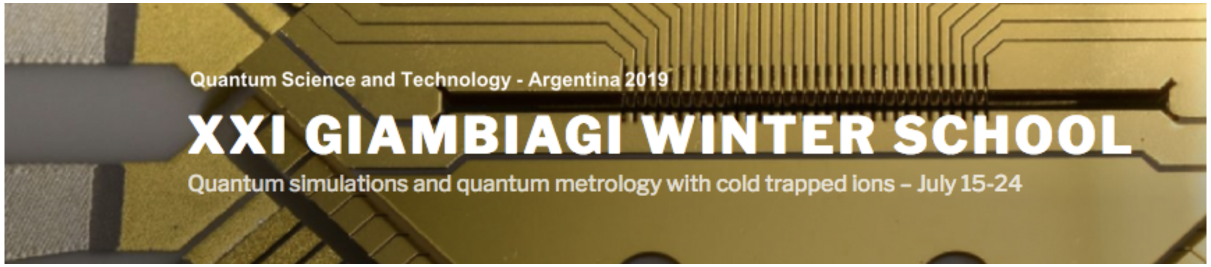


XXI Giambiagi Winter School
July 2019
University of Buenos Aires
Argentina

Quantum Thermodynamics

Janet Anders
University of Exeter, UK

joint work with :
Philipp Kammerlander
Sai Vinjanampathy
Harry Miller
....

UNIVERSITY OF EXETER

Lecture overview

I - Work extraction from quantum coherences (long)

II - Maxwell's demon and his exorcism - experimental evidence (short)

III - Thermodynamics beyond the weak coupling limit (long)

IV - Optional: Non-equilib. temperature of levitated nanospheres (short)

Outline - III

- Recap: standard thermodynamic potentials
- Violation of laws of thermodynamics in the quantum regime?
- Resolution of paradox/lessons
- (weak coupling) Stochastic thermodynamics
- Thermodynamic potentials and stochastic thermodynamics beyond weak coupling (classical) ← *a bit chewy …*
- Thermodynamic uncertainty relation (quantum)

Outline - III

- Recap: standard thermodynamic potentials
- Violation of laws of thermodynamics in the quantum regime?
- Resolution of paradox/lessons
- (weak coupling) Stochastic thermodynamics
- Thermodynamic potentials and stochastic thermodynamics beyond weak coupling (classical) ← *a bit chewy …*
- Thermodynamic uncertainty relation (quantum)

Recap: Standard thermodynamic potentials

classical description:

phase space coordinates x

Hamiltonian $H_S(x)$

partition function $Z_S = \int dx \, e^{-\beta H_S(x)}$

equilibrium distribution

$$\rho_S(x) = \frac{e^{-\beta H_S(x)}}{Z_S}$$

for equilibrium state at inverse temperature

$$\beta = 1/T$$

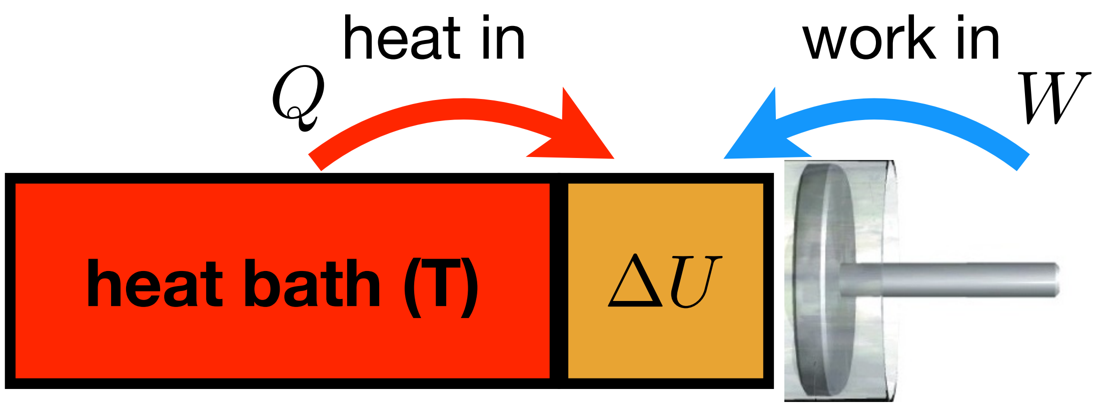
$$k_B = 1$$

internal energy $U_S = -\partial_\beta \ln Z_S$

free energy $F_S = -\frac{1}{\beta} \ln Z_S$

entropy $S_S = \beta(U_S - F_S) = -\int dx \, \rho_S(x) \ln \rho_S(x)$

Recap: Standard laws of thermodynamics



First law

$$\Delta U_S = W + Q$$

with sign conventions:

$$\Delta U = U_{\text{end}} - U_{\text{start}}$$

$$Q = Q_{\text{abs}} \qquad W = W_{\text{abs}}$$

Second law

$$\Delta S_S \geq \frac{Q}{T}$$

← for one bath at T

or $W \geq \Delta F_S$

Violation of standard thermodynamics

- The 2nd law of thermodynamics is *the* core principle in physics.

  Eddington: The law that entropy always increases, holds, I think, the supreme position among the laws of Nature. 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.

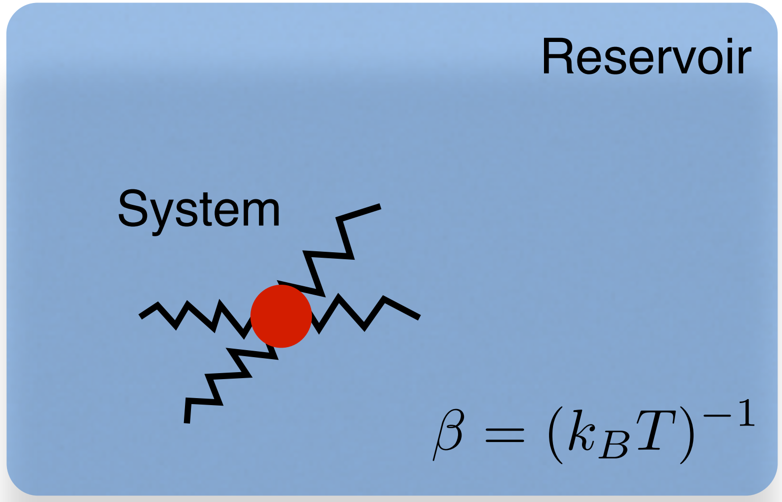
- Landauer's principle links thermodynamics with information and is equivalent to the second law.

- But there is a well-cited paper that proves that the 2nd law of thermodynamics/Landauer's erasure principle is violated in the quantum regime.

Phys. Rev. Lett. 85:1799 (2000)
Phys. Rev. E 64:056117 (2001)

The original argument

Phys. Rev. Lett. 85:1799 (2000)



Caldeira-Leggett model

$$H = H_S + H_B + H_{int}$$

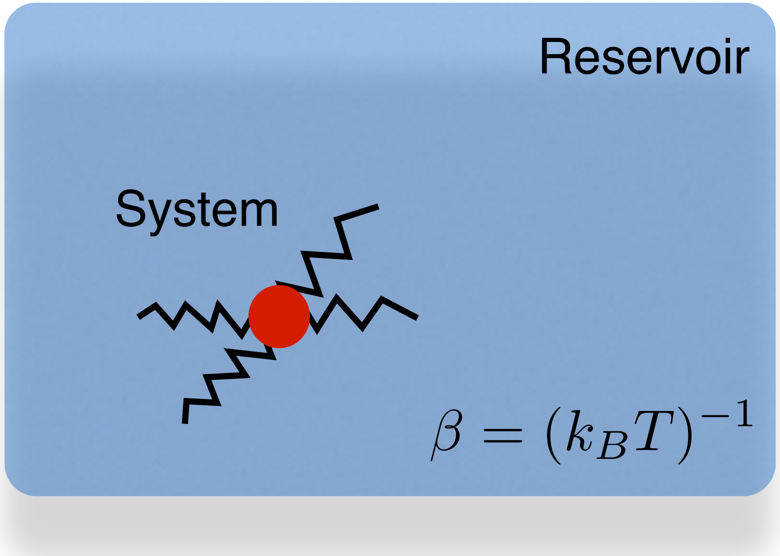
interaction term

$$H_S = \frac{p^2}{2m} + \frac{m\omega^2 q^2}{2}$$

$$H_B + H_{int} = \sum_j \left[\frac{p_j^2}{2m_j} + \frac{m_j \omega_j^2}{2} \left(q_j - \frac{c_j\, q}{m_j \omega_j^2} \right)^2 \right]$$

The original argument

Phys. Rev. Lett. 85:1799 (2000)



