Fluctuation Theorem for Arbitrary Open Quantum Systems

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Tasaki-Crooks Fluctuation Theorem and Jarzynski Equality: State of the art

Peter Hänggi, Michele Campisi, and Peter Talkner

- Classical
  - ✓ Isolated system
  - ✓ Weak coupling
  - ✓ Strong Coupling
- Quantum
  - ✓ Isolated system
  - ✓ Weak coupling
  - ✓ Strong Coupling

What are fluctuation and work theorems about?

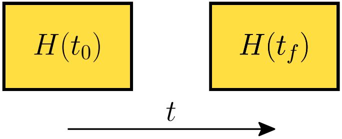
Small systems: fluctuations may become comparable to average quantities.

Can one infer thermal **equilibrium properties** from fluctuations in **nonequilibrium** processes?

Jarzynski's equality

C. Jarzynski, PRL 78, 2690 (1997)

$Z^{-1}(t_0)e^{-\beta H(t_o)}$ non-eq.



$\{H(t)\}_{t_f,t_0}$: protocol
w: work performed

$$\langle e^{-\beta w} \rangle = e^{-\beta \Delta F}$$

$$\Delta F = F(t_f) - F(t_0), \quad F(t) = -\beta^{-1} \ln Z(t)$$

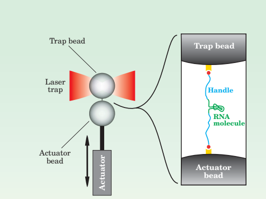
$\langle \cdot \rangle$: average over realizations of the same protocol

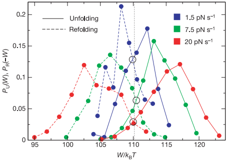
Jensen's inequality : $\Delta F \leq \langle w \rangle$ Second Law

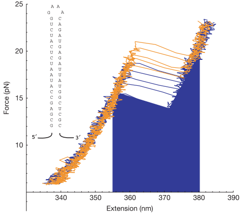
Crooks' fluctuation theorem

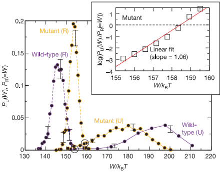
$$\frac{p_{t_f,t_0}(w)}{p_{t_0,t_f}(-w)} = e^{-\beta(\Delta F - w)}$$

G.E. Crooks, PRE **60**,2721 (1999)







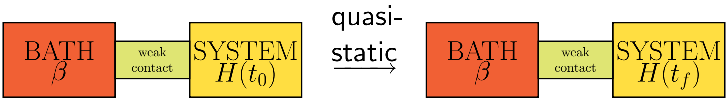


D. Colin et al. Nature **437**, 231 (2005)

Equilibrium versus nonequilibrium processes

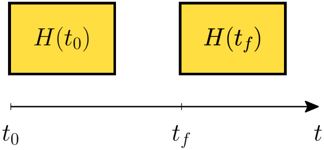
Isothermal quasistatic process:

$e^{-\beta H(t_0)}/Z(t_0)$ $\qquad$ $e^{-\beta H(t_f)}/Z(t_f)$



$$\Delta F = w = \langle w \rangle$$

Non-equilibrium process:



$p_{t_f,t_0}(w) = ?$ pdf of work

Definition of work

A. **Classical**:

$$w = \int_{t_0}^{t_f} dt\, \frac{\partial H(z(t),t)}{\partial t} = H(z(t_f),t_f) - H(z(t_0),t_0)$$

$z(t)$: Trajectory in phase space
$z(t_0)$: Starting point taken from $Z^{-1}(t_0)e^{-\beta H(z,t_0)}$

B. **Quantum mechanical**:

$$w = e_m(t_f) - e_n(t_0)$$

$$H(t)\varphi_{n,\lambda}(t) = e_n(t)\varphi_{n,\lambda}(t)$$

work is a RANDOM quantity due to the randomness inherent in the INITIAL STATE $\rho(t_0)$ and in QUANTUM MECHANICS.

