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# Nonequilibrium Jarzynski Relations Related to Quantum Systems

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## Abstract

Equilibrium statistical mechanics is now a well established theory. The area of physics of nonequilibrium and open quantum systems, known as quantum thermodynamics, is less well known and investigated here. A set of results which arises in the area of nonequilibrium processes and work fluctuations in quantum mechanics is the development of Jarzynski relations. Several novel approaches to producing these relations in the quantum case is studied here.

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# 1 Introduction

A number of results have appeared recently which can be broadly classified as fluctuation theorems and Jarzynski relations [**1-3**] in various dynamical systems. They relate nonequilibrium quantities with equilibrium free energies and contribute to the study of open quantum systems. Crooks has pointed out possible relations between Jarzynski's results and the fluctuation theorem for steady state nonequilibrium systems [**4-5**]. These turn out to be powerful results pertaining to the case of nonequilibrium statistical mechanics [**6-10**] that can hold far from equilibrium. Jarzynski originally produced his initial work within the context of classical mechanics. This relation has been further extended in other directions, for example, to the area of stochastic mechanics. Roughly speaking the result relates the distribution of the work done by a driving force of arbitrary rate on a system which is initially at equilibrium to the free energy difference between the initial and final states of the system, which is an equilibrium property. The ensemble average of the trajectory entropy production is the macroscopic entropy production of the system whereas the distribution gives rise to collection of fluctuation theorems.

The purpose ahead is to attempt to understand the nature of these kinds of relations within the rules of quantum mechanics. The entropy average of the trajectory entropy production is the macroscopic entropy production of the system whereas its distribution gives rise to various fluctuation theorems. It is the hope that one can understand the development and nature of Jarzynski relations that are produced by means of the physics of quantum mechanics. The understanding of such fundamental relations in the quantum case is not fully established as is the study of open quantum systems. Quantum Jarzynski relations have been studied and fluctuation theorems have been developed in a few restricted instances. One reason this is important is that physical quantities defined on classical trajectories are conceptually clear and can be tested experimentally. For these reasons we start by postulating a path integral formulation of the correlation function. The measurement of quantities associated with quantum processes remains open as it is closely related to the topic of quantum measurement [**11-13**].

## 2 Correlation Functions from Path Integrals

It is known that quantum mechanical states evolve by means of unitary operators. This is equivalent to evolution under the Schrödinger equation represented in the following way

$$|\psi(t)\rangle = \mathbf{U}(t,t_0)|\psi(t_0)\rangle. \tag{2.1}$$

The operator $\mathbf{U}$ is called the evolution operator, and can be written as a time ordered exponential. In the Heisenberg picture, states do not evolve, it is the observables that evolve as

$$\mathbf{A}(t) = \mathbf{U}(t)\mathbf{A}\,\mathbf{U}(t). \tag{2.2}$$

Due to path dependence that occurs in thermodynamics, for certain variables in general, it is useful that the concept of correlation function should be developed explicitly in terms of path integrals. It is known that the path integral provides a representation of the evolution operator $\mathbf{U}$

$$\langle x(t)|\mathbf{U}(t)|x(0)\rangle = \int_{x(t)=x,x(0)=x_0} Dx\, e^{iS/\hbar}. \tag{2.3}$$

The converse of this is also true. If (2.3) is used as the definition of the evolution operator, Schrödinger's equation may be derived. In the coordinate representation, where $\mathbf{U}(x,x_0,t)=\langle x|\mathbf{U}(t)|x(0)\rangle$, by linearity the density matrix evolves according to

$$\rho(x,x',t) = \langle x|\mathbf{U}(t)\,\rho\,\mathbf{U}^{\dagger}(t)|x'\rangle = \int_{x(t)=x,x(t')=x'} Dx\,Dx'\,e^{i(S[x]-S[x'])/\hbar}\,\rho(x(0),x'(0),0). \tag{2.4}$$

Considering cyclic permutations under the trace operation it follows that $\mathrm{Tr}\,\rho(t)=\mathrm{Tr}\,\rho(0)=1$ as expected.

