

(Quantum) Thermodynamics at strong coupling: Go's and NO-Go's



Peter Hänggi and Peter Talkner

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[arXiv:1911.11660]

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WALTER SCRIPTUNIAS II



Steam engines convert heat into work; physicists are debating the rules that govern how quantum-level machines could do the same thing.

HERMODYNAMICS

Clash of the physics laws

The debate over how the laws of heat and energy apply at the quantum level is hotting up.

BY DAVIDE CASTELVECCHI

The young field of quantum thermodynamics, which tries to reconcile quantum theory with the 200-year-old science of heat and entropy, is booming. It's also causing some heated disputes.

Many physicists hope that rebuilding thermodynamics from the laws of quantum mechanics will help to settle long-debated conundrums. There are practical implications, too. The field could help to resolve whether the concepts of heat and efficiency apply to tiny electronic components and even atom-sized machines.

But despite proliferating approaches — many of which were presented at the Fifth Quantum Thermodynamics Conference this month in Oxford, UK — the field is as contentious as ever. The crux of the issue is whether the fundamental laws that govern heat and energy on large scales also dictate the behaviour of nanoscale systems — or whether new laws are needed.

Interest is growing: this year, more than 100 scientists attended the quantum thermodynamics conference, says co-organizer Vlatko Vedral, a physicist at the University of Oxford. That is double the attendance in previous years.

Such meetings bring together researchers from subfields that use different technical

languages, says co-organizer Felix Binder, a theoretician at Nanyang Technological University in Singapore. “There are a lot of barriers being broken between different approaches.”

But a few physicists, such as Peter Hänggi of the University of Augsburg, Germany, caution that some of the work is misguided. “The field is growing rapidly, but also a lot of nonsense is written (and talked) about,” he says.

Physicists have argued over the meaning of the three laws of thermodynamics since they were written in the nineteenth and early twentieth centuries. The laws say that energy cannot be created or destroyed; that the amount of disorder, or entropy, in an isolated system can ▶

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

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


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

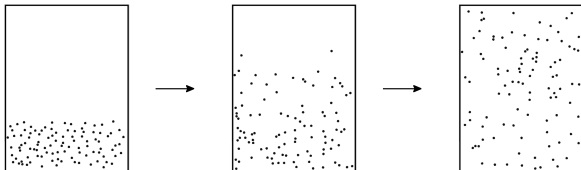


must know

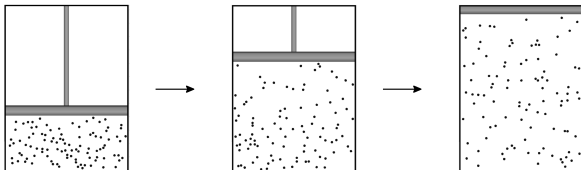


must know

MINUS FIRST LAW vs. SECOND LAW



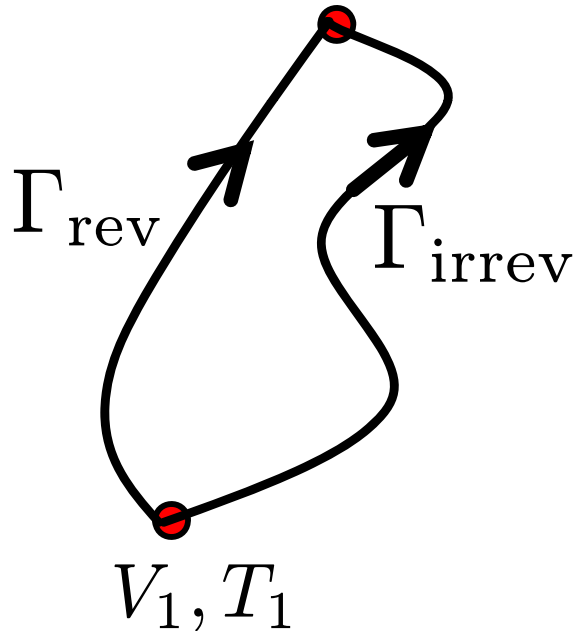
-1st Law



2nd Law

Entropy S – content of *transformation* „Verwandlungswert“

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

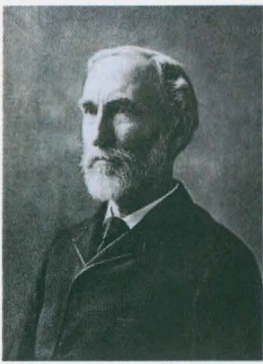


$$\oint_C \frac{\delta Q}{T} \leq 0$$

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

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

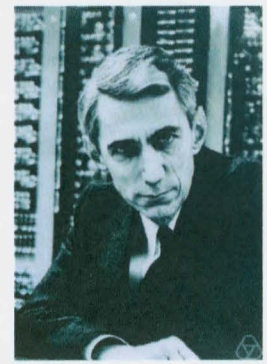
$$S(V_2, T_2) - S(V_1, T_1) = \int_{\Gamma_{\text{rev}}} \frac{\delta Q^{\text{rev}}}{T}$$



J. W. Gibbs



L. Boltzmann



C. E. Shannon

$$H_G = \int W_N \ln W_N d\Gamma_N$$

$$H_B = N \int W_i \ln W_i d\Gamma_i$$

$$S_G = k_B \ln \Omega_G$$

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

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

⊕
ZOO

Renyi
 Relative
 Kullback-Leibler
 v. NEUMANN
 COLMOGOROV-SINAI
 FISHER
 Daroczy-Harvda-Charvat-Tsallis
 WEHRL
 Hartley-Chaitin
 CLAUDIUS
 CONDITIONAL

ETC.

