Quantum Fluctuation Relations and the Arrow of Time

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M. Campisi, P. Hänggi, and P. Talkner
Colloquium: Quantum fluctuation relations: Foundations and applications
Rev. Mod. Phys. **83**, 771–791 (2011);
Addendum and Erratum: Quantum fluctuation relations: Foundations and applications
Rev. Mod. Phys. **83**, 1653 (2011).

M. Campisi and P. Hänggi
Fluctuation, Dissipation and the Arrow of Time
Entropy **13**, 2024–2035 (2012).

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The famous Laws

Equilibrium Principle -- minus first Law

An isolated, macroscopic system which is placed in an arbitrary initial state within a finite fixed volume will attain a unique state of equilibrium.

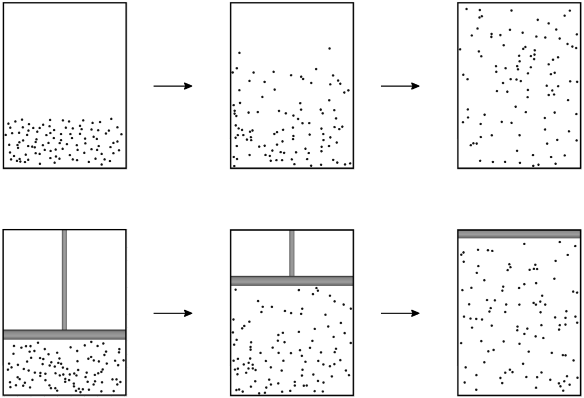
Second Law (Clausius)

For a non-quasi-static process occurring in a thermally isolated system, the entropy change between two equilibrium states is non-negative.

Second Law (Kelvin)

No work can be extracted from a closed equilibrium system during a cyclic variation of a parameter by an external source.

MINUS FIRST LAW vs. SECOND LAW



-1st Law

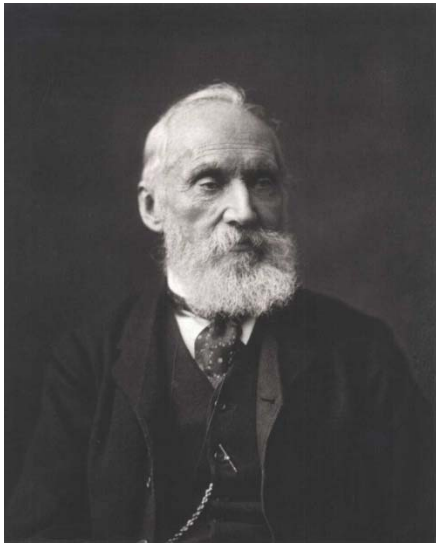
2nd Law

Second Law

Rudolf Julius Emanuel Clausius
(1822 – 1888)

Heat generally cannot spontaneously flow from a material at lower temperature to a material at higher temperature.

$$\delta Q = T\mathrm{d}S \quad (\text{Zürich, } 1865)$$

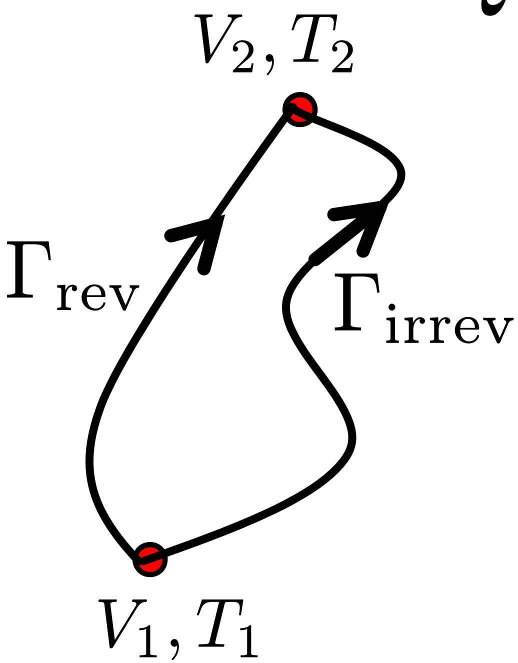


William Thomson alias Lord Kelvin
(1824 – 1907)

No cyclic process exists whose sole effect is to extract heat from a single heat bath at temperature T and convert it entirely to work.

