Transient quantum fluctuation relations

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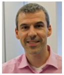
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Introduction

- Transient fluctuation relations by Jarzynski and Crooks
- Work
- Quantum work statistics and transient fluctuation relations
- Experimental verification and alternatives
- Open systems
- Summary

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Colloquium: Quantum fluctuation relations: Foundations and applications

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PERSPECTIVE | INSIGHT

The other QFT

Peter Hänggi and Peter Talkner

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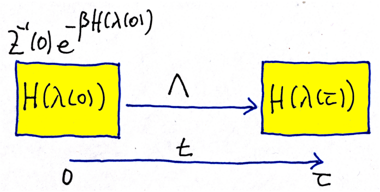
Jarzynski



$\Lambda = \{\lambda(t) | 0 \leq t \leq \tau\}$: protocol

w: Work performed on the system

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

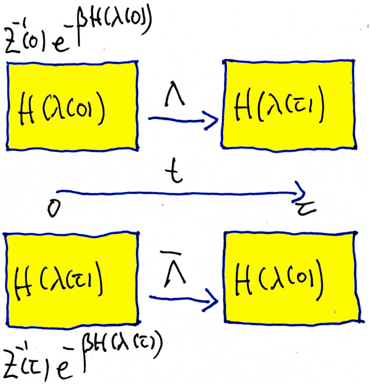
Jarzynski, PRL **78**, 2690 (1997).

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

$$\Delta F = F(\tau) - F(0), \quad F(t) = -\beta^{-1} \ln Z(t), \quad Z(t) = \mathrm{Tr} e^{-\beta H(\lambda(t))}$$

Jensen's inequality $\Longrightarrow$ $\langle w \rangle \geq \Delta F$ 2nd law

Crooks relation



$\Lambda = \{\lambda(t)|0 \leq t \leq \tau\}$ forward protocol

$\bar{\Lambda} = \{\epsilon_\lambda \lambda(\tau - t)|0 \leq t \leq \tau\}$ backward protocol

$$p_\Lambda(w) = e^{-\beta(\Delta F - w)} p_{\bar{\Lambda}}(-w)$$

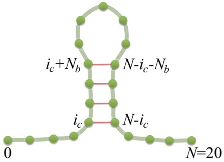
G.E. Crooks, PRE **60**, 2721 (1999)

$p_\Pi(w)$: pdf of work w during protocol $\Pi = \Lambda, \bar{\Lambda}$

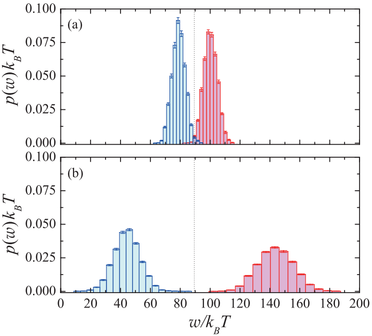
Crooks $\Rightarrow$ Jarzynski

Applications

Pulling macromolecules in order to determine free energy differencies between different confirmations: Liphardt et al., Science **296**, 1832 (2002); Collin et al., Nature **437**, 231 (2005); Douarche et al., Europhys. Lett. **70**, 593 (2005).



S. Kim, Y.W. Kim, P. Talkner, J.Yi, Phys. Rev. E **86**, 041130 (2012).



Jarzynski: $\Delta F = -\beta^{-1} \ln \langle e^{-\beta w} \rangle$
Crooks: $p_\Lambda(w) = e^{-\beta(\Delta F - w)} p_{\bar{\Lambda}}(-w) \;\Rightarrow p_\Lambda(w)$ and $p_{\bar{\Lambda}}(-w)$ cross at $w = \Delta F$

Work

Classical closed system:

$$\begin{aligned} w &= H(z(\tau), \lambda(\tau)) - H(z, \lambda(0)) \\ &= \int_0^\tau dt \frac{dH(z(t), \lambda(t))}{dt} \\ &= \int_0^\tau dt \frac{\partial H(z(t), \lambda(t))}{\partial \lambda} \dot{\lambda}(t) \end{aligned}$$

Note that a proper gauge must be used in order that the Hamiltonian yields the energy.

Work characterizes a process; it comprises information from states at distinct times. Hence it is not an observable.

The measurement of the quantum versions of power- and energy-based work definitions requires different strategies.

1. Two energy measurements:

One at the beginning, the other at the end of the protocol yield eigenvalues $e_n(0)$ and $e_m(\tau)$ of $H(\lambda(0))$ and $H(\lambda(\tau))$.

$$w^e = e_m(\tau) - e_n(0) \Longrightarrow \text{fluctuation theorems.}$$

2. Power-based work:

Requires a continuous measurement of power.

