Aspects of Quantum Thermodynamics: Facts, debatable issues and unsolved issues

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FQMT 2024 Prag

First Law – ~~Energy Conservation~~

$$\Delta U = \Delta Q + \Delta W$$

ΔU change in internal energy

ΔQ heat added on the system

ΔW work done on the system

H. von Helmholtz: “Über die Erhaltung der Kraft” (1847)

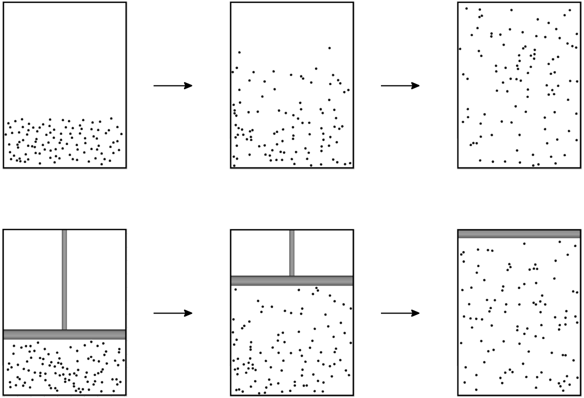
$$\Delta U = (T\Delta S)_{\text{quasi-static}} - (p\Delta V)_{\text{quasi-static}}$$

Heat in Thermodynamics

$$\Delta U = \Delta Q^{\text{irrev}} + \Delta W^{\text{noneq}}$$

$$\Rightarrow \Delta Q^{\text{irrev}} = \underset{\substack{\Big\uparrow \\ \textbf{must know}}}{\Delta U} - \underset{\substack{\Big\uparrow \\ \textbf{must know}}}{\Delta W^{\text{noneq}}}$$

MINUS FIRST LAW vs. SECOND LAW



-1st Law

2nd Law

Entropy in Stat. Mech.

$$S = k_{\mathrm{B}} \ln \Omega(E, V, \ldots)$$

QM: $\Omega_{\mathrm{G}}(E, V, \ldots) = \sum_{0 \leq E_i \leq E} 1$

classical

Gibbs: $\Omega_{\mathrm{G}} = \left(\frac{1}{N!\, h^{\mathrm{DOF}}} \right) \int \mathrm{d}\Gamma\, \Theta \left(E - H(\underline{q}, \underline{p}; V, \ldots) \right)$

Boltzmann: $\Omega_{\mathrm{B}} = \epsilon_0 \frac{\partial\, \Omega_{\mathrm{G}}}{\partial E} \propto \int \mathrm{d}\Gamma\, \delta \left(E - H(\underline{q}, \underline{p}; V, \ldots) \right)$

density of states

canonical ensemble

$$\varrho^T = \delta(E^T - H^T(\xi, Z)) / \omega^T(E^T; Z) \Rightarrow P(E^S | E^T; Z) = \frac{\omega^S(E^S)\,\omega^B(E^T - E^S)}{\omega_T(E^T)}$$

$$E^T = E^S + E^B$$

$$= \frac{\omega^S(E^S)}{\varepsilon\,\omega^T(E^T)} \exp\left[\frac{S^B_B(\overbrace{E^T - E^S}^{E^B})}{k_B}\right]$$

NEXT: $S^B_B(E^T - E^S) = S^B_B(\bar{E}^B) + \frac{1}{T^B_B(\bar{E}_B)}(E^T - E^S - \bar{E}^B) + \dots,$

$$\rightsquigarrow \quad = \frac{\omega^S(E^S)}{\varepsilon\,\omega^T(E^T)} \exp\left[\frac{S^B_B(\bar{E}^B)}{k_B} + \frac{(E^T - \bar{E}^B) - E^S}{k_B T^B_B(\bar{E}^B)} + \dots\right]$$

with $+ \dots \to 0$! $(\partial^2 S^B_B / \partial^2 E^B) = -1/T_B^2 C^B_B)$

$$\Rightarrow \quad P(E^S | E^T, Z) = \frac{\omega^S(E^S)}{Z_{can}} \exp\left[-\frac{E^S}{k_B T^B_B(\bar{E}^B)}\right]$$

note: $T^B_B(\bar{E}_B) \overset{?}{=} T^B_B(E^T)$; IF "normal": $T^B_B = T^B_G = T^S_G = T^T_G$

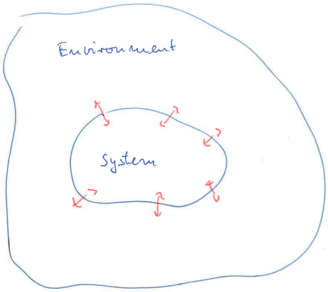
Erunt multi qui, postquam mea scripta legerint, non ad contemplandum utrum vera sint quae dixerim, mentem convertent, sed solum ad disquirendum quomodo, vel iure vel iniuria, rationes meas labefactare possent.

