



Centre for  
Quantum  
Technologies



PRESENTS

**JULY COLLOQUIUM  
2012**

DOING SMALL SYSTEMS:  
**FLUCTUATION  
RELATIONS &  
THE ARROW OF TIME**

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UNIVERSITY OF AUGSBURG

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CQT SEMINAR ROOM S15-03-15**

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# Doing small systems: 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).

# Acknowledgments

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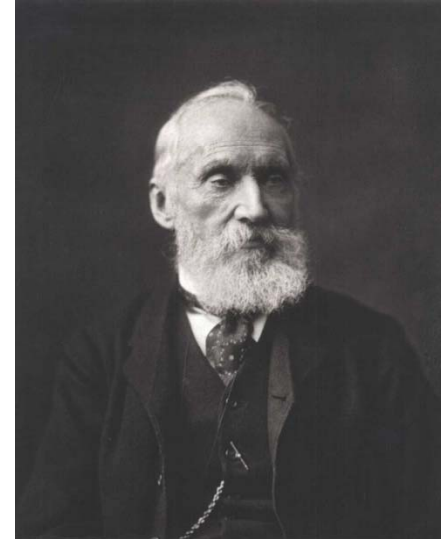
# Second Law



**Rudolf Julius Emanuel Clausius**  
(1822 – 1888)

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

$$\delta Q = TdS \quad (\text{Zürich, 1865})$$



**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.

# 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.*

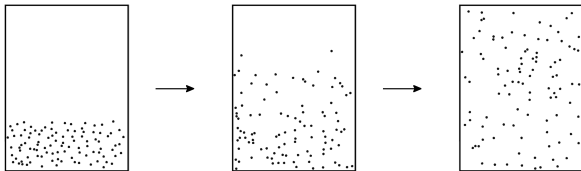
## Second Law (Clausius)

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

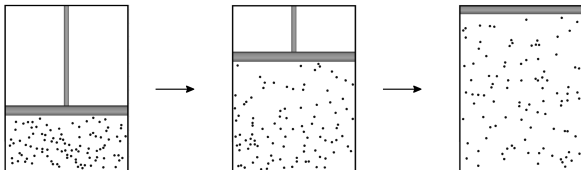
## Second Law (Kelvin)

*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



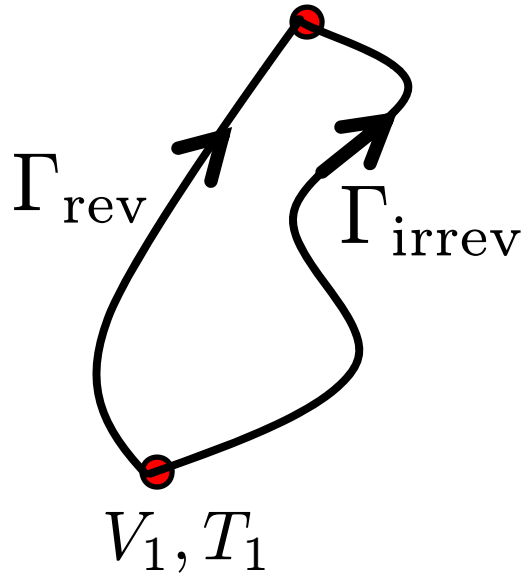
**-1st Law**



**2nd Law**

# Entropy $S$ – content of *transformation* „Verwandlungswert“

$$dS_{V_2, T_2} = \delta Q^{\text{rev}} / T; \quad \delta Q^{\text{irrev}} < \delta Q^{\text{rev}}$$



