Effect of Quantum Collapse on the Distribution of Work in Driven Single Molecules

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Two sources of quantum deviations from Jarzynski's celebrated classical relation between the free energy change and the distribution of work are analyzed using an exactly solvable harmonic model: Quantum dynamics retains the Gaussian profile of the distribution and merely gives rise to analytic corrections in $\hbar$, whereas quantum measurements (wave function collapse) induce extended power-law tails which fundamentally alter the distribution. These results may be observed in quantum information processing and in experiments involving mechanically or optically driven single quantum objects.

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Jarzynski has pointed out that the distribution of work made by a time-dependent force on classical systems may be used to obtain the free energy difference between two states, even when the force is switched on rapidly so that the system is out of equilibrium throughout the process [1,2]. Such distributions are readily obtained from repeated measurements on small systems (since bulk measurements merely give the average work). This remarkable relation between a path function (work) and a state function (free energy) has been verified experimentally [3] and triggered intense theoretical activity [4–7].

Jarzynski's original derivation and most subsequent work relied on the detailed-balance condition of a Markovian master equation for a classical system coupled to a bath. However, quantum effects which arise from both the quantum nature of the dynamics itself as well as the effects of repeated measurements [8] may be significant for single quantum objects (trapped ions, atoms, and molecules). The Jarzynski's relation was shown to hold for an isolated quantum system, when the measurement of work was treated classically [9], but its extension to more general quantum systems is still an open problem.

In this Letter we use an exactly solvable microscopic model, a collection of harmonic oscillators of which one collective coordinate is driven [10], to analyze the distribution of work and study both effects of quantum dynamics and measurement. Our results do not rely on any assumed Markovian form of reduced equations of motion or the detailed balance condition. When the measurement is treated classically we show that the distribution of work is Gaussian and the Jarzynski relation is recovered in the high-temperature limit. Quantum low-temperature corrections are expressed as a semiclassical expansion in $\hbar$. However, more dramatic effects are obtained when using von Neumann's prescription [11] which [see Eq. (1)] properly takes into account the projection (collapse of the wave function) induced by the measurement process. We then predict the breakdown of the Gaussian profile of work and the appearence of long algebraic tails which are sensitive to the measurement error bar.

We assume the Hamiltonian $\hat{H}_f(\tau) = \hat{H} + f(\tau)\hat{Q}$, where $\hat{H}$ represents the nondriven system and the second term represents the driving force $f(\tau)$ coupled to a collective coordinate $\hat{Q}$ which is a linear combination of the oscillator coordinates. (The model can be also viewed as a quantum oscillator coupled to a harmonic bath with arbitrary spectral density.) The work made by the driving force during the time interval $[0, t]$ is described by the operator $\hat{w} = -\int_0^t d\tau \dot{f}(\tau)\hat{Q}(\tau)$.

The dynamics and the measurement process are most clearly treated using superoperator algebra in Liouville space. This keeps track of time ordering and allows a smooth transition to the classical limit [12–14]. The quantum dynamics of an arbitrary variable Q in Liouville space involves two replicas: Q_L (left) and Q_R (right) that represent the ket and bra components of the density matrix $\rho(Q_L, Q_R)$, respectively. The semiclassical expansion is facilitated by introducing the variables $Q_+ = (Q_L + Q_R)/2$ and $Q_- = Q_L - Q_R$. Q_+ is a classical coordinate variable and Q_- is a quantum coordinate which carries information about coherence (phase). The classical limit can be reproduced by using the Wigner representation of the density matrix, obtained by a Fourier transformation with respect to Q_-. This results in a phase space distribution $\rho(Q_+, P)$, where P is the momentum variable conjugate to Q_-.

We now turn to a quantum treatment of the measurement [8,12,15]. Because of dissipation the work produced by an external force is a path function which can be obtained by a repeated measurement of the particle trajectory throughout the time interval. The distribution $\mathcal{P}(w)$ thus depends on how continuous measurements affect the quantum system. This issue, especially in the semiclassical regime, has drawn considerable attention [16–18]. Using the von Neumann principle, the effects of measurements may be incorporated by either collapsing the wave function of the measured variable directly (strong measurement), or by temporarily coupling the measured variable to an intermediate system (device) followed by collapsing in the intermediate system

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(weak measurement). In this Letter we focus on strong measurement and derive an expression for the probability distribution function (PDF) for stochastic trajectories (the probability of a certain outcome in a series of measurements).