G. Galilei, *Opere* (Ed. Naz., vol. I, p. 412)

There will be many who, when they will have read my paper, will apply their mind, not to examining whether what I have said is true, but only to seeking how, by hook or by crook, they could demolish my arguments.

Equilibrium Theromdynamics of Open Quantum Systems

Weakly coupled systems



$E_{\text{interaction}} \ll E_{\text{system}}$

System $\oplus$ Environment in thermal equilibrium at total energy E_{tot}

$$p_\beta(\mathbf{x}) = Z^{-1} e^{-\beta H_S(\mathbf{x})}$$

$$Z = \int d\Gamma_S e^{-\beta H_S(\mathbf{x})}$$

$\mathbf{x} \in \Gamma_S$: phase space of system

$$d\Gamma_s = \frac{d^{3N}\mathbf{q}\, d^{3N}\mathbf{p}}{h^{3N}}$$: volume element

$$\beta = k_B^{-1} \frac{\partial S_{\text{tot}}}{\partial E_{\text{tot}}}$$: inverse temperature

Standard form of canonical equilibrium of a subsystem holds for large systems with short-range interactions:

$$E_{\text{interaction}} \propto V_S^{2/3}\,, \quad E_{\text{system}} \propto V_S$$

$$F_S = -\beta^{-1} \ln Z \ : \qquad \text{free energy}$$

$$U_S = -\frac{\partial}{\partial \beta} \ln Z = \langle H_S \rangle_S \ : \qquad \text{internal energy}$$

$$S_S = k_B \ln Z_S - k_B \beta \frac{\partial}{\partial \beta} \ln Z_S = -k_B \langle \ln p_\beta \rangle_S \ : \qquad \text{entropy}$$

yielding

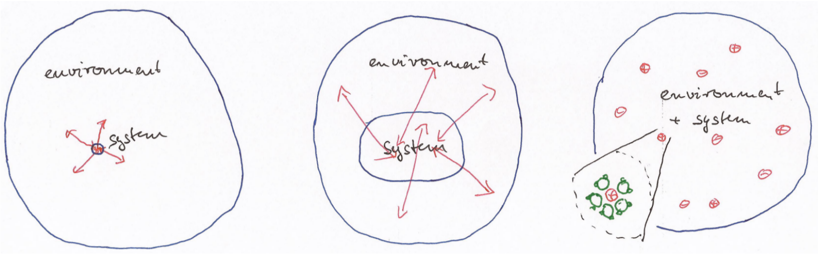
$$F_S = U_S - TS_S \tag{1}$$

$$U_S = \frac{\partial}{\partial \beta} (\beta F_S) \tag{2}$$

$$S_S = k_B \beta^2 \frac{\partial}{\partial \beta} F_S \tag{3}$$

Any pair of the three equations (1 – 3) implies the third one.
Potentials F_s, U_S and S_S satisfying (1 –3) are
THERMODYNAMICALLY CONSISTENT.

Strongly coupled systems



microscopic system

macroscopic system with long-range interactions

solvated system, e.g. pinch of salt in a pot of water

$$H_{\text{tot}}(\mathbf{x},\mathbf{y}) = H_S(\mathbf{x}) + H_i(\mathbf{x},\mathbf{y}) + H_B(\mathbf{y})$$: total system's Hamiltonian

$\mathbf{x} \in \Gamma_S$, Γ_S phase space of system

$\mathbf{y} \in \Gamma_B$, Γ_B phase space of environment

Strongly coupled systems

$H_{\text{tot}}(\mathbf{x},\mathbf{y}) = H_S(\mathbf{x}) + H_i(\mathbf{x},\mathbf{y}) + H_B(\mathbf{y})$: total system's Hamiltonian

$$\mathbf{x} \in \Gamma_S\,, \quad \Gamma_S \quad \text{phase space of system}$$

$$\mathbf{y} \in \Gamma_B\,, \quad \Gamma_B \quad \text{phase space of environment}$$