Entropy S – content of *transformation* „Verwandlungswert“

$$d\,S = \delta Q^{\mathrm{rev}}/T\,; \quad \delta Q^{\mathrm{irrev}} < \delta Q^{\mathrm{rev}}$$



$$\oint_C \frac{\delta Q}{T} \leq 0$$

$$C = \Gamma_{\mathrm{rev}}^{-1} + \Gamma_{\mathrm{irrev}}$$

$$\left.\begin{aligned} S(V_2,T_2) - S(V_1,T_1) &\geq \int_{\Gamma_{\mathrm{irrev}}} \frac{\delta Q}{T} \\ S(V_2,T_2) - S(V_1,T_1) &= \int_{\Gamma_{\mathrm{rev}}} \frac{\delta Q}{T} \end{aligned}\right\} \quad \frac{\partial S}{\partial t} \geq 0 \quad \textbf{NO !}$$

What are fluctuation and work theorems about?

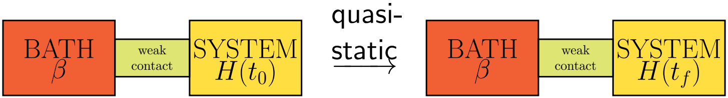
Small systems: fluctuations may become comparable to average quantities.

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

Equilibrium versus nonequilibrium processes

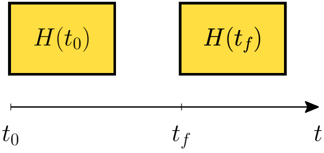
Isothermal quasistatic process:

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

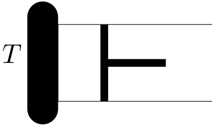


$$\Delta F = w = \langle w \rangle$$

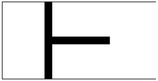
Non-equilibrium process:



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

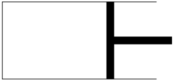


$$H = H(\mathbf{z}, \lambda_t)$$



λ_0

eq.



λ_τ

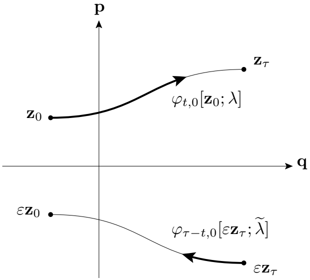
non-eq

$$\rho_0(\mathbf{z}) = \frac{e^{-\beta H(\mathbf{z}, \lambda_0)}}{Z(\lambda_0)} \qquad \rho_\tau(\mathbf{z}) \neq \frac{e^{-\beta H(\mathbf{z}, \lambda_\tau)}}{Z(\lambda_\tau)}$$

$\lambda : [0, \tau] \to R$ protocol

$t \to \lambda_t$

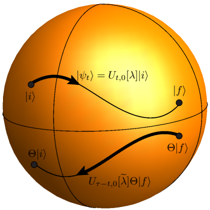
MICROREVERSIBILITY OF TIME DEPENDENT SYSTEMS



Classical

$$\varepsilon(\mathbf{q},\mathbf{p}) = (\mathbf{q},-\mathbf{p})$$

$$\varepsilon\varphi_{t,0}[\mathbf{z}_0;\lambda] = \varphi_{\tau-t,0}[\varepsilon\mathbf{z}_\tau;\widetilde{\lambda}]$$

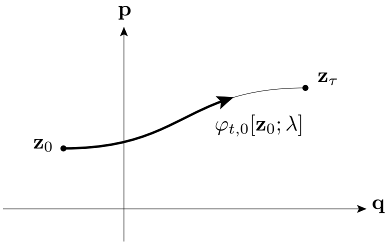


Quantum

$\Theta =$ Time reversal operator

$$U_{t,\tau}[\lambda] = \Theta^\dagger U_{\tau-t,0}[\widetilde{\lambda}]\Theta$$

CLASSICAL WORK



$$W[\mathbf{z}_0;\lambda] = H(\mathbf{z}_\tau,\lambda_\tau) - H(\mathbf{z}_0,\lambda_0) = \int \mathrm{d}t\,\dot{\lambda}_t \frac{\partial H(\varphi_{t,0}[\mathbf{z}_0;\lambda],\lambda_t)}{\partial \lambda_t}$$

$$p[W;\lambda] = \int \mathrm{d}\mathbf{z}_0 \rho_0(\mathbf{z}_0)\delta[W - H(\mathbf{z}_\tau,\lambda_\tau) + H(\mathbf{z}_0,\lambda_0)]$$

Work is a RANDOM quantity

JARZYNSKI EQUALITY

C. Jarzynski, PRL 78 2690 (1997)

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

$$\Delta F = F(\lambda_\tau) - F(\lambda_0) = -\beta^{-1} \ln \frac{Z(\lambda_\tau)}{Z(\lambda_0)}$$

$$Z(\lambda_t) = \int \mathrm{d}\mathbf{z}\, e^{-\beta H(\mathbf{z}, \lambda_t)}$$