A correlation or characteristic function can be defined as a sum over paths which join the specified initial state to a final state for one general type of evolution which in a certain limit can be used to produce a Jarzynski relation. The explicit value of the histories at these two preferred times can be stated explicitly,

$$G(\tau,\tau') =$$
$$\int dx(0)dx'(0)dx(\tau')dx(\tau)dx(t)\,\Big(\int_{0\le t\le\tau'} Dx\,e^{iS(x)/\hbar}\Big)\,e^{i(\tau-\tau')\mathbf{H}_F/\hbar}\,\Big(\int_{\tau'\le t\le\tau} Dx\,e^{iS(x)/\hbar}\Big)$$
$$e^{-i(\tau-\tau')\mathbf{H}_I/\hbar}\Big(\int_{\tau\le t\le t} Dx\,e^{iS(x)/\hbar}\Big)\Big(\int Dx'\,e^{-iS(x')/\hbar}\Big)\cdot\rho(x(0),x'(0),0). \tag{2.5}$$

Assume that $\tau>\tau'$ and let us make explicit the value of the histories based on these two different selected times

$$G(\tau,\tau') = \int dx(0)dx'(0)dx(\tau')dx(\tau)dx(t)\,\Big(\int_{0\le t\le\tau'} Dx\,e^{iS(x)/\hbar}\Big)\,e^{i(\tau-\tau')\mathbf{H}_F/\hbar}$$
$$\Big(\int_{\tau'\le t\le\tau} Dx\,e^{iS(x)\ \hbar}\Big)\,e^{-i(\tau-\tau')\mathbf{H}_I/\bar{\hbar}}\Big(\int_{\tau\le t\le t} Dx\,e^{iS(x)/\hbar}\Big)\,\Big(\int Dx'\,e^{-iS(x')/\hbar}\Big)\rho(x(0),x'(0),0). \tag{2.6}$$

Each integral in brackets can be identified with a matrix element related to evolution operator $\mathbf{U}$ as in (2.3), so (2.6) is put in the form,

$$G(\tau,\tau') = \int dx(0)dx'(0)dx(\tau')dx(t)\,\langle x(t)|\mathbf{U}(t,\tau)|x(0)\rangle e^{i(\tau-\tau')\,\mathbf{H}_F/\hbar}$$
$$\langle x(\tau)|\mathbf{U}(\tau,\tau')|x(\tau')\rangle\,e^{i(\tau-\tau')\mathbf{H}_I/\hbar}\langle x(\tau')|\mathbf{U}(\tau',0)|x(0)\rangle\langle x(0)|\rho|x'(0)\rangle\langle x'(0)|\mathbf{U}(0,t)|x(t)\rangle. \tag{2.7}$$

A particular limiting case of this process is very useful to continue the analysis, which amounts to taking a limit which produces a $G$ in one variable. To this end, let $\tau', t$ approach zero, then $G(\tau)$ reduces to one variable. The last matrix element collapses to unity and $G(\tau)$ simplifies to

$$G(\tau) = \mathrm{Tr}[\mathbf{U}(\tau) e^{-i\tau \mathbf{H}(0)} \rho(0)\, \mathbf{U}^{\dagger}(\tau)\, e^{i\tau \mathbf{H}(\tau)}]. \tag{2.8}$$

For a system that evolves under the exclusive influence of a time dependent Hamiltonian $\mathbf{H}(t)$ from an initial equilibrium state, the density matrix in (2.8) can be selected to have the Gibbs form

$$\rho(0) = \frac{1}{Z}\, e^{-\beta \mathbf{H}(0)} \tag{2.9}$$

at $t = 0$ and ending at a final time $\tau$. The work which is performed on the system is a randomly distributed quantity and $G(\tau)$ can be related to it. Its statistical properties follow from a probability density $p(\zeta)$, which can be related to the function in (2.8) by means of a Fourier transform

$$G(\tau) = \int d\zeta\, e^{i\tau\zeta}\, p(\zeta). \tag{2.10}$$

The averaged exponential work $\langle \exp(-\beta W) \rangle$ is obtained by putting (2.10) in $G(\tau)$ to obtain

$$G(\tau) = \frac{1}{Z(0)} \mathrm{Tr}[e^{i\tau \mathbf{H}(\tau)} \mathbf{U}(\tau) e^{-(i\tau+\beta)\mathbf{H}(0)} \mathbf{U}^{\dagger}(\tau)]. \tag{2.11}$$