We introduce a set $\mathcal{M}$ of outcomes and associate a set of measured values q_n for $n \in \mathcal{M}$. The effect of a measurement on the system is described by a set of functions $\{\psi_n\}_{n\in\mathcal{M}}$ of the collective coordinate Q that satisfy the property of *unit decomposition* $\sum_{n\in\mathcal{M}}|\psi_n(Q)|^2 = 1$. The effect of the measurement with an outcome $n \in \mathcal{M}$ on the system wave function $|\Psi\rangle$ is given by the action of the operator $\hat{\psi}_n$ followed by a proper normalization, whereas the outcome probability is given by the aforementioned norm. The wave function $|\Psi_n'\rangle$ and the corresponding density matrix $\hat{\rho}_n'$ after the measurement are

$$|\Psi_n'\rangle = \frac{\hat{\psi}_n|\Psi\rangle}{\sqrt{\langle\Psi|\hat{\psi}_n^\dagger\hat{\psi}_n|\Psi\rangle}}; \qquad \hat{\rho}_n' = \frac{\hat{W}_n(\hat{\rho})}{\mathrm{Tr}[\hat{W}_n(\hat{\rho})]}, \tag{1}$$

where $\hat{W}_n(\hat{\rho}) = \hat{\psi}_n\hat{\rho}\hat{\psi}_n^\dagger$, or adopting Liouville-space notation $\hat{W}_n = \hat{\psi}_{nL}\hat{\psi}_{nR}^\dagger$. The outcome probability is then $\mathcal{P}(n) = \mathrm{Tr}[\hat{W}_n(\hat{\rho})]$. This immediately results in the following Liouville-space correlation function expression for the PDF for stochastic trajectories $\mathbf{n} = (n_1, \ldots, n_N)$ that describe the measurement outcomes at times $\tau_1, \ldots, \tau_N$:

$$\mathcal{P}(\mathbf{n}) = \left\langle \prod_{j=1}^{N} \hat{W}_{n_j}(\tau_j) \right\rangle. \tag{2}$$

The angular bracket stands for the complete trace weighted with an initial canonical distribution of the complete system at the initial time when $f = 0$, and the time evolution is determined by the entire driven Hamiltonian. Conservation of probability is guaranteed by the unit decomposition property. The von Neumann prescription [11] which represents an ideal measurement where ψ_n are orthogonal corresponds to a special choice of the collapsing parameters $\mathcal{M} = Z$; $q_n = \varepsilon n$; $\psi_n(Q) = 1$ for $Q \in [-\varepsilon/2 + q_n, \varepsilon/2 + q_n]$; $\psi_n(Q) = 0$ otherwise. The reason for generalizing that prescription will be discussed below. To simplify the computation of work we assume a staircase profile of the force, i.e., $f(\tau) = f_j$ for $\tau \in [\tau_j, \tau_{j+1}]$ with $j = 1, \ldots, N$. In this case $\dot{f}(\tau) = \sum_j \Delta f_j \delta(\tau - \tau_j)$ and $w = -\sum_j \Delta f_j Q(\tau_j)$. The work is made only at discrete points (rather than continuously), which are taken to be the points of measurements. Substituting the integral representation of the collapsing operator

$$\hat{W}_n = \int dq_+ dq_- W_n(q_-, q_+) \int \frac{dp_+ dp_-}{(2\pi)^2} \times \exp[ip_+(\hat{Q}_- - q_-) + ip_-(\hat{Q}_+ - q_+)], \tag{3}$$

expressed in terms of the Liouville-space collapsing function

$$W_n(q_-, q_+) = \psi_n\left(q_+ + \frac{q_-}{2}\right)\psi_n^*\left(q_+ - \frac{q_-}{2}\right), \tag{4}$$

into Eq. (2) and expressing the Liouville space time–evolution superoperator of a driven system in terms of that of the nondriven system $[f(\tau) = 0]$, the PDF of the measurement outcomes that depends parametrically on the driving force profile $f(\tau)$ adopts the form

$$\mathcal{P}(\mathbf{n}; f) = \int d\mathbf{q}_+ d\mathbf{q}_- \prod_{j=1}^{N} W_{n_j}(q_{j-}, q_{j+}) \int \frac{d\mathbf{p}_+ d\mathbf{p}_-}{(2\pi)^{2N}} \times \exp\left[-i\sum_{j=1}^{N}(p_{j-}q_{j+} + p_{j+}q_{j-})\right] \times \left\langle \exp\left[i\sum_{j=1}^{N}[p_{j-}\hat{Q}_+(\tau_j) + p_{j+}\hat{Q}_-(\tau_j)] - \frac{i}{\hbar}\int_0^t f(\tau)\hat{Q}_-(\tau)\right]\right\rangle, \tag{5}$$