Since exp is convex, then

$$\langle W \rangle \geq \Delta F \qquad \text{Second Law}$$

INCLUSIVE VS. EXCLUSIVE VIEWPOINT

C. Jarzynski, C.R. Phys. 8 495 (2007)

$$H(\mathbf{z}, \lambda_t) = H_0(\mathbf{z}) - \lambda_t Q(\mathbf{z})$$

$$\begin{aligned} W &= -\int dt Q_t \dot{\lambda}_t \\ &= H(\mathbf{z}_\tau, \lambda_\tau) - H(\mathbf{z}_0, \lambda_0) \end{aligned}$$

Not necessarily of the textbook form $\int \mathrm{d}(\text{displ.}) \times$ (force)

$$\begin{aligned} W_0 &= \int dt \lambda_t \dot{Q}_t \\ &= H_0(\mathbf{z}_\tau) - H_0(\mathbf{z}_0) \end{aligned} \qquad \dot{\mathbf{z}}_t = \{H(\mathbf{z}_t, \lambda_t); \mathbf{z}\}$$

G.N. Bochkov and Yu. E. Kuzovlev JETP **45**, 125 (1977)

Canonical initial state

Exclusive Work:

$$\boxed{\begin{array}{ll} \dfrac{p[w_0;\lambda]}{p[-w_0;\widetilde{\lambda}]} = e^{\beta w_0} & \text{Bochkov-Kuzovlev-Crooks} \\ \langle e^{-\beta w_0}\rangle = 1 & \text{Bochkov-Kuzovlev} \end{array}}$$

G.N. Bochkov, Y.E. Kuzovlev, Sov. Phys. JETP **45**, 125 (1977);
G.N. Bochkov, Y.E. Kuzovlev, Physica A **106**, 443 (1981)

INCLUSIVE, EXCLUSIVE and DISSIPATED WORK

$$W_{diss} = W - \Delta F \qquad \langle e^{-\beta W_{diss}} \rangle = 1$$

W, W_0, W_{diss} are DISTINCT stochastic quantities

$$p[x;\lambda] \neq p_0[x;\lambda] \neq p_{diss}[x;\lambda]$$

They coincide for cyclic protocols $\lambda_0 = \lambda_\tau$

M.Campisi, P. Talkner and P. Hänggi, Phil. Trans. R. Soc. A **369**, 291 (2011)

GAUGE FREEDOM

$$\begin{aligned} H'(\mathbf{z},t) &= H(\mathbf{z},t) + g(t) \\ W' &= W + g(\tau) - g(0) \\ \Delta F' &= \Delta F + g(\tau) - g(0) \end{aligned}$$

$W, \Delta F$ are gauge dependent: **not true physical quantities**

WARNING: be consistent! use same gauge to calculate W and ΔF

$$\langle e^{-\beta W'} \rangle = e^{-\beta \Delta F'} \iff \langle e^{-\beta W} \rangle = e^{-\beta \Delta F}$$

The fluctuation theorem is gauge invariant !

Gauge: irrelevant for dynamics
crucial for ENERGY-HAMILTONIAN connection

GAUGE FREE vs. GAUGE DEPENDENT EXPRESSIONS OF CLASSICAL WORK

$$H' = H_0(\mathbf{z}) - \lambda_t Q(\mathbf{z}) + g(t)$$

Inclusive work:

$$\begin{aligned} W' &= H'(\mathbf{z}_\tau, \tau) - H'(\mathbf{z}_0, 0) \quad , \quad g\text{-dependent} \\ W^{\mathrm{phys}} &= -\int \mathrm{d}t Q_t \dot{\lambda}_t \quad , \quad g\text{-independent} \\ W^{\mathrm{phys}} &= W' - g(\tau) + g(0) \end{aligned}$$

Exclusive work:

$$\begin{aligned} W_0 &= H_0(\mathbf{z}_\tau, \lambda_\tau) - H_0(\mathbf{z}_0, \lambda_0) \\ &= \int \mathrm{d}t \lambda_t \dot{Q}_t \quad , \quad g\text{-independent} \end{aligned}$$

Dissipated work:

$$W_{\mathrm{diss}} = H'(\mathbf{z}_\tau, \tau) - H'(\mathbf{z}_0, 0) - \Delta F' \, , \quad \text{g-independent}$$