Using this form for the correlation function and (2.9), the Jarzynski equation is obtained immediately in the explicit form

$$\langle e^{-\beta W} \rangle = \frac{Z(\tau)}{Z(0)}, \tag{2.12}$$

where $Z(\tau) = \mathrm{Tr}(e^{-\beta H(\tau)})$ is the partition function of a hypothetical system with Hamiltonian $\mathbf{H}$ in a Gibbs state at inverse temperature $\beta$. By replacing the quantum correlation function by the corresponding correlation function of a classical Hamiltonian the characteristic function of the work performed on the classical system results.

When a classical system in thermal equilibrium is driven from that equilibrium by an external perturbation, the irreversible work of that process is related to the free energy of the system by Jarzynski's inequality.

## 3 Quantum Dynamics of Open Systems

To a quantum system a density matrix $\rho$ can be assigned which describes the mixed state of the system that is capable of interacting with an environment.

For an equilibrated system with Hamiltonian $\mathbf{H}$ which interacts weakly with a thermal bath at temperature $T$, the equilibrium density matrix is

$$\rho_e = \frac{e^{-\beta \mathbf{H}}}{\mathrm{Tr}(e^{-\beta \mathbf{H}})} = \frac{e^{-\beta \mathbf{H}}}{Z} = e^{\beta F \mathbf{I} - \beta \mathbf{H}}. \tag{3.1}$$

In (3.1), $Z$ the partition function and $F$ is the Helmholtz free energy and $\beta = 1/k_B T$.

The dynamics of an open quantum system can be accounted for in terms of quantum operator which maps $\rho' = \mathcal{S}\,\rho$. This is a linear tracing preserving complete positive map of operators. Any such complete positive superoperator has a represntation as a sum of operators known as a Kraus representation

$$\mathcal{S}\rho = \sum_{\alpha} \mathbf{A}_{\alpha} \rho\, \mathbf{A}_{\alpha}^{\dagger}. \tag{3.2}$$

Conversely, any operator-sum represents a complete positive superoperator. The collection $\{\mathbf{A}_{\alpha}\}$ is trace preserving and hence conserves probability according to $\sum_{\alpha} \mathbf{A}_{\alpha}^{\dagger} \mathbf{A}_{\alpha} = I$, where $I$ is the identity operator.

The objective is to study the dynamics of a quantum system accounted for by a time-dependent Hamiltonian which is coupled weakly to an extended thermal environment. The total combined system has Hamiltonian

$$\mathbf{H} = \mathbf{H}^S(t) \otimes \mathbf{I}^B + \mathbf{I}^S \otimes \mathbf{H}^B + \epsilon\, \mathbf{H}^{int}, \tag{3.3}$$

where $\mathbf{I}^S$ and $\mathbf{I}^B$ are system, bath and identity operators, $\mathbf{H}^S$ is the time dependent Hamiltonian of the system, $\mathbf{H}^B$ is the bath Hamiltonian and $\mathbf{H}^{int}$ is the bath-system interaction Hamiltonian, $\epsilon$ a small coupling constant. Initially the system and environment are uncorrelated and have initial combined state $\rho^S \otimes \rho_{eq}^B$, such that $\rho_{eq}^B$ is the thermal equilibrium density matrix of the bath.

Suppose the system and environment are uncorrelated at the beginning. The combined state is $\rho^S \otimes \rho_{eq}^B$, where $\rho_{eq}^B$ is the thermal equkibrium density matrix of the bath. A quantum operator description of the system dynamics can be developed by allowing the combined total system to undergo unitary dynamics for some finite time. At that point, the final state of the environment is reached,

$$\begin{aligned} \mathcal{S}(x,t)\rho^S = \mathrm{Tr}_B\, \mathbf{U}[\rho^S \otimes \rho^B]\mathbf{U}^{\dagger} &= \sum_f \langle b_f | \mathbf{U} \big( \rho^S \otimes \sum_i \frac{e^{-\beta\, E_i^B}}{Z^B} |b_i\rangle\langle b_i| \big) \mathbf{U}^{\dagger} |b_f\rangle \\ &= \sum_{i,f} \frac{e^{-\beta E_i^B}}{Z^B} \langle b_f | \mathbf{U} | b_i \rangle \rho^S \, \langle b_i | \mathbf{U}^{\dagger} | b_f \rangle. \end{aligned} \tag{3.4}$$

