from the following exact identity. Let G be an operator on $\mathcal{H}_S$ and write $\text{Tr}\ [G\, P_\alpha^n] \equiv G(\alpha)$. Then, as one easily checks,

$$\sum_\omega G(\alpha_n)\, e^{\beta V_{\alpha_0}^0} \text{Tr}\ [P_{\alpha_n}^n \Lambda_{n-1}(\ldots P_{\alpha_1}^1(\Lambda_1(P_{\alpha_0}^0\, \rho_0\, P_{\alpha_0}^0))P_{\alpha_1}^1 \ldots)] = \frac{\text{Tr}\ [G]}{Z} \qquad (4.19)$$

for all super-operators Λ_t (acting linearly on density matrices) that leave the identity invariant, $\Lambda_t(1) = 1$.
One can generalize (4.17) and (4.18) by choosing here

$$\Lambda_t(A) = \sum_r \mu_r^t\ U_r^S\ A\ U_r^{S\star}$$

with $\mu_r^t \geq 0$ and $\sum_r \mu_r^t = 1$, meaning that the unitary U_r^S is employed with probability μ_r^t at time t. These Λ's leave the identity invariant, so (4.19) applies and

$$\sum_\omega q_\beta^e(\omega)\, e^{\beta(V_{\alpha_0}^0 - V_{\alpha_n}^n)} = e^{-\beta\Delta F} \qquad (4.20)$$

just like in (4.17)–(4.18) but now with probabilities

$$q_\beta^e(\omega) \equiv \text{Tr}\ [P_{\alpha_n}^n \Lambda_{n-1}(\ldots P_{\alpha_1}^1(\Lambda_1(P_{\alpha_0}^0\, \rho_0\, P_{\alpha_0}^0))P_{\alpha_1}^1 \ldots)]$$

Of course, if γ in (3.1) is zero, then $U_t = U_t^S \otimes U^R$ factorizes and the treatments of Sections 4.1-4.2 reduces to the adiabatic case. The work is a difference of energies (instead of a path-dependent quantity) and there is no heat ($Q = 0$).

4.3.2. *Quasi-static regime.* We imagine then that the evolutions U_t are slow enough so that the system plus reservoirs relax into an equilibrium state with respect to H_t.
We think about the case of Section 4.2. Always,

$$p_\beta(\omega, e) = q_\beta(\omega) q_\beta(e|\omega) \tag{4.21}$$

but in the quasi-static regime we have

$$p_\beta(\alpha_t, E_t) = q_\beta(\alpha_t) q_\beta(E_t|\alpha_t) \tag{4.22}$$

which suffices to see that $\langle e^{-\beta(E_n - E_0)}\rangle(\omega)$ depends only on (ω_0, ω_n). Again, there is no path dependence in the work W.

4.3.3. *No time-dependence.* Suppose that (3.1) does not contain a parameter dependence and that the time-evolution is homogeneous ($U_t \equiv U$).
Then of course $\Delta F = 0$. For the effective Markovian dynamics of Section 4.1, one sees immediately that $W(\omega) = 0$ for each ω in (4.4). In the adiabatic case of Section 4.3.1 as well: $V^0_{\alpha_0} - V^n_{\alpha_n} = 0$ with $q^S_\beta-$probability one when we ask that in (4.17) the projections $P^t_{\alpha_t}$ and the unitary evolutions mutually commute. In the case of Section 4.2, we can use conservation of energy $V^i_{\alpha_i} + E_i =$ constant, as in the first law (4.11), when we ignore the (boundary) interaction term H^I in the energy balance. In that case we again get $W(\omega) = 0$.

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