

On the Jarzynski relation for dissipative quantum dynamics

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Abstract. In this note, we will discuss how to compactly express the Jarzynski identity for an open quantum system with dissipative dynamics. In quantum dynamics we must avoid explicitly measuring the work directly, which is tantamount to continuously monitoring the state of the system, and instead measure the heat flow from the environment. These measurements can be concisely represented with Hermitian map superoperators, which provide a convenient and compact representations of correlation functions and sequential measurements of quantum systems.

1. Introduction

When a classical system in thermal equilibrium is driven from that equilibrium by an external perturbation, then the work of that process is related to the system's free energy change by Jarzynski's equality [1, 2, 3, 4].

$$\langle e^{-\beta W} \rangle = \int p(W) e^{-\beta W} dW = e^{-\beta \Delta F}. \quad (1)$$

Here, $p(W)$ is the probability distribution of work W done on the system, $\beta = 1/k_B T$ is the inverse temperature T of the environment in natural units, (k_B is the Boltzmann constant) and ΔF is the Helmholtz free energy change of the system. In other words, a Boltzmann weighted average of the irreversible work recovers the equilibrium free energy difference from an out-of-equilibrium transformation.

The generalization of the Jarzynski identity to closed system quantum dynamics is technically straightforward [5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19]. The system is initially in thermal equilibrium with the environment, but is decoupled and isolated from the environment during the perturbation of the system. The work is then the difference in energy of the system between the beginning and end of the experiment. However, for a system that can interact with the environment this does not suffice, since the total change in energy of the system $\Delta E = Q + W$ is equal to the work W applied via the time dependent perturbation plus the flow of heat Q from the environment. Unlike a classical system, we cannot continuously measure the energy of the system without severely disturbing the dynamics of the system.

Our solution to this problem is to realize that although we cannot continuously measure the work or system energy, we can measure the heat flow from the environment [9] without directly measuring the energy eigenstate of the system. If we assume that the environment is large, rapidly decoheres and always remains at thermal equilibrium, uncorrelated and unentangled with the system, then we can measure the change in energy of the bath (i.e. $-Q$) without further disturbing the dynamics of the system. Essentially, we reexpress the open-system quantum Jarzynski identity as

$$\langle e^{-\beta W} \rangle = \langle e^{-\beta E_f} e^{+\beta Q} e^{+\beta E_i} \rangle = e^{-\beta \Delta F}. \quad (2)$$

In this note we will discuss how to represent the measurement of heat flow and the quantum Jarzynski identity using a quantum Markov dynamics to describe the system, and Hermitian maps, generalized measurement superoperators, to represent the measurements of heat flow.

2. Background: Quantum Dynamics of Open Systems

We are interested in the dynamics of a quantum system with a time dependent Hamiltonian, weakly coupled to an extended, thermal environment. Let the total Hamiltonian of the combined system be

$$H = H^S(t) \otimes I^B + I^S \otimes H^B + \epsilon H^{\text{int}}, \quad (3)$$

where I^S and I^B are system and bath identity operators, H^S is the time dependent Hamiltonian of the system, H^B is the bath Hamiltonian, H^{int} is the bath-system interaction Hamiltonian and ϵ is a small coupling constant.

If the system Hamiltonian is time-independent, the environment is in thermal equilibrium, and in the limit that the the coupling constant is small, but the

dimensionality of the environment is large, then the system relaxes to a mixed state describe by the equilibrium density matrix [20, 21]

$$\rho^{\text{eq}} = \frac{e^{-\beta H^{\text{S}}}}{\text{tr} e^{-\beta H^{\text{S}}}} = \frac{e^{-\beta H^{\text{S}}}}{Z} = e^{\beta F - \beta H^{\text{S}}}, \quad (4)$$

where $Z = \text{tr} \exp(-\beta H^{\text{S}})$ is the partition function and $F = -\frac{1}{\beta} \ln Z$ is the Helmholtz free energy of the system.