The unitary evolution operator of the total system is

$$\mathbf{U} = \exp\big( - \frac{i}{\hbar} \int_s^t \mathbf{H}(\tau)\, d\tau \big). \tag{3.5}$$

The partial trace $\mathrm{Tr}_B$ acts over the bath degrees of freedom which have energy eigenvalues $\{E_i^B\}$. As well $\{|b_i\rangle\}$ are the orthonormal energy eigenvectors of the state with $Z^B$ the bath partition function. It may be assumed the bath energy states are non-degenerate. It follows from (3.4) that for this kind of dynamics

$$A_{ij} = \frac{e^{-\frac{1}{2}\beta E_i^B}}{\sqrt{Z^B}} \langle b_j|\mathbf{U}|b_i\rangle. \tag{3.6}$$

Suppose the environment is large and has a characteristic relaxation time which is short compared with the bath-system interactions with $\epsilon$ real and small. The environment stays very close to thermal equilibrium, which is unentangled and uncorrelated with the system. The system dynamics of each consecutive time interval is then described by operators (3.4) which can then be linked together to generate the transformation

$$\rho(t) = \mathcal{S}(t-1,t) \cdots \mathcal{S}(T+1,s+2)\mathcal{S}(s,s+1)\,\rho(s). \tag{3.7}$$

## 4 Sequential Measurements arising from Hermitian maps

A collection of measurement operators characterizes the measurement of a quantum system by means of measurement results $\{a_\alpha\}$. A Hermitian operator $\mathbf{H} = \mathbf{H}^\dagger$ of a von Neumann measurement can be decomposed into a set of eigenvalues $\lambda_h$ and orthonormal projection operators $\pi_\alpha$ such that $\mathbf{H} = \sum_h \lambda_h \,\pi_\lambda$. This can be generalized to positive operator valued measure and need not be projectors nor orthonormal. The probability of observing the $\alpha$-th outcome is

$$p_\alpha = \mathrm{Tr}(\mathbf{A}_\alpha \rho\, \mathbf{A}_\alpha^\dagger). \tag{4.1}$$

The state of the system after this interaction is described by

$$\rho'_\alpha = \frac{\mathbf{A}_\alpha \rho \mathbf{A}_\alpha^\dagger}{\mathrm{Tr}(\mathbf{A}_\alpha \rho \mathbf{A}_\alpha^\dagger)}. \tag{4.2}$$

Overall this averaging over different interactions is the full quantum operation (3.2). It is common to represent the effect and result of the measurement using a Hermitian map operator, sometimes called a superoperator $\mathcal{B}$,

$$\mathcal{B}\rho = \sum_\alpha b_\alpha \,\mathbf{B}_\alpha \,\rho\, \mathbf{B}_\alpha^\dagger. \tag{4.3}$$

This type of operator-sum cannot, in general, be cast as an operator-sum, since the measurement values $\{b_\alpha\}$ may be negative. An operator valued sum maps

Hermitian operators to Hermitian operators

$$[\mathcal{B}\mathbf{H}]^\dagger = \big(\sum_\alpha b_\alpha \mathbf{B}_\alpha \mathbf{H} \mathbf{B}_\alpha^\dagger\big)^\dagger = \mathcal{B}\mathbf{H}^\dagger = \mathcal{B}\mathbf{H}. \tag{4.4}$$

Conversely any Hermitian map has an operator-value sum representation.