Entropy in Stat. Mech.

$$S = k_B \ln \Omega(E, V, \dots)$$

QM: $\Omega_G(E, V, \dots) = \sum_{0 \leq E_i \leq E} 1$



classical

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

Boltzmann: $\Omega_B = \epsilon_0 \frac{\partial \Omega_G}{\partial E} \propto \int d\Gamma \delta(E - H(\underline{q}, \underline{p}; V, \dots))$
density of states

First law


$$dE = \delta Q + \delta A = T dS - \sum_n p_n dZ_n$$

↖ = dE - \delta A = 0 if ADIABATIC

$$p_j = T \left(\frac{\partial S}{\partial Z_j} \right)_{E, Z_n \neq Z_j} \stackrel{!}{=} - \left\langle \frac{\partial H}{\partial Z_j} \right\rangle_E$$

From: "Thermodynamic Laws in **ISOLATED** Systems"
S. HILBERT, P. H., J. Dunkel, PRE 90, 02116 (2014)

Gibbs

$$\begin{aligned} T_G \left(\frac{\partial S_G}{\partial Z_j} \right) &= \frac{1}{\omega} \frac{\partial}{\partial Z_j} \text{Tr} \left[\Theta(E - H) \right] = -\frac{1}{\omega} \text{Tr} \left[-\frac{\partial}{\partial Z_j} \Theta(E - H) \right] \\ &= -\text{Tr} \left[\left(\frac{\partial H}{\partial Z_j} \right) \frac{\delta(E - H)}{\omega} \right] = - \left\langle \frac{\partial H}{\partial Z_j} \right\rangle \end{aligned}$$


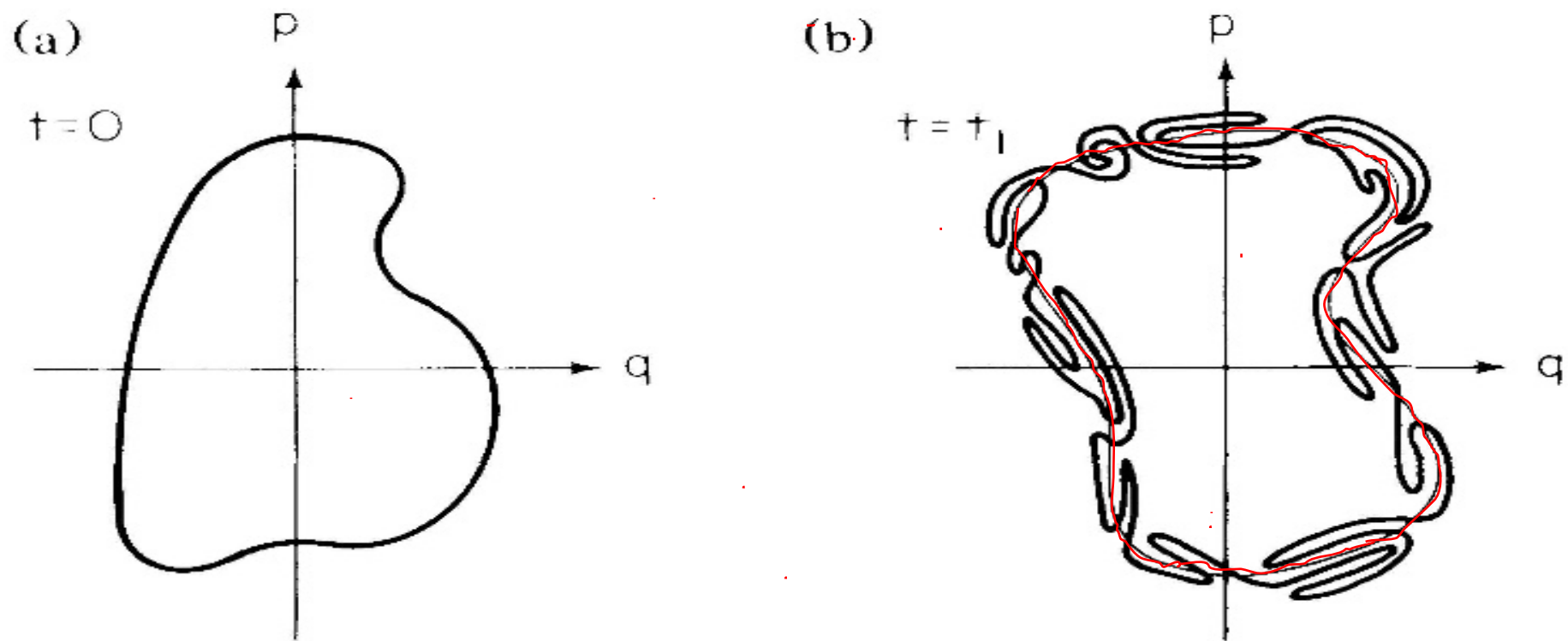


FIG. 1. (a) Initial $H=E_0$ surface at $t=0$ evolves under the exact dynamics into the convoluted surface shown in (b) which is close to an energy surface $H=E(t_1)$, where $E(t_1)$ is obtained from the constancy of μ .