QUANTUM WORK FLUCTUATION RELATIONS

$$H(\mathbf{z}, \lambda_t) \longrightarrow \mathcal{H}(\lambda_t)$$

$$\rho(\mathbf{z}, \lambda_t) \longrightarrow \varrho(\lambda_t) = \frac{e^{-\beta\mathcal{H}(\lambda_t)}}{\mathcal{Z}(\lambda_t)}$$

$$Z(\lambda_t) \longrightarrow \mathcal{Z}(\lambda_t) = \mathrm{Tr} e^{-\beta\mathcal{H}(\lambda_t)}$$

$$\varphi_{t,0}[\mathbf{z}_0; \lambda] \longrightarrow U_{t,0}[\lambda] = \mathcal{T} \exp\left[-\frac{i}{\hbar}\int_0^t ds \mathcal{H}(\lambda_s)\right]$$

$$W[\mathbf{z}_0; \lambda] \longrightarrow ?$$

$$
\begin{aligned}
\mathcal{W}[\lambda] &= U_{t,0}^{\dagger}[\lambda]\mathcal{H}(\lambda_t)U_{t,0}[\lambda] - \mathcal{H}(\lambda_0) \\
&= \mathcal{H}_t^H(\lambda_t) - \mathcal{H}(\lambda_0) \\
&= \int_0^t \mathrm{d}t\dot{\lambda}_t \frac{\partial \mathcal{H}_t^H(\lambda_t)}{\partial \lambda_t}
\end{aligned}
$$

WORK IS NOT AN OBSERVABLE

P. Talkner et al. PRE 75 050102 (2007)

Work characterizes PROCESSES, not states!
(δW is not exact)

Work cannot be represented by a Hermitean operator $\mathcal{W}$

$W[\mathbf{z}_0; \lambda] \longrightarrow w = E_m^{\lambda_\tau} - E_n^{\lambda_0}$ two-measurements

$E_n^{\lambda_t}$ =instantaneous eigenvalue: $\mathcal{H}(\lambda_t)|\psi_n^{\lambda_t}\rangle = E_n^{\lambda_t}|\psi_n^{\lambda_t}\rangle$

Probability of inclusive quantum work

recall: $H(\lambda_t)\varphi_{n,\nu}(\lambda_t) = e_n(\lambda_t)\varphi_{n,\nu}(\lambda_t)$,
$P_n(t) = \sum_\nu |\varphi_{n,\nu}(\lambda_t)\rangle\langle\varphi_{n,\nu}(\lambda_t)|$

1st measurement of energy: $e_n(\lambda_0)$ with prob $p_n = \mathrm{Tr}\, P_n(t_0)\rho(t_0)$,
state after measurement: $\rho_n = P_n(t_0)\rho(t_0)P_n(t_0)/p_n$

$t_0 \to t_f$:
$\rho_n(t_f) = U_{t_f,t_0}\rho_n U^\dagger_{t_f,t_0}, \quad i\hbar\partial U_{t,t_0}/\partial t = H(\lambda_t)U_{t,t_0}, \quad U_{t_0,t_0} = 1$

2nd measurement of energy: $e_m(t_f)$ with prob.
$p(m|n) = \mathrm{Tr}\, P_m(t_f)\rho_n(t_f)$

$$\boxed{p_{t_f,t_0}(w) = \sum_{n,m} \delta(w - [e_m(\lambda_\tau) - e_n(\lambda_0)])p(m|n)p_n}$$

Characteristic function of work

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

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

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

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)

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)

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

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

Microcanonical initial state

$$\rho(t_0) = \omega_E^{-1}(t_0)\delta(H(t_0) - E),$$

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

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

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

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

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

PROBLEM

Projective quantum measurement of:

$\Delta E =$TOTAL energy
$\Delta N =$ TOTAL number of particles

in MACROSCOPIC systems !!!

Measurements

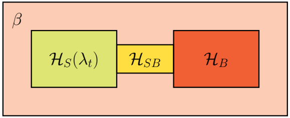
A projective measurement of an observable $A = \sum_i a_i P_i^A$, $P_i^A P_j^A = \delta_{i,j} P_i^A$:

$$\rho \longrightarrow \sum_i P_i^A \rho P_i^A$$

while a force protocol is running leads to a change of the statistics of work but leaves unchanged the Crooks relation and the Jarzyninski equality.

M. Campisi, P. Talkner, P. Hänggi, Phys. Rev. Lett. **105**, 140601 (2010);
M. Campisi, P. Talkner, P. Hänggi, Phys. Rev. E **83**, 041114, (2011).