The main point as far as this is concerned is that it makes for a compact and convenient representation of sequential measurements and correlation functions. Let $\mathcal{A}$ be a Hermitian map representing a measurement at 0 and $\mathcal{B}$ a different measurement of the same system at time $t$. The expectation value of a single measurement is,

$$\mathrm{Tr}(\mathcal{A}\rho) = \sum_\alpha b_\alpha \,\mathrm{Tr}(\mathbf{A}_\alpha \rho \mathbf{A}^\dagger) = \sum_\alpha p(\alpha)\, b_\alpha. \tag{4.5}$$

A correlation function $\langle b(t) a(0)\rangle$ may be expressed as

$$\langle b(t)\, a(0)\rangle = \mathrm{Tr}\big(\mathbf{B}\mathcal{S}_t \mathcal{A}\,\rho(0)\big) = \sum_{\alpha,\beta} p(\alpha,\beta)\, a_\alpha b_\beta. \tag{4.6}$$

Just as every Hermitian operator represents some measurement on the Hilbert space of pure states, every Hermitian map can be associated with some measurements on the Liouville space of mixed states.

# 5 Heat Flow Measurement

A representation of heat flow by means of Hermitian maps exists. This holds under the assumptions that the bath and system Hamiltonians are constant during the measurement procedure and that the bath-system coupling is small. A measurement has to be constructed on the whole system, so the bath degrees of freedom are projected out. What is left is a Hermitian map operator that acts on the system density matrix alone. This process is outlined step by step after which it is expressed in mathematical form. Start with the bath in thermal equilibrium and weakly coulped to the system. The initial energy eigenstate of the bath is measured, then allowed to evolve for a time interval. The final energy eigenstate of the bath is then measured. The trace $\mathrm{Tr}_B$ over the bath degree of freedom produces the last unrenormalized system density matrix. Its trace $\mathrm{Tr}_S$ gives the probability of observing the given and final bath energy eigenstates. For the final step, one multiplies by the Boltzmann weighted heat, then it is summed over all initial and final bath states to obtain the average Boltzmann weighted heat flow. Stated explicitly as an equation,

$$\langle e^{\beta Q}\rangle = \sum_{i,f} e^{-\beta(E_f^B - E_i^B)} \mathrm{Tr}_S\,\mathrm{Tr}_B\,\big[\mathbf{I}^S \otimes |b_f\rangle\langle b_f|\big]\,\mathbf{U}\big[\mathbf{I}^S \otimes |b_i\rangle\langle b_i|\big]\,\big[\rho^S \otimes \rho_e^B q\big]$$

$$\big[\mathbf{I}^S \otimes |b_i\rangle\langle b_i|\big]\mathbf{U}^\dagger\,\big[\mathbf{I}^S \otimes |b_f\rangle\langle b_f|\big]. \tag{5.1}$$

The sums over initial and final states can be split into separate sums on the right and left. Then (5.1) can be rewritten just with the bath Hamiltonian

$$\langle e^{\beta Q}\rangle = \mathrm{Tr}_S\mathrm{Tr}_B\,\big[\mathbf{I}^S\otimes e^{-\frac{\beta}{2}\mathbf{H}^B}\big]\mathbf{U}\big[\mathbf{I}^S\otimes e^{\frac{\beta}{2}\mathbf{H}^B}\big]\cdot\big[\rho^B\otimes\rho^B_{eq}\big]\cdot\big[\mathbf{I}^S\otimes e^{\frac{\beta}{2}\mathbf{H}^B}\big]\mathbf{U}^\dagger\big[\mathbf{I}^S\otimes e^{-\frac{\beta}{2}\mathbf{H}^B}\big]. \tag{5.2}$$

If the bath Hamiltonian is substituted with $\mathbf{I}^S\otimes\mathbf{H}^B = \mathbf{H}-\mathbf{H}^S(t)\otimes\mathbf{I}^B-\epsilon\,\mathbf{H}^{int}$. Total Hamiltonian $\mathbf{H}$ commutes with the unitary dynamics and drops out of the picture, so when $\epsilon$ is very small, that term can be neglected