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

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

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

# Small system – single realizations

**1-st law:**  $\Delta E_\omega = \Delta Q_\omega + \Delta W_\omega$

**! random quantities i**

$$\langle \dots \rangle \Rightarrow \Delta U = \Delta Q + \Delta W$$

Note:  $\Delta Q = \Delta U - \Delta W$   $\Delta U = ?$  &  $\Delta W = ?$

weak coupling:  $\Delta Q = -\Delta Q_{\text{bath}}$

**2-nd law:**  $\Delta S_{A \rightarrow B}^{\text{REV}} \geq \frac{\Delta Q}{T}$

$$\Delta S_{A \rightarrow B}^{\text{REV}} = \frac{\Delta Q}{T} + \sum^{\text{IRREV}} (\geq 0)$$

$$= \frac{\Delta U - \Delta W}{T} + \sum^{\text{IRREV}}$$

$$= \frac{-\Delta Q_{\text{bath}}}{T} + \sum^{\text{IRREV}} ; \text{ for weak coupling}$$



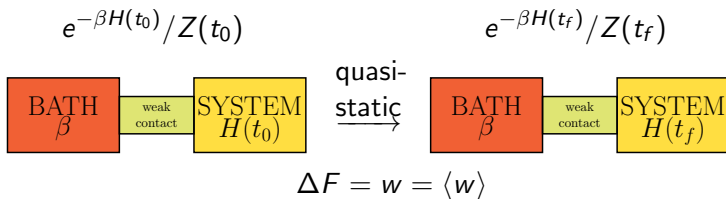
# What are fluctuation and work theorems about?

**Small systems:** fluctuations may become comparable to average quantities.

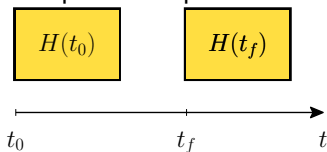
Can one infer thermal **equilibrium properties** from fluctuations in **nonequilibrium** processes?

# Equilibrium versus nonequilibrium processes

Isothermal quasistatic process:



Non-equilibrium process:



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



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



$\lambda_0$   
eq.

$$\rho_0(\mathbf{z}) = \frac{e^{-\beta H(\mathbf{z}, \lambda_0)}}{Z(\lambda_0)}$$



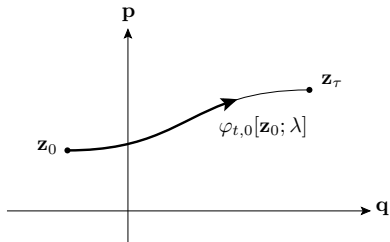
$\lambda_\tau$   
non-eq

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

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

$t \rightarrow \lambda_t$

# CLASSICAL WORK

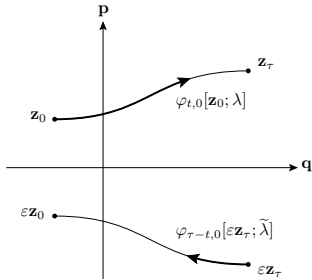


$$W[\mathbf{z}_0; \lambda] = H(\mathbf{z}_\tau, \lambda_\tau) - H(\mathbf{z}_0, \lambda_0) = \int dt \dot{\lambda}_t \frac{\partial H(\varphi_{t,0}[\mathbf{z}_0; \lambda], \lambda_t)}{\partial \lambda_t}$$

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

Work is a RANDOM quantity

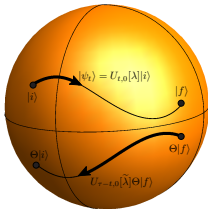
# MICROREVERSIBILITY OF TIME DEPENDENT SYSTEMS



**Classical**

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

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



**Quantum**

$\Theta$  = Time reversal operator

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

# 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  $\int d(\text{displ.}) \times (\text{force})$

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

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

# JARZYNSKI EQUALITY

C. Jarzynski, PRL 78 2690 (1997)

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

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

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

Since exp is convex, then

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

# Canonical initial state

Exclusive Work:

$$\frac{p[w_0; \lambda]}{p[-w_0; \tilde{\lambda}]} = e^{\beta w_0} \quad \text{Bochkov-Kuzovlev-Crooks}$$
$$\langle e^{-\beta w_0} \rangle = 1 \quad \text{Bochkov-Kuzovlev}$$

