Quantum Fluctuation Relations

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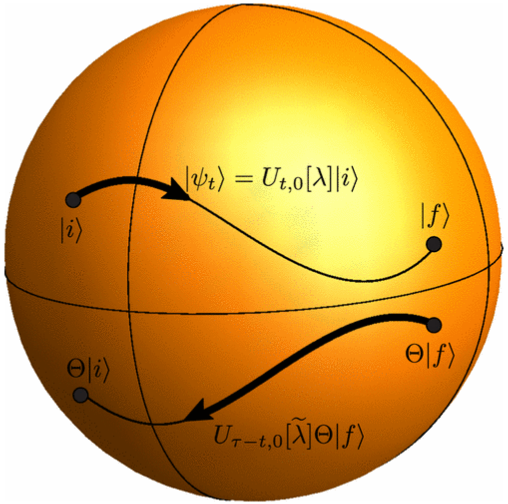

REVIEWS OF MODERN PHYSICS, VOLUME 83, JULY–SEPTEMBER 2011

Colloquium: Quantum fluctuation relations: Foundations and applications

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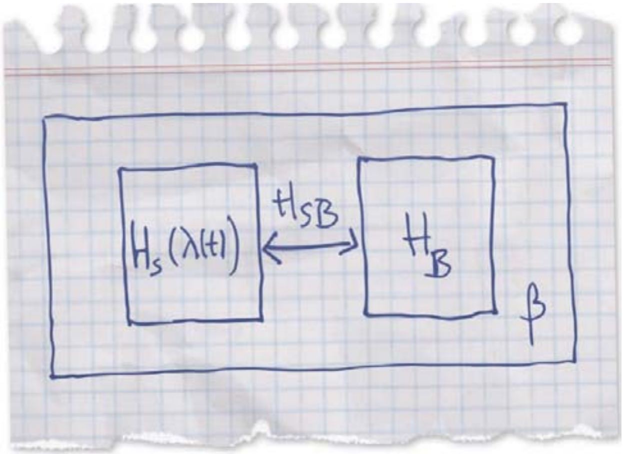
P. Hänggi and P. Talkner, Nature Physics **11**, 108 -110 (2015)



PERSPECTIVE | INSIGHT

The other QFT

Peter Hänggi and Peter Talkner

Fluctuation theorems go beyond the linear response regime to describe systems far from equilibrium. But what happens to these theorems when we enter the quantum realm? The answers, it seems, are now coming thick and fast.

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.

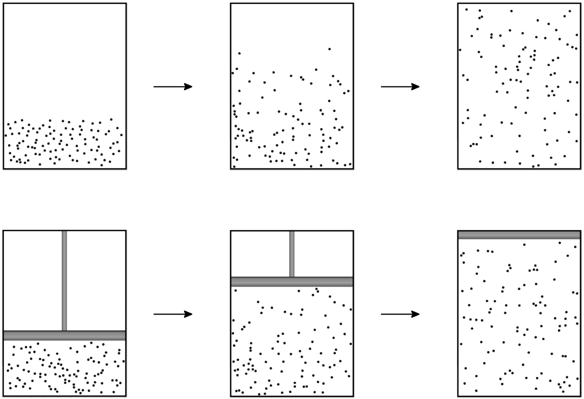
Second Law (Clausius)

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

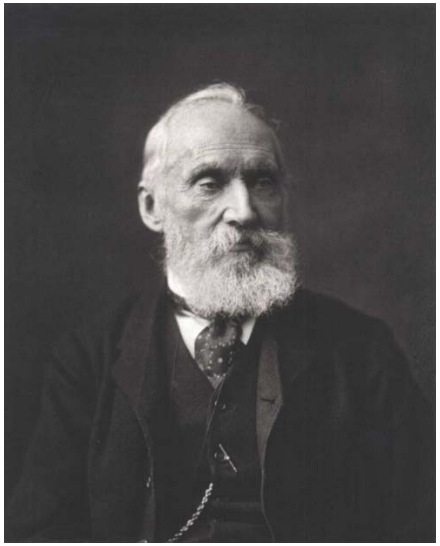


-1st Law

2nd Law

Second Law

Rudolf Julius Emanuel Clausius
(1822 – 1888)



William Thomson alias Lord Kelvin
(1824 – 1907)