If we further assume that the environment rapidly decoheres with a characteristic relaxation time short compared with the relevant bath-system interactions, then the environment remains very near thermal equilibrium, unentangled and uncorrelated with the system, irrespective of any perturbation applied to the system. Consequently, the system dynamics can be described by a quantum Markov chain [22, 23, 21]

$$\rho(t) = \mathcal{S}(t-1, t) \cdots \mathcal{S}(s+1, s+2) \mathcal{S}(s, s+1) \rho(s) \quad (5)$$

where each \mathcal{S} is a quantum operation $\rho' = \mathcal{S}\rho$, a linear, trace preserving, completely positive map of operators [24, 25, 26, 27]. Any such completely positive superoperator has operator-sum representations,

$$\mathcal{S}\rho \equiv \sum_{\alpha} A_{\alpha} \rho A_{\alpha}^{\dagger}. \quad (6)$$

Conversely, any operator-sum represents a completely positive superoperator. The collection $\{A_{\alpha}\}$ are known as Kraus operators. The superoperator is trace preserving, and therefore conserves probability, if $\sum_{\alpha} A_{\alpha}^{\dagger} A_{\alpha} = I$, where I is the identity operator. In the simplest case, the dynamics of a isolated quantum system is described by a single unitary operator $U^{\dagger} = U^{-1}$.

We can derive a quantum operator description of the system dynamics by following the unitary dynamics of the combined total system for a finite time and then measuring the final state of the environment. We assume that initially the system and environment are uncorrelated and that the initial combined state is $\rho^{\text{S}} \otimes \rho_{\text{eq}}^{\text{B}}$, where $\rho_{\text{eq}}^{\text{B}}$ is the thermal equilibrium density matrix of the bath.

$$\begin{aligned} \mathcal{S}(s, t) \rho^{\text{S}} &= \text{tr}_{\text{B}} U [\rho^{\text{S}} \otimes \rho^{\text{B}}] U^{\dagger} \\ &= \sum_f \langle b_f | U \left(\rho^{\text{S}} \otimes \left[\sum_i \frac{e^{-\beta E_i^{\text{B}}}}{Z^{\text{B}}} |b_i\rangle \langle b_i| \right] \right) U^{\dagger} | b_f \rangle \\ &= \sum_{if} \frac{e^{-\beta E_i^{\text{B}}}}{Z^{\text{B}}} \langle b_f | U | b_i \rangle \rho^{\text{S}} \langle b_i | U^{\dagger} | b_f \rangle \end{aligned} \quad (7)$$

Here, U is the unitary evolution operator of the total system

$$U = \mathcal{T} \exp \left(-\frac{i}{\hbar} \int_s^t H(\tau) d\tau \right), \quad (8)$$

where \mathcal{T} is the time-ordering operator, tr_{B} is a partial trace over the bath degrees of freedom, $\{E_i^{\text{B}}\}$ are the energy eigenvalues and $\{|b_i\rangle\}$ are the orthonormal energy eigenvectors of the bath, and Z^{B} is the bath partition function. For simplicity, and without loss of generality, we assume that the bath energy states are non-degenerate.

It follows from the last line of Eq. (7) that the Kraus operators for this dynamics are

$$A_{ij} = \frac{e^{-\frac{1}{2}\beta E_i^{\text{B}}}}{\sqrt{Z^{\text{B}}}} \langle b_j | U | b_i \rangle \quad (9)$$

In the limit of small time interval we obtain a continuous time quantum Markovian dynamics,

$$\rho(t) = \mathcal{T} \exp \left(\int_s^t \mathcal{L}(\tau) d\tau \right) \rho(s) \quad (10)$$

where \mathcal{L} is the Lindbladian superoperator [23, 22, 27].

3. Hermitian Maps and Sequential Measurements

If we describe the system dynamics using quantum operations, then it proves very convenient to describe measurements using superoperator Hermitian maps. A measurement of a quantum system can be characterized by a collection of measurement operators $\{A_\alpha\}$, where $\sum_\alpha A_\alpha^\dagger A_\alpha = I$, and associated real valued measurement results, a_α . For example, the Hermitian operator $H = H^\dagger$ of a standard von Neumann measurement can be decomposed into a collection of eigenvalues h and orthonormal projection operators P_h , such that $H = \sum_h h P_h$. More generally, the measurement operators of a POVM (Positive Operator Valued Measure) need not be projectors nor orthonormal [27].

The probability of observing the α th outcome is

$$p_\alpha = \text{tr} A_\alpha \rho A_\alpha^\dagger \quad (11)$$

and the state of the system after this particular interaction is

$$\rho'_\alpha = \frac{A_\alpha \rho A_\alpha^\dagger}{\text{tr} A_\alpha \rho A_\alpha^\dagger}. \quad (12)$$

The overall effect of the dynamics, averaging over different interactions, is a quantum operation, Eq. (6).