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

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

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

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

They coincide for cyclic protocols  $\lambda_0 = \lambda_T$

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  $\Delta F$

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

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:

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

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

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

Exclusive work:

$$W_0 = H_0(\mathbf{z}_\tau, \lambda_\tau) - H_0(\mathbf{z}_0, \lambda_0)$$

$$= \int dt \lambda_t \dot{Q}_t \quad , \quad g\text{-independent}$$

Dissipated work:

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

# QUANTUM WORK FLUCTUATION RELATIONS

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

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

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

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

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

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



# WORK IS NOT AN OBSERVABLE

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

Work characterizes PROCESSES, not states!  
( $\delta W$  is not exact)

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



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

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

# 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  $p_n = \text{Tr } P_n(t_0)\rho(t_0)$ ,  
state after measurement:  $\rho_n = P_n(t_0)\rho(t_0)P_n(t_0)/p_n$

$t_0 \rightarrow t_f$ :

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

2nd measurement of energy:  $e_m(t_f)$  with prob.

$$p(m|n) = \text{Tr } P_m(t_f)\rho_n(t_f)$$

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

# Characteristic function of work

$$\begin{aligned}G_{t_f, t_0}(u) &= \int dw e^{i u w} p_{t_f, t_0}(w) \\&= \sum_{m, n} e^{i u e_m(t_f)} e^{-i u e_n(t_0)} \text{Tr} P_m(t_f) U_{t_f, t_0} \rho_n U_{t_f, t_0}^\dagger P_n \\&= \sum_{m, n} \text{Tr} e^{i u H(t_f)} P_m(t_f) U_{t_f, t_0} e^{-i H(t_0)} \rho_n U_{t_f, t_0}^\dagger P_n \\&= \text{Tr} e^{i u H_H(t_f)} e^{-i u H(t_0)} \bar{\rho}(t_0) \\&\equiv \langle e^{i u H(t_f)} e^{-i u H(t_0)} \rangle_{t_0}\end{aligned}$$

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

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

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

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

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  $u = i\beta$

$$\langle e^{-\beta w} \rangle = \int dw e^{-\beta w} p_{t_f, t_0}(w)$$

$$= G_{t_f, t_0}^c(i\beta)$$

$$= \text{Tr} e^{-\beta H_H(t_f)} e^{\beta H(t_0)} Z^{-1}(t_0) e^{-\beta H(t_0)}$$

$$= \text{Tr} e^{-\beta H(t_f)} / Z(t_0)$$

$$= Z(t_f) / Z(t_0)$$

$$= e^{-\beta \Delta F}$$

quantum  
Jarzynski  
equality

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

$$\begin{aligned} Z(t_0)G_{t_f, t_0}^c(u) &= \text{Tr } U_{t_f, t_0}^+ e^{iuH(t_f)} U_{t_f, t_0} e^{i(-u+i\beta)H(t_0)} \\ &= \text{Tr } e^{-i(-u+i\beta)H(t_f)} e^{-\beta H(t_f)} U_{t_0, t_f}^+ e^{i(-u+i\beta)H(t_0)} U_{t_0, t_f} \\ &= Z(t_f)G_{t_0, t_f}^c(-u + i\beta) \end{aligned}$$

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

Tasaki-Crooks  
theorem

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

# 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  $A = \sum_i a_i P_i^A$ ,  
 $P_i^A P_j^A = \delta_{ij} P_i^A$ :

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

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

# Microcanonical initial state

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

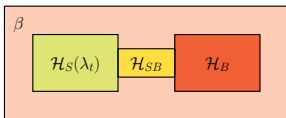
$$\omega_E(t_0) = \text{Tr} \delta(H(t_0) - E) = e^{S(E, t_0)/k_B}$$