where hereafter $\langle\ldots\rangle$ denotes the time-ordered Liouville-space correlation function (that constitutes a full trace with respect to the complete density matrix and also performs time odering) of the nondriven system whose time evolution is determined by the nondriven Hamiltonian $\hat{H}$. We shall evaluate Eq. (5) using the second order cumulant expansion which is exact for a linearly driven harmonic system linearly coupled to a harmonic bath at arbitrary temperature [10]. Since in our case the force profile $f(\tau)$ is determined by the force vector $\mathbf{f} = (f_1, \ldots, f_N)$, the PDF (which only depends on $f_1, \ldots, f_{N-1}$) can be represented as

$$\mathcal{P}(\mathbf{n}; \mathbf{f}) = \int d\mathbf{q}_+ d\mathbf{q}_- \prod_{j=1}^{N} W_{n_j}(q_{j-}, q_{j+}) \int \frac{d\mathbf{p}_+ d\mathbf{p}_-}{(2\pi)^{2N}} \times \exp\left(-\frac{1}{2}\sum_{jk}\bar{M}_{jk}^{(+)}p_{j-}p_{k-} - i\hbar\sum_{jk}^{k<j}\bar{M}_{jk}^{(-)}p_{j-}p_{k+}\right) \times \exp\left[-i\sum_{j}(p_{j+}q_{j-} + p_{j-}q_{j+}) + i\sum_{jk}^{k+1<j}u_{jk}p_{j-}f_k\right], \tag{6}$$

with $u_{jk} = \int_{\tau_k}^{\tau_{k+1}} d\tau G_-(\tau_j - \tau)$, $\bar{M}_{jk}^{(\pm)} = G_\pm(\tau_j - \tau_k)$. Here $G_+(t) = \langle\hat{Q}_+(t)\hat{Q}_+(0)\rangle$ and $G_-(t) = -i\hbar^{-1}\langle\hat{Q}_+(t)\hat{Q}_-(0)\rangle$ are two-point Liouville-space correlation function and response function of the collective coordinate, respectively, in the nondriven system. They are related by the fluctuation-dissipation theorem and both can be computed by a complete trace with respect to the total density matrix, and keeping track of time ordering. Usually they are expressed in terms of the bath spectral density [10]. The measurement effects enter through the Liouville-space collapsing function $W_n(q_-, q_+)$ [Eq. (4)]. Ignoring quantum measurement effects is equivalent to adopting the following form for the collapsing function: $W_n(q_-, q_+) = 1$ for $q_+ \in [-\varepsilon/2 + q_n, \varepsilon/2 + q_n]$ and 0 otherwise. In this case Eq. (2) has a well-defined limit of infinitely frequent (continuous) measurements and the PDF for a stochastic trajectory $q(\tau)$ that represents the measurement outcome then becomes

$$\bar{\mathcal{P}}(q; f) = \int \mathcal{D}p \exp\left[-i\int_0^t d\tau p(\tau)q(\tau)\right] \times \left\langle \exp\left(i\int_0^t d\tau\left[p(\tau)\hat{Q}_+(\tau) - \hbar^{-1}f(\tau)\hat{Q}_-(\tau)\right]\right)\right\rangle. \quad (7)$$

Equation (7) can be rationalized as follows: the path integral over the functions $p(\tau)$ constitutes a Fourier-transform representation of the functional δ function that collapses the classical coordinate trajectory $Q_+(\tau)$ to the stochastic (observed) trajectory $q(\tau)$, whereas the $\hat{Q}_-(\tau)$ term accounts for the effects of the driving force. The PDF of work can be represented in a path-integral form where integration goes over the stochastic trajectories $q(\tau)$ obtained as a result of continuous measurements of the collective coordinate:

$$\mathcal{P}(w, f) = \int \mathcal{D}q\delta[\bar{w}(f, q) - w]\bar{\mathcal{P}}(q; f) = \int_{-\infty}^{\infty} \frac{d\lambda}{2\pi}\exp(-i\lambda w)S(\lambda; f), \quad (8)$$

where we have introduced the work generating function $S(\lambda; f)$. Combining Eqs. (7) and (8) leads to the following Liouville-space correlation function expression for the generating function $S_0(\lambda, f)$ in the classical measurement limit:

$$S_0(\lambda; f) = \left\langle \exp\left[-i\int_0^t d\tau[\lambda\dot{f}(\tau)\hat{Q}_+(\tau) + \hbar^{-1}f(\tau)\hat{Q}_-(\tau)]\right]\right\rangle. \quad (9)$$

Equation (9) is exact for any quantum system (not necessarily harmonic) and at arbitrary temperature; the only approximation made is the classical treatment of the meaurement.