Let the total system stay in a canonical equilibrium state at inverse temperature β:

$$\rho_\beta(\mathbf{x},\mathbf{y}) = Z_{\text{tot}}^{-1} e^{-\beta H_{\text{tot}}(\mathbf{x},\mathbf{y})}$$

$$Z_{\text{tot}} = \int d\Gamma_S d\Gamma_B e^{-\beta H_{\text{tot}}(\mathbf{x},\mathbf{y})}$$

Then the system is in the state

$$p_\beta(\mathbf{x}) = \int d\Gamma_B \rho_\beta(\mathbf{x},\mathbf{y})$$

The reduced state $p_\beta(\mathbf{x})$ in general differs from the Gibbs state $Z_S^{-1} e^{-\beta H(\mathbf{x})}$ of a weakly coupled system. To write $p_\beta(\mathbf{x})$ in the form of a Gibbs state one introduces the Hamiltonian of mean force $H^*(\mathbf{x})$ defined by

$$
\begin{aligned}
e^{-\beta H^*(\mathbf{x})} &= \langle e^{-\beta(H_S(\mathbf{x})+H_i(\mathbf{x},\mathbf{y}))} \rangle_B \\
&= Z_B^{-1} \int d\Gamma_B \, e^{-\beta(H_S(\mathbf{x})+H_i(\mathbf{x},\mathbf{y})+H_B(\mathbf{y}))} \\
Z_B &= \int d\Gamma_B \, e^{-\beta H_B(\mathbf{y})} \\
H^*(\mathbf{x}) &= H_S(\mathbf{x}) - \beta^{-1} \ln \langle e^{-\beta H_i(\mathbf{x},\mathbf{y})} \rangle_B \\
p_\beta(\mathbf{x}) &= Z_S^{-1} e^{-\beta H^*(\mathbf{x})} \\
Z_S &= \int d\Gamma_S \, e^{-\beta H^*(\mathbf{x})} = Z_{\text{tot}}/Z_B
\end{aligned}
$$

Quantum interlude

$$\begin{aligned} \Gamma_S \otimes \Gamma_B &\Rightarrow \mathcal{H}_S \otimes \mathcal{H}_B \\ \int d\Gamma_s \int d\Gamma_b &\Rightarrow \mathrm{Tr}_S \mathrm{Tr}_B \\ \rho(\mathbf{x}, \mathbf{y}) &\Rightarrow \hat{\rho} \\ H_{\mathrm{tot}} &\Rightarrow \hat{H}_{\mathrm{tot}} \end{aligned}$$

$$\begin{aligned} \hat{H}^* &= -\beta^{-1} \ln \mathrm{Tr}_B e^{-\beta \hat{H}_{\mathrm{tot}}} / \mathrm{Tr} e^{-\beta H_B} \\ \hat{p}_\beta &= Z_S^{-1} e^{-\beta \hat{H}^*} \\ Z_S &= Z_{\mathrm{tot}} / Z_B = \mathrm{Tr}_B \mathrm{Tr}_S e^{-\beta \hat{H}_{\mathrm{tot}}} / \mathrm{Tr}_B e^{-\beta \hat{H}_B} \end{aligned}$$

For quantum systems, the Hamiltonian of mean force ALWAYS depends on temperature.

Warning

W1 Note that $\hat{H}^*$ ($H^*(\mathbf{x})$) determines $\hat{p}_\beta$ ($p_\beta(\mathbf{x})$) but not vice versa:

$$\ln p_\beta = -\beta H^* - \ln Z_S$$

In other words, H_S^* cannot be inferred from the intrinsic point of view of the open system, say in terms of tomography of the open system density matrix. Additional information from the environment in the form of $Z_S = Z_{\text{tot}}/Z_B$ is required.

Thermodynamics

$$F_S = -\beta^{-1}\ln Z_s = F_{\text{tot}} - F_B$$

$$U_s = \frac{\partial}{\partial\beta}\beta F_S = U_{\text{tot}} - U_B$$

$$S_S = k_B\beta^2\frac{\partial}{\partial\beta}F_S = S_{\text{tot}} - S_B$$

$$C_S = -k_B\beta^2\frac{\partial^2}{\partial\beta^2}\beta F_S = C_{\text{tot}} - C_B$$

The potentials F_S, U_S and S_S are thermodynamically consistent because they follow from a partition function.