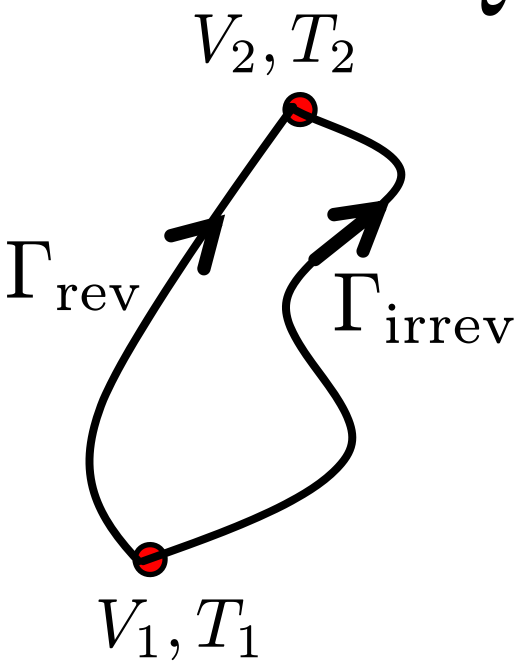
Heat generally cannot spontaneously flow from a material at lower temperature to a material at higher temperature.

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.

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

Entropy S – content of *transformation* „Verwandlungswert“

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



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

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

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

SECOND LAW

Quote by Sir Arthur Stanley Eddington:

“If someone points out to you that your pet theory of the universe is in disagreement with Maxwell’s equations – then so much the worse for Maxwell’s equations. If it is found to be contradicted by observation – well, these experimentalists do bungle things sometimes. But if your theory is found to be against the second law of thermodynamics I can give you no hope; there is nothing for it but to collapse in deepest humiliation.“

Freely translated into German:

Falls Ihnen jemand zeigt, dass Ihre Lieblingstheorie des Universums nicht mit den Maxwellgleichungen übereinstimmt - Pech für die Maxwellgleichungen. Falls die Beobachtungen ihr widersprechen - nun ja, diese Experimentatoren bauen manchmal Mist. -- Aber wenn Ihre Theorie nicht mit dem zweiten Hauptsatz der Thermodynamik übereinstimmt, dann kann ich Ihnen keine Hoffnung machen; ihr bleibt nichts übrig als in tiefster Schande aufzugeben.

What are fluctuation and work theorems about?

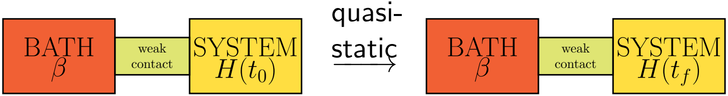
Small systems: fluctuations may become comparable to average quantities.

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

Equilibrium versus nonequilibrium processes

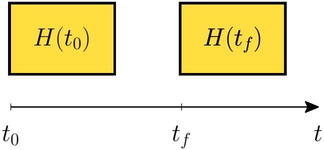
Isothermal quasistatic process:

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



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

Non-equilibrium process:



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

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 $\int \mathrm{d}$(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)

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

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

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

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

$W, \Delta F$ 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:

$$W' = H'(\mathbf{z}_\tau, \tau) - H'(\mathbf{z}_0, 0) \quad , \quad g\text{-dependent}$$

$$W^{\mathrm{phys}} = -\int \mathrm{d}t Q_t \dot{\lambda}_t \quad , \quad g\text{-independent}$$

$$W^{\mathrm{phys}} = W' - g(\tau) + g(0)$$

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

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

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

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

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

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

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

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 work

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

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

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

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

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

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

Probability of work

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

Characteristic function of work

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

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

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

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)

REVIEWS OF MODERN PHYSICS, VOLUME 83, OCTOBER–DECEMBER 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

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

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

Quite surprisingly, notwithstanding the identity

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

one finds that generally ≠!

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

"=" IS WRONG

As a consequence, it is not allowed to replace $\mathcal{H}_\tau^H(\lambda_\tau) - \mathcal{H}(\lambda_0)$, with $\int_0^\tau dt\dot{\lambda}_t\partial\mathcal{H}_t^H(\lambda_t)/\partial\lambda_t$ 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 $A(t) = iu\mathcal{H}_t^H(\lambda_t)$]. 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).

