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Frontiers in Non-equilibrium Physics 2024

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Hierarchical structure of fluctuation theorems for a driven system in contact with multiple heat reservoirs

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Peking University

Refs: Phys. Rev. E 92, 012131 (2015)

Phys. Rev. Lett. 120, 080602 (2018)

Phys. Rev. E 107, 024135 (2023)

outline

- Background and Motivation
- Hierarchical Structure of Fluctuation Theorems for Multiple Heat Reservoirs
- Properties of Fluctuation Theorems for Multiple Heat Reservoirs
- Calculation of Joint Distributions of Work and Heat
- Summary

Background

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NEWS AND VIEWS | 04 April 2022

Twenty-five years of nanoscale thermodynamics

A paper published in 1997 brought the thermodynamics of the nineteenth century into the twenty-first century — expanding the physics of transformations involved in the operation of steam engines to the realm of molecular motors.

Fluctuation theorems concerning work (partial list)

(There is only one reservoir, and the system is driven)

- Jarzynski equality

$$\left\langle e^{-\beta(W-\Delta F)} \right\rangle = 1$$

C. Jarzynski, PRL, 78, 2690, (1997)

- Crooks Fluctuation Theorem

G. E. Crooks, PRE, 60, 2721, (1999)

$$\frac{\bar{P}_\tau(-W)}{P_\tau(W)} = e^{-\beta(W-\Delta F)}$$

- Hummer-Szabo Relation

G. Hummer, A. Szabo, PNAS, 98, 3658 (2001)

$$\left\langle \delta(\Gamma' - \Gamma_\tau) e^{-\beta W} \right\rangle = \frac{e^{-\beta U_B(\Gamma')}}{Z_A}$$

- Differential Fluctuation Theorem

P. Maragakis, M. Spichty, and M. Karplus, J. Phys. Chem. B, 112, 6168 (2008)

$$P_F(W, \Gamma_0 \to \Gamma_\tau) e^{-\beta(W-\Delta F)} = P_R(-W, \Gamma_\tau^* \to \Gamma_0^*)$$

- Sagawa-Ueda Fluctuation Theorems (with feedback)

T. Sagawa and M. Ueda, Phys. Rev. Lett. 109, 180602 (2012)

$$\left\langle e^{-\beta(W-\Delta F)-I} \right\rangle = 1$$

Fluctuation theorems concerning heat

(There are more than one reservoirs, but the system is not driven)

VOLUME 92, NUMBER 23 PHYSICAL REVIEW LETTERS week ending 11 JUNE 2004

Classical and Quantum Fluctuation Theorems for Heat Exchange

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Theoretical Division, T-13, MS B213, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

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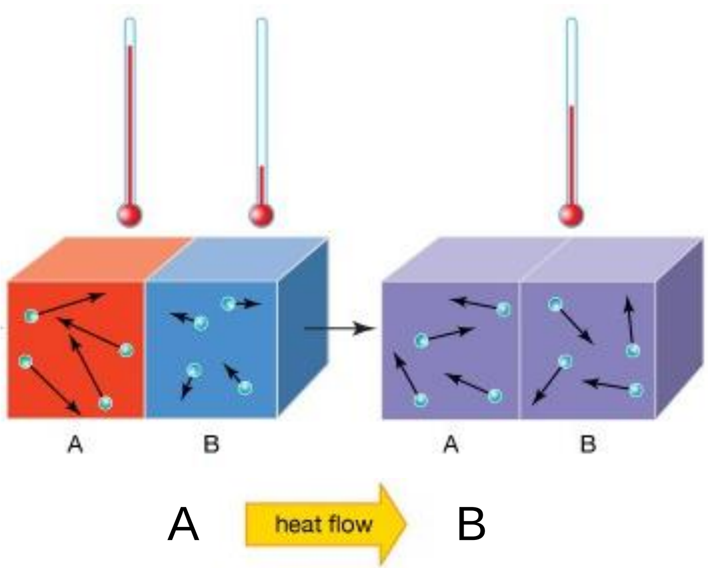
October 2003; published 11 June 2004)

ɣeen two classical or quantum finite systems initially prepared at
ɔbey a fluctuation theorem.



$$\left\langle e^{(\beta-\beta_S)\, q}\right\rangle = 1$$

$$\Rightarrow \quad (\beta-\beta_S)\langle q\rangle \geq 0$$

C. Jarzynski and D. K. Wójcik, PRL, 92, 230602 (2004)

Motivation

Is there any fluctuation theorem concerning work and/or heat when the system is in contact with multiple heat reservoirs?