R.P. Feynman, F.L. Vernon, Ann. Phys. (N.Y.) **24**, 118 (1963).
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**, 061105 (2009).

Further warnings

W2 INTERNAL ENERGY

$$U_S = -\frac{\partial}{\partial \beta} \ln Z_S = \langle \frac{\partial}{\partial \beta} \beta H^* \rangle_S = \langle H^* \rangle_S + \beta \langle \partial H^* / \partial \beta \rangle_s$$

$$\langle \cdot \rangle_S = Z_S^{-1} \int d\Gamma_S \cdot e^{-\beta H^*}$$

The internal energy in general does not agree with the average of the Hamiltonian of mean force. The temperature dependence of H^* entails an additional contribution.

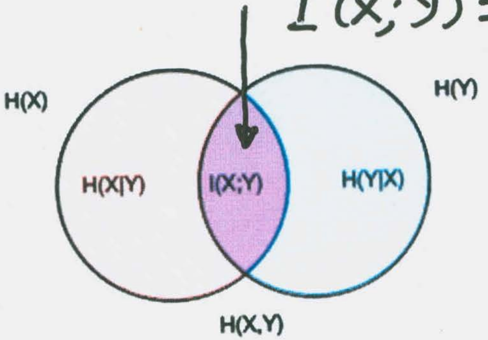
W3 ENTROPY

$$S_S = -k_B \langle \ln p_\beta \rangle_S + k_B \beta^2 \langle \partial H^* / \partial \beta \rangle_S$$

The entropy in general deviates from the Shannon-Gibbs (von Neumann) entropy due to the temperature dependence of the Hamiltonian of mean force.

Conditional Entropy

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

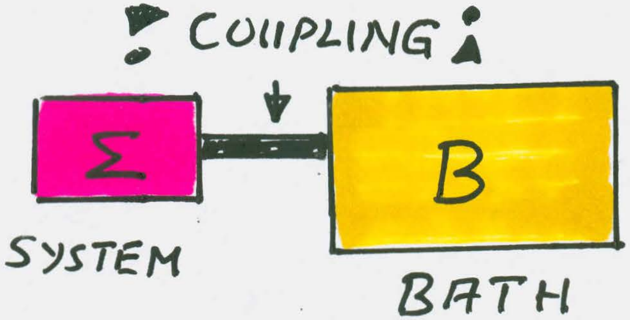


$$H(y|x) = -\sum_{x,y} p(x,y) \ln p(x,y) - \left(-\sum_{x} p(x) \ln p(x)\right)$$

