Fluctuation theorems: Work is not an observable

Peter Talkner, Eric Lutz, Peter Hänggi

Institute of Physics, University of Augsburg, D-86135 Augsburg, Germany
(Dated: February 6, 2008)

The characteristic function of the work performed by an external time-dependent force on a Hamiltonian quantum system is identified with the *time-ordered correlation function* of the exponentiated system's Hamiltonian. A similar expression is obtained for the averaged exponential work which is related to the free energy difference of equilibrium systems by the Jarzynski work theorem.

Deep relations between nonequilibrium fluctuations and thermal equilibrium properties of small systems have recently been discovered and formulated in terms of so-called fluctuation theorems [1, 2]. These theorems are not only of basic theoretical relevance but provide novel ground for experimental investigations of small systems in physics, chemistry and biology [3]

In this rapid communication we want to preclude a possible confusion about the notion of work in the context of fluctuation theorems for quantum mechanical Hamiltonian systems. To be precise, we consider a quantum system which was in thermal contact with a heat bath at inverse temperature β until a time t_0. Then the contact with the bath is switched off and a classical force acts on the otherwise isolated Hamiltonian system until the time t_f according to a prescribed protocol. We demonstrate that the exponential average of the total work performed on the system as well as the characteristic function of this work are given by *time-ordered correlation functions* of the exponentiated Hamiltonian rather than by expectation values of an operator representing the work as a pretended observable.

For a system that evolves under the exclusive influence of a time dependent Hamiltonian $H(t)$ from an initial thermal equilibrium state

$$\rho(0) = Z(0)^{-1} \exp\left\{-\beta H(0)\right\}, \qquad (1)$$

at time $t_0 = 0$ until a final time $t = t_f$, the work performed on the system is a randomly distributed quantity w. Its statistical properties follow from a probability density $p(w)$ or, equivalently, from the corresponding characteristic function $G(u)$ which is defined as the Fourier transform of the probability density, i.e.

$$G(u) = \int dw\, e^{iuw} p(w) \qquad (2)$$

We will demonstrate that the characteristic function is given by the following quantum correlation function:

$$\begin{aligned}
G(u) &= \langle e^{iuH(t_f)} e^{-iuH(0)} \rangle \\
&\equiv \mathrm{Tr}\, e^{iuH_H(t_f)} e^{-iuH(0)} \rho(0) \\
&= \mathrm{Tr}\, e^{iuH(t_f)} U(t_f) e^{-iuH(0)} \rho(0) U^+(t_f) \\
&= \mathrm{Tr}\, e^{iuH(t_f)} U(t_f) e^{-(iu+\beta)H(0)} U^+(t_f)/Z(0)
\end{aligned} \qquad (3)$$

where Tr denotes the trace over the system's Hilbert space $\mathcal{H}$, $U(t)$ the unitary time evolution governed by the Schrödinger equation $i\hbar \partial U(t)/\partial t = H(t)U(t)$ with $U(0) = 1$, and $H_H(t) = U^+(t)H(t)U(t)$ is the Hamiltonian in the Heisenberg picture. The third equality follows from the second line by the cyclic invariance of the trace and the last line follows with eq. (1).

The characteristic function has the form of a time-ordered correlation function of the two operators $\exp\{iuH(t_f)\}$ and $\exp\{-iuH(0)\}$. We note that this correlation function in general *differs* from the averaged exponential of the difference of the Hamiltonians $W = H_H(t_f) - H(0)$, which sometimes is referred to as the operator of work [4]. It is possible though to formally rewrite the characteristic function in terms of the difference between the Hamiltonians. In the second line of eq.(3) the product of the operators $\exp\{iuH_H(t)\}$ and $\exp\{-iuH(0)\}$ occurs in chronological order and may be written as $\exp\{iuH_H(t)\} \exp\{-iuH(0)\} = \mathcal{T}_> \exp\{iuH_H(t)\} \exp\{-iuH(0)\}$. Under the protection of the time ordering operator $\mathcal{T}_>$ the usual rule for exponentials of commutative quantities holds [5] to yield the following equivalent forms of the characteristic function of work

$$\begin{aligned}
G(u) &= \mathrm{Tr}\, \mathcal{T}_> e^{iu(H_H(t_f)-H(0))} \rho(0) \\
&= \mathrm{Tr}\, \mathcal{T}_> \exp\{iu \int_0^{t_f} \frac{\partial H_H(s)}{\partial s} ds\} \rho(0)
\end{aligned} \qquad (4)$$

The second equality is a consequence of the known fact that the total derivative of the Hamiltonian in the Heisenberg picture coincides with its partial time derivative.

The averaged exponentiated work $\langle \exp\{-\beta w\} \rangle$ is obtained from the characteristic function by putting $u = i\beta$, cf. eq. (2). Using the correlation function expression (3) together with the canonical initial density matrix (1) we immediately recover the Jarzynski equation in its known form [6]

$$\langle e^{-\beta w} \rangle = \frac{Z(t_f)}{Z(0)} \qquad (5)$$

where $Z(t_f) = \mathrm{Tr}\, e^{-\beta H(t_f)}$ is the partition function of a hypothetical system with Hamiltonian $H(t_f)$ in a Gibbs state at inverse temperature β.

