

Quantum Extension of the Jarzynski Relation: Analogy with Stochastic Dephasing

Shaul Mukamel*

*Department of Chemistry and Department of Physics and Astronomy, University of Rochester,
P.O. RC Box 270216, Rochester, New York 14627-0216, USA*

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The relation between the distribution of work performed on a classical system by an external force switched on an arbitrary time scale and the corresponding equilibrium free energy difference is generalized to quantum systems. Using the adiabatic representation, we show that this relation holds for isolated systems as well as for systems coupled to a bath described by a master equation. A close formal analogy is established between the present “classical trajectory” picture over populations of adiabatic states and phase fluctuations (dephasing) of a quantum coherence in spectral line shapes, described by the stochastic Liouville equation.

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Jarzynski [1,2] had established a remarkably simple and general relationship between the distribution of work performed on a classical system by an external force and the free energy difference between the initial and final states [3–5]. This interesting prediction, connecting equilibrium quantities (free energies) to nonequilibrium trajectories corresponding to measurements performed on an arbitrary time scale, has recently been verified in single molecule measurements [6].

In this Letter we utilize the adiabatic representation [7] to prove that this relation holds equally for quantum systems. For an isolated driven quantum system (i.e., not coupled to a bath) the work does not depend on the path, and the proof follows directly from a sum rule of nonadiabatic couplings. We further develop a path integral representation of systems coupled to a bath described by a master equation in the adiabatic basis using “trajectories” over adiabatic state populations, and generalize Jarzynski’s relation to obtain the joint distribution of work and energy in a nonequilibrium measurement. A close resemblance is established between the physical picture underlying the distribution of work and the distribution of phase acquired by a quantum coherence due to coupling to a bath.

Consider a quantum system coupled to an external force which changes its Hamiltonian $H(t)$ by switching a parameter $\lambda(t)$ from $\lambda = 0$ at $t = 0$ to $\lambda = 1$ at time t . Initially the system is in thermal equilibrium and the instantaneous energy levels [eigenvalues of $H(t)$] are denoted $\epsilon_n(t)$, with the corresponding eigenstates $|\varphi_n(t)\rangle$. The canonical partition function for a given value of λ is

$$Z_\lambda = \sum_n \exp[-\beta\epsilon_n(t)] \equiv \exp(-\beta F_\lambda), \quad (1)$$

where F_λ is the Helmholtz free energy.

Let us consider an externally driven, but otherwise isolated, system. In the adiabatic representation [7] we expand its density matrix as

$$\rho(t) = \sum_{nm} \rho_{nm}(t) |\varphi_n(t)\rangle \langle \varphi_m(t)|, \quad (2)$$

where the coefficients $\rho_{nm}(t)$ satisfy the Liouville equation

$$\frac{d}{dt} \rho_{kl}(t) = -i\omega_{kl}(t)\rho_{kl}(t) - \sum_{mn} S_{kl,mn}(t)\rho_{mn}(t) \quad (3)$$

with $\omega_{kl}(t) \equiv \epsilon_k(t) - \epsilon_l(t)$ and

$$S_{kl,mn}(t) = \langle \varphi_k(t) | \dot{\varphi}_m(t) \rangle \delta_{ln} + \langle \dot{\varphi}_n(t) | \varphi_l(t) \rangle \delta_{km}. \quad (4)$$

The nonadiabatic coupling S is of purely quantum origin and has no classical analog.

For a given realization of $\lambda(t)$, the solution of Eq. (3) allows us to compute the conditional probability $K_{mn}(t)$ of the system to be in the state $|\varphi_m(t)\rangle$ at time t given that it started at state $|\varphi_n(0)\rangle$, so that $\rho_{mn}(t) = K_{mn}(t)\rho_{nn}(0)$. This probability is normalized by summing over *final* states $\sum_m K_{mn}(t) = 1$. A second, less obvious, sum rule is obtained by summation over *initial* states $\sum_n K_{mn}(t) = 1$. When the external force varies slowly, it follows from the adiabatic theorem [7] that no nonadiabatic transitions take place, $K_{mn}(t) = \delta_{mn}$, and this sum rule trivially holds. For finite switching time scales there are nonadiabatic transitions and the instantaneous eigenstates $|\varphi_n(t)\rangle$ are no longer the solutions of the time dependent Schrödinger equation. Nevertheless, the second sum rule follows from the relation

$$\sum_n S_{kl,mn}(t) = \frac{d}{dt} \langle \varphi_k(t) | \varphi_l(t) \rangle = 0. \quad (5)$$