Merits and qualms of work fluctuations in classical fluctuation theorems

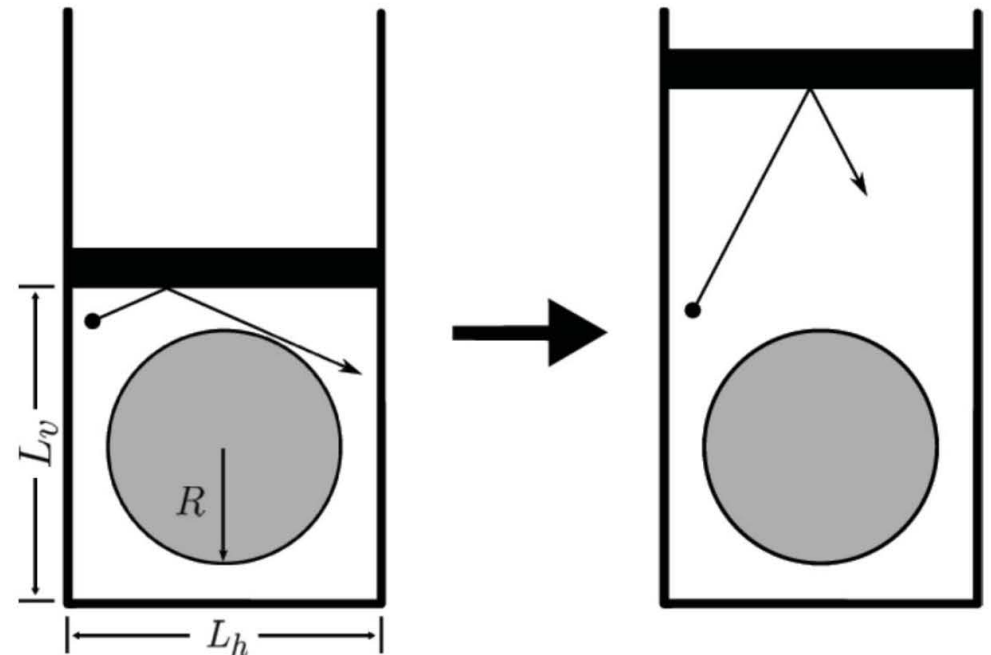
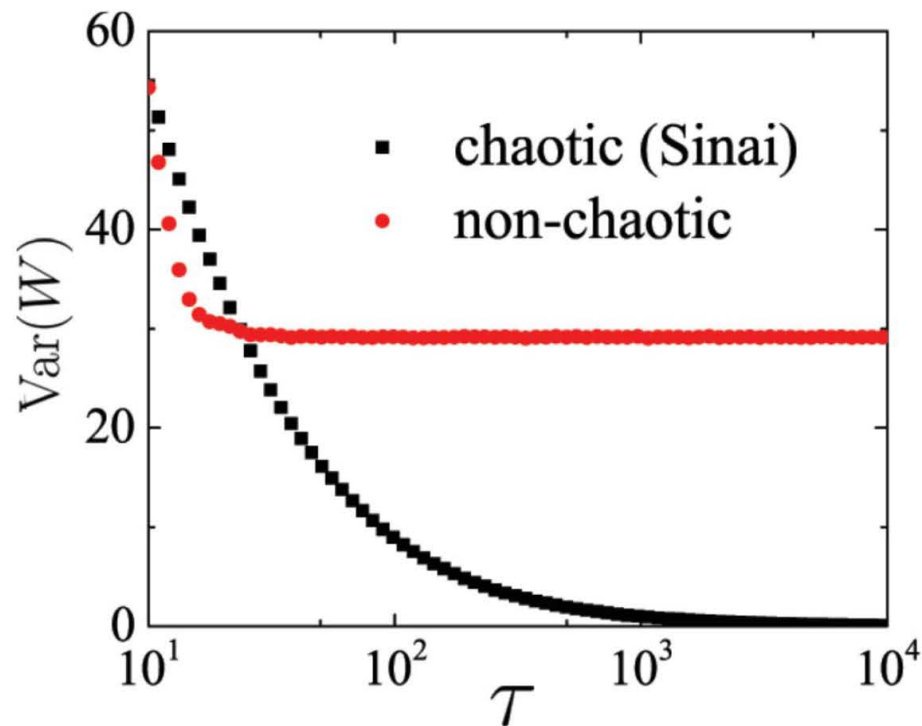
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canonical ensemble

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

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

$$= \frac{\omega^S(E^S)}{\mathcal{Z} \omega^T(E^T)} \exp \left[\frac{S_B^B(E^T - E^S)}{k_B} \right]$$

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

$$\Rightarrow \frac{\omega^S(E^S)}{\mathcal{Z} \omega^T(E^T)} \exp \left[\frac{S_B^B(\bar{E}^B)}{k_B} + \frac{(E^T - \bar{E}^B) - E^S}{k_B T_B^B(\bar{E}^B)} + \dots \right]$$