OPEN QUANTUM SYSTEM: WEAK COUPLING



$$\mathcal{H}(\lambda_t) = \mathcal{H}_S(\lambda_t) + \mathcal{H}_B + \mathcal{H}_{SB}$$

$$\varrho(\lambda_0) = e^{-\beta\mathcal{H}(\lambda_0)}/Y(\lambda_0)$$

$$\Delta E = E_m^{\lambda_\tau} - E_n^{\lambda_0} \qquad \text{system energy change}$$

$$\Delta E^B = E_\mu^B - E_\nu^B = -Q \qquad \text{bath energy change}$$

$$p[\Delta E, Q; \lambda] = \sum_{m,n,\mu,\nu} \delta[\Delta E - E_m^{\lambda_\tau} + E_n^{\lambda_0}]\delta[Q + E_\mu^B - E_\nu^B] p_{m\mu|n\nu}[\lambda] p_{n\nu}^0$$

$$\frac{p[\Delta E, Q; \lambda]}{p[-\Delta E, -Q; \widetilde{\lambda}]} = e^{\beta(\Delta E - Q - \Delta F_S)} \qquad \Delta F_S = -\beta^{-1} \ln \frac{\mathcal{Z}_S(\lambda_\tau)}{\mathcal{Z}_S(\lambda_0)}$$

$$\Delta E = w + Q \qquad \frac{p[w, Q; \lambda]}{p[-w, -Q; \widetilde{\lambda}]} = e^{\beta(w - \Delta F_S)}$$

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

Strong coupling: Quantum Treatment

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

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:

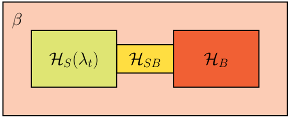
$$Y(t) = \mathrm{Tr} e^{-\beta(H_S(t)+H_{SB}+H_B)}$$

and

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

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

OPEN QUANTUM SYSTEM: STRONG COUPLING



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

$$w = \mathcal{E}_m^{\lambda_\tau} - \mathcal{E}_n^{\lambda_0} = \text{work on total system=work on } \mathcal{S}$$

$$Y(\lambda_t) = \mathrm{Tr} e^{-\beta H(\lambda_t)} = \text{partition function of total system}$$

$$\mathcal{Z}_S(\lambda_t) = \frac{Y(\lambda_t)}{\mathcal{Z}_B} \neq \mathrm{Tr}_S e^{-\beta \mathcal{H}_S(\lambda_t)} = \text{partition function of } \mathcal{S}$$

$$F_S(\lambda_t) = -\beta^{-1} \ln \mathcal{Z}_S(\lambda_t) \text{ proper free energy of open system}$$

$$\frac{p[w;\lambda]}{p[-w;\widetilde{\lambda}]} = \frac{Y(\lambda_\tau)}{Y(\lambda_0)} e^{\beta w} = \frac{\mathcal{Z}(\lambda_\tau)}{\mathcal{Z}(\lambda_0)} e^{\beta w} = e^{\beta(w - \Delta F_S)}$$

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

Partition function

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

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

Free energy of a system strongly coupled to an environment

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).

An important difference

Route I

$$E \doteq E_\mathrm{S} = \langle H_\mathrm{S} \rangle = \frac{\mathrm{Tr}_{\mathrm{S+B}}(H_\mathrm{S} \mathrm{e}^{-\beta H})}{\mathrm{Tr}_{\mathrm{S+B}}(\mathrm{e}^{-\beta H})}$$

Route II

$$\mathcal{Z} = \frac{\mathrm{Tr}_{\mathrm{S+B}}(\mathrm{e}^{-\beta H})}{\mathrm{Tr}_\mathrm{B}(\mathrm{e}^{-\beta H_\mathrm{B}})} \qquad U = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}$$

$$\begin{aligned} \Rightarrow U &= \langle H \rangle - \langle H_\mathrm{B} \rangle_\mathrm{B} \\ &= E_\mathrm{S} + \left[\langle H_{\mathrm{SB}} \rangle + \boxed{\langle H_\mathrm{B} \rangle - \langle H_\mathrm{B} \rangle_\mathrm{B}} \right] \end{aligned}$$

For finite coupling E and U differ!

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).

ARROW OF TIME

$$+ : \text{movie in forward direction}$$

$$- : \text{movie in backward direction}$$

frame "t": λ_t and Q_t

Forward: $\beta W_0 \gg 1$

Backward: $\beta W_0 \ll -1$ (W_0 is odd under time reversal!)