A direct consequence of Eq. (5) is that the following uniform distribution in adiabatic population space, obtained by setting $\rho_{nm}(t) = \delta_{nm}$ at all times in Eq. (2),

$$\rho(t) = \sum_n |\varphi_n(t)\rangle \langle \varphi_n(t)|, \quad (6)$$

satisfies the Liouville equation. This interesting identity

gives rise to the second sum rule, which holds despite the nonadiabatic transitions and is the key for proving the quantum Jarzynski identity. Alternatively, Eq. (6) can be viewed as a unitary transformation of the unit operator between adiabatic basis sets at different times. This equation then simply states that the unit operator is invariant to a unitary transformation.

We shall now compute the ensemble average of $\exp(-\beta W)$ where W is the cumulative work performed up to time t . If the system starts in state $|\varphi_n(0)\rangle$ and ends up at time t in the state $|\varphi_m(t)\rangle$, then the work made by the external force is $W = \epsilon_m(t) - \epsilon_n(0)$, and we have

$$\langle \exp(-\beta W) \rangle = \frac{1}{Z_0} \sum_{mn} \exp[-\beta \epsilon_n(0)] \times K_{mn}(t) \exp\{-\beta[\epsilon_m(t) - \epsilon_n(0)]\}. \quad (7)$$

This gives

$$\langle \exp(-\beta W) \rangle = \frac{1}{Z_0} \sum_{mn} K_{mn}(t) \exp[-\beta \epsilon_m(t)]. \quad (8)$$

Using the second sum rule we can carry out the n summation and obtain Jarzynski relation

$$\langle \exp(-\beta W) \rangle = Z_1/Z_0, \quad (9)$$

where Z_1 is the final state partition function for $\lambda = 1$. Equation (8) implies that it is generally possible to compute the free energy change $F_1 - F_0 \equiv -\beta^{-1} \log(Z_1/Z_0)$ using the distribution of work.

We next turn to a system coupled to a bath and described by a master equation in the adiabatic basis [2,5]. We denote the transition rate from state n' to n by $R_{nn'}(t)$. R depends on t since it is recast in the time dependent, adiabatic, basis. It further satisfies the detailed balance condition [8]

$$R_{nn'}(t)/R_{n'n}(t) = \exp(-\beta \omega_{nn'}(t)). \quad (10)$$

For an isolated system the work equals the energy change and is therefore a state function. When the system is not isolated, the work becomes path dependent and may not be computed from the initial and final states alone, as was done in Eq. (7). For our model, the change in energy along the path stems from the variation of the eigenvalues $\epsilon_n(t)$ which is induced by the driving force, as well as the changes in their occupations, which are induced by the coupling to the bath (Fig. 1). The former is the work, whereas the latter is the heat. Both work and heat are path dependent, whereas the overall energy change $\epsilon_m(t) - \epsilon_n(0)$ is a state function.

We shall compute the joint distribution of work performed (W) and the change in the system's energy (E) in the process by defining the joint energy-work generating function

$$S(\gamma, \delta; t) = \langle \exp[-\gamma W(t) - \delta E(t)] \rangle, \quad (11)$$