$$\begin{aligned}\langle e^{\beta Q}\rangle &= \mathrm{Tr}_S\mathrm{Tr}_B\,\big[e^{\frac{\beta}{2}\mathbf{H}^S}\otimes\mathbf{I}^B\big]\mathbf{U}\big[e^{-\frac{\beta}{2}\mathbf{H}^S}\otimes\mathbf{I}^B\big]\big[\rho^S\otimes\rho^B_e\big]\big[e^{-\frac{\beta}{2}\mathbf{H}^S}\otimes\mathbf{I}^B\big]\mathbf{U}^\dagger\big[e^{\frac{\beta}{2}\mathbf{H}^S}\otimes\mathbf{I}^B\big]\\ &= \mathrm{Tr}_S\,e^{\frac{\beta}{2}\mathbf{H}^S}\big[\mathrm{Tr}_B\mathbf{U}\big(\big[e^{-\frac{\beta}{2}\mathbf{H}^S}\rho^S e^{-\frac{\beta}{2}\mathbf{H}^S}\big]\otimes\rho^B_e\big)\mathbf{U}^\dagger\big]e^{\frac{\beta}{2}\mathbf{H}^S} \qquad (5.3)\\ &= \mathrm{Tr}_S\sum_\alpha e^{\frac{\beta}{2}\mathbf{H}^S}\mathbf{A}_\alpha e^{-\frac{\beta}{2}\mathbf{H}^S}\rho^S e^{\frac{\beta}{2}\mathbf{H}^S}\mathbf{A}^\dagger_\alpha e^{-\frac{\beta}{2}\mathbf{H}^S}.\end{aligned}$$

The second line of (5.3) comes from collecting terms acting on the bath or system alone to yield the Kraus operators in the last line. The last line comes out using the operators $\{\mathbf{A}_\alpha\}$ to reach the reduced dynamics of the system.

The average Boltzmann weighted heat flow can be presented in terms of the reduced system dynamics $\mathcal{S}$ of the system and a Hermitian map operator $\mathcal{R}$ which is defined as

$$\langle E^{\beta\,Q}\rangle = \mathrm{Tr}\,\mathcal{R}^{-1}\mathcal{S}\,\mathcal{R}\rho^S, \qquad \mathcal{R}_t\,\rho = e^{-\frac{\beta}{2}\mathbf{H}(t)}\rho\,e^{-\frac{\beta}{2}\mathbf{H}(t)}. \tag{5.4}$$

These Hermitian map operators act at the beginning and end of a time interval and measure the change in the system energy over that interval.

To obtain the quantum Jarzynski identity this way, divide the total experimental time into a series of discrete intervals indexed by an integer $n$. The system Hamiltonian is fixed within each time interval and changes at the ends of an interval. Over each time interval, heat flow is measured by taking the time evolution operator $\mathcal{S}_t$ with the corresponding Hermitean map measurements, $\mathcal{R}_t^{-1}\mathcal{S}_t\mathcal{R}_t$. The measurement of the Boltzmann weighted change in energy with $\exp(-\beta\Delta E) = \mathrm{Tr}(\mathcal{R}_\tau\mathcal{S}\mathcal{R}_0^{-1})$.

The averaged Boltzmann weighted work of a driven dissipative quantum system is expressed

$$\langle e^{-\beta W}\rangle = \mathrm{Tr}[\mathcal{R}_\tau\big(\prod_t \mathcal{R}_t^{-1}\mathcal{S}_t\mathcal{R}_t\big)\mathcal{R}_0^{-1}\rho_0^e q], \tag{5.5}$$

where $\rho_t^e$ is the equilibrium density matrix with system Hamiltonian $\mathbf{H}_t^S$. This product collapses on account of the structure of (5.4) and equilibrium density matrix (3.1). After this we are left with only the free energy difference between initial and final equilibrium ensembles,

$$\begin{aligned}\langle e^{-\beta W}\rangle &= \mathrm{Tr}\big(\mathcal{R}_\tau[\mathcal{R}_\tau^{-1}\mathcal{S}_\tau\mathcal{R}]\cdots[\mathcal{R}_2^{-1}\mathcal{S}_2\mathcal{R}_2][\mathcal{R}_1^{-1}\mathcal{S}_1\mathcal{R}_1]\mathcal{R}_0^{-1}\rho_0^{eq}\big)\\ &= \mathrm{Tr}(\mathcal{R}_\tau[\mathcal{R}_\tau^{-1}\mathcal{S}_\tau\mathcal{R}_\tau]\cdots[\mathcal{R}_2\mathcal{S}_2\mathcal{R}_2]\,\mathcal{R}_1^{-1}\rho_1^{eq}\,\frac{Z(1)}{Z(0)}) \qquad (5.6)\\ &= \frac{Z(\tau)}{Z(0)} = e^{-\beta\Delta F}.\end{aligned}$$