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

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

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

# OPEN QUANTUM SYSTEM: WEAK COUPLING



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

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

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

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

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

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

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

# Small system – single realizations

**1-st law:**  $\Delta E_\omega = \Delta Q_\omega + \Delta W_\omega$

**! random quantities i**

$$\langle \dots \rangle \Rightarrow \Delta U = \Delta Q + \Delta W$$

Note:  $\Delta Q = \Delta U - \Delta W$   $\Delta U = ?$  &  $\Delta W = ?$

weak coupling:  $\Delta Q = -\Delta Q_{\text{bath}}$

**2-nd law:**  $\Delta S_{A \rightarrow B}^{\text{REV}} \geq \frac{\Delta Q}{T}$

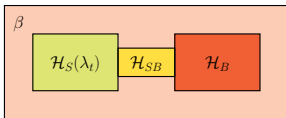
$$\Delta S_{A \rightarrow B}^{\text{REV}} = \frac{\Delta Q}{T} + \sum^{\text{IRREV}} (\geq 0)$$

$$= \frac{\Delta U - \Delta W}{T} + \sum^{\text{IRREV}}$$

$$= \frac{-\Delta Q_{\text{bath}}}{T} + \sum^{\text{IRREV}} ; \text{ for weak coupling}$$



# OPEN QUANTUM SYSTEM: STRONG COUPLING



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

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

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

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

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

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

# Partition function

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

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

# Quantum Hamiltonian of Mean Force

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

where

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

also

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

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

# 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.

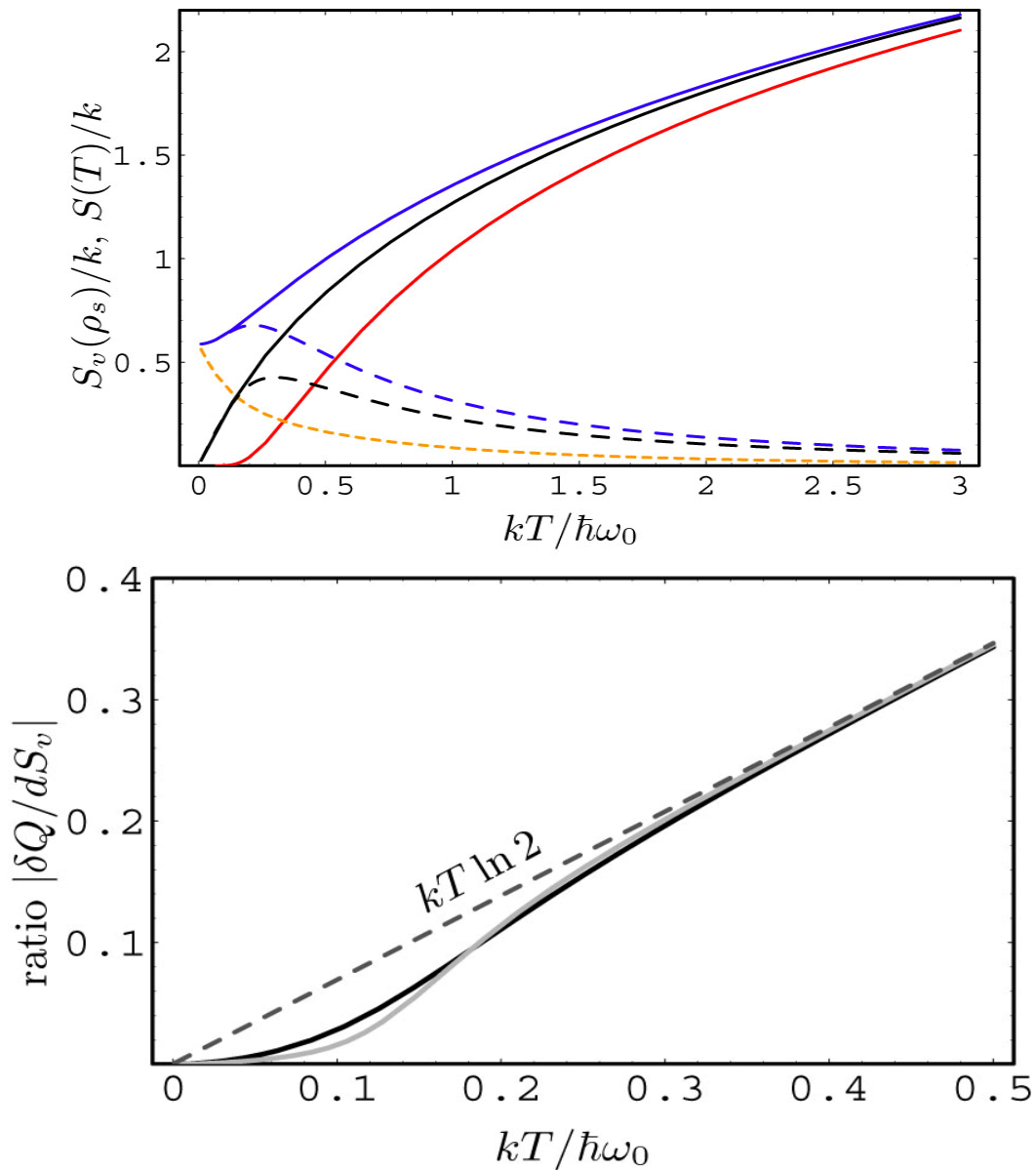
With this form of free energy the three laws of thermodynamics are fulfilled.