By replacing the quantum correlation function by the corresponding correlation function of a classical Hamiltonian system the characteristic function of the work performed on the classical system is obtained. Its inverse Fourier transform yields the known classical expression for the probability density of work, cf. Ref. [7]

$$
\begin{aligned}
p_{\text{cl}}(w) \;=\; & Z_{\text{cl}}^{-1}(0) \int d\mathbf{z}(0) \\
& \delta\big(w - [H(\mathbf{z}(t_f), t_f) - H(\mathbf{z}(0), 0)]\big) \\
& \times e^{-\beta H(\mathbf{z}(0), 0)}
\end{aligned} \tag{6}
$$

where $Z_{\text{cl}}(0) = \int d\mathbf{z}\exp\{-\beta H(\mathbf{z},0)\}$ denotes the classical partition function, $\mathbf{z} = (\mathbf{p}, \mathbf{q})$ a point in phase space which serves as the initial condition of the trajectory $\mathbf{z}(t)$ evolving according to Hamilton's equations of motion.

The fluctuation theorem has long been known for a sudden switch of the Hamiltonian of a classical system [8]. For a quantum system with a Hamiltonian changing from H_0 at time $t_0 = 0^-$ to H_1 at $t_f = 0^+$ the time-evolution operator becomes $U(t_f) = 1$. The characteristic function (3) then simplifies to

$$
G(u) = \text{Tr}\, e^{iuH_1} e^{-iuH_0} e^{-\beta H_0}/Z(0) \tag{7}
$$

and the Jarzynski equation (5) again follows with $u = i\beta$. In all nontrivial cases, when the two Hamiltonians do not commute, the averaged exponential of the difference operator $H_1 - H_0$ does not yield this result.

The proof of eq. (3) essentially follows an argument given by Kurchan [9], see also Refs. [10–12]. It is based on the elementary observation that two energy measurements are required in order to determine the work performed on the system by an external force. In the first measurement, the energy is determined in the initial Gibbs state $Z(0)^{-1}\exp\{-\beta H(0)\}$. The outcome of this measurement is one of the eigenvalues $e_n(0)$ of the Hamiltonian $H(0)$ with the probability

$$
p_n = \exp\{-\beta e_n(0)\}/Z(0). \tag{8}
$$

After the measurement the system is found in the corresponding eigenstate $\varphi_n(0)$ of $H(0)$ satisfying $H(0)\varphi_n(0) = e_n(0)\varphi_n(0)$. This state evolves according to $\psi(t) = U(t)\varphi_n(0)$ until the second energy measurement is performed at the time t_f. It produces an eigenvalue $e_m(t_f)$ with the probability

$$
p(m, t_f|n) = |(\varphi_m(t_f)|U(t_f)\varphi_n(0))|^2, \tag{9}
$$

where $(\cdot|\cdot)$ denotes the scalar product of the Hilbert space $\mathcal{H}$. Here, $e_m(t_f)$ and $\varphi_m(t_f)$ are the eigenvalues and eigenfunctions, respectively, of the Hamiltonian $H(t_f)$. Hence, the energies $e_m(t_f)$ and $e_n(0)$ are measured with the probability $p(m, t|n)p_n$ such that the probability density of the work, which is the difference of the measured energies, becomes

$$
p(w) = \sum_{n,m} \delta\big(w - [e_m(t_f) - e_n(0)]\big)\, p(m, t_f|n)p_n \tag{10}
$$

One then finds for the characteristic function from the definition (2)

$$
\begin{aligned}
G(u) &= \sum_{n,m} e^{iu(e_m(t_f) - e_n(0))} \\
&\quad \times \big(\varphi_m(t_f)|U(t_f)\varphi_n(0)\big) \\
&\quad \times \big(\varphi_n(0)|U^+(t_f)\varphi_m(t_f)\big) e^{-\beta e_n(0)}/Z(0) \\
&= \sum_{n,m} \big(\varphi_m(t_f)|U(t_f)e^{-iuH(0)}\rho(0)\varphi_n(0)\big) \\
&\quad \times \big(\varphi_n(0)|U^+(t_f)e^{iuH(t_f)}\varphi_m(t_f)\big) \\
&= \text{Tr}\, U(t_f)e^{-iuH(0)}\rho(0)U^+(t_f)e^{iuH(t_f)}
\end{aligned} \tag{11}
$$

In going to the last line, the sum over the complete set of eigenstates $\{\varphi_m(t)\}$ was written as the trace and the completeness of the eigenstates $\varphi_n(0)$ was used. By use of the cyclic invariance of the trace the quantum correlation function expression (3) for the characteristic function is proved.

This expression for the characteristic function contains all available statistical information about the work performed by an external force on an isolated quantum system, such as the averaged exponentiated work, cf. eq. (5). All moments of the work follow from the derivatives of the characteristic function.

[1] C. Jarzynski, J. Stat. Phys, in press; cond-mat/0612305v1;
[2] C. Jarzynski, Lect. Notes Phys. **711**, 201 (2007).
[3] C. Bustamante, J. Liphardt, F. Ritort, Physics Today **58** (7), 43 (2005)
[4] A.E. Allahverdyan, T.M. Nieuwenhuizen, Phys. Rev. E **71**, 066102 (2005).
[5] J.M. Ziman, *Elements of Advanced Quantum Theory*, Cambridge University Press, Cambridge 1969.
[6] C. Jarzynski, Phys. Rev. Lett. **78**, 2690 (1997).
[7] C. Jarzynski, Phys. Rev. E **56**, 5018 (1997).
[8] R. Zwanzig, J. Chem. Phys. **22**, 1420 (1954).
[9] J. Kurchan, cond-mat/0007360v2.
[10] H. Tasaki, cond-mat/0009244v2.
[11] S. Mukamel, Phys. Rev. Lett. **90**, 170604 (2003).
[12] T. Monnai, Phys. Rev. E, **72**, 027102 (2005).