Caldeira-Leggett model

$$H = H_S + H_B + H_{int}$$

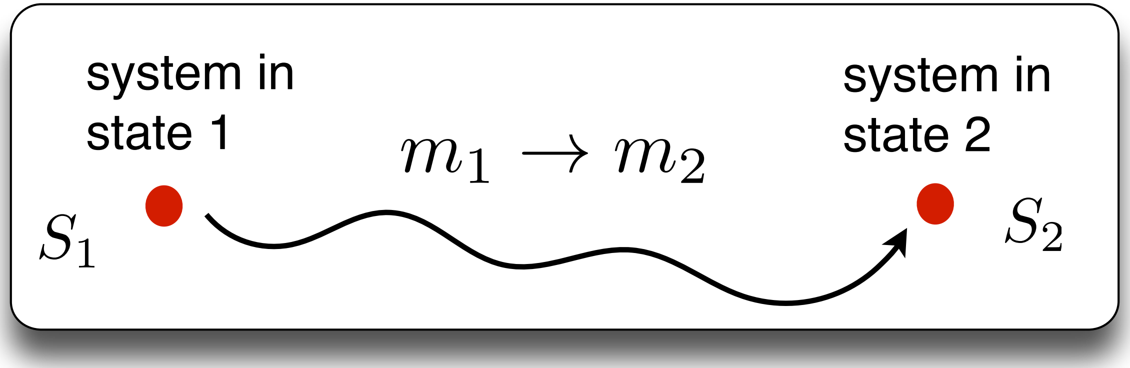
global thermal state

$$\rho = \frac{e^{-\beta H}}{Z}$$

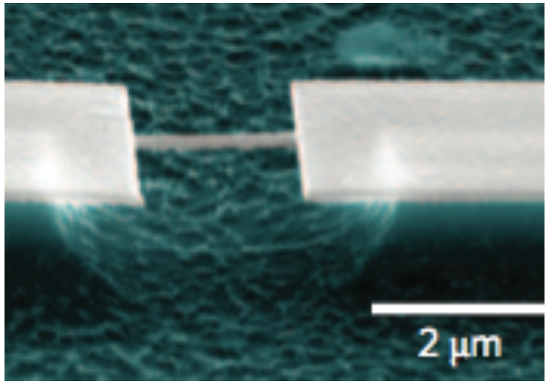
reduced state of the oscillator

$$\rho_S = tr_B[\rho]$$

The paradox



increase of oscillator mass



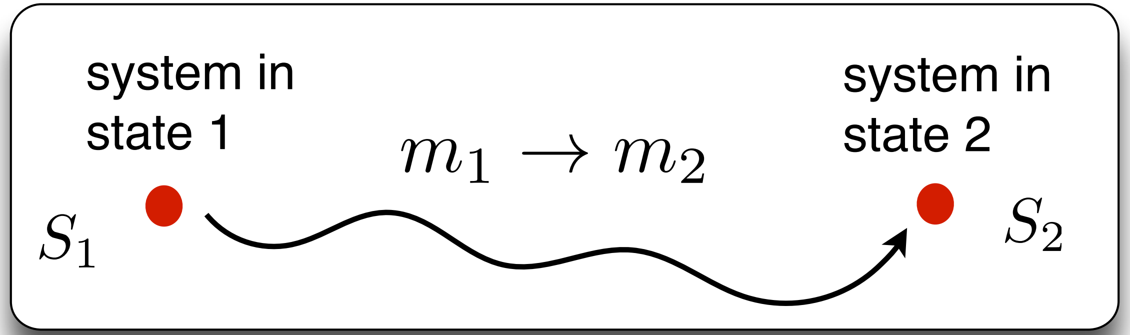
Naik, et al, Nature Nanotechnology 445 (2009)
Cleland et al, Nature **464**:697 (2010)

nature nanotechnology ARTICLES
PUBLISHED ONLINE: 21 JUNE 2009 | DOI: 10.1038/NNANO.2009.152

Towards single-molecule nanomechanical mass spectrometry

A. K. Naik[1†], M. S. Hanay[1†], W. K. Hiebert[1,2†], X. L. Feng[1] and M. L. Roukes[1*]

The paradox



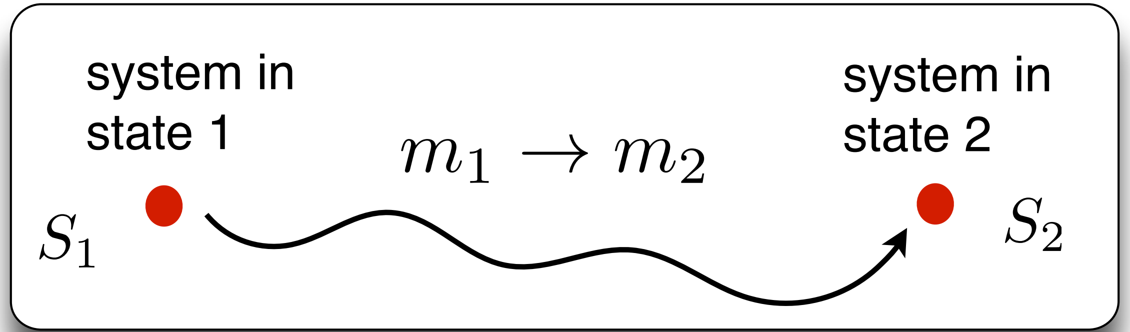
increase of oscillator mass

Clausius inequality

$$\Delta S \geq \frac{Q_{abs}}{T}$$

$$0 \geq \Delta := Q_{abs} - T\Delta S$$

The paradox



increase of oscillator mass

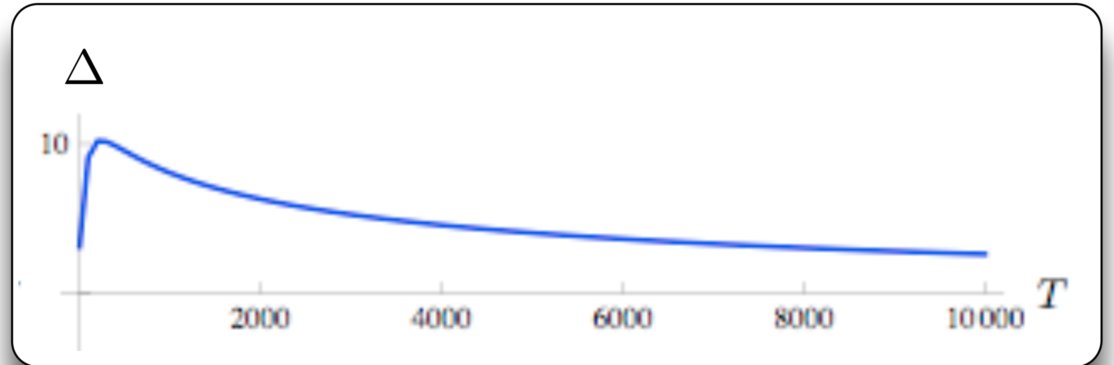
Clausius inequality

$$\Delta S \geq \frac{Q_{abs}}{T}$$

$$0 \geq \Delta := Q_{abs} - T\Delta S$$

calculate ΔS and Q_{abs} for this process

Phys. Rev. Lett. 85:1799 (2000)



$\Rightarrow$ violation of Clausius inequality

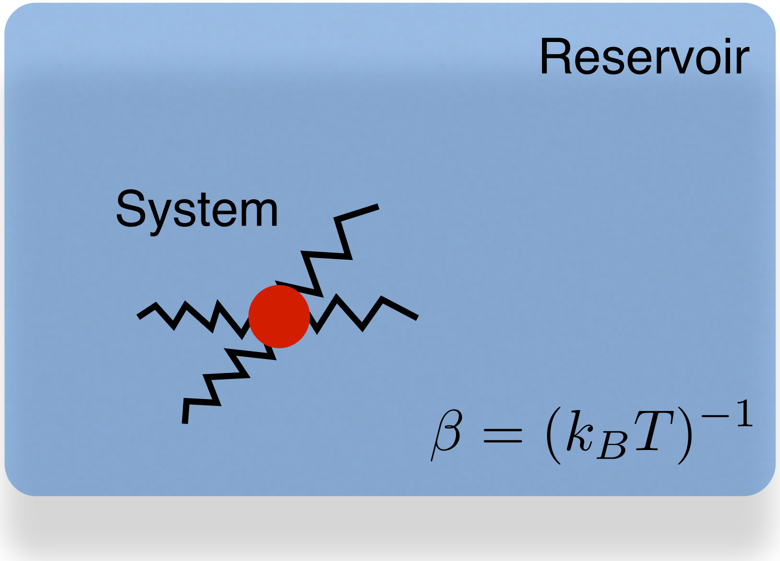
& Landauer’s erasure principle

Outline - III

- Recap: standard thermodynamic potentials
- Violation of laws of thermodynamics in the quantum regime?
- Resolution of paradox/lessons
- (weak coupling) Stochastic thermodynamics
- Thermodynamic potentials and stochastic thermodynamics beyond weak coupling (classical) ← *a bit chewy …*
- Thermodynamic uncertainty relation (quantum)

The original argument

Phys. Rev. Lett. 85:1799 (2000)