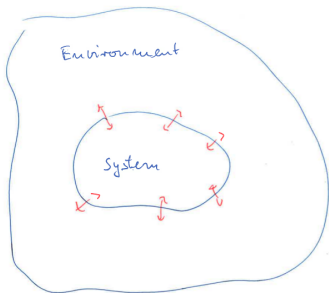
with $+\dots \rightarrow 0$! $(\partial^2 S_B^B / \partial^2 E^B) = -1/T_B^2 C_B^B$



$$P(E^S | E^T, Z) = \frac{\omega^S(E^S)}{\mathcal{Z}_{can}} \exp \left[- \frac{E^S}{k_B T_B^B(\bar{E}^B)} \right]$$

note: $T_B^B(\bar{E}^B) \stackrel{?}{=} T_B^B(E^T)$; IF "normal": $T_B^B = T_G^B = T_G^S = T_G^T$

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

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

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

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

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

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

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

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

yielding

$$F_S = U_S - TS_S \quad (1)$$

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

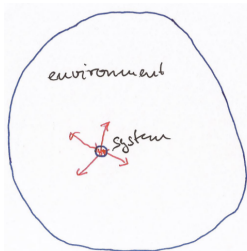
$$S_S = k_B \beta^2 \frac{\partial}{\partial \beta} F_S \quad (3)$$

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.

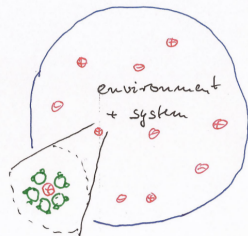
Strongly coupled systems



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

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

$\mathbf{y} \in \Gamma_B$, Γ_B 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

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

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).

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

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

$$Z_B = \int d\Gamma_B e^{-\beta H_B(\mathbf{y})}$$

$$H^*(\mathbf{x}) = H_S(\mathbf{x}) - \beta^{-1} \ln \langle e^{-\beta H_i(\mathbf{x},\mathbf{y})} \rangle_B$$

$$p_\beta(\mathbf{x}) = Z_S^{-1} e^{-\beta H^*(\mathbf{x})}$$

$$Z_S = \int d\Gamma_S e^{-\beta H^*(\mathbf{x})} = Z_{\text{tot}}/Z_B$$

Warning

W1 Note that \hat{H}^* ($H^*(\mathbf{x})$) determines \hat{p}_β ($p_\beta(\mathbf{x})$) 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.

Further warnings

W2 INTERNAL ENERGY

$$U_S = -\frac{\partial}{\partial \beta} \ln Z_S = \left\langle \frac{\partial}{\partial \beta} \beta H^* \right\rangle_S = \langle H^* \rangle_S + \beta \langle \partial H^* / \partial \beta \rangle_S$$
$$\langle \cdot \rangle_S = Z_S^{-1} \int d\Gamma_S \cdot e^{-\beta H^*}$$

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.



Beware of continuous entropy



$$p(x, \lambda) = p(y, \lambda) \left| \frac{dy}{dx} \right| \Leftrightarrow p(x, \lambda) dx = p(y, \lambda) dy$$

$$S_y(\lambda) = - \int dy p(y, \lambda) \ln p(y, \lambda)$$

$$= - \int dx p(x, \lambda) \left| \frac{dx}{dy} \right| \ln \left\{ p(x, \lambda) \left| \frac{dx}{dy} \right| \right\}$$

$$= - \int dx p(x, \lambda) \ln p(x, \lambda) - \int dx p(x, \lambda) \ln \left| \frac{dx}{dy} \right|$$

$$= S_x(\lambda) - \int p(x, \lambda) \ln \left| \frac{dx}{dy} \right| dx$$

$$\equiv \langle \ln \left| \frac{dx}{dy} \right| \rangle = C(\lambda; \beta)$$

$$\rightarrow S_y(\lambda; \beta) = S_x(\lambda; \beta) = C(\lambda; \beta) \neq 0 !!$$

Summary

- ▶ Equilibrium statistical mechanics and thermodynamics of open systems in strong contact with the environment
 - ▶ Hamiltonian of mean force $H^*(\mathbf{x})$ replaces H_S . It is defined in terms of a renormalized Boltzmann factor and hence, depends on temperature, in general.
 - ▶ W1: $H^*(\mathbf{x})$ cannot be determined from an intrinsic open system point of view
 - ▶ W2: $U_S = \langle H^* \rangle_S + \beta \langle \frac{\partial}{\partial \beta} H^* \rangle_S$
 - ▶ W3: Thermodynamic entropy may deviate from Shannon-Gibbs entropy
- ▶ Stochastic energetics and thermodynamics
 - ▶ Fluctuating internal energy must be DEFINED such that its equilibrium average equals the internal energy. There are no stringent arguments for a particular choice.
 - ▶ Fluctuating energy and fluctuating work can be used to define fluctuating heat by means of a first law-like balance requiring a closed total system. The ambiguity of the fluctuating internal energy is consequently inherited by the heat.

Summary (cont.)

- ▶ Thermodynamic consistency allows one to construct compatible families of fluctuating internal energy, fluctuating free energy and fluctuating entropy. For a given fluctuating internal energy one may choose virtually any second fluctuating thermodynamic potential with a matching third one.
- ▶ For other initial preparation classes than the stationary preparation class there is no obvious way of introducing a Hamiltonian of mean force.