Probability of work

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$$H(t)\varphi_{n,\lambda}(t) = e_n(t)\varphi_{n,\lambda}(t)$$

$$P_n(t) = \sum_\lambda |\varphi_{n,\lambda}(t)\rangle\langle\varphi_{n,\lambda}(t)|$$

$$\begin{aligned} p_n &= \mathrm{Tr}\, P_n(t_0)\rho(t_0) \\ &= \text{probability of being at energy } e_n(t_0) \text{ at } t = t_0 \end{aligned}$$

$$\begin{aligned} \rho_n &= P_n(t_0)\rho(t_0)P_n(t_0)/p_n \\ &= \text{state after measurement} \end{aligned}$$

$$\rho_n(t_f) = U_{t_f,t_0}\rho_n U^+_{t_f,t_0}$$

$$\begin{aligned} p(m|n) &= \mathrm{Tr} P_m(t_f)\rho_n(t_f) \\ &= \text{conditional probability of getting to energy } e_m(t_f) \end{aligned}$$

Probability of work

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$$p_{t_f,t_0}(w) = \sum_{n,m} \delta(w - [e_m(t_f) - e_n(t_0)])\, p(m|n)\, p_n$$

Characteristic function of work

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$$
\begin{aligned}
G_{t_f,t_0}(u) &= \int dw\, e^{iuw} p_{t_f,t_0}(w) \\
&= \sum_{m,n} e^{iue_m(t_f)} e^{-iue_n(t_0)} \mathrm{Tr} P_m(t_f) U_{t_f,t_0} \rho_n U^{+}_{t_f,t_0} p_n \\
&= \sum_{m,n} \mathrm{Tr} e^{iuH(t_f)} P_m(t_f) U_{t_f,t_0} e^{-iH(t_0)} \rho_n U^{+}_{t_f,t_0} p_n \\
&= \mathrm{Tr} e^{iuH_H(t_f)} e^{-iuH(t_0)} \bar{\rho}(t_0) \\
&\equiv \langle e^{iuH(t_f)} e^{-iuH(t_0)} \rangle_{t_0}
\end{aligned}
$$

$$
H_H(t_f) = U^{\dagger}_{t_f,t_0} H(t_f) U_{t_f,t_0},
$$

$$
\bar{\rho}(t_0) = \sum_n P_n(t_0)\rho(t_0)P_n(t_0), \quad \bar{\rho}(t_0) = \rho(t_0) \iff [\rho(t_0), H(t_0)]
$$

Work is not an observable

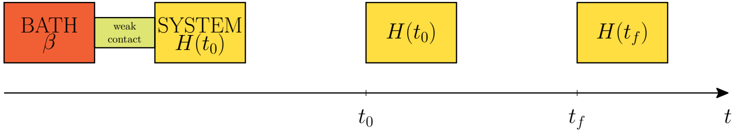
Note: $G_{t_f,t_0}(u)$ is a CORRELATION FUNCTION. If work was an observable, i.e. if a hermitean operator W existed then the characteristic function would be of the form of an EXPECTATION VALUE

$$G_W(u) = \langle e^{iuW} \rangle = \mathrm{Tr} e^{iuW} \rho(t_0)$$

Hence, work is not an observable.

P. Talkner, P. Hänggi, M. Morillo, Phys. Rev. E **77**, 051131 (2008)
P.Talkner, E. Lutz, P. Hänggi, Phys. Rev. E **75**, 050102(R) (2007)

Canonical initial state



$$\rho(t_0) = Z^{-1}(t_0)e^{-\beta H(t_0)}, \quad Z(t_0) = \mathrm{Tr} e^{-\beta H(t_0)}, \quad \bar{\rho}(t_0) = \rho(t_0)$$

$$G^c_{t_f,t_0}(\beta, u) = Z^{-1}(t_0)\mathrm{Tr} e^{iuH_H(t_f)} e^{-iuH(t_0)} e^{-\beta H(t_0)}$$