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

Quantum Jarzynski equality

The Jarzynski equality holds for systems with infinite-dimensional Hilbert space and for universal measurement operators iff

(i) $M_n(0)$ is error-free ($p(n'|n) = \delta_{n',n}$), $M_n(0) = |\psi_n(0)\rangle\langle n; 0|$

(ii) $\{|\psi_n(0)\rangle\}$ form a complete orthonormal basis, i.e.
$\langle\psi_n(0)|\psi_k(0)\rangle = \delta_{n,k}$ and $\sum_n |\psi_n\rangle\langle\psi_n| = \mathbb{1}$

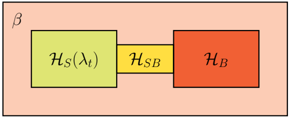
(iii) $\mathrm{Tr} M_m^\dagger(\tau) M_m(\tau) = 1$

P. Hänggi and P. Talkner, Nature Phys. **11**, 108 (2015).

OPEN SYSTEMS

$$H(\lambda(t)) \longrightarrow H_{SYSTEM}(\lambda(t)) + H_{BATH} + H_{S\text{-}B}$$

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

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

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

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

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

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

$$\boxed{G^{E,Q}_{t_f,t_0}(u,v) = \mathrm{Tr} e^{i\left(uH_H^S(t_f)-vH_H^B(t_f)\right)} e^{-i\left(uH^S(t_0)-vH^B\right)}\rho_0^0}$$

Crooks theorem for energy and heat

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

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

$$\Delta E = E^{\lambda_t}_m - E^{\lambda_0}_n$$

$$Q = -\Delta E^B = -E^B_\mu + E^B_\nu$$

$$w = \Delta E - Q : \qquad \text{work}$$

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

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

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

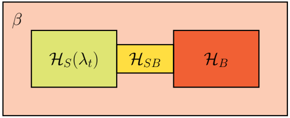
$$\frac{p_{t_f,t_0}(w|Q)}{p_{t_0,t_f}(-w|-Q)} = e^{\beta Q}\langle e^{-\beta w}|Q\rangle$$

$$\langle e^{\beta Q}\rangle = \frac{\mathrm{Tr} e^{-\beta H^S(t_0)} e^{-\beta H^B_H(t_f)}}{Z_S(t_0) Z_B}$$

$$\langle e^{-\beta E}\rangle = \frac{\mathrm{Tr} e^{-\beta H^S_H(t_f)} e^{-\beta H^B}}{Z_S(t_0) Z_B}$$

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

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).

Main results

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

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

OPEN SYSTEMS

no

$$\mathcal{H}(\lambda_t) = \mathcal{H}_S(\lambda_t) + \mathcal{H}_B + \mathcal{H}_{S-B}(\cancel{\lambda_t})$$

CLASSICAL WORK: $\mathcal{H}(\Gamma_\tau;\lambda_\tau) - \mathcal{H}(\Gamma_0;\lambda_0)$

with $\frac{d\mathcal{H}}{dt} = \frac{\partial\mathcal{H}}{\partial t} = \frac{\partial\mathcal{H}}{\partial\lambda}\dot{\lambda} = \frac{\partial\mathcal{H}_S}{\partial\lambda}\dot{\lambda} \Rightarrow$ $= \int_0^\tau dt \underbrace{\frac{\partial\mathcal{H}_S^*(\Gamma_t^S;\lambda(t))}{\partial\lambda(t)}}_{=\frac{\partial\mathcal{H}_S}{\partial\lambda}} \dot{\lambda}(t)$

! NOT ! SO FOR QUANTUM

by the way: $\mathcal{H}_S^*(\Gamma_\tau^S;\lambda_\tau) - \mathcal{H}_S^*(\Gamma_0^S;\lambda_0) = \int_0^\tau dt\,\dot{\lambda}\frac{\partial\mathcal{H}_S(\Gamma_t^S;\lambda_t)}{\partial\lambda(t)} + \int_0^\tau dt\,\dot{\Gamma}_t^S\frac{\partial\mathcal{H}_S^*(\Gamma_t^S;\lambda_t)}{\partial\Gamma_t^S}$

2-nd LAW – WORK ??

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).