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

Quantum Conditional Entropy

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



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

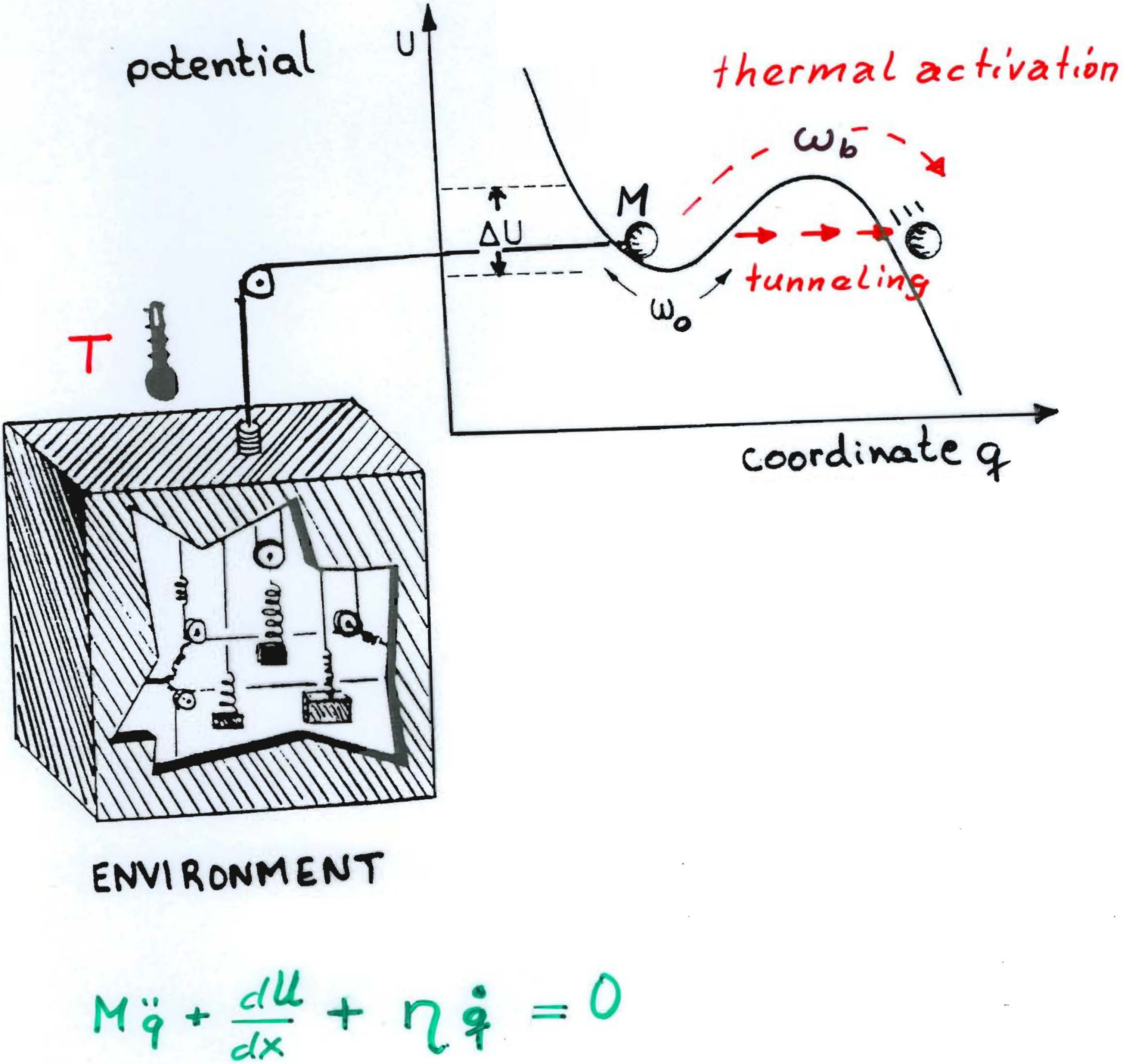
can. thermod. entropy

quantum cond. entropy

$$\overset{?!}{=} S_{vN}\left(\varrho^{can}_{\Sigma\times B}\right) - S_{vN}\left(\varrho_B = Tr_{\Sigma}\, \varrho^{can}_{\Sigma\times B}\right)$$

$$\uparrow \neq \varrho_B^{can}$$

THE PROBLEM



$$M\ddot{q} + \frac{d\mathcal{U}}{dx} + \eta\dot{q} = 0$$

"simple" example Damped harmonic Oscillator

$$\boxed{\mathbb{H}^{*}_{osc} = \mathbb{H}_{eff} + kT\ln\left(Z_{eff}/Z_{s}\right)\cdot \mathbb{1}_{s}}$$

with $\varrho_s = \frac{\exp(-\beta\,\mathbb{H}^{*}_{osc})}{Z_s} = \frac{\exp(-\beta\,\mathbb{H}_{eff})}{Z_{eff}}$

$$\underline{Z_s \cdot Z_B^{0} \overset{!}{=} Z_T}$$

$$\mathbb{H}_{eff} = \frac{p^2}{2m_{eff}} + \frac{1}{2} m_{eff}\,\omega_{eff}^2\, q^2$$

$$m_{eff} = \frac{\sqrt{\langle p^2\rangle / \langle q^2\rangle}}{\omega_{eff}}$$

$$Z_{eff}^{-1} = 2\sinh(\hbar\beta\omega_{eff}/2)$$

$$\omega_{eff} = \frac{2}{\hbar\beta}\,\mathrm{arcoth}\left(\frac{2}{\hbar}\sqrt{\langle p^2\rangle\langle q^2\rangle}\right)$$

$$\mathbb{H}_{eff}\,|n\rangle = \hbar\omega_{eff}\,(n + 1/2)\,|n\rangle$$

Grabert et al. Z. Phys. B 55, 87-94 (1984)

PHYSICAL REVIEW A **69**, 052109 (2004)

Is the dynamics of open quantum systems always linear?