# 6 Jarzynski Inequalities and the Second Law

A Jarzynski relation is derived in the form of an inequality and shown it has applications to the second law of thermodynamics. Suppose $\mathbf{H}(t)$ is an arbitrary time-dependent Hamiltonian with $t_{init} \leq t \leq t_{fin}$ and denote its normalized eigenstates $|\varphi_i\rangle_I$ and $|\varphi_i\rangle_F$. of $H_I = \mathbf{H}(t_{init})$ and $\mathbf{H}_F = \mathbf{H}(t_{fin})$, respectively, with eigenvalues $e_i^I$ and $e_i^F$. Let $\mathbf{U}$ be the unitary operator producing time evolution over the whole time interval.

Let the system be in the Gibbs state at $t = t_{init}$ with inverse temperature $\beta$ described by the density matrix

$$\rho_{init} = \frac{e^{-\beta\mathbf{H}}}{Z(\beta)}, \qquad Z(\beta) = \sum_{i=1}^{N} e^{-\beta e_i^I}. \tag{6.1}$$

Define variables $p_{ij}$ as

$$p_{ij} = \frac{e^{-\beta e_i^I}}{Z(\beta)}|{}_F\langle\varphi_j|\mathbf{U}|\varphi_i\rangle_I|^2. \tag{6.2}$$

This can be interpreted as the probability that the system is found in the $i$-th eigenstate of $\mathbf{H}$ at $t = t_{init}$ and then in the $j$-th eigenstate of $\mathbf{H}$ at $t = t_{fin}$ and this is normalized. For any function $\chi(E, E')$ of two energy variables, its classical average is defined as

$$\overline{\chi(E,E')} = \sum_{i,j=1}^{N} p_{ij}\, F(e_i^I, e_j^F). \tag{6.3}$$

In a general situation in which $\mathbf{H}^I$ and $\mathbf{U}^{-1}\mathbf{H}^F\mathbf{U}$ do not commute, the classical average (6.3) does not correspond to quantum mechanical expectation in a direct way. The averaging brackets are defined by setting $\langle\cdot\rangle_{init} = \mathrm{Tr}[(\cdot)\rho_{init}]$ the expectation at $t = t_{init}$ and $\langle\cdot\rangle_{fin} = \mathrm{Tr}[(\cdot)\mathbf{U}\rho_{init}\mathbf{U}^{-1}]$ at $t = t_{fin}$. For $\chi$ an identity function, the following hold

$$\bar{E}^I = \langle\mathbf{H}\rangle_{init}, \qquad \bar{E}^F = \langle\mathbf{H}\rangle_{fin}. \tag{6.4}$$

For the definitions of (6.3) and (6.5), for any real $\beta^*$

$$\overline{e^{\beta\, E^I - \beta^* E^F}} = \sum_{i,j=1}^{N} e^{\beta e_i^I - \beta^* e_j^F} \frac{e^{-\beta e_i^I}}{Z(\beta)} |{}_F\langle \varphi_j | \mathbf{U} | \varphi_i \rangle_I|^2 = \frac{1}{Z(\beta)} \sum_{j=1}^{N} e^{-\beta^* e_i^F} = \frac{Z'(\beta^*)}{Z(\beta)} \tag{6.5}$$

Unitarity gives rise to the third term and $Z'(\beta^*) = \sum_{j=1}^{N} e^{-\beta^* e_j^F}$. Then (6.5) is another form of Jarzynski equality.

Recalling Jensen's inequality, $\overline{\exp(\xi)} \geq \exp(\overline{\xi})$, it follows from (6.5) that

$$e^{\beta\, \overline{E^I} - \beta^* \overline{E^F}} \leq \frac{Z'(\beta^*)}{Z(\beta)} \tag{6.6}$$

Using (6.4), inequality (6.6) produces an inequality for quantum mechanical expectation values for any $\beta^*$

$$\beta \langle \mathbf{H}_I \rangle_{init} - \beta^* \langle \mathbf{H}_F \rangle_{fin} \leq \log\, Z'(\beta^*) - \log\, Z(\beta), \tag{6.7}$$

Note that the basic Jarzynski equality can contain much stronger information than the corresponding inequality.