Prior: $P(+) = 1/2; \quad P(-) = 1/2$

After Seeing movie

$$\text{Posterior:} \quad P(+|W_0) = \frac{P(W_0|+)P(+)}{P(W_0)} =$$

$$= \frac{P(W_0|+)P(+)}{P(W_0|+)P(+) + P(W_0|-)P(-)}$$

USING EXCLUSIVE WORK

$$H(\mathbf{q},\mathbf{p};\lambda_t) = H_0(\mathbf{q},\mathbf{p}) - \lambda_t Q(\mathbf{q},\mathbf{p})$$

$\lambda_t = 0$ at $t = 0$; Protocol: $\lambda_t : 0 \to t = \tau$

$$\varrho_0(\mathbf{q},\mathbf{p}) = e^{-\beta H_0(\mathbf{q},\mathbf{p})}/Z_0(\beta)$$

$\Longrightarrow$ F.-T. $\boxed{P[\Gamma,\lambda] = P[\widetilde{\Gamma},\widetilde{\lambda}]e^{\beta W_0}}$ B.-K. (1977)

$$W_0 = \int_0^\tau dt \lambda_t \dot{Q}_t \qquad \widetilde{\lambda}_t = \lambda_{\tau-t}$$

$\Longrightarrow$ $\boxed{\langle e^{-\beta W_0}\rangle_\lambda = 1}$ "equality" (2$^{\text{nd}}$ Law)

with $\langle \exp(x)\rangle \geq \exp(\langle x\rangle)$

$\Longrightarrow$ $\langle e^{-\beta W_0}\rangle_\lambda \geq e^{\langle -\beta W_0\rangle_\lambda}$ $\Longrightarrow$ $0 \geq -\beta\langle W_0\rangle_\lambda$

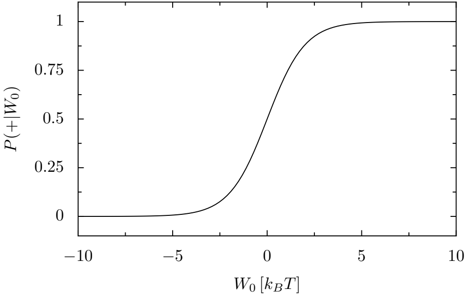
$\boxed{\langle W_0\rangle_\lambda \geq 0}$ "inequality"

ARROW OF TIME

$$\text{F.-T.:} \qquad \frac{P(W_0|+)}{P(W_0|-)} = \exp(\beta W_0)$$

$$W_0 \text{ Odd:} \qquad P(-W_0|-) = P(W_0|+)$$

$$\Longrightarrow \boxed{P(+|W_0) = \frac{1}{e^{-\beta W_0} + 1}}$$



ARROW OF TIME

1) $H_0(\mathbf{q}, \mathbf{p}) \longrightarrow H(\mathbf{q}, \mathbf{p}; t)$: „emergence of an arrow“

2) preparation, here canonical $\Longrightarrow$ „determines its direction“

conventional :

- coarse graining of quantities <-> breaking det.-balance
- Stoßzahlansatz
- initial molecular chaos (Bogoliubov)
- Fokker-Planck eqs.; master eqs.

All contain ad hoc elements that induce the time arrow : „future“ $\neq$ „past“

Summary

- Classical and quantum mechanical expressions for the distribution of work for arbitrary initial states
- The characteristic function of work is given by a correlation function
- Work is not an observable.
- Fluctuation theorems (Crooks and Jarzynski) for thermal equilibrium states and microscopic reversibility
- Open Systems
  - Strong coupling: Fluctuation and work theorems
  - Weak coupling: Fluctuation theorems for energy and heat as well as work and heat
- Measurements do not affect Crooks relation and Jarzynski equality

References

P. Talkner, E. Lutz, P. Hänggi, Phys. Rev. E, **75**, 050102(R) (2007).
P. Talkner, P. Hänggi, J Phys. A **40**, F569 (2007).
P. Talkner, P. Hänggi, M. Morillo, Phys. Rev. E **77**, 051131 (2008).
P. Talkner, P.S. Burada, P. Hänggi, Phys. Rev. E **78**, 011115 (2008).
P. Hänggi, G.-L. Ingold, P. Talkner, New J. Phys. **10**, 115008 (2008).
P. Talkner, M. Campisi, P. Hänggi, J. Stat. Mech., P02025 (2009).
G.-L. Ingold, P. Talkner, P. Hänggi, Phys. Rev. E **79**, 0611505 (2009).
M. Campisi, P. Talkner, P. Hänggi, Phys. Rev. Lett. **102**, 210401 (2009).
M. Campisi, P. Talkner, P. Hänggi, J. Phys. A **42**, F392002 (2009).
M. Campisi, D. Zueco, P. Talkner, Chem. Phys. **375**, 187 (2010).
M. Campisi, P. Talkner, P. Hänggi, Phil. Trans. Roy. Soc. **369**, 291 (2011).
M. Campisi, P. Talkner, P. Hänggi, Phys. Rev. Lett. **105**, 140601 (2010).
M. Campisi, P. Hänggi, P. Talkner, Rev. Mod. Phys. **83**, 771 (2011).
M. Campisi, P. Talkner, P. Hänggi, Phys. Rev. E, **83**, 041114 (2011).
J. Yi, P. Talkner, Phys. Rev. E **83**, 41119 (2011).
J. Yi, P. Talkner, M. Campisi, Phys. Rev. E, **84**, 011138 (2011).