E.g. for $H(\lambda) = H_0 + \lambda Q$, a continuous observation of the generalized coordinate Q is required leading to a freezing of the systems dynamics in an eigenstate of Q.

$$w^p_N = \sum_{k=1}^{N} \dot{\lambda}(t_k) q_{\alpha_k} \frac{\tau}{N}\,, \quad Q = \sum_\alpha q_\alpha \Pi^Q_\alpha$$

Fluctuation theorems hold only if $[H_0, Q] = 0$ or equivalently $[H(\lambda(t)), H(\lambda(s))] = 0$ for all $t, s \in (0, \tau)$.

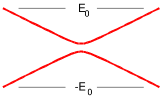
Hence the equivalence of the power- and energy-based work definitions for classical systems fails to hold in quantum mechanics.

Example: LANDAU-ZENER : $H(t) = \frac{vt}{2}\sigma_z + \Delta\sigma_x, \; -\tau/2 \le t \le \tau/2$

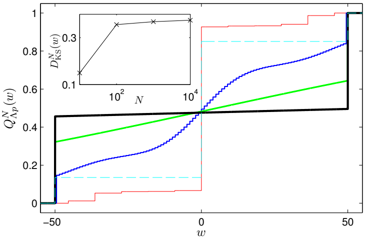
possible work-values:

$$\mathcal{W}^e = \{-E_0, 0, E_0\}, \; E_0 = \left((v\tau/2)^2 + \Delta^2\right)^{1/2}$$ energy-based

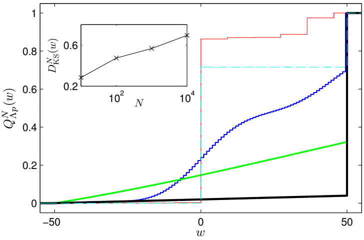
$$\mathcal{W}^p = \left\{\frac{v\tau}{2(N+1)}g, g = -N, -N+2, \ldots, N\right\}$$ power-based



$2\beta E_0 = 10^{-1}$



$2\beta E_0 = 10$



$v = 5\Delta^2/\hbar, \; \tau = 20\hbar/\Delta, \; N = 10, \; 10^2, \; 10^3, \; 10^4,$ energy based.

B.P. Venkatesh, G. Watanabe, P. Talkner, arXiv:1503.03228

Work pdf

$$p_\Lambda(w) = \sum_{n,m} \delta\big(w - e_m(\tau) + e_n(0)\big) P_\Lambda(m|n) p(n) \ : \qquad \text{work pdf}$$

$$P_\Lambda(m|n) = \mathrm{Tr} P_m(\tau) U(\Lambda) P_n(0) U^\dagger(\Lambda)/d_n(0) \qquad \text{transition prob.}$$

$$H(\lambda(t)) = \sum_n e_n(t) P_n(t), \quad d_n(t) = \mathrm{Tr} P_n(t)$$

$$p(n) = \mathrm{Tr} P_n(0)\rho(0) = d_n(0) e^{-\beta e_n(0)}/Z(0), \qquad \text{can. in. st.}$$

$$Z(0) = \sum_n d_n(0) e^{-\beta e_n(0)}$$

$$\Lambda = \{\lambda(t) | 0 \le t \le \tau\} \ : \qquad \text{protocol}$$

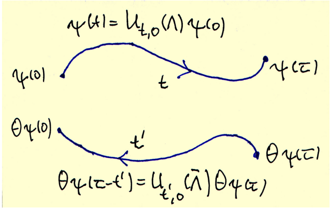
$$U(\Lambda) = U_{\tau,0}(\Lambda)\,, \quad i\hbar \frac{\partial}{\partial t} U_{t,s}(\Lambda) = H(\lambda(t)) U_{t,s}(\Lambda)\,, \quad U_{s,s}(\Lambda) = \mathbb{1}$$

J. Kurchan, arXiv:cond-mat/0007360.

H. Tasaki arXiv:cond-mat/0009244.

CROOKS RELATION, $p_\Lambda(w) = e^{-\beta(\Delta F - w)} p_{\bar\Lambda}(-w)$, follows from

(i) time-reversal invariance



$$H(\lambda(t)) = \theta H(\epsilon_\lambda \lambda(t))\theta^\dagger$$
$$\Longrightarrow$$
$$U_{s,t}(\Lambda) = U^\dagger_{t,s}(\Lambda) = \theta^\dagger U_{\tau-s,\tau-t}(\bar\Lambda)\theta$$

D. Andrieux, P. Gaspard, Phys. Rev. Lett. **100**, 230404. P. Talkner, M. Morillo, J. Yi, P. Hänggi, New J. Phys. 15, 095001 (2013).

$$P_\Lambda(m|n)d_n(\tau) = P_{\bar\Lambda}(n|m)d_m(0)\,,\ \text{generalized detailed balance}$$