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!

$$\boxed{\varrho_S = \frac{\exp -\beta \mathbb{H}_S^*}{Z_S}} \; ; \quad Z_T = Z_S \cdot Z_B$$

$$F_S = F_T - F_B^\circ \quad ; \quad U_S = U_T - U_B^\circ \quad ; \quad S_S = S_T - S_B^\circ$$

$$\rightarrow \boxed{C_S = \frac{\partial U_S}{\partial T} = C_T - C_B^\circ}$$

NOW:

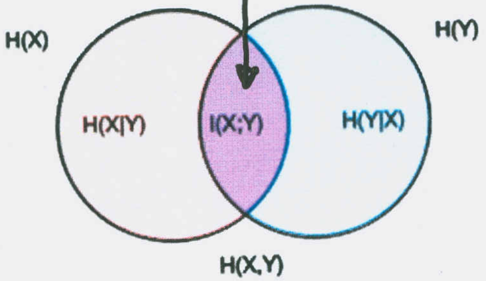
$$U_S = \langle \mathbb{H}_S \rangle_S + U_{INT} = \langle \mathbb{H}_S \rangle_S + \underbrace{\left[\langle H_{Int} \rangle_T + \langle \mathbb{H}_B \rangle_T - \langle \mathbb{H}_B \rangle_B^\circ \right]}_{U_{INT}}$$

1-st LAW:

$$\frac{d \mathbb{H}_T}{dt} = \frac{\partial \mathbb{H}_S(\lambda)}{\partial \lambda} \dot{\lambda}$$

$$\begin{aligned} dU_S &= \langle \delta W^{rev} \rangle + \langle \delta Q^{rev} \rangle \\ &= \langle \delta W^{rev} \rangle + T\, dS_S \\ &= d\langle \mathbb{H}_S \rangle_S + dU_{INT} \\ dU_S &= \underbrace{Tr(\varrho_S\, d\mathbb{H}_S)}_{\langle \delta W^{rev} \rangle} + \underbrace{Tr(\mathbb{H}_S\, d\varrho_S) + dU_{INT}}_{\langle \delta Q^{rev} \rangle = T\, dS_S} \end{aligned}$$

Conditional Entropy



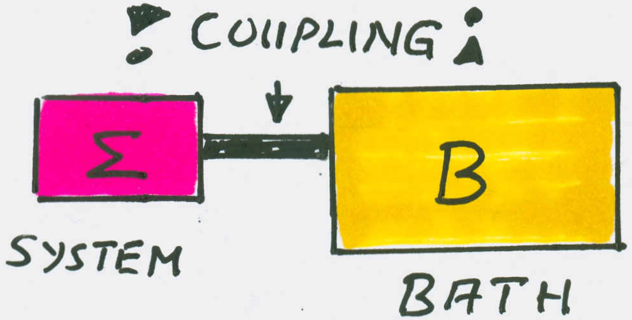
$$I(x;y) = H(x,y) - H(x|y) - H(y|x)$$

$$H(y|x) = -\sum_{x,y} p(x,y) \ln p(x,y) - \left(-\sum_{x} p(x) \ln p(x)\right)$$

$$= -\sum_{x,y} p(x,y) \ln p(y|x) \geq 0$$

Quantum Conditional Entropy

von NEUMANN: $S_{vN}(\varrho_\Sigma) = -\mathrm{Tr}\, \varrho_\Sigma \ln \varrho_\Sigma$

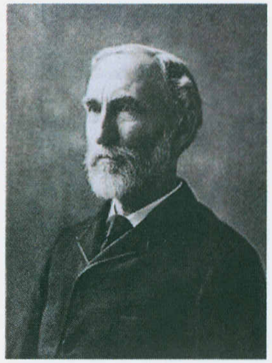


$$S_\Sigma = S_{vN}(\varrho^{can}_{\Sigma\times B}) - S_{vN}(\varrho^{can}_{B})$$

can. thermod. entropy

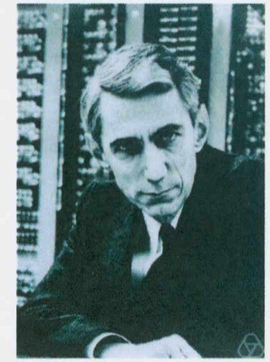
$$\overset{?!}{=} S_{vN}(\varrho^{can}_{\Sigma\times B}) - S_{vN}(\underbrace{\varrho_B = \mathrm{Tr}_\Sigma\, \varrho^{can}_{\Sigma\times B}}_{\neq \varrho_B^{can}})$$

quantum cond. entropy



J. W. Gibbs

L. Boltzmann



C. E. Shannon

$$H_G = \int W_N \ln W_N \, d\Gamma_N \qquad H_B = N \int w_1 \ln w_1 \, d\Gamma_1$$

$$S_S = - \sum_i p_i \log_2 p_i$$

$$S_G = k_B \ln \Omega_G \qquad S_B = k_B \ln \left(\frac{\partial \Omega_G}{\partial E} \right) \delta E$$