Erratum: *Colloquium*: Quantum fluctuation relations: Foundations and applications [Rev. Mod. Phys. 83, 771 (2011)]

Michele Campisi, Peter Hänggi, and Peter Talkner

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The first line of Eq. (51) contains some typos: it correctly reads

$$G[u;\lambda] = \mathrm{Tr}\,\mathcal{T}\, e^{iu[\mathcal{H}^H_\tau(\lambda_\tau)-\mathcal{H}(\lambda_0)]}e^{-\beta\mathcal{H}(\lambda_0)}/Z(\lambda_0). \tag{51}$$

This compares with its classical analog, i.e., the second line of Eq. (27).

Quite surprisingly, notwithstanding the identity

$$\mathcal{H}^H_\tau(\lambda_\tau) - \mathcal{H}(\lambda_0) = \int_0^\tau dt\,\dot{\lambda}_t \frac{\partial \mathcal{H}^H_t(\lambda_t)}{\partial \lambda_t}, \tag{1}$$

one finds that generally

$$\mathcal{T}\, e^{iu[\mathcal{H}^H_\tau(\lambda_\tau)-\mathcal{H}(\lambda_0)]} \neq \mathcal{T}\exp\left[iu\int_0^\tau dt\,\dot{\lambda}_t \frac{\partial \mathcal{H}^H_t(\lambda_t)}{\partial \lambda_t}\right]. \tag{2}$$

¡WRONG!

As a consequence, it is not allowed to replace $\mathcal{H}^H_\tau(\lambda_\tau) - \mathcal{H}(\lambda_0)$, with $\int_0^\tau dt\dot{\lambda}_t \partial\mathcal{H}^H_t(\lambda_t)/\partial\lambda_t$ in Eq. (51). Thus, there is no quantum analog of the classical expression in the third line of Eq. (27). This is yet another indication that "work is not an observable" (Talkner, Lutz, and Hänggi, 2007)). This observation also corrects the second line of Eq. (4) of the original reference (Talkner, Lutz, and Hänggi, 2007).

The correct expression is obtained from the general formula

$$\mathcal{T}\exp[A(\tau) - A(0)] = \mathcal{T}\exp\left[\int_0^\tau dt\left(\frac{d}{dt}e^{A(t)}\right)e^{-A(t)}\right], \tag{3}$$

where $A(t)$ is any time dependent operator [in our case $A(t) = iu\mathcal{H}^H_t(\lambda_t)$]. Equation (3) can be proved by demonstrating that the operator expressions on either side of Eq. (3) obey the same differential equation with the identity operator as the initial condition. This can be accomplished by using the operator identity $de^{A(t)}/dt = \int_0^1 ds e^{sA(t)}\dot{A}(t)e^{(1-s)A(t)}$.

There are also a few minor misprints: (i) The symbol ds in the integral appearing in the first line of Eq. (55) should read dt. (ii) The correct year of the reference (Morikuni and Tasaki, 2010) is 2011 (not 2010).

The authors are grateful to Professor Yu. E. Kuzovlev for providing them with this insight, and for pointing out the error in the second line of Eq. (51).

REFERENCES

Talkner P., E. Lutz, and P. Hänggi, 2007, Phys. Rev. E **75**, 050102(R).

Definition of work

A. **Classical**:

$$w^{\text{in}} = \int_{t_0}^{\tau} dt\, \frac{dH(z(t), \lambda_t)}{dt} = H(z(t_f), \lambda_\tau) - H(z(t_0), \lambda_0) \quad \text{inclusive}$$

$$w^{\text{ex}} = \int_{t_0}^{\tau} dt\, \frac{dH(z(t), \lambda_0)}{dt} = H(z(t_f), \lambda_0) - H(z(t_0), \lambda_0) \quad \text{exclusive}$$