Let $\rho_{init}$ be any density matrix, $\mathbf{U}$ an arbitrary unitary operator with $\rho_{fin} = \mathbf{U}\rho_{init}\mathbf{U}^{-1}$, then we have

$$\mathrm{Tr}\,[\rho_{init}\, \log\, \rho_{init}] = \mathrm{Tr}[\rho_{fin}\, \log\, \rho_{fin}]. \tag{6.8}$$

This is just stating that von Neumann entropy is invariant in $t$. Suppose $\rho'$ is an arbitrary density matrix. The relative entropy satisfies,

$$S(\rho' | \rho_{fin}) = \mathrm{Tr}\,[\rho_{fin}(\log\, \rho_{fin} - \log\, \rho')] \geq 0. \tag{6.9}$$

Combining the last two relations (6.8), and (6.9), the following inequality is obtained

$$\mathrm{Tr}\,[\rho_{init}\, \log\, \rho_{init}] \geq \mathrm{Tr}[\rho_{fin}\, \log\, \rho']. \tag{6.10}$$

A Jarzynski inequality results if both the initial density matrix and reference density matrix are chosen to be Gibbs states.

A fundamental application of these results to quantum thermodynamics exists. Suppose the quantum system is macroscopic in size and the time dependent Hamiltonian $\mathbf{H}(t)$ describes an adiabatic operation in thermodynamics. Suppose further $\mathbf{H}(t)$ stays at $\mathbf{H}_F$ for a sufficiently long time at the end of the operation such that the system reaches macroscopic equilibrium. Set $\beta^* = \beta$ at first to yield an inequality for the expectation value of the work $W(\mathcal{U})$ done by the external agent on the system which has control of the Hamiltonian, hence

$$W(\mathcal{U}) = \langle \mathbf{H}^F \rangle_{fin} - \langle \mathbf{H}^I \rangle_{int} \geq \frac{1}{\beta}\big( \log\, Z(\beta) - \log\, Z'(\beta) \big). \tag{6.11}$$

For the case of a thermodynamic system whose energy is known to be $\mathcal{U}$, the entropy can be determined by means of a Legendre transformation in the following way

$$S(\mathcal{U}) = \min_{\beta} \beta(\mathcal{U} - F(\beta)) = \overline{\beta}(\mathcal{U} - F(\bar{\beta})). \tag{6.12}$$

In (6.12), $F(\beta)$ is the Helmholtz free energy and $\overline{\beta}$ is the unique temperature at which the minimum is attained. In other words, it is the equilibrium value of the inverse temperature. From the basic inequality (6.7) the following inequality must hold for any $\beta^*$,

$$\beta \left( \langle \mathbf{H}^I \rangle - F^I(\beta) \right) \leq \beta^* \left( \langle \mathbf{H}^F \rangle - F^F(\beta^*) \right). \tag{6.13}$$

Here $F^I(\beta) = -\beta^{-1} \log Z(\beta)$ and $F^F(\beta^*) = -\beta^{*-1} \log Z^*(\beta^*)$. Now the left-hand side of this is just the entropy of the initial state $S^I$ and the minimum over $\beta^*$ on the right-hand side is the entropy $S^F$ of the final state. Then (6.14) implies the inequality which enforces the law of entropy increase for Gibbs states

$$S^I \leq S^F. \tag{6.14}$$

Not to say this proves the second law, but there is clearly a deep connection between these relations that have been studied here and the second law of thermodynamics.

# 7 Conclusions

It is apparent that the approach explored here can yield a lot of knowledge with regard to quantum thermodynamics and systems not at equilibrium. The path integral approach at the start could incorporate processes that may violate the second law over very small time scales. There are other factors at work however which keep this from getting out of control. These factors may come from quantum mechanics itself, and may even lead to new developments in this area of physics.

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