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(Received 1 December 2003; published 17 May 2004)

We study the influence of the preparation of an open quantum system on its reduced time evolution. In contrast to the frequently considered case of an initial preparation where the total density matrix factorizes into a product of a system density matrix and a bath density matrix the time evolution generally is no longer governed by a linear map nor is this map affine. Put differently, the evolution is truly nonlinear and cannot be cast into the form of a linear map plus a term that is independent of the initial density matrix of the open quantum system. As a consequence, the inhomogeneity that emerges in formally exact generalized master equations is in fact a nonlinear term that vanishes for a factorizing initial state. The general results are elucidated with the example of two interacting spins prepared at thermal equilibrium with one spin subjected to an external field. The second spin represents the environment. The field allows the preparation of mixed density matrices of the first spin that can be represented as a convex combination of two limiting pure states, i.e., the preparable reduced density matrices make up a convex set. Moreover, the map from these reduced density matrices onto the corresponding density matrices of the total system is affine only for vanishing coupling between the spins. In general, the set of the accessible total density matrices is nonconvex.

Examples

Jaynes Cummings model

$$\hat{H}_{\text{tot}} = \underbrace{\frac{\epsilon}{2}\sigma_z}_{\hat{H}_S} + \underbrace{\Omega\left(a^\dagger a + \frac{1}{2}\right)}_{\hat{H}_B} + \underbrace{\chi\sigma_z\left(a^\dagger a + \frac{1}{2}\right)}_{\hat{H}_i}$$

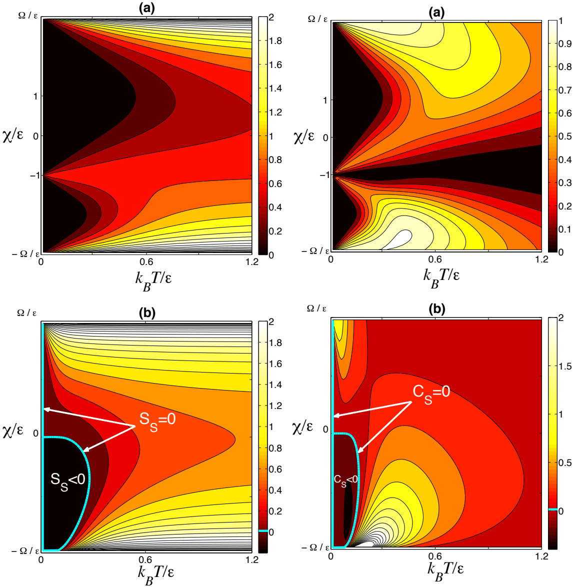
partition functions

$$Z_{\text{tot}} = q_+ + q_- \,, \quad q_\pm = \frac{e^{\beta\Omega/2} e^{\mp\beta(\epsilon+\chi)/2}}{1 - e^{-\beta(\Omega\pm\chi)}}$$

$$Z_B = \frac{1}{2\sinh(\beta\Omega/2)}$$

$$Z_S = 2(q_+ + q_-)\sinh(\beta\Omega/2)$$

Entropy and specific heat



$\Omega/\epsilon = 3$

$\Omega/\epsilon = 1/3$

Nonequilibrium aspects of work and heat fluctuations

Aspects of work fluctutions: classical case

Work

Classical closed system:

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

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

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

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

thermal equilibrium: mean values vs. fluctuations

depends on β & γ

internal energy: $$U_S = -\frac{\partial}{\partial\beta}\ln Z_S = \left\langle \frac{\partial}{\partial\beta}\beta H^* \right\rangle_{\rho_\beta}$$

$\rho_\beta \equiv \varrho^{eq}_{system}$
$\doteq$ "S"

$$= \langle H_S\rangle_S + \left[\langle H_{INT}\rangle + \langle H_B\rangle_{tot} - \langle H_B\rangle_B\right]$$

fluctuating internal energy $$E(x;\lambda) = \frac{\partial}{\partial\beta}\left[\beta H^*(x;\lambda)\right]; \quad U_S = \langle E(x;\lambda)\rangle_S$$

Talkner & H. PRE $\underline{94}$ 022143 (2016)
App. B

$$= \langle H_{tot}|x\rangle_{w^{eq}} - \langle H_B\rangle_B$$

$$\underline{w^{eq}(y|\underline{x}) = \frac{\varrho^{eq}_{tot}(x,y)}{\varrho^{eq}_{system}(x)}}$$