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).

$$S_{vN} = -k \text{Tr} (\rho_s \ln \rho_s) \geq S(T)$$



C. Hörhammer & H. Büttner, arXiv:0710.1716

*Temperature dependence of the ratio  $|\delta Q/dS_v|$  (in bits) with the heat defined by  $\delta Q = TdS(T)$  for quasi-static variations of the oscillator frequency  $d\omega_0$ . The system-bath-couplings are chosen to be  $\gamma = m\omega_0^2/\Gamma = 0.1$  (dark line) and  $\gamma = m\omega_0^2/\Gamma = 0.5$  (gray line). At low  $T$  deviations from the Landauer bound  $kT \ln 2$  (dashed line) occur.*

$$? \quad | \delta Q/dS_{vN} | \geq k T \ln 2 \quad ?$$

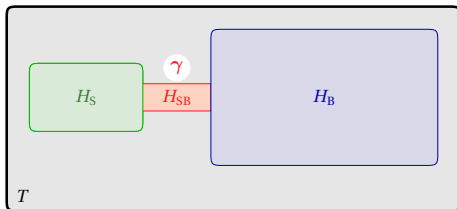
Thermal Casimir  
forces and  
quantum  
dissipation

Introduction

Quantum  
dissipation

Thermal Casimir  
effect

Conclusions



The definition of thermodynamic quantities for systems coupled to a bath with finite coupling strength is not unique.

P. Hänggi, GLI, Acta Phys. Pol. B **37**, 1537 (2006)

# An important difference



Route I

$$E \doteq E_S = \langle H_S \rangle = \frac{\text{Tr}_{S+B}(H_S e^{-\beta H})}{\text{Tr}_{S+B}(e^{-\beta H})}$$

Route II

$$\mathcal{Z} = \frac{\text{Tr}_{S+B}(e^{-\beta H})}{\text{Tr}_B(e^{-\beta H_B})} \quad U = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}$$

$$\begin{aligned} \Rightarrow U &= \langle H \rangle - \langle H_B \rangle_B \\ &= E_S + \left[ \langle H_{SB} \rangle + \langle H_B \rangle - \langle H_B \rangle_B \right] \end{aligned}$$

For finite coupling  $E$  and  $U$  differ!