Caldeira-Leggett model

$$H = H_S + H_B + H_{int}$$

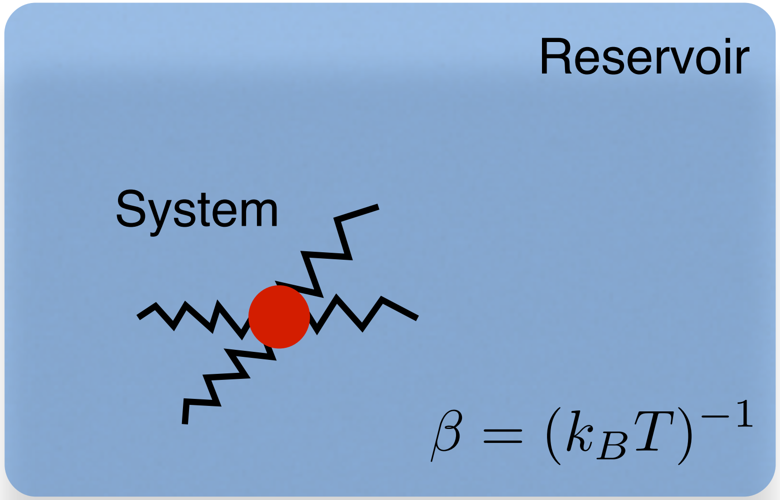
global thermal state

$$\rho = \frac{e^{-\beta H}}{Z}$$

reduced state of the oscillator

$$\rho_S = tr_B[\rho]$$

Resolution of paradox



Caldeira-Leggett model

$$H = H_S + H_B + H_{int}$$

global thermal state

$$\rho = \frac{e^{-\beta H}}{Z}$$

reduced state of the oscillator

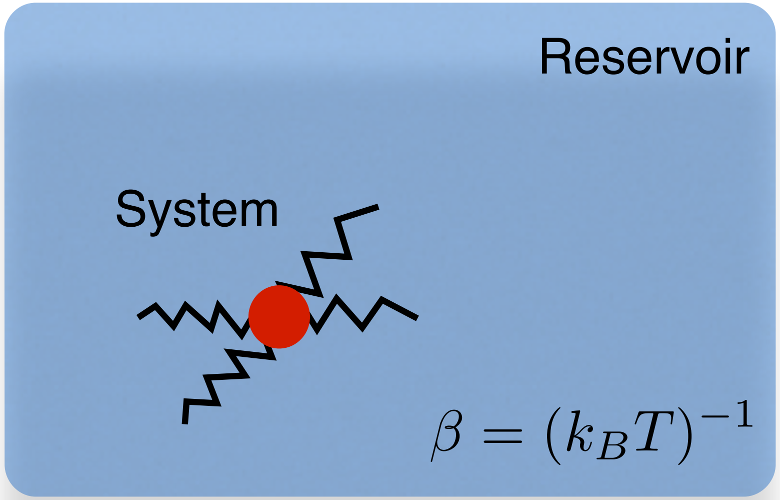
$$\rho_S = tr_B[\rho]$$

coupling process leads to correlations => non-Gibbsian state

is not thermal

$$\neq \frac{e^{-\beta H_S}}{Z_S}$$

Resolution of paradox



Caldeira-Leggett model

$$H = H_S + H_B + H_{int}$$

global thermal state

$$\rho = \frac{e^{-\beta H}}{Z}$$

reduced state of the oscillator

$$\rho_S = tr_B[\rho]$$

coupling process leads to correlations => non-Gibbsian state

is not thermal

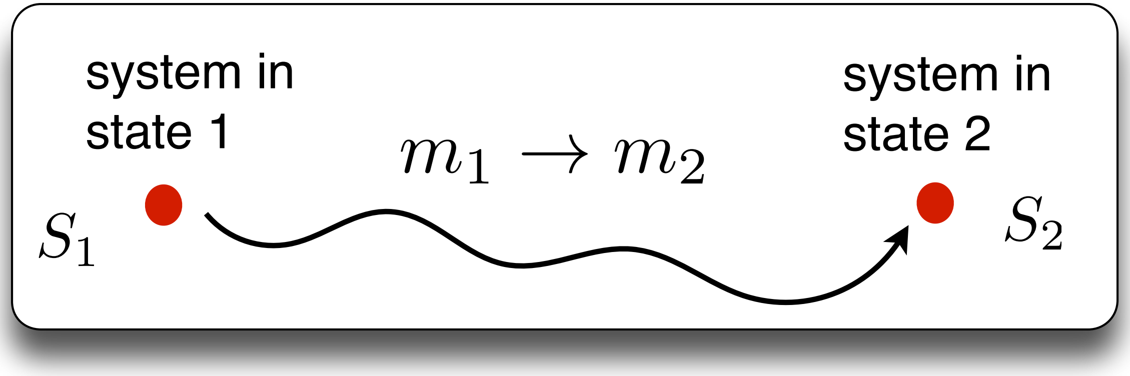
$$\neq \frac{e^{-\beta H_S}}{Z_S}$$

??

no well-defined local temperature

$$Q \leq k_B T \Delta S$$

Resolution of paradox



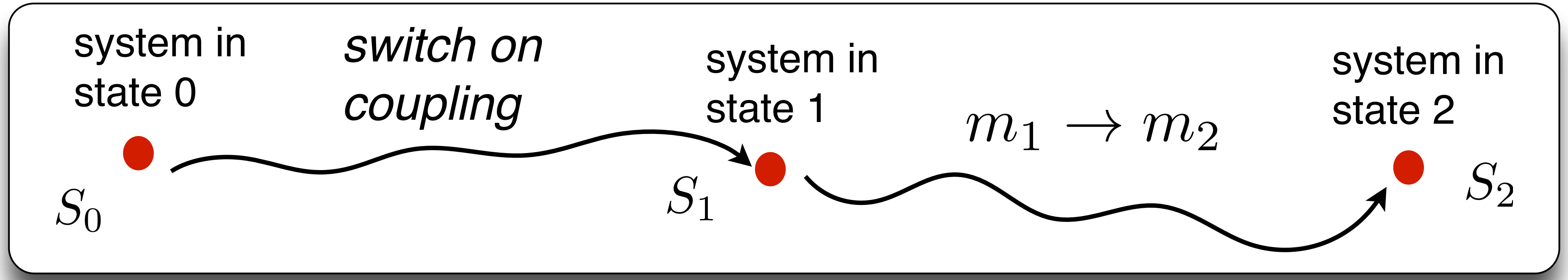
oscillator
non-thermal

$$H = H_S + H_B + H_{int}$$

no temperature,
no Clausius inequality

Hilt, Shabbir, Anders, Lutz Phys Rev E (R) (2011)

Resolution of paradox



thermal,
well-defined T

oscillator
non-thermal

$$H = H_S + H_B$$

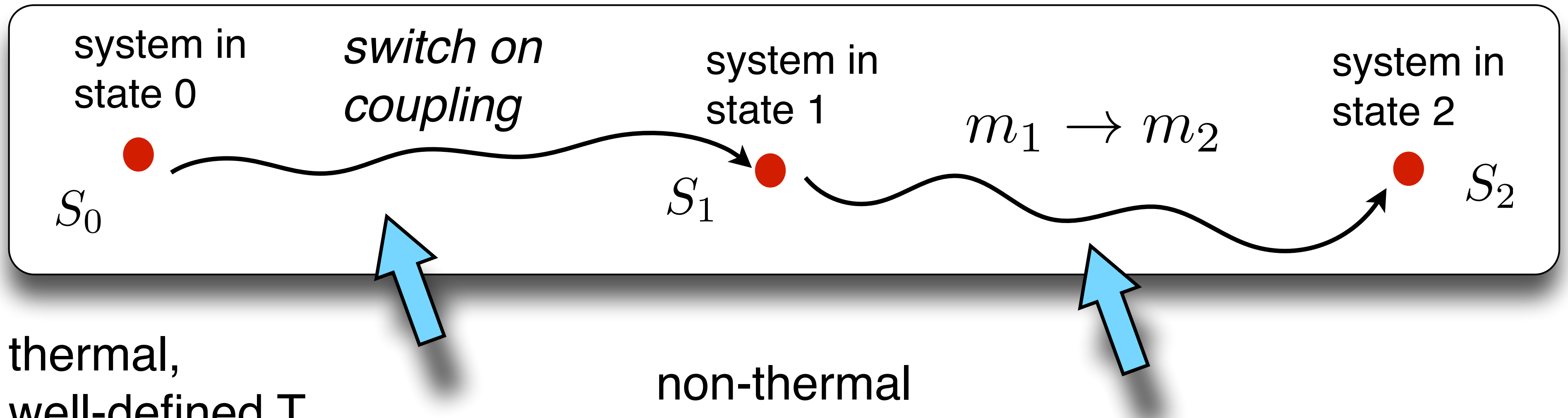
$$H = H_S + H_B + H_{int}$$

have initial temperature,
can use Clausius inequality

no temperature,
no Clausius inequality

Hilt, Shabbir, Anders, Lutz Phys Rev E (R) (2011)

Resolution of paradox



thermal, well-defined T

non-thermal

$Q^{(c)}$

$Q^{(m)}$

coupling to bath

increasing mass

creating correlations requires additional entropy and heat component:

$$\Delta S = \Delta S^{(c)} + \Delta S^{(m)}$$

$$Q = Q^{(c)} + Q^{(m)}$$

Clausius inequality

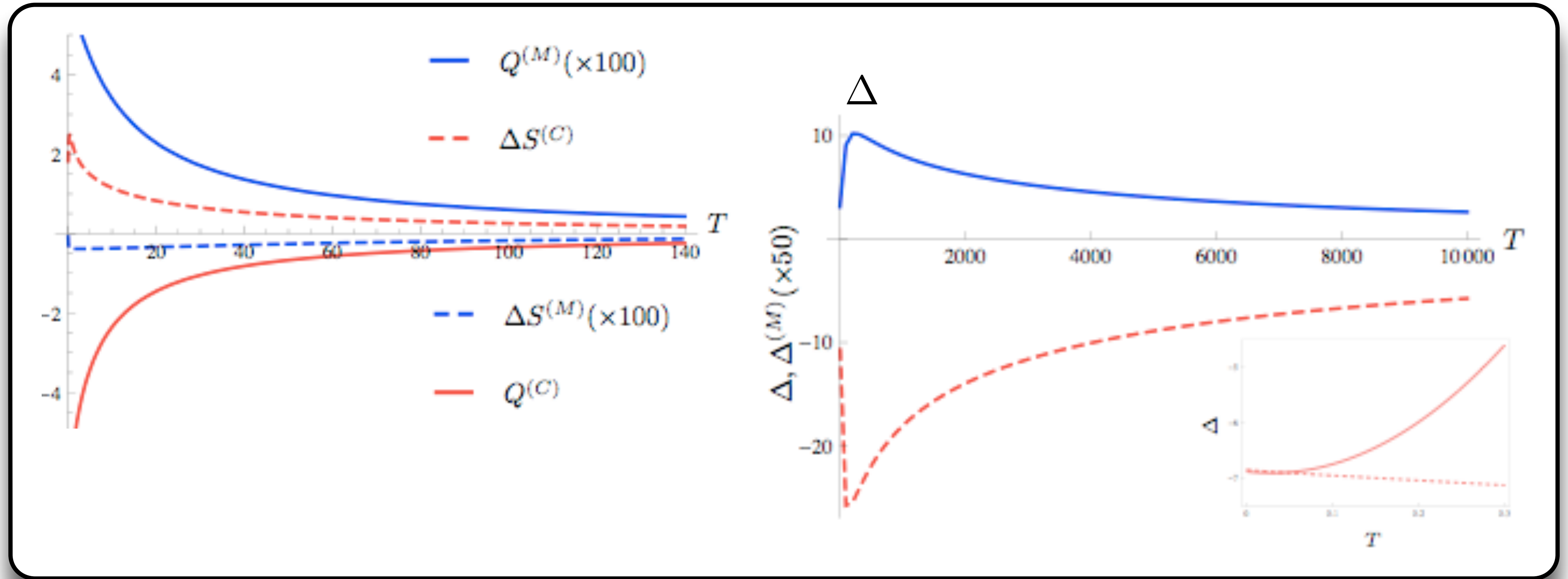
$$\Delta S \geq \frac{Q_{abs}}{T}$$

$$0 \geq \Delta := Q_{abs} - T \Delta S$$

$$\Delta = -T S_{irr}$$

Hilt, Shabbir, Anders, Lutz Phys Rev E (R) (2011)

Resolution of paradox



creating correlations requires additional entropy and heat component:

$$\Delta S = \Delta S^{(c)} + \Delta S^{(m)}$$

$$Q = Q^{(c)} + Q^{(m)}$$

Clausius inequality

$$\Delta S \geq \frac{Q_{abs}}{T}$$

$$0 \geq \Delta := Q_{abs} - T\Delta S$$

$$\Delta = -TS_{irr}$$

Hilt, Shabbir, Anders, Lutz Phys Rev E (R) (2011)

Summary

i.e. Clausius difference Δ is: $\Delta = \Delta^{(m)} + \Delta^{(c)}$

this alone is positive = looks like violation

including this term due to coupling makes Δ negative = correct with 2nd law

➤ Thermodynamic process on **quantum** brownian oscillator does ***not*** violate 2nd law.