(ii) Canonical initial states $\rho(t) = Z^{-1}(t)e^{-\beta H(\lambda(t))}$ for the forward $(t=0)$ and backward $(t=\tau)$ processes.

$$\sum_{m,n}\delta(w-e_m(\tau)+e_n(0))P_\Lambda(m|n)p_n(0) = \sum_{m,n}\delta(w-e_m(\tau)+e_n(0))$$
$$\times P_{\bar\Lambda}(m|n)p_m(\tau)\frac{p_n(0)}{p_m(\tau)}\,, \qquad \frac{p_n(0)}{p_m(\tau)} = e^{-\beta(\Delta F + e_n(0) - e_m(\tau))}$$

The Crooks relation implies the Jarzynski equality:

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

Both fluctuation theorems can be expressed in terms of the characteristic function

$$G_\Lambda(u) = \int dw e^{iuw} p_\Lambda(w)$$

$$Z(0) G_\Lambda(u) = Z(\tau) G_{\bar{\Lambda}}(-u + i\beta) \;:\quad \text{Crooks}$$

$$G_\Lambda(i\beta) = \langle e^{-\beta w} \rangle \;:\quad \text{Jarzynski}$$

P. Talkner, E. Lutz, P. Hänggi, Phys. Rev. E **75**, 050102 (2007);
P.Talkner, P. Hänggi, J. Phys. A **40**, F569 (2008).

Experiments

The classical fluctuation relations are experimentally confirmed for mechanical, electrical and molecular systems and are the basis of a method to determine free energy differences.

In quantum systems, projective energy measurements pose a severe problem.

Proposal of an experiment:

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

First experiment:

S. An et al. Nat. Phys. **11**, 193 (2015).

Alternative method avoiding projective measurements:

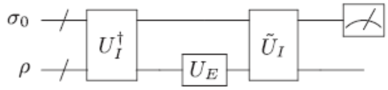
R. Dorner, S.R. Clark, L. Heaney, R. Fazio, J. Goold, V. Vedral, Phys. Rev. Lett. **110**, 230601 (2013); L. Mazzola, G. De Chiara, M. Paternostro, Phys. Rev. Lett. **110**, 230602 (2013); M. Campisi, R. Blattmann, S. Kohler, D. Zueco, P. Hänggi, New J. Phys. **15**, 105028 (2013).

Experimental confirmation:

T. Batalhão et al., Phys. Rev. Lett. **113**, 140601 (2014).

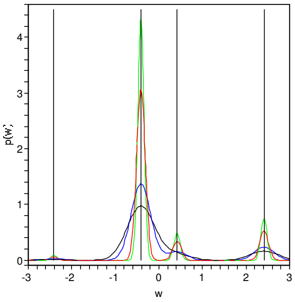
Single weak work measurement

G. De Chiara, A.J. Roncaglia, J.P. Paz, New J. Phys. **17**, 035004 (2015).



$$U_I = e^{i\kappa H_S(0)P},$$
$$\tilde{U}_I = e^{i\kappa H_S(\tau)P},$$
$$U_E \equiv U(\Lambda),\ \rho \equiv \rho(0)$$

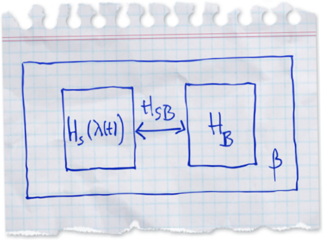
P momentum conjugate to the pointer position X.



$$p^X_\Lambda(x) = \sum_{m,n} \sigma_0(x - \hbar\kappa w_{m,n}) P_\Lambda(m|n) p_n$$
$$+ \underbrace{\text{correction term}}_{=0 \text{ if } [\rho(0), H(\lambda(0))]=0}$$

$\sigma_0(x) = \langle x|\sigma_0|x\rangle$ diagonal element of the initial pointer state wrt to the pointer-position basis. Gaussian with different variances.

Open systems



$$H_{\text{tot}}(\lambda(t)) = H_S(\lambda(t)) + H_B + H_{SB}$$

initial states:

$$\rho_{\text{tot}}(t) = Z_{\text{tot}}^{-1}(t)e^{-\beta H_{\text{tot}}(\lambda(t))}$$

$$Z_{\text{tot}}(t) = \text{Tr}e^{-\beta H_{\text{tot}}(\lambda(t))}, \quad t = 0, \tau$$

$$p_\Lambda(w) = e^{-\beta \Delta F_{\text{tot}} - w} p_{\bar{\Lambda}}(-w)$$

w = work done on the total system = work done on S

$$\Delta F_{\text{tot}} = \underbrace{F_{\text{tot}}(\tau)}_{F_S(\tau)+F_B} - \underbrace{F_{\text{tot}}(0)}_{F_S(0)+F_B} = \underbrace{\Delta F_S}_{F_S(\tau)-F_S(0)}$$