Quantum  
Brownian  
motion and  
the 3<sup>rd</sup> law

Specific heat and  
dissipation

Two approaches  
Microscopic model

Route I

Route II  
specific heat  
density of states

Conclusions



# Strong coupling: Example

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

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

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

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

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

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

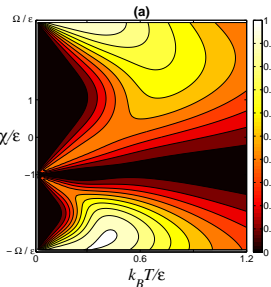
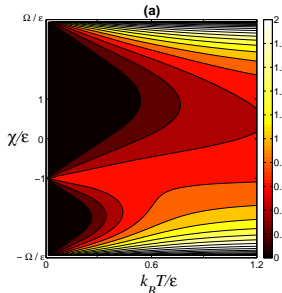
$$S_S = -\frac{\partial F_S}{\partial T} \quad C_S = T \frac{\partial S_S}{\partial T}$$



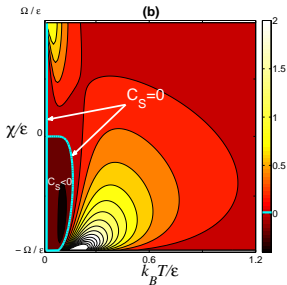
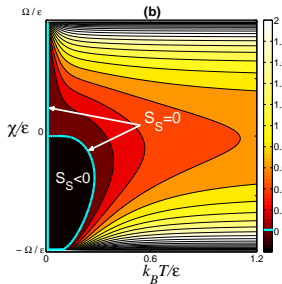
# Entropy and specific heat

Fluctuation  
Theorem for  
Arbitrary  
Open  
Quantum  
Systems

Peter Hänggi,  
Michele  
Campisi, and  
Peter Talkner



$$\Omega/\epsilon = 3$$



$$\Omega/\epsilon = 1/3$$

# USING EXCLUSIVE WORK

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

$$\lambda_t = 0 \text{ at } t = 0; \quad \text{Protocol: } \lambda_t : 0 \rightarrow t = \tau$$

$$\rho_0(\mathbf{q}, \mathbf{p}) = e^{-\beta H_0(\mathbf{q}, \mathbf{p})} / Z_0(\beta)$$

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

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

$$\Rightarrow \boxed{\langle e^{-\beta W_0} \rangle_\lambda = 1} \quad \text{“equality” (2<sup>nd</sup> Law)}$$

$$\text{with } \langle \exp(x) \rangle \geq \exp(\langle x \rangle)$$

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

$$\boxed{\langle W_0 \rangle_\lambda \geq 0} \quad \text{“inequality”}$$

# ARROW OF TIME

+ : movie in forward direction

- : movie in backward direction

frame "t":  $\lambda_t$  and  $Q_t$

Forward:  $\beta W_0 \gg 1$

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

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

After Seeing movie

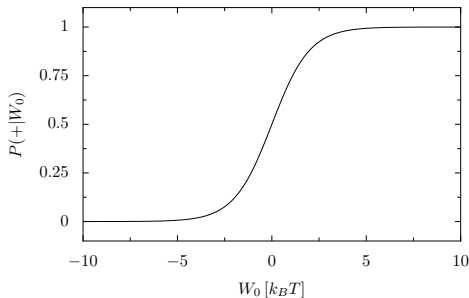
$$\begin{aligned} \text{Posterior: } P(+|W_0) &= \frac{P(W_0|+)P(+)}{P(W_0)} = \\ &= \frac{P(W_0|+)P(+)}{P(W_0|+)P(+)+P(W_0|-)P(-)} \end{aligned}$$

# ARROW OF TIME

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

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

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



# ARROW OF TIME

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

2) preparation, here canonical  $\longrightarrow \text{„determines its direction“}$

## conventional :

- coarse graining of quantities  $\leftrightarrow$  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“



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

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

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

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

Quite surprisingly, notwithstanding the identity

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

one finds that generally

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

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

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

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).

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