Can one “synthesis” the above fluctuation theorems concerning work and those concerning heat?

What are the logic relations between various fluctuation theorems?

Is there any fundamental principle underlying various fluctuation theorems?

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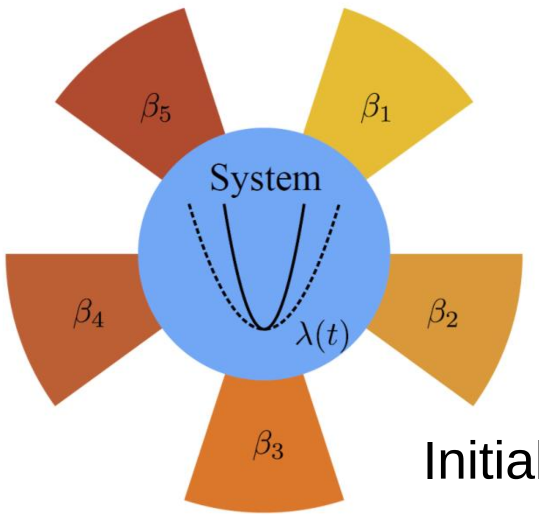
Basic setup: the model

- Consider classical stochastic thermodynamics with unambiguous definitions of microscopic work and heat.
- Weak interactions between the system and the heat reservoirs.



Hamiltonians: $H = H_S + \sum_{\nu} H_\nu + H_{int}$

$$H_S(\gamma_S(t), \lambda(t)) \qquad H_\nu(\gamma_\nu(t)),\ 1 \le \nu \le N$$

Trajectory in phase space

$$\Gamma = (\gamma_S, \gamma_1, \ldots, \gamma_N)$$

$$\gamma_S = (x_S, p_S),\ \gamma_\nu = (x_\nu, p_\nu)$$

Initial state: $\rho^{\mathrm{i}}_{\mathrm{tot}}(\Gamma(0)) = \pi^{\mathrm{i}}_S(\gamma_S(0)) \otimes \pi_1(\gamma_1(0)) \otimes \ldots \otimes \pi_N(\gamma_N(0))$

$$\pi^{\mathrm{i}}_S(\gamma_S(0)) = \frac{e^{-\beta_S H_S(\gamma_S(0), \lambda(0))}}{Z^{\mathrm{i}}_S(\beta_S)},\ \pi_\nu(\gamma_\nu(0)) = \frac{e^{-\beta_\nu H_\nu(\gamma_\nu(0))}}{Z_\nu(\beta_\nu)}$$

Total system consists of the system and heat reservoirs.

The system and heat reservoirs are in local equilibrium initially

Basic setup: work and heat on trajectories

- On a trajectory Γ of the total system

- Heat exchanged with the ν-th heat reservoir

$$q_\nu(\Gamma) := H_\nu(\gamma_\nu(0)) - H_\nu(\gamma_\nu(\tau)),$$

- Work performed by the external driving

$$w(\Gamma) := \int_0^\tau \dot{\lambda} \frac{\partial H_S}{\partial \lambda} dt.$$

- The first law holds on the trajectory level

$$H_S(\gamma_S(\tau), \lambda(\tau)) - H_S(\gamma_S(0), \lambda(0)) = w(\Gamma) + \sum_\nu q_\nu(\Gamma).$$

Detailed fluctuation theorems on trajectories

- Define the conditional probability density $\mathcal{P}(\Gamma|\Gamma(0))$ in the trajectory space.