Rather than simply representing the *effect* of the measurement with the appropriate quantum operation, we can represent the *effect* and *result* of the measurement using a Hermitian map superoperator \mathcal{A} :

$$\mathcal{A}\rho = \sum_\alpha a_\alpha A_\alpha \rho A_\alpha^\dagger \quad (13)$$

Note that this operator-value-sum cannot, in general, be recast as an operator-sum, since the measurement values $\{a_\alpha\}$ may be negative. An operator-value-sum maps Hermitian operators to Hermitian operators ($H = H^\dagger$),

$$[\mathcal{A}H]^\dagger = \left[\sum_\alpha a_\alpha A_\alpha H A_\alpha^\dagger \right]^\dagger = \mathcal{A}H^\dagger = \mathcal{A}H. \quad (14)$$

Conversely, any Hermitian map has an operator-value-sum representation [28].

Hermitian maps provide a particularly compact and convenient representation of sequential measurements and correlation functions. Let the Hermitian map \mathcal{A} representing a measurement at time 0, \mathcal{B} a different measurement of the same system at time t , and the quantum operation S_t represent the system evolution between these two measurements. The expectation value of a single measurement is

$$\langle a \rangle = \text{tr} \mathcal{A}\rho = \sum_\alpha a_\alpha \text{tr} A_\alpha \rho A_\alpha^\dagger = \sum_\alpha p(\alpha) a_\alpha \quad (15)$$

and the correlation function $\langle b(t)a(0) \rangle$ can be expressed as

$$\begin{aligned}
 \langle b(t)a(0) \rangle &= \text{tr } \mathcal{BS}_t \mathcal{A} \rho(0) \\
 &= \sum_{\alpha\beta} a_\alpha b_\beta \text{tr } B_\beta [S_t [A_\alpha \rho(0) A_\alpha^\dagger]] B_\beta^\dagger \\
 &= \sum_{\alpha\beta} p(\alpha, \beta) a_\alpha b_\beta .
 \end{aligned} \tag{16}$$

Note that expressions such as $\text{tr } AB\rho$, where A and B are Hermitian operators, often appear in perturbation expansions and are frequently referred to as quantum correlation functions. However, since AB is not in general Hermitian these expressions do not directly represent a physical measurement.

Here we establish that, just as every Hermitian operator represents some measurement on the Hilbert space of pure states, every Hermitian map can be associated with some measurement on the Liouville space of mixed states. Suppose that we have already decomposed the Hermitian map \mathcal{A} into a operator-value-sum with values $\{a_\alpha\}$ and operators $\{A_\alpha\}$. Probability conservation requires that $\sum_\alpha A_\alpha^\dagger A_\alpha = I$. If this condition is not met we can supplement the Kraus operators with an additional operator whose corresponding measurement value is zero. Note that $A_\alpha^\dagger A_\alpha$ is a positive operator and consequently $B^\dagger B = I - \frac{1}{c} \sum_\alpha A_\alpha^\dagger A_\alpha$ is also a positive operator provided that c is a real number larger than the largest eigenvalue of $\sum_\alpha A_\alpha^\dagger A_\alpha$. Therefore, we can rescale the measurement outcomes $\{ca_\alpha\}$ and Kraus operators $\{\frac{A_\alpha}{\sqrt{c}}\}$, append the additional operator B with measurement outcome 0, and associate the superoperator \mathcal{A} with the measurement

$$\mathcal{A}\rho = 0 B\rho B^\dagger + \sum_i ca_\alpha \frac{A_\alpha}{\sqrt{c}} \rho \frac{A_\alpha^\dagger}{\sqrt{c}} \tag{17}$$

Note that the decomposition of a Hermitian map into an operator-value-sum representation is not unique [27, 28].

4. Measurements of Heat Flow

We can now construct a Hermitian map representation of heat flow, under the assumptions that the bath and system Hamiltonians are constant during the measurement procedure and that the system dynamics can be described by a quantum Markov dynamics. We construct a measurement on the total system and then project out the bath degrees of freedom, leaving a Hermitian map superoperator that acts on the system density matrix alone.