For a linearly driven harmonic system the second-order cumulant expansion yields a Gaussian form for the generating function in λ which results in a Gaussian profile of work $\mathcal{P}(w; \mathbf{f}) = (1/\sigma\sqrt{2\pi})\exp(-[(w - \bar{w})^2/2\sigma^2])$ where $\bar{w} = -\int_0^t d\tau'' \int_0^{\tau''} d\tau' G_-(\tau'' - \tau')\dot{f}(\tau'')f(\tau')$ and $\sigma^2 = 2\int_0^t d\tau'' \int_0^t d\tau' G_+(\tau'' - \tau')\dot{f}(\tau'')\dot{f}(\tau')$. A semiclassical expansion is obtained by partitioning the Green function $G_+(t) = G_0(t) + G_q(t)$ into a sum of its classical limit $G_0(t)$ and quantum corrections $G_q(t)$, and making use of a relation $G_-(t) = -\beta d_t G_0(t)$ for $t > 0$. Representing the generating function as $S_0(\lambda; f) = \exp[-\beta\mathcal{F}_0(\lambda; f)]$ with $\beta = (kT)^{-1}$ and $\mathcal{F}_0(\lambda; f) = \mathcal{F}_c(\lambda; f) + \mathcal{F}_q(\lambda; f)$, and using $f(0) = 0$ we obtain after some straightforward transformations

$$\mathcal{F}_c(\lambda; f) = \frac{\lambda^2}{2\beta}G_0(0)[f(t)]^2 + i\lambda\beta^{-1}\left(1 - \frac{i\lambda}{\beta}\right) \times \int_0^t d\tau'' \int_0^{\tau''} d\tau' G_-(\tau'' - \tau')\dot{f}(\tau'')f(\tau'). \quad (10)$$

To establish the connection with Jarzynski's relation we examine the Helmholtz free energy $\bar{\mathcal{F}}(t)$ computed by assuming that the system is equilibrated with the instantaneous external force $f(t)$:

$$-\beta[\overline{\mathcal{F}}(t) - \overline{\mathcal{F}}(0)] = \beta^2\frac{G_+(0)[f(t)]^2}{2}. \quad (11)$$

Combining this with the identity $-\beta\mathcal{F}_0(-i\beta; f) = \ln\langle\exp[-\beta w(f)]\rangle$ which follows directly from the definition of $\mathcal{F}_0$ we get

$$\ln\langle\exp[-\beta w(f)]\rangle = -\beta[\bar{\mathcal{F}}(t) - \bar{\mathcal{F}}(0)] + \mathcal{R}_q. \quad (12)$$

The Jarzynski relation is obtained by setting $\mathcal{R}_q = 0$, $G_+ = G_0$, and $\mathcal{F}_0 = \mathcal{F}_c$ in the high-temperature (classical) limit and making use of Eq. (10) that implies $\mathcal{F}_c(-i\beta; f) = -\beta G_0(0)[f(t)]^2/2$. The quantum correction

$$\mathcal{R}_q(f) = \beta^2\int_0^t d\tau'' \int_0^{\tau''} d\tau' \dot{G}_q(\tau'' - \tau')\dot{f}(\tau'')f(\tau') \quad (13)$$

is analytic in $\hbar$ and represents deviations from the Jarzynski relation. To lowest nonvanishing order in $\hbar$ we have $\dot{G}_q = (\hbar^2\beta/3)\ddot{G}_-$. Equation (13) then gives an $\sim\hbar^2$ deviation from Jarzynski's relation. In general $\langle\exp[-\beta w(f)]\rangle$ is a path function that depends on the entire time profile of the force and only in the classical limit does it solely depend on its value at the boundary [$f(0)$ and $f(t)$], which is required for the Jarzynski relation to hold. This path dependence enters through $\mathcal{R}_q$. A semiclassical expansion can be also developed for a general (anharmonic) system by keeping all variables (including the bath) and considering a quantum counterpart of the generating function used in [2] to derive the relation for a Markovian (local-in-time) equation of motion. We can use the fact that the quantum canonical distribution $\exp(-\beta\hat{H})$ is obviously a stationary solution of the quantum Liouville equation. The proof of Jarzynski [2] breaks down in the quantum case because of the noncommuting nature of quantum operators. Expanding the commutators results in a regular expansion in $\hbar$ of the corrections to the Jarzynski relation.