$z(t) \equiv z(t, z)$: Trajectory in phase space: $\dot{z} = \{H(z, \lambda_t), z\}$
$z \equiv z(t_0)$: Starting point taken from $Z^{-1}(t_0) e^{-\beta H(\lambda_0)}$

for $H(z, \lambda_t) = H_0(z) - \lambda_t Q(z)$:

$$w^{\text{in}} = -\int_{t_0}^{\tau} dt\, Q(z(t)) \dot{\lambda}_t$$

$$w^{\text{ex}} = \int_{t_0}^{\tau} dt\, \dot{Q}(z(t)) \lambda_t$$

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INCLUSIVE VS. EXCLUSIVE VIEWPOINT

C. Jarzynski, C.R. Phys. **8** 495 (2007)

$$H(\mathbf{z}, \lambda_t) = H_0(\mathbf{z}) - \lambda_t Q(\mathbf{z})$$

$$\begin{aligned} W &= H(\mathbf{z}_\tau, \lambda_\tau) - H(\mathbf{z}_0, \lambda_0) \\ &= -\int dt Q_t \dot{\lambda}_t \end{aligned}$$

$$\begin{aligned} W_0 &= H_0(\mathbf{z}_\tau) - H_0(\mathbf{z}_0) \\ &= \int dt \lambda_t \dot{Q}_t \quad \Rightarrow \quad \langle e^{-\beta W_0} \rangle = 1 \end{aligned}$$

G.N. Bochkov and Yu. E. Kuzovlev JETP **45**, 125 (1977)

Strong coupling: Example

System: Two-level atom; “bath”: Harmonic oscillator

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

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

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

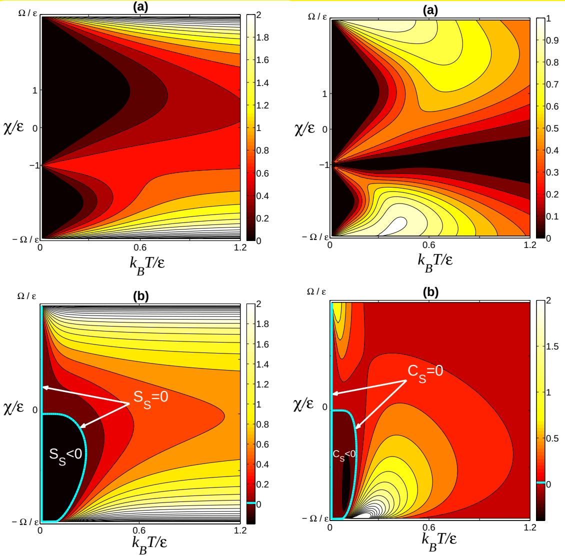
$$\gamma = \frac{1}{2\beta}\ln\left(\frac{1 - 2e^{-\beta\Omega}\cosh(\beta\chi) + e^{-2\beta\Omega}}{(1 - e^{-\beta\Omega})^2}\right)$$

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

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

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

Entropy and specific heat



$\Omega/\epsilon = 3$

$\Omega/\epsilon = 1/3$

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

Doing small systems: Fluctuation relations and the arrow of time

Peter Hänggi, Institut für Physik, Universität Augsburg

M. Campisi, P. Hänggi, and P. Talkner
Colloquium: Quantum fluctuation relations: Foundations and applications
Rev. Mod. Phys. **83**, 771–791 (2011);
Addendum and Erratum: Quantum fluctuation relations: Foundations and applications
Rev. Mod. Phys. **83**, 1653 (2011).

M. Campisi and P. Hänggi
Fluctuation, Dissipation and the Arrow of Time
Entropy **13**, 2024–2035 (2012).
G. L. Ingold, P. Hänggi, and P. Talkner
Specific heat anomalies of open quantum systems
Phys. Rev. E **79**, 061105 (2009)

Characteristic function of work

$$G_{t_f,t_0}(u) = \int dw\, e^{iuw} p_{t_f,t_0}(w)$$
$$= \mathrm{Tr} e^{iuH_H(\lambda_\tau)} e^{-iuH(\lambda_0)} \bar{\rho}(t_0)$$
$$\equiv \langle e^{iuH_H(\lambda_\tau)} e^{-iuH(\lambda_0)} \rangle_{t_0}$$

$$H_H(\lambda_\tau) = U^\dagger_{t_f,t_0} H(\lambda_\tau) U_{t_f,t_0}, \quad \bar{\rho}(t_0) = \sum_n P_n(t_0)\rho(t_0)P_n(t_0)$$

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

MORE ON GAUGE FREEDOM

$$W^{\mathsf{phys}} = -\int \mathrm{d}t Q_t \dot{\lambda}_t$$

Corresponds to the choice $g = 0$. Other physical expressions are possible corresponding to different choices of g.

The experimental conditions determine uniquely the SPECIFIC gauge one must choose !!!