Choose $u = i\beta$

$$
\begin{aligned}
\langle e^{-\beta w} \rangle &= \int dw\, e^{-\beta w} p_{t_f,t_0}(w) \\
&= G^c_{t_f,t_0}(i\beta) \\
&= \mathrm{Tr} e^{-\beta H_H(t_f)} e^{\beta H(t_0)} Z^{-1}(t_0) e^{-\beta H(t_0)} \\
&= \mathrm{Tr} e^{-\beta H(t_f)} / Z(t_0) \\
&= Z(t_f)/Z(t_0) \\
&= e^{-\beta \Delta F}
\end{aligned}
$$

quantum Jarzynski equality

$u \to -u + i\beta$ and time-reversal

$$\begin{aligned} Z(t_0) G^c_{t_f,t_0}(u) &= \mathrm{Tr}\, U^+_{t_f,t_0} e^{iuH(t_f)} U_{t_f,t_0} e^{i(-u+i\beta)H(t_0)} \\ &= \mathrm{Tr}\, e^{-i(-u+i\beta)H(t_f)} e^{-\beta H(t_f)} U^+_{t_0,t_f} e^{i(-u+i\beta)H(t_0)} U_{t_0,t_f} \\ &= Z(t_f) G^c_{t_0,t_f}(-u+i\beta) \end{aligned}$$

$$\boxed{\frac{p_{t_f,t_0}(w)}{p_{t_0,t_f}(-w)} = \frac{Z(t_f)}{Z(t_0)} e^{\beta w} = e^{-\beta(\Delta F - w)}}$$

Tasaki-Crooks theorem

H. Tasaki, cond-mat/0009244.

P. Talkner, P. Hänggi, J. Phys. A **40**, F569 (2007).

Microcanonical initial state

Peter Hänggi, Michele Campisi, and Peter Talkner

$$\rho(t_0) = \omega_E^{-1}(t_0)\delta(H(t_0) - E),$$
$$\omega_E(t_0) = \mathrm{Tr}\,\delta(H(t_0 - E)) = e^{S(E,t_0)/k_B}$$

$\omega_E(t_0)$: Density of states, $S(E, t_0)$: Entropy

$$p^{\mathrm{mc}}_{t_f,t_0}(E, w) = \omega_E^{-1}(t_0)\mathrm{Tr}\,\delta(H_H(t_f) - E - w)\delta(H(t_0) - E)$$

$$\frac{p^{\mathrm{mc}}_{t_f,t_0}(E, w)}{p^{\mathrm{mc}}_{t_0,t_f}(E + w, -w)} = \frac{\omega_{E+w}(t_f)}{\omega_E(t_0)} = e^{[S(E+w,t_f)-S(E,t_0)]/k_B}$$

P.Talkner, P. Hänggi, M. Morillo, Phys. Rev. E **77**, 051131 (2008)

Example

Driven harmonic oscillator

$$H(t) = \hbar\omega a^+ a + f^*(t) a + f(t) a^+, \qquad f(t) = 0 \text{ for } t < t_0$$

$$G_{t_f,t_0}(u) = \exp\left[-iu\frac{|f(t_f)|^2}{\hbar\omega} + \left(e^{iu\hbar\omega} - 1\right)|z|^2\right]\sum_{n=0}^{\infty} p_n L_n\left(4|z|^2 \sin^2\frac{\hbar\omega u}{2}\right)$$

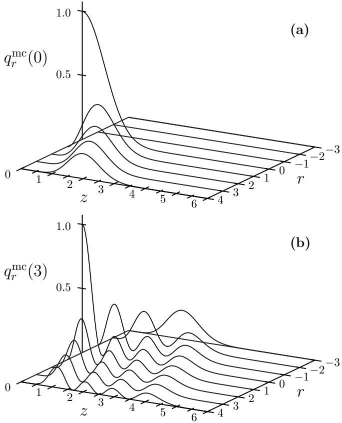
$$p_n = \mathrm{Tr} P_n(t_0)\rho(t_0) = \langle n|\rho(t_0)|n\rangle, \qquad z = \frac{1}{\hbar\omega}\int_{t_0}^{t_f} ds \frac{df(s)}{ds} e^{i\omega s}$$

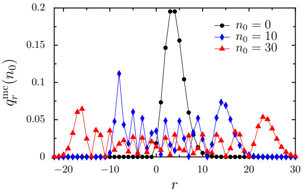
$$\langle w\rangle = \hbar\omega|z|^2 - \frac{|f(t_f)|^2}{\hbar\omega}, \quad \langle w^2\rangle - \langle w\rangle^2 = 2(\hbar\omega)^2|z|^2(\langle a^+ a\rangle_0 + \frac{1}{2})$$

$\langle w\rangle$: independent of initial state;
$\langle\cdot\rangle$: average w.r.t. initial state $\bar{\rho}(t_0) = \sum_n p_n |n\rangle\langle n|$.