$\underline{e}$q. $\underline{p}$reparation $\underline{c}$lass
G.+H.+T. Z. Physik $\underline{B26}$ 389 (1977) ($\underline{epc}$)

Now $$\delta H_{INT}(x,y) = H_{INT}(x,y) - \langle H_{INT}(x,y)|x\rangle_{w^{eq}}$$

$\int dy\, H_{INT}(x,y)\, w^{eq}(y|x)$

with $\varrho^\circ_{epc} = w^{eq}(y|x)\,\rho^\circ(x)$

arbitrary

$$\boxed{\langle \delta H_{INT}(x,y)\rangle_{\varrho^\circ_{epc}} \overset{!}{=} 0; \quad \forall \varrho^\circ_{epc}}$$

ambiguity for fluctuating potentials: $E(x;\lambda)$; etc.

$$E(x;\lambda) \Rightarrow e(x,y;\lambda) = E(x;\lambda) + \alpha(x)\,\delta H_{INT}(x,y) + h_E(x;\lambda)$$

set $\left\{ h(x;\lambda);\ \int dx\, h(x;\lambda)\,\rho^{eq}(x;\lambda) = 0 \right\}$

null-space $\uparrow$ fix!

T. & H. PRE 94 (2016)

$$\boxed{\langle e(x,y;\lambda)\rangle_{\rho^{eq}_{tot}} \overset{!}{=} \langle E(x;\lambda)\rangle_{\rho^{eq}_{S} \equiv p_\beta} = U_S}$$

but $\langle e^n(x,y;\lambda)\rangle_{\rho^{eq}_{tot}} \neq \langle E^n(x,\cancel{y};\lambda)\rangle$; $n > 1$

$$\int dx\,d\underline{\underline{y}}\ \alpha(x) \left\{ H_{INT} \frac{\rho^{eq}_{tot}(x,y)}{\rho^{eq}_{S}(x)} \cdot p^0(x) - \langle H_{INT}(x,y)|x\rangle \frac{\rho^{eq}_{tot}(x,y)}{\rho^{eq}_{S}(x)} p^0(x) \right\}$$

$$= \int dx\, \alpha(x)\, p^0(x) \underbrace{\left\{ \langle H_{INT}(x,y)|x\rangle - \langle H_{INT}(x,y)|x\rangle \cdot 1 \right\}}_{0} = 0$$

Aspects of quantum work

Projective & generalized measurements

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

3. “UNTOUCHED” WORK:

$$\langle w \rangle = \int dz[H(z(t),\lambda(t)) - H(z,\lambda(0))]\rho(z) \qquad \text{valid !}$$

$$\langle w \rangle = \mathrm{Tr}[H^H(\lambda(t)) - H(\lambda(0))]\rho(0) \qquad ????????$$

There is no operational definition of untouched work as a proper random variable.

With untouched work it would be possible to extract energy from quantum correlation and in particular from entanglement in multipartite systems.

A. Allahverdyan, Phys. Rev. E **90**, 032137 (2014).

K.V. Hovhannisyan, M. Perarnau-Llobet, M. Huber, A. Acín, Phys. Rev. Lett. **111**, 240401 (2013).

A first **NO-GO** Theorem

M Perarnau-Llobet. E Bäumer, KV Hovhannisyan, M Huber and Acin,

Phys. Rev. Lett. **118**, 070601 (2017) ; Quoted from our RMP 2020:

"Perarnau-Llobet et al. (2017) demonstrated that no measurement scheme of work exists that is linear in the initial state of the system and for which the following two conditions are simultaneously satisfied: (1) The average work agrees with the difference of the average final and initial energies for any initial state, and (2) the resulting work statistics agrees for diagonal initial states (i.e., \bar ρ(0) = ρ(0) with the TPPEMS result [Eq. (89)]."

Probability of work

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

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

More facts, open problems, pitfalls

A. The holy grail for classical/quantum **non**-equilibrium thermodynamics will never be realized (in my lifetime). In contrast to equilibrium thermodynamics with its Grande Laws; -- it rather will be characterized by a hapless search for unifying principles and cumbersome experimental challenges.

B. Thermal quantum machines: How to go beyond the usual scenario used for weak coupling scenarios where individual (work)-strokes are implemented by strict thermally ***adiabatic*** (i.e. with no heat exchange), i.e. strict **unitary** work strokes, **followed by** strict **heat exchanges** (i.e. in absence of any simultaneously present work and heat exchanges (thermalization) -- such as in those stylized quantum Otto-cycles.