Hilt, Shabbir, Anders, Lutz Phys Rev E (R) (2011)

Summary

i.e. Clausius difference Δ is: $\Delta = \Delta^{(m)} + \Delta^{(c)}$

this alone is positive = looks like violation

including this term due to coupling makes Δ negative = correct with 2nd law

➤ Thermodynamic process on **quantum** brownian oscillator does ***not*** violate 2nd law.

actually: mathematical identity $\Delta^{(c)} = -\langle \Delta H_S \rangle$

with Hamiltonian difference: $\Delta H_S = H_S^* - H_S$

where **H* is the mean force Hamiltonian** defined through: $\rho_S =: \frac{e^{-\beta H_S^*}}{Z^*}$

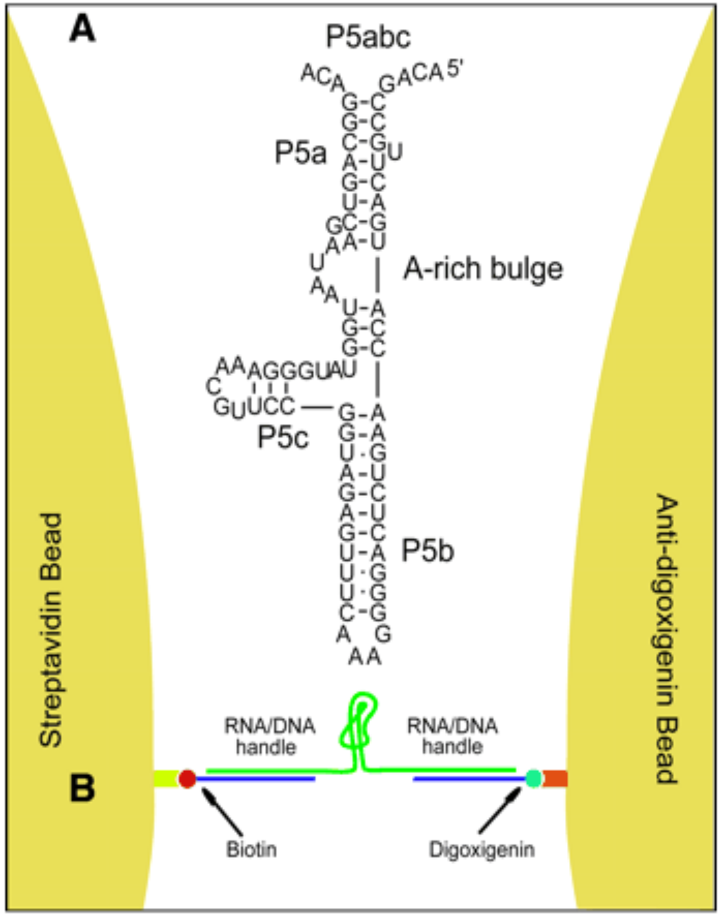
Hilt, Shabbir, Anders, Lutz Phys Rev E (R) (2011)

Outline - III

- Recap: standard thermodynamic potentials
- Violation of laws of thermodynamics in the quantum regime?
- Resolution of paradox/lessons
- (weak coupling) Stochastic thermodynamics
- Thermodynamic potentials and stochastic thermodynamics beyond weak coupling (classical) ← *a bit chewy …*
- Thermodynamic uncertainty relation (quantum)

U. Seifert, Rep. Prog. Phys 75, 126001 (2012)

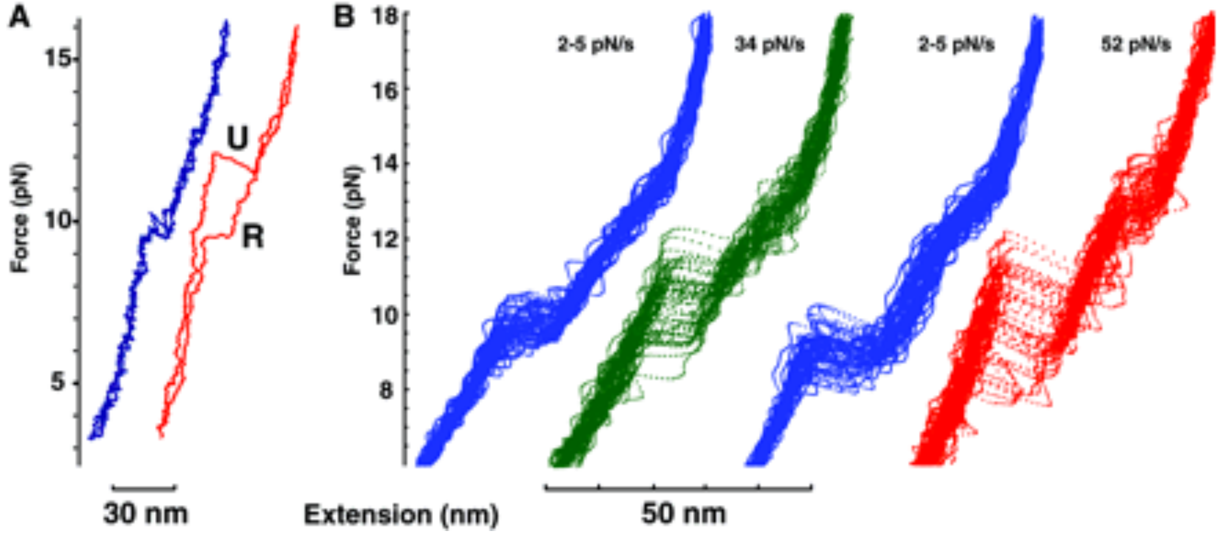
Micro: Stochastic thermodynamics



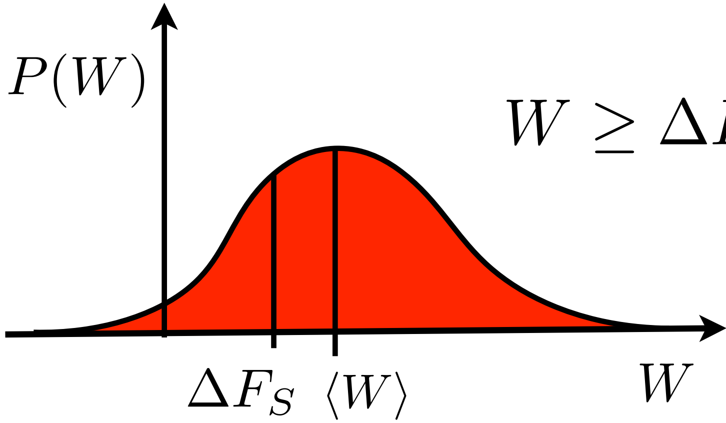
Liphardt, *et al.*,

Science **296**, 1832 (2002)

work becomes a stochastic variable



get work distribution rather than just one “work”



$$W \geq \Delta F_S$$

also: stochastic energy, entropy, …

Stochastic thermodynamics

not just for the entire distribution,
but for each phase space point *x* define:

stochastic internal energy $u_S(x) = H_S(x)$

stochastic free energy $f_S(x) = u_S(x) - \frac{s_S(x)}{\beta}$

stochastic entropy $s_S(x) = -\ln \rho_S(x)$

stochastic work $W_{x_0 \to x_\tau} = \int_0^\tau dt \, \frac{\partial H_S(x_t, t)}{\partial t}$

partial derivative for Hamiltonian that changes in time

work for particular trajectory in phase space

Example: harmonic osci with time-dependent frequency

$$H_S(\underbrace{(q_t, p_t)}_{x_t}, t) = \frac{p_t^2}{2m} + \frac{m\omega_t^2 \, q_t^2}{2}$$

sampling generates probability distribution $P(W)$

Stochastic thermodynamics

not just for the entire distribution,
but for each phase space point *x* define:

macro thermo limit

stochastic internal energy → $$U_S = \int dx \, u_S(x) \, \rho_S(x)$$

stochastic free energy →

stochastic entropy →

get standard (macroscopic) thermo potentials from averaging over thermal distribution

stochastic work $W_{x_0 \to x_\tau}$ →

work for particular trajectory in phase space

get standard (macroscopic) work from averaging over all trajectories during protocol

$$\langle W \rangle = \int dW \;\; W \, P(W)$$

sampling generates probability distribution $P(W)$

U. Seifert, Rep. Prog. Phys 75, 126001 (2012)

Micro: Stochastic thermodynamics

for initial **thermal** states (Gibbs state for $H_S(x)$)

Crooks relation

$$P^f(W) = P^b(-W)\, e^{\beta(W-\Delta F)}$$

forward work distribution — backward work distribution — exponentiell factor

protocol: controlled change of time-dependent parameter, e.g. in/de-crease of h.o. frequency

$\omega_0 \to \omega_\tau$ (forward)

$\omega_\tau \to \omega_0$ (backward)

averaging over all initial phase space points/ phase space trajectories:

Jarzynski equality

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

non-equilibrium work — inverse temperature — equilibrium free energy

Jensen's inequality

$$\langle W \rangle \geq \Delta F$$

Crooks and Jarzynski relations are more fundamental than 2nd law

Outline - III

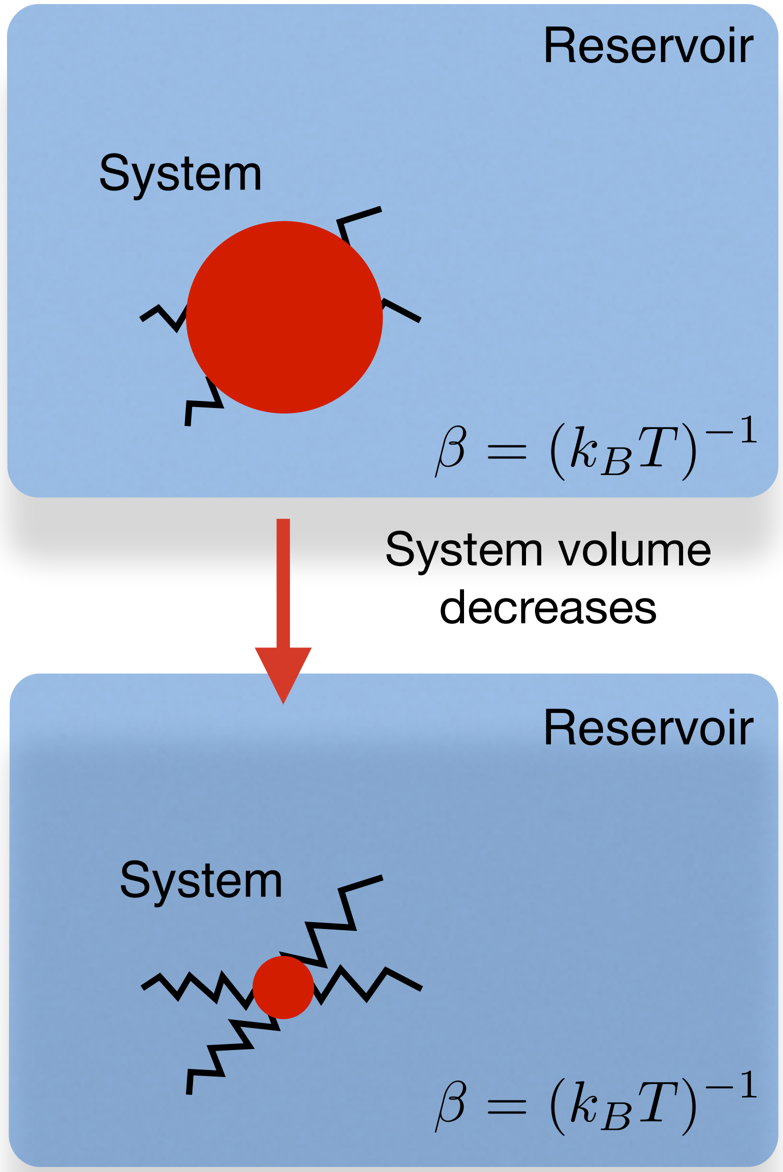
- Recap: standard thermodynamic potentials
- Violation of laws of thermodynamics in the quantum regime?
- Resolution of paradox/lessons
- (weak coupling) Stochastic thermodynamics
- Thermodynamic potentials and stochastic thermodynamics beyond weak coupling (classical) ← *a bit chewy …*
- Thermodynamic uncertainty relation (quantum)

Beyond the weak coupling limit

For a **macroscopic** system its **coupling** to the environment can be **neglected**.

For a **smaller** scale system its **coupling** to the environment becomes **relevant**.

Task: Identify corrections to **thermodynamic potentials** (e.g. energy) and **stochastic thermo relations**. (e.g. Crooks relation)



Beyond weak coupling:

need to describe system and bath

phase space coordinates for system and bath $z = (x, y)$

global Hamiltonian

$$H_{tot}(x, y) = H_S(x) + H_B(y) + V_{int}(x, y)$$

bare system Hamiltonian

interaction term

global equilibrium distribution

$$\rho_{tot}^{eq}(x, y) = \frac{e^{-\beta H_{tot}(x,y)}}{Z_{tot}}$$

for equilibrium state at inverse temperature

$$\beta = 1/T$$

$$k_B = 1$$

Beyond weak coupling:

need to describe system and bath

phase space coordinates for system and bath $z = (x, y)$

global Hamiltonian

$$H_{tot}(x,y) = H_S(x) + H_B(y) + \boxed{V_{int}(x,y)}$$

bare system Hamiltonian

interaction term

reduced state of the system

$$\rho_S^{eq}(x) = \int dy\ \rho_{tot}^{eq}(x,y) \neq \frac{e^{-\beta H_S(x)}}{Z_S}$$

global equilibrium distribution

$$\rho_{tot}^{eq}(x,y) = \frac{e^{-\beta H_{tot}(x,y)}}{Z_{tot}}$$

for equilibrium state at inverse temperature

$$\beta = 1/T$$

$$k_B = 1$$

Beyond weak coupling:
need to describe system and bath

phase space coordinates for system and bath $z = (x, y)$

global Hamiltonian

$$H_{tot}(x,y) = H_S(x) + H_B(y) + \boxed{V_{int}(x,y)}$$

bare system Hamiltonian

interaction term

global equilibrium distribution

$$\rho_{tot}^{eq}(x,y) = \frac{e^{-\beta H_{tot}(x,y)}}{Z_{tot}}$$

for equilibrium state at inverse temperature

$$\beta = 1/T$$

$$k_B = 1$$

reduced state of the system

$$\rho_S^{eq}(x) = \int dy\ \rho_{tot}^{eq}(x,y) \neq \frac{e^{-\beta H_S(x)}}{Z_S}$$

$$\rho_S^{eq}(x) =: \frac{e^{-\beta H_S^*(x)}}{Z_S^*}$$

defines mean force Hamiltonian (function of *T*)

effective system partition function

$$Z_S^* = \int dx\, e^{-\beta H_S^*(x)}$$

$$H_S^*(x) = H_S(x) - \boxed{\frac{1}{\beta} \ln \langle e^{-\beta V_{int}(x,y)} \rangle_B}$$

average over uncoupled thermal phase space distribution of bath

Beyond weak coupling:

Def: Stochastic thermodynamic potentials
for **strongly coupled systems**

stochastic internal energy $u_S(x) = H_S(x)$

stochastic free energy $f_S(x) = u_S(x) - \frac{s_S(x)}{\beta}$

stochastic entropy $s_S(x) = -\ln \rho_S(x)$

Beyond weak coupling:

Def: Stochastic thermodynamic potentials
for **strongly coupled systems**

stochastic internal energy $u_S(x) = H_S(x)$

$$u_S^*(x) = \partial_\beta[\beta H_S^*(x)] = H_S(x) - \partial_\beta \ln\langle e^{-\beta V_{int}(x,y)}\rangle_B$$

stochastic free energy $f_S(x) = u_S(x) - \frac{s_S(x)}{\beta}$

stochastic entropy $s_S(x) = -\ln \rho_S(x)$

coupling corrections to potentials

Seifert, PRL 116, 020601 (2016)

Beyond weak coupling:

UNIVERSITY OF EXETER

Def: Stochastic thermodynamic potentials
for **strongly coupled systems**

stochastic internal energy $u_S(x) = H_S(x)$

$$u_S^*(x) = \partial_\beta[\beta H_S^*(x)] = H_S(x) - \boxed{\partial_\beta \ln\langle e^{-\beta V_{int}(x,y)}\rangle_B}$$

stochastic free energy $f_S(x) = u_S(x) - \frac{s_S(x)}{\beta}$

$$f_S^*(x) = u_S^*(x) - \frac{s_S^*(x)}{\beta}$$

stochastic entropy $s_S(x) = -\ln \rho_S(x)$

$$s_S^*(x) = -\ln \rho_S(x) + \boxed{\beta^2 \partial_\beta H_S^*(x)}$$

coupling corrections to potentials

Seifert, PRL 116, 020601 (2016)

Beyond weak coupling:

Def: Stochastic thermodynamic potentials
for **strongly coupled systems**

stochastic internal energy

$$u_S^*(x) = \partial_\beta[\beta H_S^*(x)]$$

stochastic free energy

$$f_S^*(x) = u_S^*(x) - \frac{s_S^*(x)}{\beta}$$

stochastic entropy

$$s_S^*(x) = -\ln \rho_S(x) + \boxed{\beta^2 \partial_\beta H_S^*(x)}$$

Seifert, PRL 116, 020601 (2016)

Beyond weak coupling:

Def: Stochastic thermodynamic potentials
for **strongly coupled systems**

macro thermo limit

stochastic internal energy

$$u_S^*(x) = \partial_\beta[\beta H_S^*(x)] \longrightarrow U_S = \int dx\, u_S^*(x)\, \rho_S^{eq}(x) = -\partial_\beta \ln Z_S^*$$

stochastic free energy

$$f_S^*(x) = u_S^*(x) - \frac{s_S^*(x)}{\beta} \longrightarrow$$

stochastic entropy

$$s_S^*(x) = -\ln \rho_S(x) + \beta^2 \partial_\beta H_S^*(x) \longrightarrow$$

Seifert, PRL 116, 020601 (2016)

Beyond weak coupling:

Def: Stochastic thermodynamic potentials
for **strongly coupled systems**

macro thermo limit

stochastic internal energy

$$u_S^*(x) = \partial_\beta[\beta H_S^*(x)] \longrightarrow U_S = \int dx\, u_S^*(x)\, \rho_S^{eq}(x) = -\partial_\beta \ln Z_S^*$$

stochastic free energy

$$f_S^*(x) = u_S^*(x) - \frac{s_S^*(x)}{\beta} \longrightarrow F_S = -\frac{1}{\beta} \ln Z_S^*$$

stochastic entropy

$$s_S^*(x) = -\ln \rho_S(x) + \boxed{\beta^2 \partial_\beta H_S^*(x)} \longrightarrow S_S = \beta(U_S - F_S)$$

Seifert, PRL 116, 020601 (2016)

Result: Additivity of potentials

Def: class D_β (stationary preparation class/conditional states)

= the global state takes the form $\sigma(x,y) = \rho_S(x)\ \rho_B^{eq}(y|x)$

where $\rho_B^{eq}(y|x) = \frac{\rho_{tot}(x,y)}{\int dy\ \rho_{tot}(x,y)}$ with $\rho_{tot}(x,y) = \frac{e^{-\beta H_{tot}(x,y)}}{Z_{tot}}$

Talkner, Hanggi, PRE 94 (2016)

Result: Additivity of potentials

Def: class D_β (stationary preparation class/conditional states)

= the global state takes the form $\sigma(x,y) = \rho_S(x)\ \rho_B^{eq}(y|x)$

where $\rho_B^{eq}(y|x) = \frac{\rho_{tot}(x,y)}{\int dy\ \rho_{tot}(x,y)}$ with $\rho_{tot}(x,y) = \frac{e^{-\beta H_{tot}(x,y)}}{Z_{tot}}$

Talkner, Hanggi, PRE 94 (2016)

For this class: the **bath** is in a **thermal state** conditioned on the system phase space value, but tracing the bath gives an **arbitrary system state** $\rho_S(x)$