Once the fluctuating internal energy of the system is defined as $E(\mathbf{x}, \lambda)$ the remaining energy $G(\mathbf{x}, \mathbf{y})$ may be assigned to the environment

$$\begin{aligned} G(\mathbf{x}, \mathbf{y}) &= H_{\text{tot}}(\mathbf{x}, \mathbf{y}) - E(\mathbf{x}, \lambda) \\ &= \delta H_i(\mathbf{x}, \mathbf{y}) + \delta H_B(\mathbf{x}, \mathbf{y}) + \langle H_B \rangle_B \\ \delta H_i(\mathbf{x}, \mathbf{y}) &= H_i(\mathbf{x}, \mathbf{y}) - \langle H_i(\mathbf{x}, \mathbf{y}) | \mathbf{x} \rangle \\ \delta H_B(\mathbf{x}, \mathbf{y}) &= H_B(\mathbf{y}) - \langle H_B(\mathbf{y}) | \mathbf{x} \rangle \end{aligned}$$

This division though is not mandatory: a part of the interaction energy $\delta H_i(\mathbf{x}, \mathbf{y})$ could be attributed to the system, as well as an additional contribution from the null-space \mathcal{N}_β yielding a truly fluctuating internal energy expression

$$e(\mathbf{x}, \mathbf{y}, \lambda) = E(\mathbf{x}, \lambda) + \alpha(\mathbf{x})\delta H_i(\mathbf{x}, \mathbf{y}) + h_E(\mathbf{x}, \lambda)$$

which is a random field due to the dependence on the environmental coordinates \mathbf{y} which are distributed according to $w(\mathbf{y}|\mathbf{x})$.

Examples

Jaynes Cummings model

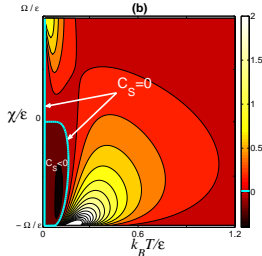
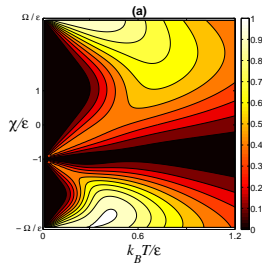
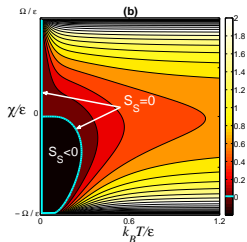
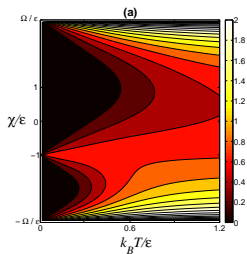
$$\hat{H}_{\text{tot}} = \underbrace{\frac{\epsilon}{2}\sigma_z}_{\hat{H}_S} + \underbrace{\Omega\left(a^\dagger a + \frac{1}{2}\right)}_{\hat{H}_B} + \underbrace{\chi\sigma_z\left(a^\dagger a + \frac{1}{2}\right)}_{\hat{H}_i}$$

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

(a): $\Omega/\epsilon = 3$, (b): $\Omega/\epsilon = 1/3$

Specific heat

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

"simple" example Damped Harmonic Oscillator

$$H_{osc}^* = H_{eff} + kT \ln(Z_{eff} / Z_S) \cdot \mathbb{1}_S$$

with $S_S = \frac{\exp(-\beta H_{osc}^*)}{Z_S} = \frac{\exp(-\beta H_{eff})}{Z_{eff}}$ $Z_S \cdot Z_B^0 \stackrel{!}{=} Z_T$

$$H_{eff} = \frac{p^2}{2m_{eff}} + \frac{1}{2} m_{eff} \omega_{eff}^2 q^2$$

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

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

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

$$H_{eff} |n\rangle = \hbar \omega_{eff} (n + 1/2) |n\rangle$$

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

ASPECTS OF QUANTUM WORK

P. Talkner and P.H. PRE E 93, 022131 (2016)

Projective & generalized
Measurements

Thermodynamics with system trajectories?

Work supplied to a system by a change of a system's parameter:

$$\begin{aligned}w &= H_{\text{tot}}(\mathbf{Z}(\tau, \mathbf{z}), \lambda(\tau)) - H(\mathbf{z}, \lambda(0)) \\ &= \int_0^\tau dt \frac{\partial H_s(\mathbf{X}(t, \mathbf{z}), \lambda(t))}{\partial \lambda(t)} \dot{\lambda}(t)\end{aligned}$$

$$\dot{\mathbf{Z}} = \{H(\mathbf{Z}, \lambda), \mathbf{Z}\}, \quad \mathbf{Z}(0) = \mathbf{z} \equiv (\mathbf{x}, \mathbf{y})$$

$$\{f(\mathbf{z}), g(\mathbf{z})\} = \sum_i \frac{\partial f}{\partial z_i^p} \frac{\partial g}{\partial z_i^q} - \frac{\partial f}{\partial z_i^q} \frac{\partial g}{\partial z_i^p} : \quad \text{Poisson bracket}$$

Note that

$$\frac{\partial H_{\text{tot}}}{\partial \lambda} = \frac{\partial H_s}{\partial \lambda} = \frac{\partial H^*}{\partial \lambda}$$

Work characterizes a **process**; it comprises information from states at distinct times. Hence it is **not** an **observable**. As such it would only present information about the state at a single instant of time.