C. Jarzynski, J. Stat. Mech. P09005 (2004);

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

Statistical mechanics of an open system is based on the Hamiltonian of mean force:

$$e^{-\beta H^*} = \frac{\mathrm{Tr}_B e^{-\beta H_{\mathrm{tot}}}}{Z_B}$$
$$Z_B = \mathrm{Tr} e^{-\beta H_B}$$

H^* in general is different from H_S; it yields the reduced density matrix:

$$\rho_S = Z_S^{-1} e^{-\beta H^*}$$
$$Z_S = \mathrm{Tr}_S e^{-\beta H^*}$$
$$= Z_{\mathrm{tot}}/Z_B$$

with $F_S = -\beta^{-1} \ln Z_s$ one obtains

$$F_S = F_{\mathrm{tot}} - F_B$$

G.W. Ford, J.T. Lewis, R.F. OConnell, Ann. Phys. (N.Y.) **185**, 270 (1988);
P. Hänggi, G.-L. Ingold, P. Talkner, New J. Phys. **10**, 115008 (2008).

Weak coupling

$$H_{\mathrm{tot}}(\lambda(t)) = H_S(\lambda(t)) + H_B + H_{SB}$$

In the weak coupling limit the interaction Hamiltonian H_{SB} is vanishingly small of the order ϵ. $\langle H_{SB} \rangle_B = 0$ (without loss of generality) $\Longrightarrow$

$$Z_{\mathrm{tot}}(t) = Z_S^0(t) Z_B (1 + \mathcal{O}(\epsilon^2))$$

Change of internal energy, ΔE and exchanged heat Q can be expressed in terms of the eigenvalues $e_i^S(t)$ and e_α^B of $H_S(\lambda(t))$ and H_B as

$$\Delta E = e_{i'}^S(\tau) - e_i^S(0)$$
$$Q = e_i^B - e_{i'}^B$$

$$w = \Delta E + Q + \mathcal{O}(\epsilon^2)$$

$H_S(t)$ and H_B can be simultaneously measured, hence there is a joint probability $p_\Lambda^{\Delta E,Q}(\Delta E, Q)$ for ΔE and Q and consequently also one for W and Q, $p_\Lambda^{w,Q}(e,Q)$, satisfying

$$p_\Lambda^{w,Q}(w,Q) = e^{-\beta(\Delta F_S - w)} p_{\bar\Lambda}^{w,Q}(-w,-Q)$$

implying for the marginal $p_\Lambda(w) = \int dQ p_\Lambda^{w,Q}(w,Q)$

$$p_\Lambda(w) = e^{-\beta(\Delta F_S - w)} p_{\bar\Lambda}(-w)$$

Neither for ΔE nor for Q analogous relations do exist. Rather one obtains PROTOCOL DEPENDENT correction factors:

$$p_\Lambda^E(E) = e^{-\beta(\Delta F_S - E)} \int dQ e^{\beta Q} \frac{P_{\bar\Lambda}(-E,Q)}{p_{\bar\Lambda}^E(-E)} p_{\bar\Lambda}^E(-E)$$

$$p_\Lambda^E(E) = \int dQ p_\Lambda^{E,Q}(E,Q)$$

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

Conclusions

- Two energy measurements for obtaining work $= e_m(\tau) - e_n(0)$.
- Closed system starting from canonical initial state undergoing time-reversal Hamiltonian dynamics $\Rightarrow$ fluctuation relations.
  canonical initial state $\Rightarrow$ free energy change;
  micro-canonical initial state $\Rightarrow$ entropy change;
  P. Talkner, P. Hänggi, M. Morillo, Phys. Rev. E **77**, 051131 (2008);
  P. Talkner, M. Morillo, J. Yi, P. Hänggi, New J. Phys. **15**, 095001 (2013).
  grand-canonical initial state $\Rightarrow$ grand potential change.
  J. Yi, Y.W. Kim, P. Talkner, Phys. Rev. E **85**, 051107
- In general, other than projective energy measurements (generalized or weak) don't give fluctuation relations.
  Measurement of power also does not lead to fluctuation relations for quantum mechanical systems.

Conclusions (cont.)

- Single generalized measurements of work a la Paz allow one to reconstruct the two-energy-measurement based work distribution.
- Fluctuation relations hold for general open systems, independent of the coupling strength between system and environment. Only requirement is canonical initial state and time-reversal Hamiltonian dynamics of the total system.
- For open systems coupling weakly to the environment the joint distribution of work and heat exists but not for heat alone, nor for the internal energy only.