P. Talkner, S. Burada, P. Hänggi, PRE **78**, 011115 (2008).

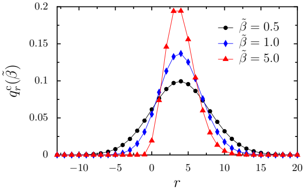
$$p_{t_f,t_0}(w) = \sum_{r\in\mathbb{Z}} q_r \,\delta\big[w - \big(\hbar\omega r - |f(t_f)|^2/(\hbar\omega)\big)\big]$$





mc.i.s.

$z = 2$

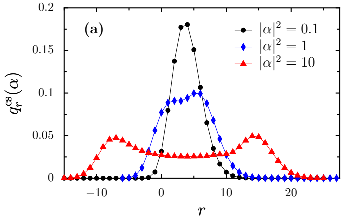


$\tilde\beta = \beta\hbar\omega$

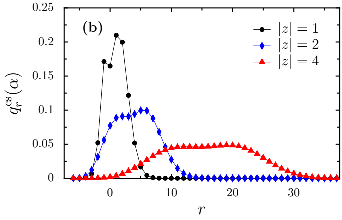
c.i.s.

$z = 2$

mc.i.s. $n_0 = 0, 3$



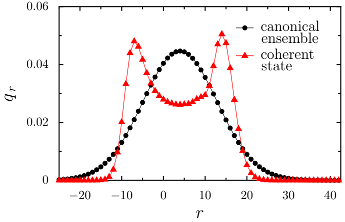
coherent i.s. $|z| = 2$



coherent i. s. $|\alpha| = 1$

$$|\alpha\rangle = e^{\alpha a^+ - \alpha^* a}|0\rangle$$

$$p_n = \frac{|\alpha|^{2n}}{n!} e^{-|\alpha|^2}$$



coherent $(|\alpha|^2 \approx 9.51)$ versus canonical $(\beta\hbar\omega = 0.1)$, $|z| = 2$

Candidate experimental check of Jarzynski equality in the quantum regime

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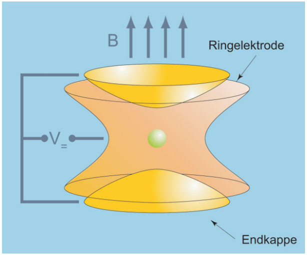
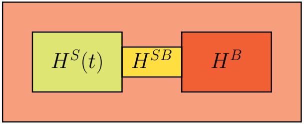
Atom in Paul Trap: Quantum Harmonic Oscillator



- Prepare oscillator in thermal state
- Probe the oscillator initial eigenstate
- Change trap stiffness
- Probe the oscillator final eigenstate
- Construct $p_{t_f,t_0}(W)$

G. Huber, F. Schmidt-Kaler, S. Deffner, E.Lutz, PRL **101** 070403 (2008)

Open Quantum Systems: Weak Coupling



$$H(t) = H^S(t) + H^B + H^{SB}$$

$$H^S(t) P_{i,\alpha}(t) = e_i^S(t) P_{i,\alpha}(t),$$

$$H^B P_{i,\alpha}(t) = e_\alpha^B P_{i,\alpha}(t),$$

$$e_i^S(t_f) - e_j^S(t_0) = E = \text{internal energy change}$$

$$e_\alpha^B - e_\beta^B = -Q = \text{exchanged heat}$$

$$\bar{\rho}_0 = \sum_{i,\alpha} P_{i,\alpha}(t_0) \rho_0 P_{i,\alpha}(t_0)$$

$$p_{t_f,t_0}(E, Q) = \text{joint PDF for E and Q}$$

$$G^{E,Q}_{t_f,t_0}(u, v) = \mathrm{Tr} e^{i\left(u H_H^S(t_f) - v H_H^B(t_f)\right)} e^{-i\left(u H^S(t_0) - v H^B\right)} \bar{\rho}_0$$