+ 200

Renyi

Relative-Kullback-Leibler

v. NEUMANN

KOLMOGOROV-SINAI

CONDITIONAL

CLAUSIUS

FISHER

Daroczy-Harvda-Charvat-Tsallis

WEHRL

Hartley-chaitin

ETC.

Strong coupling: Example

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

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

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

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

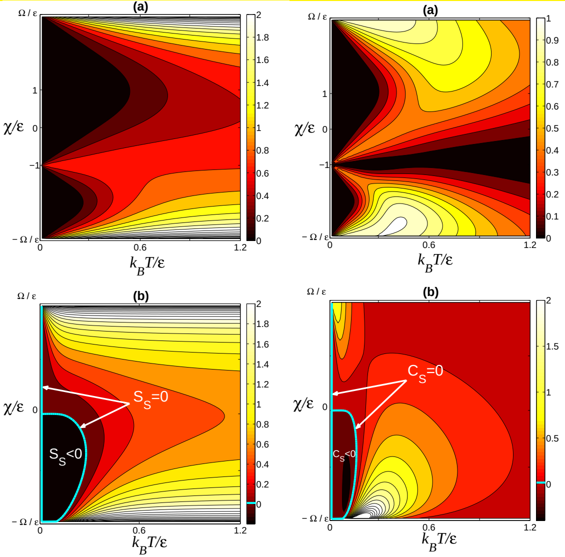
$$\gamma = \frac{1}{2\beta}\ln\left(\frac{1 - 2e^{-\beta\Omega}\cosh(\beta\chi) + e^{-2\beta\Omega}}{(1 - e^{-\beta\Omega})^2}\right)$$

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

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

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

Entropy and specific heat



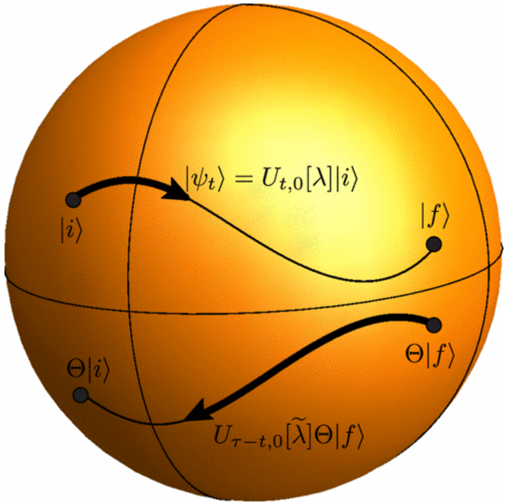
$\Omega/\epsilon = 3$

$\Omega/\epsilon = 1/3$

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

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



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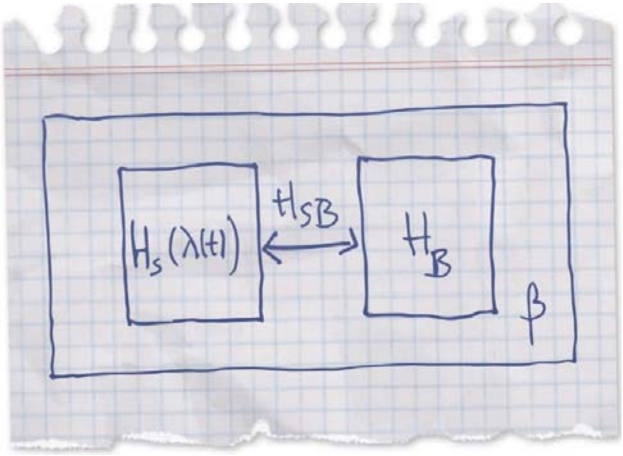

PERSPECTIVE | INSIGHT

The other QFT

Peter Hänggi and Peter Talkner

Fluctuation theorems go beyond the linear response regime to describe systems far from equilibrium. But what happens to these theorems when we enter the quantum realm? The answers, it seems, are now coming thick and fast.

A QUESTION ?

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