Result: Miller, Anders, PRE (2017)

For states in class D_β the **effective system** and **free bath potentials add**

$$\chi_{tot} = \chi_S + \chi_B^{eq} \quad \text{for} \quad \chi = U, F, S$$

(i.e. thermodynamically extensive)

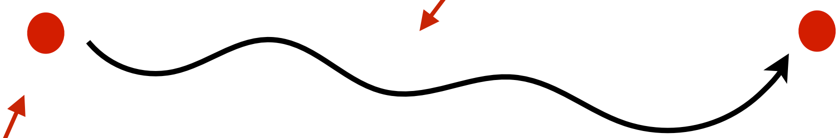
Recall: Non-equilibrium fluctuation relation

Consider dynamics generated by a time-varying Hamiltonian:

weak coupling: $H_S(x, \lambda_t)$

thermal state

non-thermal state



$\rho_S(x_t, \lambda_t)$

differs from the thermal state for the final Hamiltonian

$$\rho_S^{eq}(x_0, \lambda_0) = \frac{e^{-\beta H_S(x_0,\lambda_0)}}{Z_S(\lambda_0)}$$

$$\rho_S^{eq}(x_t, \lambda_t) = \frac{e^{-\beta H_S(x_t,\lambda_t)}}{Z_S(\lambda_t)}$$

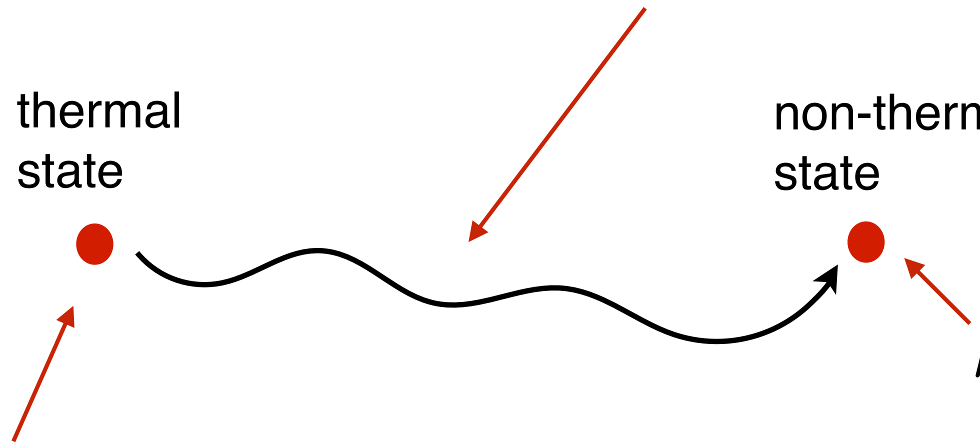
Recall: Non-equilibrium fluctuation relation

Consider dynamics generated by a time-varying Hamiltonian:

weak coupling: $H_S(x, \lambda_t)$

thermal state

non-thermal state



$\rho_S(x_t, \lambda_t)$

differs from the thermal state for the final Hamiltonian

$$\rho_S^{eq}(x_0, \lambda_0) = \frac{e^{-\beta H_S(x_0,\lambda_0)}}{Z_S(\lambda_0)}$$

$$\rho_S^{eq}(x_t, \lambda_t) = \frac{e^{-\beta H_S(x_t,\lambda_t)}}{Z_S(\lambda_t)}$$

It holds: **Crooks relation** for entropy production

$$\frac{\overrightarrow{P}(+\Sigma)}{\overleftarrow{P}(-\Sigma)} = e^{+\Sigma}$$

$$\Sigma(x) = s_S(x_t, \lambda_t) - s_S(x_0, \lambda_0) + \beta\, Q(x_0 \to x_t)$$

$$Q(x_0 \to x_t) = u_S(x_t, \lambda_t) - u_S(x_0, \lambda_0) + \int_0^t d\tau\; \partial_{\lambda_\tau} u_S(x_\tau, \lambda_\tau)\; \dot{\lambda}_\tau$$

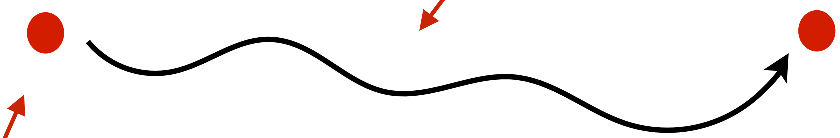
Result: Non-equilibrium fluctuation relation

Consider dynamics generated by a time-varying Hamiltonian:

strong coupling: $H_{tot}(x, y, \lambda_t) = H_S(x, \lambda_t) + H_B(y) + V_{int}(x, y)$

global state in D_β

general global state



$\rho(x_t, y_t, \lambda_t)$

$$\sigma(x_0, y_0, \lambda_0) = \rho_S(x_0, \lambda_0)\ \rho_B^{eq}(y_0|x_0; \lambda_0)$$

differs from the global **conditional** thermal state for the final Hamiltonian

$$\sigma(x_t, y_t, \lambda_t) = \rho_S(x_t, \lambda_t)\ \rho_B^{eq}(y_t|x_t; \lambda_t)$$

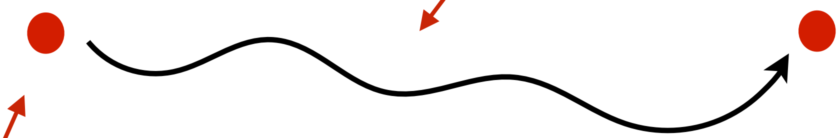
Result: Non-equilibrium fluctuation relation

Consider dynamics generated by a time-varying Hamiltonian:

strong coupling: $H_{tot}(x, y, \lambda_t) = H_S(x, \lambda_t) + H_B(y) + V_{int}(x, y)$

global state in D_β

general global state



$\rho(x_t, y_t, \lambda_t)$

$$\sigma(x_0, y_0, \lambda_0) = \rho_S(x_0, \lambda_0)\ \rho_B^{eq}(y_0|x_0; \lambda_0)$$

differs from the global **conditional** thermal state for the final Hamiltonian

$$\sigma(x_t, y_t, \lambda_t) = \rho_S(x_t, \lambda_t)\ \rho_B^{eq}(y_t|x_t; \lambda_t)$$

Miller, Anders PRE (2017)

It holds: **Crooks relation** for entropy production **incl corrections ***

$$\frac{\overrightarrow{P}(+\Sigma)}{\overleftarrow{P}(-\Sigma)} = e^{+\Sigma}$$

$$\Sigma(x) = s_S^*(x_t, \lambda_t) - s_S^*(x_0, \lambda_0) + \beta\, Q^*(x_0 \to x_t)$$

$$Q^*(x_0 \to x_t) = u_S^*(x_t, \lambda_t) - u_S^*(x_0, \lambda_0) + \int_0^t d\tau\ \partial_{\lambda_\tau} u_S^*(x_\tau, \lambda_\tau)\ \dot{\lambda}_\tau$$

Result: Non-equilibrium fluctuation relation

Miller, Anders PRE (2017)

It holds: **Crooks relation** for entropy production **incl corrections ***

$$\frac{\overrightarrow{P}(+\Sigma)}{\overleftarrow{P}(-\Sigma)} = e^{+\Sigma}$$

$$\Sigma(x) = s^*_S(x_t, \lambda_t) - s^*_S(x_0, \lambda_0) + \beta\, Q^*(x_0 \to x_t)$$

$$Q^*(x_0 \to x_t) = u^*_S(x_t, \lambda_t) - u^*_S(x_0, \lambda_0) + \int_0^t d\tau\; \partial_{\lambda_\tau} u^*_S(x_\tau, \lambda_\tau)\; \dot{\lambda}_\tau$$

Result: Non-equilibrium fluctuation relation

UNIVERSITY OF EXETER

and hence: average entropy production
= KL divergence between entropy production distributions

entropy production measures irreversibility

$$\langle \Sigma(\lambda_t) \rangle = S\left[\overrightarrow{P}(+\Sigma) \middle|\middle| \overleftarrow{P}(-\Sigma)\right]$$

i.e. discrepancy between forwards and backwards entropy production

Miller, Anders PRE (2017)

It holds: **Crooks relation** for entropy production **incl corrections** *

$$\frac{\overrightarrow{P}(+\Sigma)}{\overleftarrow{P}(-\Sigma)} = e^{+\Sigma}$$

$$\Sigma(x) = s_S^*(x_t, \lambda_t) - s_S^*(x_0, \lambda_0) + \beta\, Q^*(x_0 \to x_t)$$

$$Q^*(x_0 \to x_t) = u_S^*(x_t, \lambda_t) - u_S^*(x_0, \lambda_0) + \int_0^t d\tau\ \partial_{\lambda_\tau} u_S^*(x_\tau, \lambda_\tau)\ \dot{\lambda}_\tau$$

Result: Effective 2nd law

Miller, Anders PRE (2017)

It holds: **Crooks relation** for entropy production **incl corrections ***

$$\frac{\overrightarrow{P}(+\Sigma)}{\overleftarrow{P}(-\Sigma)} = e^{+\Sigma}$$

$$\Sigma(x) = s_S^*(x_t, \lambda_t) - s_S^*(x_0, \lambda_0) + \beta\, Q^*(x_0 \to x_t)$$

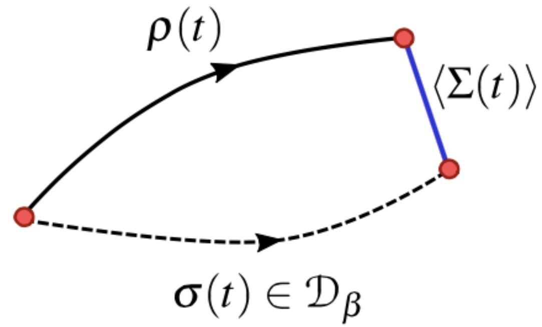
$$Q^*(x_0 \to x_t) = u_S^*(x_t, \lambda_t) - u_S^*(x_0, \lambda_0) + \int_0^t d\tau\; \partial_{\lambda_\tau} u_S^*(x_\tau, \lambda_\tau)\; \dot{\lambda}_\tau$$

Result: Effective 2nd law

Result: Miller, Anders, PRE (2017) Strasberg, Esposito PRE (2017)