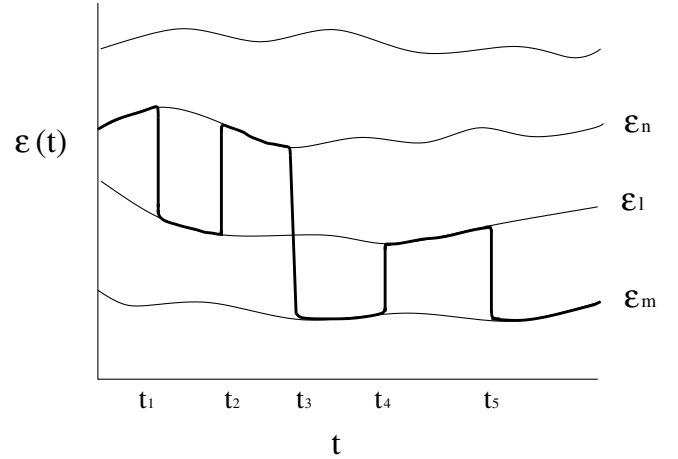


FIG. 1. A “classical trajectory” in population space of adiabatic states. Shown is a trajectory which starts at state $|\varphi_n(0)\rangle$, ends in state $|\varphi_m(t)\rangle$, and undergoes $j = 5$ jumps at time t_1, \dots, t_5 . The solution of the master equation is given by a path integral over all possible trajectories (sum over all possible values of $j = 0, 1, 2, \dots$ and integration over t_j).

where $\langle \dots \rangle$ denotes an ensemble average over trajectories for a fixed realization of $\lambda(t)$. The moments of W and E can then be computed as derivatives with respect to the parameters γ and δ ,

$$\langle W(t)^p E^q(t) \rangle = (-1)^{p+q} \frac{\partial^p}{\partial \gamma^p} \frac{\partial^q}{\partial \delta^q} S(\gamma, \delta; t) |_{\gamma=\delta=0}. \quad (12)$$

By expanding the solution of the master equation perturbatively in the off diagonal elements of $R_{nn'}(n \neq n')$ it can be represented as a path integral in the adiabatic population space (see Fig. 1): Consider a family of trajectories which start at state $|\varphi_n(0)\rangle$ at $t = 0$ and end in state $|\varphi_m(t)\rangle$ at time t . In the course of a given trajectory the system had jumped j times between different adiabatic states with $j = 0, 1, 2, \dots$. The conditional probability of the system to start at state $|\varphi_n(0)\rangle$ and end in state $|\varphi_m(t)\rangle$ is then given by a sum over all possible values of j . The work can be computed by integrating $\partial \epsilon_n / \partial t$ along the continuous segments of each trajectory. The contribution of this family to the generating function can be calculated by solving the equation of motion for the following Green function:

$$\frac{dG_{mn}(t)}{dt} = \sum_{n'} R_{nn'}(t) G_{n'n}(t) - \gamma \frac{\partial \epsilon_m}{\partial t} G_{mn}(t) \quad (13)$$

with the initial condition $G_{mn}(0) = \delta_{mn}$. It immediately follows from the path integral representation of the solution of the master equation that the generating function is given by averaging the Green function over the equilibrium distribution of initial states and a weighted summation over final states,

$$S(\gamma, \delta; t) = \sum_{nm} \exp\{-\delta[\epsilon_m(t) - \epsilon_n(0)]\} \\ \times G_{mn}(t; \gamma) \frac{\exp(-\beta\epsilon_n(0))}{Z_0}. \quad (14)$$

Equation (14) provides the following physical picture for the process: We consider an ensemble of trajectories over adiabatic state populations. In the classical case [1] the ensemble is generated by the distribution of initial states, whereas here the ensemble originates from the random nature of the stochastic jumps among adiabatic states. The Green function represents an open system where population can flow to (or from) state m with a rate $-\gamma\partial\epsilon_m/\partial t$ which depends on the variation of the adiabatic energies with time and on the parameter γ . As a result, the total population $\sum_m G_{mn}(t)$ is not conserved, and its value determines the generating function for the work and energy. The adiabatic representation thus provides a classical trajectory picture for the joint distribution of work and energy. To recover the Jarzynski relation we set $\gamma = \beta$ and $\delta = 0$ in Eq. (14) which then assumes the form

$$S(\beta; 0, t) = \sum_m G_m(\beta, t), \quad (15)$$

where

$$G_m(\beta, t) = \sum_n G_{mn}(\beta, t) \frac{\exp(-\beta\epsilon_n(0))}{Z_0}. \quad (16)$$

Let us consider the (unnormalized) distribution of states m ,

$$G_m(\beta, t) = \frac{\exp(-\beta\epsilon_m(t))}{Z_0}. \quad (17)$$

It can be easily verified that Eq. (17) is a solution to Eq. (13); this follows from the detailed balance of R that guarantees that the first term in the right-hand side of Eq. (13) vanishes when acting on Eq. (17). Substituting Eq. (17) in Eq. (15) immediately gives the Jarzynski relation [Eq. (9)]. It will be interesting to extend these results to systems described by more elaborate kinetic schemes such as fractional kinetics [9] rather than the ordinary master equation.