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

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} : unselective pm state
$\text{Tr} \Pi_n \rho \Pi_n$	$\text{Tr} M_n \rho M_n^\dagger$	$p_n = \text{Prob}(n \text{ in } \rho)$
$\Pi_n \rho \Pi_n / p_n$	$\rho_n = M_n \rho M_n^\dagger / p_n$	ρ_n : selective pm state
$\sum_n \Pi_n = \mathbb{1}$	$\sum_n M_n^\dagger M_n = \mathbb{1}$	normalization

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

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

projective energy
measurements

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 $t = t_0$

$$\rho_n = P_n(t_0)\rho(t_0)P_n(t_0)/p_n$$

= 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 $e_m(t_f)$

Probability of work

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

Characteristic function of work

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

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

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

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)

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

1. TWO ENERGY MEASUREMENTS:

One at the beginning, the other at the end of the protocol yield eigenvalues $e_n(0)$ and $e_m(\tau)$ of $H(\lambda(0))$ and $H(\lambda(\tau))$.

$$w^e = e_m(\tau) - e_n(0) \implies \text{fluctuation theorems.}$$

2. POWER-BASED WORK:

Requires a **continuous measurement** of power.

E.g. for $H(\lambda) = H_0 + \lambda Q$, a continuous observation of the generalized coordinate Q is required leading to a **freezing of the systems dynamics** in an eigenstate of Q .

$$w_N^p = \sum_{k=1}^N \dot{\lambda}(t_k) q_{\alpha_k} \frac{\tau}{N+1}, \quad Q = \sum_{\alpha} q_{\alpha} \Pi_{\alpha}^Q$$

Fluctuation theorems hold only if $[H_0, Q] = 0$ or equivalently $[H(\lambda(t)), H(\lambda(s))] = 0$ for all $t, s \in (0, \tau)$.

Hence the **equivalence** of the **power- and energy-based work** definitions for classical systems **fails** to hold in **quantum mechanics**.

3. “UNTOUCHED” WORK:

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

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

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

Another NO-GO

$$H_{tot} = H_{\text{System}}(\lambda(t)) + H_{INT} + H_{ENV}; \quad \underline{t \in [0, \tau]}$$

NO state fct.

$$\frac{\partial H_{tot}}{\partial t} = \frac{\partial H_S}{\partial t} = dH_{tot}/dt$$

ΔE_{System} = $\int_0^\tau dt T_r [g_S(t) H_S(t)] = \langle H_S(\tau) \rangle_{g_S(\tau)} - \langle H_S(0) \rangle_{g_S(0)} \neq \Delta U_S^{eq}$

$$= \int_0^\tau dt T_r [\dot{g}_S(t) H_S(t)] + \int_0^\tau dt T_r [g_S(t) \dot{H}_S(t)]$$

NO $\leftarrow \langle Q \rangle ?$

$$\leftarrow = \langle H_{tot}(\tau) \rangle_{g_{tot}(\tau)} - \langle H_{tot}(0) \rangle_{g_{tot}(0)}$$

OK ONLY for Heat weak coupling

$$= \langle W \rangle \doteq \langle W \rangle_{TPPEMS}$$

$$\langle Q \rangle = - \langle Q \rangle_{ENV} \quad (H_S = H_S^*)$$

$$\underline{IF} [H_{tot}(\lambda(0)), g_{tot}(0)] \equiv 0$$

Note: thermally isolated

$$\langle Q \rangle = 0 \quad \& \quad \dot{g} = \frac{i}{\hbar} [H_S(t), g_S(t)] \Rightarrow T_r [\dot{g}_S H_S] = 0 !$$

$\xrightarrow{\text{cyclic}}$

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



Work-Operator WO

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

(B) $G(u) = \text{Tr} \exp(iu (W - WO)) \rho$
with

$$WO = \sum_n \Pi_n (H^\wedge H_\tau - H_0) \Pi_n$$

and

$$\rho = \sum_n p(n) \Pi_n = \exp(-\beta H_0) / Z_0$$

(B)

(C)

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

(D)

$H^\wedge H_\tau$ is the Hamilton operator in the Heisenberg picture at time τ ; Π_n are the projection operators on the energy-eigenstates of H_0 .

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

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

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:

$$H_0 = \epsilonpsilon_0 \sigma_z / 2 \Rightarrow H_1 = \epsilonpsilon_1 \sigma_x / 2$$

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

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

$$WO = -H_0$$

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.