The full, explicit measurement is

$$\begin{aligned}
 \langle e^{+\beta Q} \rangle &= \sum_{if} \overbrace{e^{-\beta(E_f^B - E_i^B)}}^g \overbrace{\text{tr}_S}^f \overbrace{\text{tr}_B}^e \overbrace{[I^S \otimes |b_f\rangle\langle b_f|]}^d \overbrace{U}^c \overbrace{[I^S \otimes |b_i\rangle\langle b_i|]}^b \\
 &\quad \cdot \overbrace{[\rho^S \otimes \rho_{\text{eq}}^B]}^a \cdot \overbrace{[I^S \otimes |b_i\rangle\langle b_i|]}^b \overbrace{U^\dagger}^c \overbrace{[I^S \otimes |b_f\rangle\langle b_f|]}^d
 \end{aligned}$$

We start with a composite system consisting of the bath, initially in thermal equilibrium, weakly coupled to the system (a). We measure the initial energy eigenstate of the bath (b), allow the system and bath to evolve together for some time (c), and then measure the final energy eigenstate of the bath (d). The trace over

the bath degrees of freedom (e) yields the final, unnormalized system density matrix, whose trace in turn (f) gives the probability of observing the given initial and final bath energy eigenstates. We then multiply by the Boltzmann weighted heat (g) and sum over all initial and final bath states (h) to obtain the desired average Boltzmann weighted heat flow.

The sum over initial states can be split into separate sums on the left and right projectors, since the bath is initially diagonal. Similarly, the sum over the final states can be split into separate sums on the right and left due to the final trace over bath degrees of freedom. As a consequence, we can rewrite the previous expression using the bath Hamiltonian.

$$= \text{tr}_S \text{tr}_B [I^S \otimes e^{-\frac{\beta}{2} H^B}] U [I^S \otimes e^{+\frac{\beta}{2} H^B}] \cdot [\rho^S \otimes \rho_{\text{eq}}^B] \cdot [I^S \otimes e^{+\frac{\beta}{2} H^B}] U^\dagger [I^S \otimes e^{-\frac{\beta}{2} H^B}]$$

Since the total Hamiltonian commutes with the unitary dynamics, and is time independent over the time interval under consideration, we can write

$$U = e^{+\frac{\beta}{2} H} U e^{-\frac{\beta}{2} H}.$$

Furthermore, since $e^A e^B = \exp\{A + B + \frac{1}{2}[A, B] + \dots\}$

$$[I^S \otimes e^{-\frac{\beta}{2} H^B}] e^{+\frac{\beta}{2} H} = [e^{+\frac{\beta}{2} H^S + O(\epsilon)} \otimes I^B]$$

Therefore, in the small coupling limit $\epsilon \rightarrow 0$ the heat flow measurement is approximately

$$\approx \text{tr}_S \text{tr}_B [e^{+\frac{\beta}{2} H^S} \otimes I^B] U [e^{-\frac{\beta}{2} H^S} \otimes I^B] \cdot [\rho^S \otimes \rho_{\text{eq}}^B] \cdot [e^{-\frac{\beta}{2} H^S} \otimes I^B] U^\dagger [e^{+\frac{\beta}{2} H^S} \otimes I^B],$$

with errors of order ϵ . Taking the limit of small coupling constant does not represent an additional constraint, since we already require that the system-bath coupling be small in order to justify a quantum Markov chain dynamic, Eqs. (5) and (10).

We now collect terms acting on the bath or system alone

$$= \text{tr}_S e^{+\frac{\beta}{2} H^S} \left[\text{tr}_B U \left[[e^{-\frac{\beta}{2} H^S} \rho^S e^{-\frac{\beta}{2} H^S}] \otimes \rho_{\text{eq}}^B \right] U^\dagger \right] e^{+\frac{\beta}{2} H^S}$$

and recover the Kraus operators $\{A_{ij}\}$ describing the reduced dynamics of the system, Eq. (9).

$$= \text{tr}_S \sum_{ij} e^{+\frac{\beta}{2} H^S} A_{ij} e^{-\frac{\beta}{2} H^S} \rho^S e^{+\frac{\beta}{2} H^S} A_{ij}^\dagger e^{-\frac{\beta}{2} H^S}$$

Finally, we have found that the average Boltzmann weighted heat flow can be represented by

$$\langle e^{+\beta Q} \rangle = \text{tr} \mathcal{R}^{-1} \mathcal{S} \mathcal{R} \rho^S \quad (18)$$

where \mathcal{S} is the reduced dynamics of the system and the Hermitian map measurement superoperator \mathcal{R} is

$$\mathcal{R} \rho = e^{-\frac{\beta}{2} H^S} \rho e^{-\frac{\beta}{2} H^S} \quad (19)$$

The paired Hermitian map superoperators act at the beginning and end of a time interval and measure the change in system energy during that interval. This does not disturb the system beyond the disturbance already induced by coupling the system to the environment.