For initial states in class D_β and Ham. dynamics in full phase space

$$\langle \Sigma(\lambda_t) \rangle = S[\rho(x_t, y_t, \lambda_t) || \sigma(x_t, y_t, \lambda_t)]$$



since Kullbeck-Leibler divergence is positive ⇒ $\langle \Sigma(\lambda_t) \rangle \geq 0$

implying $\Delta S_S^* \geq \frac{Q^*}{T}$ (2nd law)

Miller, Anders PRE (2017)

It holds: **Crooks relation** for entropy production **incl corrections ***

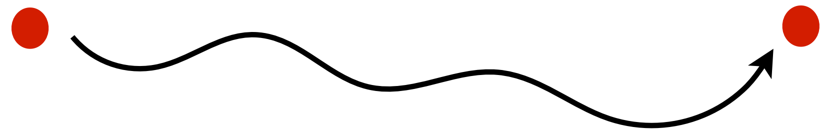
$$\frac{\overrightarrow{P}(+\Sigma)}{\overleftarrow{P}(-\Sigma)} = e^{+\Sigma}$$

$$\Sigma(x) = s_S^*(x_t, \lambda_t) - s_S^*(x_0, \lambda_0) + \beta\, Q^*(x_0 \to x_t)$$

$$Q^*(x_0 \to x_t) = u_S^*(x_t, \lambda_t) - u_S^*(x_0, \lambda_0) + \int_0^t d\tau\; \partial_{\lambda_\tau} u_S^*(x_\tau, \lambda_\tau)\; \dot{\lambda}_\tau$$

Summary: **strong coupling stoch. thermo**

Defining appropriate stochastic thermodynamic potentials, including **strong coupling corrections,** one obtains effective standard stochastic thermodynamics results.



Crooks relation holds $$\frac{\overrightarrow{P}(+\Sigma)}{\overleftarrow{P}(-\Sigma)} = e^{+\Sigma}$$

Miller, Anders PRE (2017)

entropy production measures irreversibility $$\langle \Sigma(\lambda_t) \rangle = S\left[\overrightarrow{P}(+\Sigma) || \overleftarrow{P}(-\Sigma)\right]$$

Strasberg, Esposito PRE (2017)

entropy production measures distance from "equilibrium" $$\langle \Sigma(\lambda_t) \rangle = S[\rho(x_t, y_t, \lambda_t) || \sigma(x_t, y_t, \lambda_t)]$$

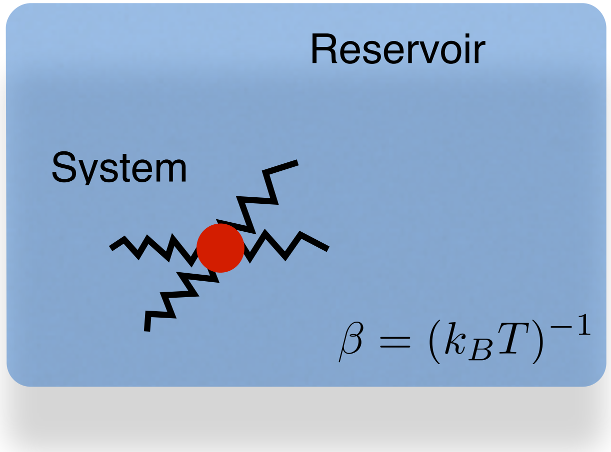
Outline - III

- Recap: standard thermodynamic potentials
- Violation of laws of thermodynamics in the quantum regime?
- Resolution of paradox/lessons
- (weak coupling) Stochastic thermodynamics
- Thermodynamic potentials and stochastic thermodynamics beyond weak coupling (classical) ← *a bit chewy …*
- Thermodynamic uncertainty relation (quantum)

Energy-temperature uncertainty relation

Bohr $\Delta\beta\,\Delta U \geq 1$ for thermal states

valid for systems weakly coupled to environment



(quantum notation)

$$\hat{H} = \hat{H}_S + \hat{H}_E + \hat{V}_{SE}$$

when this term becomes important

with system state

$$\rho_S \approx \frac{e^{-\beta \hat{H}_S}}{Z_S}$$

Correction for systems **strongly** coupled to their environment?

Energy uncertainty

reduced system state $\rho_S := tr_E \left[\frac{e^{-\beta(\hat{H}_S + \hat{H}_E + \hat{V}_{SE})}}{Z} \right]$

mean force Hamiltonian $\rho_S =: \frac{e^{-\beta \hat{H}_S^*}}{Z_S^*}$

Kirkwood, …, Jarzynski, Lutz,
Aurell, Seifert, Esposito …

mean system energy $U_S := -\partial_\beta \ln Z_S^*$ additive with bare environment

Energy uncertainty

reduced system state $$\rho_S := tr_E\left[\frac{e^{-\beta(\hat{H}_S+\hat{H}_E+\hat{V}_{SE})}}{Z}\right]$$

mean force Hamiltonian $$\rho_S =: \frac{e^{-\beta \hat{H}_S^*}}{Z_S^*}$$

Kirkwood, …, Jarzynski, Lutz, Aurell, Seifert, Esposito …

mean system energy $$U_S := -\partial_\beta \ln Z_S^*$$ additive with bare environment

but $$U_S \neq tr[\hat{H}_S^* \rho_S]$$

instead $$U_S = tr[\hat{E}_S \rho_S]$$

Seifert, PRL (2016)

$$\hat{E}_S := \partial_\beta \left(\beta \hat{H}_S^*\right)$$ effective energy operator of system

energy uncertainty

$$\Delta U_S = \sqrt{\mathrm{Var}_{\rho_S}[\hat{E}_S]}$$

Mean force *H* and effective energy operator

UNIVERSITY OF EXETER

weak coupling

state

$$\rho_S = \frac{e^{-\beta \hat{H}_S}}{Z_S}$$

energy

$$U_S = tr[\hat{H}_S \rho_S]$$

strong coupling

$$\rho_S = \frac{e^{-\beta \hat{H}^*_S}}{Z^*_S}$$

Hamiltonian of mean force

$$U_S = tr[\hat{E}_S \rho_S]$$

effective energy operator

Example: Damped Harmonic Oscillator

$$\hat{H}_{\mathcal{S}} = \frac{\hat{p}^2}{2M} + \frac{M\omega^2\hat{x}^2}{2} \longrightarrow \hat{H}^*_{\mathcal{S}}(T) = \frac{\hat{p}^2}{2M_T} + \frac{M_T\omega_T^2\hat{x}^2}{2}$$

$$\hat{H}_{\mathcal{R}} = \sum_{j=1}^{N}\left(\frac{\hat{p}_j^2}{2M_j} + \frac{M_j\omega_j^2\hat{x}_j^2}{2}\right)$$

$$M_T = \omega_T^{-1}\sqrt{\frac{\hat{p}^2}{\hat{x}^2}}$$

$$\hat{V}_{\mathcal{S}\cup\mathcal{R}} = \sum_{j=1}^{N}\left(-\lambda_j\hat{x}\otimes\hat{x}_j + \frac{\lambda_j^2}{2M_j\omega_j^2}\hat{x}^2\right)$$

$$\omega_T = 2T\operatorname{arcoth}(2\sqrt{\langle\hat{p}^2\rangle\langle\hat{x}^2\rangle})$$

Drude-Ullersma spectrum

$$\lambda_j = \sqrt{\frac{2\gamma M_j M\omega_j^2\Delta}{\pi}\frac{\omega_D^2}{\omega_D^2+\omega_j^2}}$$

Grabert, Weiss, Talkner, Z. Phys. B. (1983)

$$\hat{E}^*_{\mathcal{S}}(T) := \partial_\beta\left[\beta\hat{H}^*_{\mathcal{S}}(T)\right] = \alpha_T\hat{H}^*_{\mathcal{S}}(T) - g_T\frac{\hat{a}_T^2 + (\hat{a}_T^\dagger)^2}{2}$$

Constants dependent on effective mass and frequency

T-dependent annihilation operator

Temperature uncertainty

optimal parameter estimation:

considering all possible measurements (POVMs) on the quantum system, what is the ultimate precision that we can hope for?

$$\beta = 1/(k_B T)$$

Get bound on $\Delta\beta$ for states

$$\rho_S =: \frac{e^{-\beta \hat{H}_S^*}}{Z_S^*}$$

General answer: *Cramer-Rao* bound

$$\Delta\theta \geq \frac{1}{\sqrt{nF(\theta)}}$$

Rao (1945), Cramer (1946)

Temperature uncertainty

UNIVERSITY OF EXETER

optimal parameter estimation:

considering all possible measurements (POVMs) on the quantum system, what is the ultimate precision that we can hope for?

$$\beta = 1/(k_B T)$$

General answer: *Cramer-Rao* bound

Get bound on $\Delta\beta$ for states

$$\rho_S =: \frac{e^{-\beta \hat{H}_S^*}}{Z_S^*}$$

Miller, Anders, Nat. Comms. 9:2203 (2018)

$$\Delta\beta \geq \frac{1}{\sqrt{\Delta U_S{}^2 - Q[\hat{E}_S, \rho_S]}} \geq \frac{1}{\Delta U_S}$$

strongly coupled   weakly coupled

With the *skew information*:

$$Q[\hat{E}_S, \rho_S] = -\frac{1}{2}\int_0^1 da\, \mathrm{tr}\{[\hat{E}_S, (\rho_S)^a]\ [\hat{E}_S, (\rho_S)^{1-a}]\}$$

commutators

Wigner, Yanase, J. Phys. Chem. (1963)

Li, et al, Eur Phys Jour D (2011)