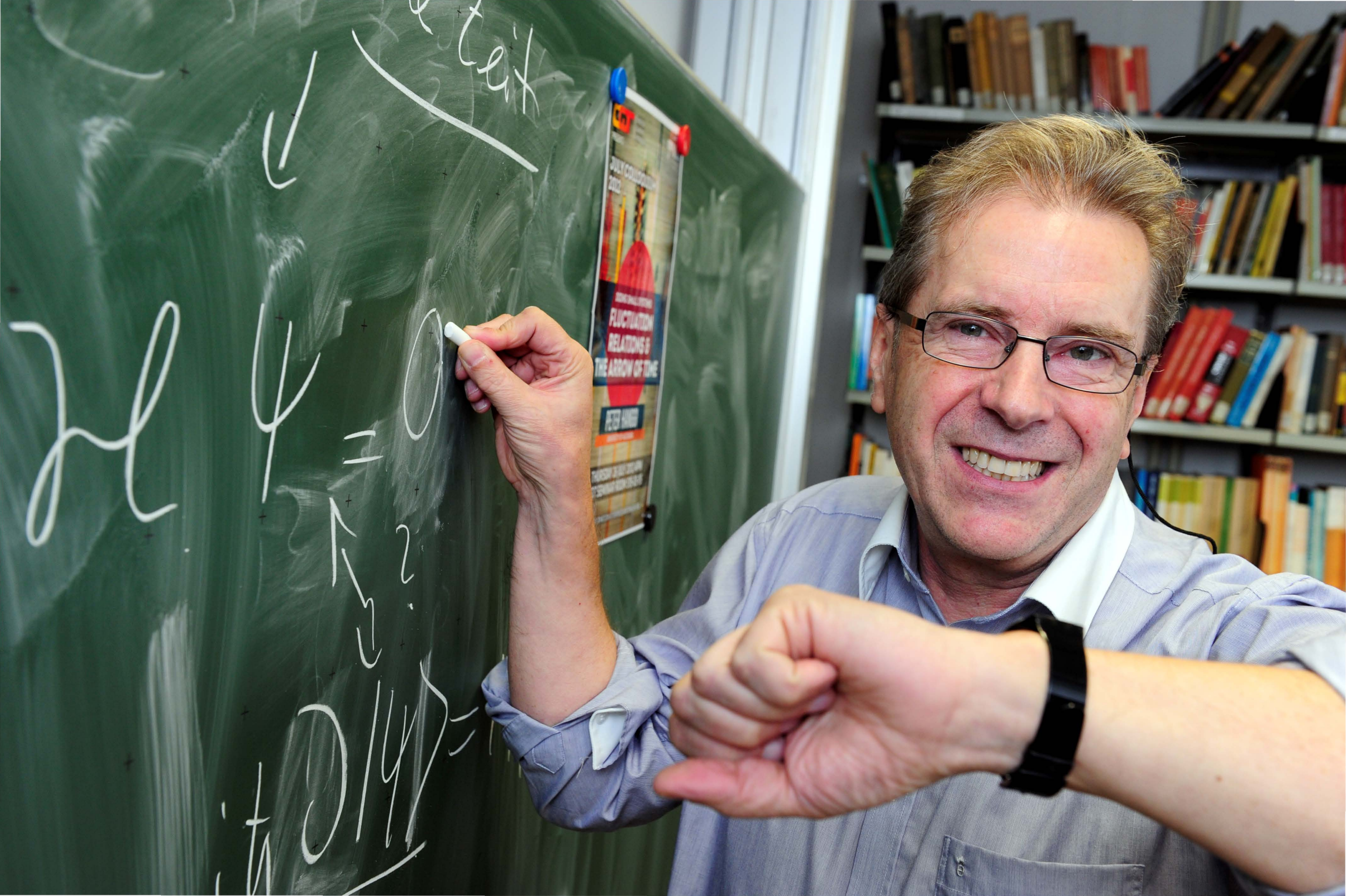
Finally let me come back to your email, at the end of which you say that you take into account the cost of measurement. But where in your theory is the measurement? In the abstract of your paper you say "we completely omit quantum measurements in the definition of quantum work". I see here a contradiction.

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.

Conclusions

- ▶ Generalized energy measurements lead to work distributions which typically do not satisfy the Crooks relation relations.
- ▶ Exceptions are error-free measurements protocol-dependent post-measurement satisfying a detailed balance relation
- ▶ Imposing only the JE poses a weaker requirement: 1st set of measurements must be error-free with a complete orthogonal set of post-measurement states and second measurements must have with “effects” $M_n^\dagger(0)M_n(0)$ having unit trace.
- ▶ Continuous measurements with Gaussian measurement operators and constant variance obey modified fluctuation relations with protocol-independent modifications.
- ▶ Fluctuation relations continue to hold in presence of measurements during the force protocol under mild conditions on the measurement operators.



JULY COLLECTION 2012
FLUCTUATION RELATIONS & THE ARROW OF TIME
PETER HÄNGGI
FRESH JULY 2012
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Zeit

Fluctuating entropy

Fluctuating entropy is a central notion of stochastic thermodynamics¹. Usually it is assumed to be proportional to the logarithm of the system pdf

$$s_0^{\text{sth}}(\mathbf{x}) = -k_B \ln p(\mathbf{x})$$

such that its average coincides with the Shannon entropy $-k_B \int d\Gamma_S p(\mathbf{x}) \ln p(\mathbf{x})$.

However, this violates W3: $\langle s_0^{\text{sth}}(\mathbf{x}) \rangle_\beta \neq S_S$.

Recent attempt² to cure this deficit:

$$s^{\text{sth}}(\mathbf{x}) = -k_B \ln p(\mathbf{x}) + k_B \beta^2 \frac{\partial}{\partial \beta} H^*(\mathbf{x}, \beta)$$

¹ U. Seifert, Phys. Rev. Lett. **95**, 040602 (2005).