P. Talkner, M. Campisi, P. Hänggi, J.Stat.Mech. (2009) P02025

$$\rho_0 = Z^{-1}(t_0) e^{-\beta\left(H^S(t_0) + H^{SB} + H^B\right)} \qquad \text{therm. eq. at } t_0$$

$$\approx \rho_0^0 \left[1 - \int_0^\beta d\beta' e^{\beta'\left(H^S(t_0)+H^B\right)} \delta H^{SB} e^{-\beta'\left(H^S(t_0)+H^B\right)} \right]$$

$$\rho_0^0 = Z_S^{-1}(t_0) Z_B^{-1} e^{-\beta\left(H^S(t_0)+H^B\right)}$$

$$\bar{\rho}_0 = \sum_{i,\alpha} P_{i,\alpha}(t_0) \rho_0 P_{i,\alpha}(t_0)$$

$$= \rho_0^0 + \mathcal{O}\left((\delta H^{SB})^2 \right)$$

$$G_{t_f,t_0}^{E,Q}(u,v) = \mathrm{Tr} e^{i\left(u H_H^S(t_f) - v H_H^B(t_f)\right)} e^{-i\left(u H^S(t_0) - v H^B\right)} \rho_0^0$$

Crooks theorem for energy and heat

Peter Hänggi, Michele Campisi, and Peter Talkner

$$Z_S(t_0)G^{E,Q}_{t_f,t_0}(u,v) = Z_S(t_f)G^{E,Q}_{t_0,t_f}(-u+i\beta,-v-i\beta)$$

$$\frac{p_{t_f,t_0}(E,Q)}{p_{t_0,t_f}(-E,-Q)} = \frac{Z_S(t_f)}{Z_S(t_0)}e^{\beta(E-Q)} = e^{-\beta(\Delta F_S - E + Q)}$$

$w = E - Q$: work

$$\frac{p^{Q,w}_{t_f,t_0}(Q,w)}{p^{Q,w}_{t_0,t_f}(-Q,-w)} = e^{-\beta(\Delta F_S - w)}, \qquad \frac{p^{w}_{t_f,t_0}(w)}{p^{w}_{t_0,t_f}(-w)} = e^{-\beta(\Delta F_S - w)}$$

$$p_{t_f,t_0}(Q|w) = p_{t_0,t_f}(-Q|-w), \qquad p_{t_f,t_0}(Q|w) = \frac{p^{Q,w}_{t_f,t_0}(Q,w)}{p^{w}_{t_f,t_0}(w)}$$

Strong coupling: Quantum Treatment

Peter Hänggi, Michele Campisi, and Peter Talkner

$$H(t) = H_S(t) + H_{SB} + H_B$$

Fluctuation Theorem for the total system:

$$\frac{p_{t_f,t_0}(w)}{p_{t_0,t_f}(-w)} = \frac{Y(t_f)}{Y(t_i)} e^{\beta w}$$

where:

$$Y(t) = \mathrm{Tr} e^{-\beta(H_S(t)+H_{SB}+H_B)}$$

and

$$w = e_m(t_f) - e_n(t_0)$$

$e_n(t)$= instantaneous eigenvalues of total system

Free energy of a system strongly coupled to an environment

Peter Hänggi, Michele Campisi, and Peter Talkner

Thermodynamic argument:

$$F_S = F - F_B^0$$

F total system free energy
F_B bare bath free energy.

With this form of free energy the three laws of thermodynamics are fulfilled.

G.W. Ford, J.T. Lewis, R.F. O'Connell, Phys. Rev. Lett. **55**, 2273 (1985);
P. Hänggi, G.L. Ingold, P. Talkner, New J. Phys. **10**,115008 (2008);
G.L. Ingold, P. Hänggi, P. Talkner, Phys. Rev. E **79**, 0611505 (2009).