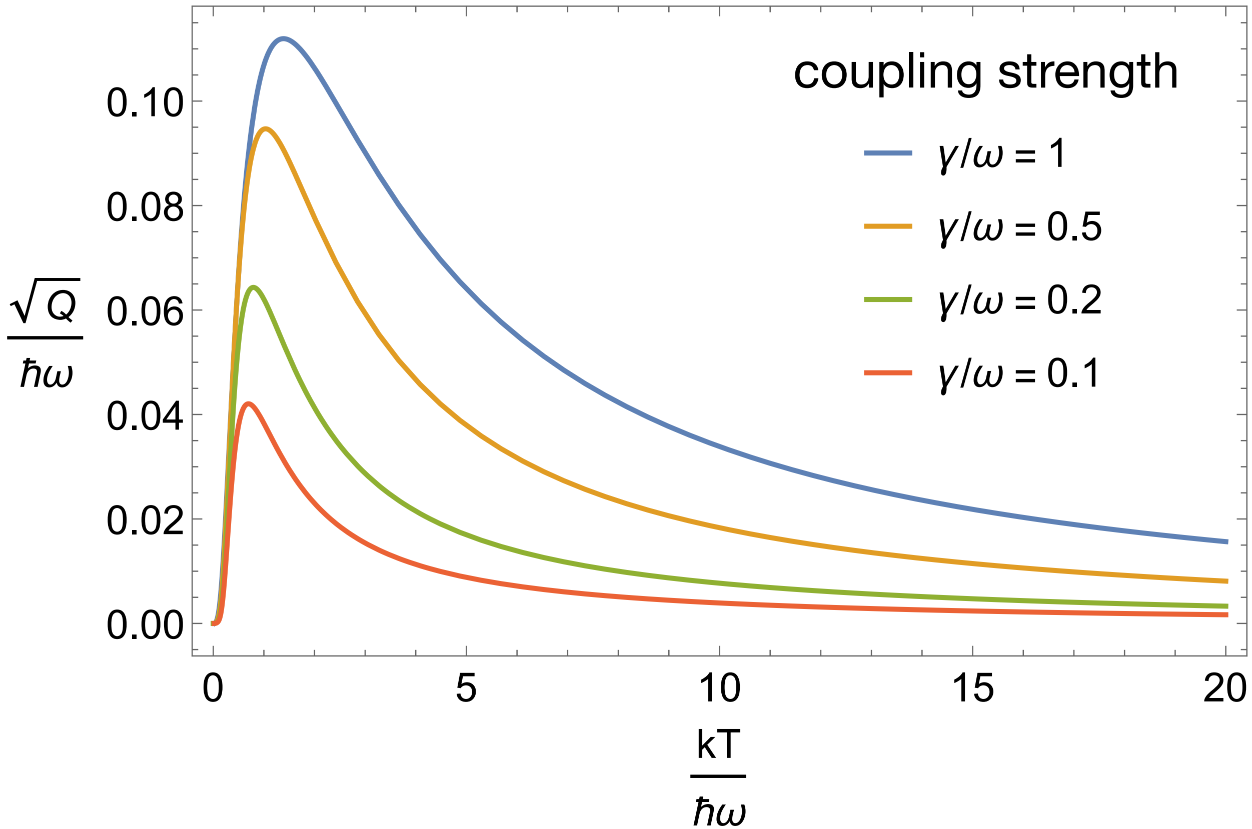
Skew information

$$Q[\hat{E}_S, \rho_S] = -\frac{1}{2}\int_0^1 da\,\mathrm{tr}\{[\hat{E}_S, (\rho_S)^a]\ \ [\hat{E}_S, (\rho_S)^{1-a}]\}$$

Wigner, Yanase, J. Phys. Chem. (1963)
Li, et al, Eur Phys Jour D (2011)

commutators

for damped quantum harmonic oscillator



$$\hat{H}^*_S(T) = \frac{\hat{p}^2}{2M_T} + \frac{M_T\omega_T^2\hat{x}^2}{2}$$

$$\hat{E}_S(T) = \alpha_T \hat{H}^*_S(T) - g_T\frac{\hat{a}_T^2 + (\hat{a}_T^\dagger)^2}{2}$$

Grabert, Weiss, Talkner,
Z. Phys. B. (1983)

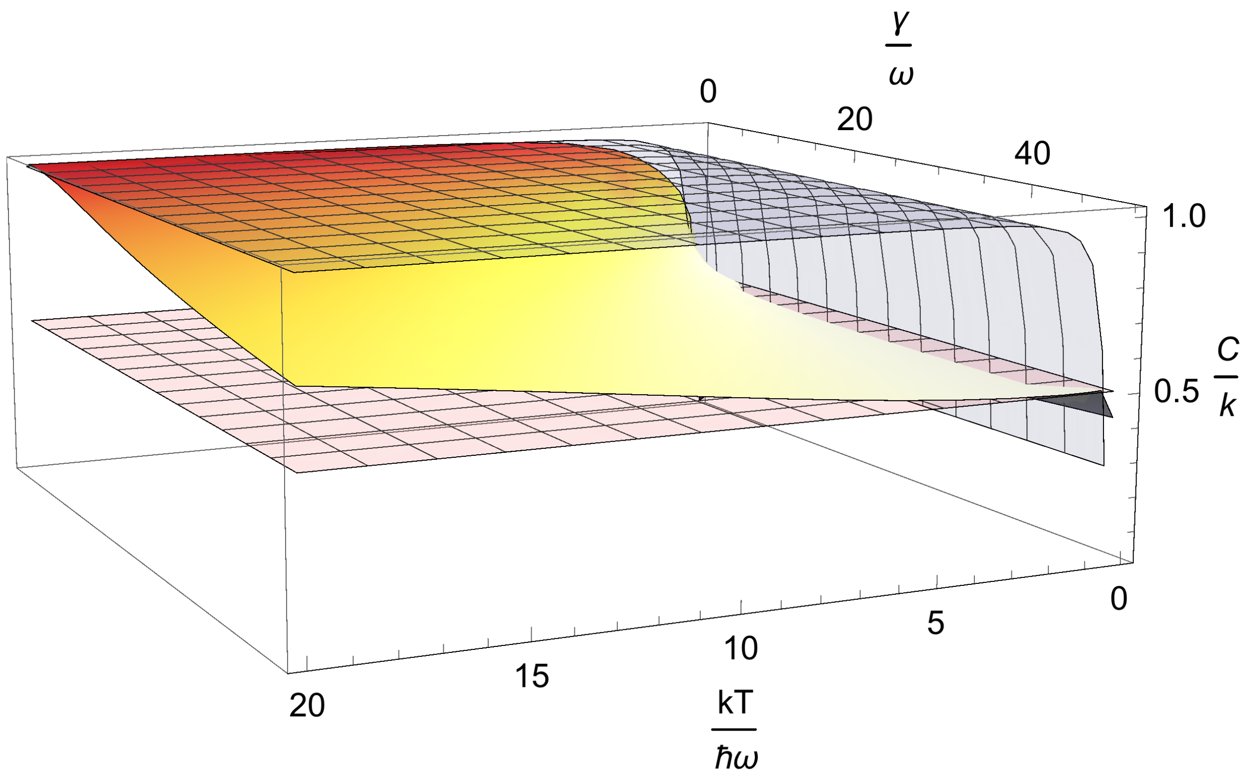
Heat capacity $C_S(T) := \frac{\partial U_S}{\partial T}$

weakly coupled: $C_S(T) = \frac{\Delta U_S^2}{T^2}$

strongly coupled: $C_S(T) = \frac{\Delta U_S^2}{T^2} - \frac{Q[\hat{E}_S, \rho_S]}{T^2} + \langle \partial_T \hat{E}_S \rangle$

quantum correction

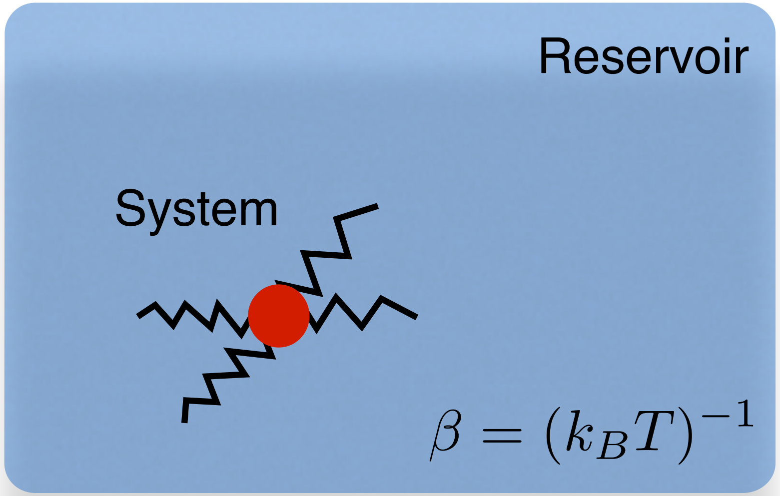
classical correction



for damped quantum harmonic oscillator

Summary: QuTh. beyond weak coupling

It is possible to include a system's **coupling** to environmental degrees of freedom in a **generalised thermodynamic framework.**



The energy operator that includes **strong coupling** corrections may not commute with Gibbs state (⇒ skew information $Q[\hat{E}_S, \rho_S]$).

$$\hat{E}_S := \partial_\beta \left(\beta \hat{H}_S^* \right)$$

$$\rho_S = \frac{e^{-\beta \hat{H}_S^*}}{Z_S^*}$$

Thermodynamic **uncertainty relation** with strong coupling corrections:

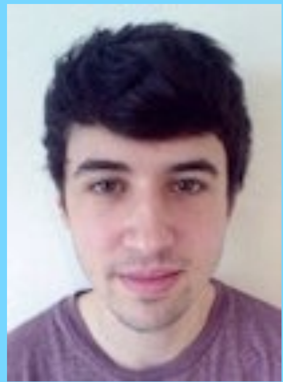
$$\Delta\beta \geq \frac{1}{\sqrt{\Delta U_S{}^2 - Q[\hat{E}_S, \rho_S]}} \geq \frac{1}{\Delta U_S}$$

Miller, Anders, Nat. Comms. 9:2203 (2018)

Strong coupling stochastic thermodynamics
PRE **95**, 062123 (2017)

$$\rho_S = \frac{e^{-\beta \hat{H}_S^*}}{Z_S^*}$$

$$U_S = tr[\hat{E}_S \rho_S]$$



Harry Miller
Exeter

Uncertainty relation
Nature Comms **9**, 2203 (2018)

Further reading:

Seifert, *PRL* **116**, 020601 (2016)

Jarzynski, *PRX* **7**, 011008 (2017)

Strasberg, Esposito,
PRE **95**, 062101(2017)

Thank you!

EPSRC
Engineering and Physical Sciences Research Council

cost
EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY
MPNS COST Action MP1209
Thermodynamics in the quantum regime

THE ROYAL SOCIETY