² U. Seifert Phys. Rev. Lett. **116**, 020601 (2016).

The Hamiltonian of mean force in general depends on temperature, the parameters specifying the coupling of system and environment as well as on properties of the environment.

If $H_S(\mathbf{x}) = T(\mathbf{p}) + V(\mathbf{q})$ and $H_i(\mathbf{q}, \mathbf{y})$, ($\mathbf{x} \equiv (\mathbf{q}, \mathbf{p})$) then

$$H^*(\mathbf{x}) = T(\mathbf{p}) + V^*(\mathbf{q})$$

$$V^*(\mathbf{q}) = V(\mathbf{q}) - \beta^{-1} \ln \langle e^{-\beta H_i(\mathbf{q}, \mathbf{y})} \rangle_B : \text{potential of mean force}^*$$

In this case the reduced position pdf $p_\beta(\mathbf{q})$ is determined by the potential of mean force

$$p_\beta(\mathbf{q}) = e^{-\beta V^*(\mathbf{q})} / Z_S^{\text{conf}}$$
$$Z_S^{\text{conf}} = Z_S / \int d\mathbf{p} e^{-\beta T(\mathbf{p})}$$

* J.G. Kirkwood, J. Chem. Phys. **3**, 300 (1935).

For example, if

$$H_S(\mathbf{x}, \lambda) = H_0(\mathbf{x}) + Q\lambda, \quad Q : \text{a coordinate of } S$$

the work done on the system by a parameter variation extending over the time span $(0, \tau)$ is given by

$$w = \int_0^\tau dt Q(t, \mathbf{z}) \dot{\lambda}(t)$$

requiring to monitor the trajectory $Q(t, \mathbf{z})$ for $0 \leq t \leq \tau$.

Provided an energy-expression $E(\mathbf{x}, \lambda)$ exists that on average agrees with the internal energy

$$U_S = \langle E(\mathbf{x}, \lambda) \rangle_S$$

then the first law-like energy balance

$$dE = \delta W + \delta Q$$

would define a **fluctuating heat** Q . Accordingly, the hypothetical $E(\mathbf{x}, \lambda)$ may be denoted as a **fluctuating internal energy**.

In stochastic energetics and stochastic thermodynamics a possible temperature dependence of the potential $U(q, \lambda)$ is disregarded and $U(q, \lambda)$ is assumed to represent the fluctuating internal energy. Recently, Seifert¹ reformulated stochastic thermodynamics on the basis of thermodynamics of open systems with the Hamiltonian of mean force as a central element. He postulates the form of the fluctuating internal energy as

$$E(\mathbf{x}, \lambda) = \frac{\partial}{\partial \beta} \beta H^*(\mathbf{x})$$

Its thermal average yields the correct thermodynamic internal energy

$$\langle E(\mathbf{x}, \lambda) \rangle_S = U_S$$

Note that in spite of its name, the fluctuating internal energy is a deterministic function of the phase-space variable \mathbf{x} . A randomness appears only through the stochasticity of the time-evolution of \mathbf{x} .

¹ U. Seifert, Phys. Rev. Lett. **116**, 020601 (2016).

However, any other function

$$\tilde{E}(\mathbf{x}, \lambda) = E(\mathbf{x}, \lambda) + h_E(\mathbf{x}, \lambda)$$

where $h_E(\mathbf{x}, \lambda) \in \mathcal{N}_\beta = \{h(\mathbf{x}) | \int d\Gamma_S h(\mathbf{x}) p_\beta(\mathbf{x}) = 0\}$ equally has the required average $\langle \tilde{E}(\mathbf{x}, \lambda) \rangle_S = U_S$.

Another form of $E(\mathbf{x}, \lambda)$ can be given in terms of a conditional average over the environment

$$E(\mathbf{x}, \lambda) = \langle H_{\text{tot}} | \mathbf{x} \rangle - \langle H_B \rangle_B$$

$$\langle \cdot | \mathbf{x} \rangle = d\Gamma_B \cdot w(\mathbf{y} | \mathbf{x})$$

$$\begin{aligned} w(\mathbf{y} | \mathbf{x}) &= \frac{\rho_\beta(\mathbf{x}, \mathbf{y})}{\int d\Gamma_B \rho_\beta(\mathbf{x}, \mathbf{y})} \\ &= \frac{e^{-\beta(H_i(\mathbf{x}, \mathbf{y}) + H_B(\mathbf{y}))}}{\int d\Gamma_B e^{-\beta(H_i(\mathbf{x}, \mathbf{y}) + H_B(\mathbf{y}))}} \\ &= Z_B^{-1} e^{-\beta(H_{\text{tot}} - H^*(\mathbf{x}))} \end{aligned}$$

$w(\mathbf{y}|\mathbf{x})$: distribution of bath degrees of freedom \mathbf{y} under the condition of a fixed system state \mathbf{x} . It defines the stationary preparation class¹ consisting of all microscopic initial phase-space distributions of the form $w(\mathbf{y}|\mathbf{x})p_0(\mathbf{x})$ with arbitrary $p_0(\mathbf{x})$.

H. Grabert, P. Talkner, P. Hänggi, Z. Phys. B **26** 389 (1977)