Typically is however, that both - heat and work – are acting both during a corresponding stroke-duration. Likewise, simultaneous work-heat exchanges occur while coupling TO and coupling OFF thermal baths (e.g. with the two isothermal strokes in the Carnot cycle.

Work-Operator WO

by Deffner-Paz-Zurek
PRE 94, 010103 (2016)

G(u) = Tr exp(iu (W - WO) rho (B)
with
WO = sum_n Pi_n (H^H_tau -H_0) Pi_n (C)
and
rho = \sum_n p(n) Pi_n = exp(- beta H_0)/Z_0 (D)

$$\Rightarrow \tilde{W}_{n_0} = \langle n_0 | U^{+} H(\tau) U_\tau | n_0 \rangle - \varepsilon(n_0; \lambda_0)$$

H^H_tau is the Hamilton operator in the Heisenberg picture at time tau; Pi_n are the projection operators on the energy-eigenstates of H_0.

$$\langle e^{-\beta \tilde{W}} \rangle = e^{-\beta \Delta F} e^{-S(\tilde{\rho}_\tau \| \rho^{eq}_{-H(\tau)})}$$

Note that (A) and (7) imply (B) and (C) and vice versa.

Obviously, (B) is the characteristic function of the hermitian operator WO
defined in (C) which is the **old work operator projected onto the eigenbasis of H_0.** Hence, you have introduced a new work operator in spite of your initial statement that work operators are deficient.

Let me close with the simple example of a spin 1/2 in a magnetic field which undergoes a sudden change:
H_0 = epsilon_0 sigma_z/2 ==> H_1 = epsilon_1 \sigma_x/2

In this case the final Hamiltonian projected onto the eigenbasis of the initial one vanishes and the work operator (7) becomes

$$WO = -H_0 \quad !?!$$

WO = - H_0
and the **possible work values just coincide with the spectrum of the initial Hamiltonian in contrast to the result of the two measurement scheme consisting of four possible work values** given by the differences of the initial and final energy eigenvalues.

Finally let me come back to your email, at the end of which you say that you take into account the cost of measurement. But where in your theory is the measurement? In the abstract of your paper you say "we completely omit quantum measurements in the definition of quantum work". I see here a contradiction.
Or do I misunderstand?

I hope this message finds you in good spirit. If I have been critical it merely has been for the sake of science and understanding but it is not meant in any personal way.

A QUESTION ?

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

(published 19 December 2011)

DOI: 10.1103/RevModPhys.83.1653 PACS numbers: 05.30.−d, 05.40.−a, 05.60.Gg, 05.70.Ln, 99.10.Cd

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

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

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).

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

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)

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Generalized energy measurements

Positive operator valued measures (POVM) as generalized measurements

projective	POVM	
Π_n	$M_n, \; M_n^\dagger$	measurement operators
$\sum_n \Pi_n \rho \Pi_n$	$\sum_n M_n \rho M_n^\dagger$	ρ_{pm}: unselectice pm state
$\mathrm{Tr} \Pi_n \rho \Pi_n$	$\mathrm{Tr} M_n \rho M_n^\dagger$	$p_n = \mathrm{Prob}(n \text{ in } \rho)$
$\Pi_n \rho \Pi_n / p_n$	$\rho_n = M_n \rho M_n^\dagger / p_n$	ρ_n: selective pm state
$\sum_n \Pi_n = \mathbb{1}$	$\sum_n M_n^\dagger M_n = \mathbb{1}$	normalization

[redacted]

[redacted]

[redacted]

[redacted]

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$\sum_n \Pi_n = \mathbb{1}$	$\sum_n M_n^\dagger M_n = \mathbb{1}$	normalization

measurement error:

$$p(n|m) = \text{Tr} M_n \Pi_m M_n^\dagger / \text{Tr}\Pi_m = \text{Tr} M_n^\dagger M_n \Pi_m / \text{Tr}\Pi_m$$

A measurement is ERROR-FREE if

$$p(n|m) = \delta_{n,m}$$

Probability of work

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

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

p_n $= \text{Tr } P_n(t_0)\rho(t_0)$
$=$ probability of being at energy $e_n(t_0)$ at $t = t_0$

ρ_n $= P_n(t_0)\rho(t_0)P_n(t_0)/p_n$
$=$ state after measurement

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

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