The validity of the Jarzynski relation for a system coupled to a bath at constant temperature has been established by Jarzynski [2] and Crooks [5]. The present derivation and the definition of work closely resemble Jarzynski's master equation approach. However, the path integral picture of continuous segments with discrete jumps provides a new insight for quantum systems and helps establish an interesting analogy with the theory of pure dephasing of quantum coherence, as will be shown next.

Equation (13) closely resembles the stochastic Liouville equation of Kubo [10–12], which has been

widely used in the theory of NMR and optical line shapes as well as in single molecule spectroscopy [13]. Computing the work generating function is then formally equivalent to computing the dephasing of a two level system (g and e) coupled to a bath. In that problem we consider equilibrium fluctuations of a quantum coherence σ between the two levels which are coupled to a classical bath represented by a phase space Γ . σ satisfies the stochastic Liouville equation [10]

$$\frac{d\sigma(\Gamma, t)}{dt} = \sum_{\Gamma'} W(\Gamma, \Gamma')\sigma(\Gamma', t) - iU(\Gamma)\sigma(\Gamma, t). \quad (18)$$

Here W is a Markovian rate matrix and $U(\Gamma)$ is the fluctuating energy gap between the two levels. σ serves as a generating function for the absorption line shape which is given by the Fourier transform of its zeroth moment $J(t) \equiv \int \sigma(\Gamma, t)d\Gamma$. The normalization of σ is thus the physically interesting quantity whose Fourier transform gives the spectral line shape.

Equations (13) and (18) describe very different physical phenomena: The former corresponds to an externally driven nonequilibrium system, whereas the latter represents a nondriven system at equilibrium. However, the two equations have a close formal connection. To better see the analogy we recast the solution of Eq. (18) as

$$\sigma(\Gamma, t) = \left\langle \exp\left[-i \int_0^t d\tau U(\tau)\right] \right\rangle, \quad (19)$$

where the averaging is over a subensemble of trajectories which assume the same value Γ at time t . For comparison we write the solution of Eq. (13) as

$$G_m(\gamma, t) = \left\langle \exp\left[-\gamma \int_0^t d\tau \partial\epsilon/\partial\tau\right] \right\rangle. \quad (20)$$

The average here is over a subensemble of trajectories (Fig. 1) which start at thermal equilibrium at $t = 0$ and end up in state m at time t . We reiterate that $\partial\epsilon/\partial\tau$ corresponds only to the continuous part of the trajectory; the jumps should be excluded.

In both equations we compute a phase space distribution whose time dependent normalization gives the generating function for the quantity of interest (either work or absorption spectrum). The first term in the right-hand side of Eq. (13) or (18) represents a regular dynamics which conserves the normalization, whereas the second term is responsible for varying the normalization, which is the physically interesting property. In Eq. (13) or (20) this comes from the flow of adiabatic state populations in and out of the system, originating from the time dependence of adiabatic energies. In the dephasing problem [Eq. (18) or (19)], the coherence σ acquires a random phase (U) which is different for different trajectories and it thus constitutes path function. This translates to loss of magnitude (dephasing and decoherence) upon ensemble averaging. The work in the nonadiabatic dynamics is

related to an integral over the continuous part of the energy trajectory in the same way that the phase in the line shape problem is obtained by an integral over the fluctuating two level frequency. This analogy suggests that it should be possible to carry out nonequilibrium line shape measurements by, for example, switching on an electric field for a solute in a polar solvent and observing the spectroscopic analogs of the Jarzynski relations by looking, for example, at the time dependent Stokes shift.

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*Email address: mukamel@chem.rochester.edu

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