Partition function

$$Z_S(t) = \frac{Y(t)}{Z_B}$$

where $Z_B = \mathrm{Tr}_B e^{-\beta H_B}$

Main results

Peter Hänggi, Michele Campisi, and Peter Talkner

$$\frac{p_{t_f,t_0}(w)}{p_{t_0,t_f}(-w)} = e^{\beta w}\frac{Y(t_f)}{Y(t_0)} = e^{\beta w}\frac{Z_S(t_f)}{Z_S(t_0)} = e^{\beta(w-\Delta F_S)}$$

$$\langle e^{-\beta w}\rangle = e^{-\beta \Delta F_S}$$

Quantum Hamiltonian of Mean Force

$$Z_S(t) := \frac{Y(t)}{Z_B} = \mathrm{Tr}_S\, e^{-\beta H^*(t)}$$

where

$$H^*(t) := -\frac{1}{\beta} \ln \frac{\mathrm{Tr}_B\, e^{-\beta(H_S(t)+H_{SB}+H_B)}}{\mathrm{Tr}_B\, e^{-\beta H_B}}$$

also

$$\frac{e^{-\beta H^*(t)}}{Z_S(t)} = \frac{\mathrm{Tr}_B\, e^{-\beta H(t)}}{Y(t)}$$

M. Campisi, P. Talkner, P. Hänggi, Phys. Rev. Lett. **102**, 210401 (2009).

Strong coupling: Example

System: Two-level atom; "bath": Harmonic oscillator

$$H = \frac{\epsilon}{2}\sigma_z + \Omega\left(a^\dagger a + \frac{1}{2}\right) \quad + \chi\sigma_z\left(a^\dagger a + \frac{1}{2}\right)$$

$$H^* = \frac{\epsilon^*}{2}\sigma_z + \gamma$$

$$\epsilon^* = \epsilon + \chi + \frac{2}{\beta}\text{artanh}\left(\frac{e^{-\beta\Omega}\sinh(\beta\chi)}{1 - e^{-\beta\Omega}\cosh(\beta\chi)}\right)$$

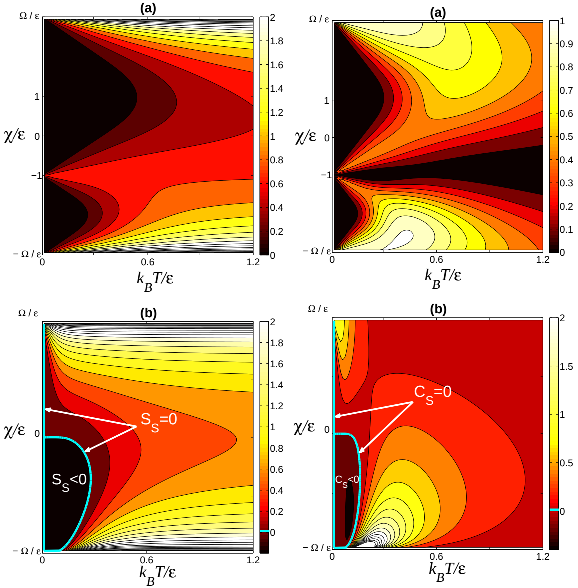
$$\gamma = \frac{1}{2\beta}\ln\left(\frac{1 - 2e^{-\beta\Omega}\cosh(\beta\chi) + e^{-2\beta\Omega}}{(1 - e^{-\beta\Omega})^2}\right)$$

$$Z_S = \text{Tr}e^{-\beta H^*} \quad F_S = -k_b T \ln Z_S$$

$$S_S = -\frac{\partial F_S}{\partial T} \quad C_S = T\frac{\partial S_S}{\partial T}$$

M. Campisi, P. Talkner, P. Hänggi, J. Phys. A: Math. Theor. **42** 392002 (2009)

Entropy and specific heat



$\Omega/\epsilon = 3$

$\Omega/\epsilon = 1/3$

Summary

- Correlation function expression of characteristic function of work valid for all initial states of a closed system.
- Work is not an oservable.
- Canonical initial states.
  - Quantum Crooks' fluctuation theorem.
  - Quantum Jarzynski's work theorem.
- Microcanonical state:
  - Crooks type theorem yields microcanonical entropy changes.
- Open Systems
  - Weak coupling: Fluctuation theorems for energy and heat and work and heat
  - Strong coupling: Fluctuation and work theorems

References

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