5. Quantum Jarzynski Identity

We are now in a position to derive the quantum Jarzynski identity [Eq. (2)] using Hermitian maps and the quantum operator formalism. We split the total experimental time into τ intervals, labeled by the integer t . The system Hamiltonian is fixed within each time interval, and only changes in discrete jumps at the interval boundaries [2]. We can therefore measure the heat flow by wrapping the superoperator time evolution of each time interval \mathcal{S}_t with the corresponding Hermitian map measurements $\mathcal{R}_t^{-1}\mathcal{S}_t\mathcal{R}_t$. Similarly, we can represent the measurement of the Boltzmann weighted change in energy of the system with

$$\begin{aligned}\langle e^{-\beta\Delta E} \rangle &= \text{tr } \mathcal{R}_\tau \mathcal{S} \mathcal{R}_0^{-1} \rho \\ &= \sum_{if} e^{-\beta(E_f^S - E_i^S)} \langle s_f | \mathcal{S} \left(|s_i\rangle \langle s_i| \rho |s_i\rangle \langle s_i| \right) |s_f\rangle\end{aligned}$$

The initial energy measurement does not disturb the system, nor influence subsequent measurements of the heat flow, since the system begins at thermal equilibrium with a density matrix diagonal in the energy eigenbasis. The final energy measurement projects the system into an energy eigenstate of the final Hamiltonian, but this does not influence the preceding heat flow measurements.

The average Boltzmann weighted work of a driven, dissipative quantum system can therefore be compactly expressed as

$$\langle e^{-\beta W} \rangle = \text{tr} \left[\mathcal{R}_\tau \left(\prod_t [\mathcal{R}_t^{-1} \mathcal{S}_t \mathcal{R}_t] \right) \mathcal{R}_0^{-1} \rho_0^{\text{eq}} \right] \quad (20)$$

where ρ_t^{eq} is the system equilibrium density matrix with system Hamiltonian H_t^S .

Due to the structure of the energy change Hermitian maps \mathcal{R} [Eq. (19)] and the equilibrium density matrix [Eq. (4)] this product of superoperators telescopes, leaving only the free energy difference between the initial and final equilibrium ensembles.

$$\begin{aligned}\langle e^{-\beta W} \rangle &= \text{tr} \left[\mathcal{R}_\tau [\mathcal{R}_\tau^{-1} \mathcal{S}_\tau \mathcal{R}_\tau] \cdots [\mathcal{R}_2^{-1} \mathcal{S}_2 \mathcal{R}_2] [\mathcal{R}_1^{-1} \mathcal{S}_1 \mathcal{R}_1] \mathcal{R}_0^{-1} \rho_0^{\text{eq}} \right] \\ &= \text{tr} \left[\mathcal{R}_\tau [\mathcal{R}_\tau^{-1} \mathcal{S}_\tau \mathcal{R}_\tau] \cdots [\mathcal{R}_2^{-1} \mathcal{S}_2 \mathcal{R}_2] [\mathcal{R}_1^{-1} \mathcal{S}_1 \mathcal{R}_1] \frac{I}{Z(0)} \right] \\ &= \text{tr} \left[\mathcal{R}_\tau [\mathcal{R}_\tau^{-1} \mathcal{S}_\tau \mathcal{R}_\tau] \cdots [\mathcal{R}_2^{-1} \mathcal{S}_2 \mathcal{R}_2] \mathcal{R}_1^{-1} \mathcal{S}_1 \rho_1^{\text{eq}} \frac{Z(1)}{Z(0)} \right] \\ &= \text{tr} \left[\mathcal{R}_\tau [\mathcal{R}_\tau^{-1} \mathcal{S}_\tau \mathcal{R}_\tau] \cdots [\mathcal{R}_2^{-1} \mathcal{S}_2 \mathcal{R}_2] \mathcal{R}_1^{-1} \rho_1^{\text{eq}} \frac{Z(1)}{Z(0)} \right] \\ &= \frac{Z(\tau)}{Z(0)} = \exp\{-\beta\Delta F\}\end{aligned}$$

We can recover a continuous time description by taking the limit where the time intervals and jumps are infinitesimally small. In this we can express the quantum Jarzynski identity in the continuous time Lindblad form.

$$\begin{aligned}\langle e^{-\beta W} \rangle &= \text{tr} \mathcal{R}(t) \exp \left\{ \int_0^\tau R(t)^{-1} \mathcal{L}(t) \mathcal{R}(t) dt \right\} \mathcal{R}(0)^{-1} \rho_0^{\text{eq}} \\ &= e^{-\beta\Delta F}\end{aligned} \quad (21)$$

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