So far we considered a quantum system subjected to a classical measurement. Quantum measurements are discrete and we shall illustrate their effects by applying the von Neumann prescription for $N = 2$ measurements. We note that in this case performing integrations over q_{1+} and q_{2+} leads to a continuous function of q_{1-} that has jumps of the first derivative at $q_{1-} = 0$ and $q_{1-} = \varepsilon_1/\sqrt{2}$ (note that in the semiclassical case the second jump is negligible with respect to the first) that determines the $\mathcal{P}(n_1, n_2) \sim (n_2)^{-2}$ asymptotic. Computing the first derivative jump at q_{1-} yields the following asymptotic expressions for large n_1 and n_2:

$$\mathcal{P}(n_1, n_2; f) \approx \frac{\hbar \bar{M}^{(-)}}{\pi(\varepsilon_2 n_2 + \zeta\varepsilon_1 n_1 + uf)^2} \times \frac{\varepsilon_2}{\sqrt{2\pi \bar{M}^{(+)}}} \exp\left[-\frac{1}{2\bar{M}^{(+)}}(\varepsilon_1 n_1)^2\right]. \quad (14)$$

For simplicity we assume different error bars ε_1 and ε_2 chosen such that the work produced at both jumps is measured with the same precision $\bar{\varepsilon}$ so that $w = f_1\varepsilon_1 n_1 + (f_2 - f_1)\varepsilon_2 n_2 = \bar{\varepsilon}\,\bar{n}$; $\bar{n} = n_1 + n_2$. The distribution of work is then computed by $\mathcal{P}(\bar{n}; f_1, f_2) = \sum_{n=-\infty}^{\infty} \mathcal{P}(n, \bar{n} - n; f_1)$. Equation (14) then gives

$$\mathcal{P}(\bar{n}, t) \approx \frac{\hbar G_-(t)|f_1||f_2 - f_1|}{\pi\bar{\varepsilon}^2\bar{n}^2};$$
$$\mathcal{P}(w, t)dw \approx \frac{\hbar G_-(t)|f_1||f_2 - f_1|}{w^2}\frac{dw}{\pi\bar{\varepsilon}}. \quad (15)$$

Unlike quantum dynamics which only makes small semicalssical corrections to the distribution of work, the quantum measurement induces an extended tail of $\mathcal{P}(n_1, n_2)$ with respect to n_2, which results in a power law decay of $\mathcal{P}(w)$. The origin of this algebraic tail can be understood as follows: Classical coordinate measurement selects a particular value of the classical coordinate Q_+ but does not affect the quantum variable Q_-. We can then divide the phase space (Q_L, Q_R) [or (Q_+, Q_-)] into bins; stripes of width $\sqrt{2}\varepsilon$ along Q_+. The total distribution $\rho = \sum_m N_m(\rho)$ is simply the sum of the various bins and is not affected by the measurement. Since no information is lost about the distribution, classical measurement involves no collapse, just binning. In a quantum measurement, in contrast, we retain boxes of width $\sim\varepsilon$ in both diagonal and off-diagonal directions. This implies that both the classical Q_+ and quantum Q_- variables are collapsed in a similar fashion. Since Q_- is conjugated to the particle momentum, measuring the coordinate (necessary to keep track of the work performed) affects not only the particle coordinate, but its momentum as well, as required by the Heisenberg uncertainty principle. We thus discard the information about the coherence ($|Q_-| > \varepsilon$) each time we make a measurement and the total distribution changes since some coherence is necessarily erased by the measurement. This is how collapse is viewed in Liouville space. Because of this, even a harmonic system that starts as a Gaussian distribution in phase space becomes non-Gaussian once subjected to the measurement.

The long tails arise from the sharp edges of the von Neumann binning, which represents an ideal measurement whereby the functions ψ_n are orthogonal. It is possible to use a smoother set of functions provided we retain the property of unit decomposition. In that case we introduce some uncertainty into the measurement, since the bins in (Q_+, Q_-) space overlap and the functions ψ_n are no longer orthogonal. However, this fuzziness allows one to truncate the coherence more gradually. Smoothing the collapsing functions will eliminate the long tails in the PDF, however if the smoothing regions are narrow, Eq. (14) will still represent the intermediate regime. At larger values of of w, $\mathcal{P}(w)$ will cross over to a different asymptotic behavior which will depend on the details of collapsing functions ψ_n. The present analysis may be applied to quantum computing where repeated measurements are essential for the control, retrieval, and manipulation of quantum information. These effects may also be observed in single molecule spectroscopy with mechanical forces (tweezers) or by using photon counting statistics.

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