Γ : an arbitrary trajectory

$\Gamma(0)$: the initial condition

Full information of the initial state $\Gamma(0)$
+
Classical dynamics of the total system

→

Deterministic evolution according to the initial state

$$\mathcal{P}(\Gamma|\Gamma(0)) = \delta_{\Gamma,\Gamma_{\mathrm{d}}}$$

Detailed fluctuation theorems on trajectories

- The time-reversal process

Jacobbi

$$\tilde{\Gamma}(t) = \Theta[\Gamma(\tau - t)]$$

Time reversal operation Θ :

$$\tilde{x}(t) = \Theta[x(\tau - t)] = x(\tau - t),$$
$$\tilde{p}(t) = \Theta[p(\tau - t)] = -p(\tau - t).$$

- Consider the even control parameter (e.g. the frequency of harmonic potential)

$$\tilde{\lambda}(t) = \lambda(\tau - t)$$

Liouville

- Microreversibility

$$\tilde{\mathcal{P}}(\tilde{\Gamma}|\tilde{\Gamma}(0)) = \mathcal{P}(\Gamma|\Gamma(0)),$$

↓

the most detailed fluctuation theorem

Detailed fluctuation theorems on trajectories

- Sum over the reservoir trajectories, the conditional probability density of the system trajectory is

$$\mathcal{P}_S(\gamma_S; \{\gamma_\nu(\tau)\}, \{\gamma_\nu(0)\}|\gamma_S(0)) := \sum_{\{\gamma_\nu\}} \underbrace{\mathcal{P}(\gamma_S, \{\gamma_\nu\}|\gamma_S(0), \{\gamma_\nu(0)\})}_{= \mathcal{P}(\Gamma|\Gamma(0))} \prod_\nu \pi_\nu(\gamma_\nu(0)),$$

- Integrate over $\gamma_\nu(0)$ and $\gamma_\nu(\tau)$, we obtain the coarse-grained conditional probability density

$$\mathcal{P}_S(\gamma_S; \{q_\nu\}|\gamma_S(0)) := \int \dots \int \mathcal{P}_S(\gamma_S; \{\gamma_\nu(0)\}, \{\gamma_\nu(\tau)\}|\gamma_S(0)) \times \prod_\nu \{d\gamma_\nu(0) d\gamma_\nu(\tau) \delta[q_\nu - H_\nu(\gamma_\nu(0)) + H_\nu(\gamma_\nu(\tau))]\}.$$

- The detailed fluctuation theorem

$$\frac{\tilde{\mathcal{P}}_S(\tilde{\gamma}_S; \{-q_\nu\}|\tilde{\gamma}_S(0))}{\mathcal{P}_S(\gamma_S; \{q_\nu\}|\gamma_S(0))} = e^{\sum_\nu \beta_\nu q_\nu}.$$

$q_\nu(-q_\nu)$: the heat exchange with the ν-th heat reservoir in the forward (reverse) process.

Detailed fluctuation theorems on trajectories

- With the complete trajectory probability density

$$\mathcal{P}_S(\gamma_S; \{q_\nu\}) \coloneqq \mathcal{P}_S(\gamma_S; \{q_\nu\} | \gamma_S(0)) \pi^{\mathrm{i}}_S(\gamma_S(0)),$$

we can also obtain

$$\frac{\tilde{\mathcal{P}}_S(\tilde{\gamma}_S; \{-q_\nu\})}{\mathcal{P}_S(\gamma_S; \{q_\nu\})} = e^{-\beta_S[w(\gamma_S) - \Delta F_S] + \sum_\nu (\beta_\nu - \beta_S) q_\nu}.$$

- These are two detailed fluctuation theorems expressed by the probability density of the system trajectory.

- After a coarse-grained procedure, we can obtain a family of fluctuation theorems at different coarse-grained levels.

Differential fluctuation theorems of joint distributions

- Let us consider the joint distribution of work and heat.
- Sum over the system trajectories, we obtain the conditional joint distribution

$$P(w,\{q_\nu\},\gamma_S(\tau)|\gamma_S(0)) := \sum_{\{\gamma_S\}} \mathcal{P}_S(\gamma_S;\{q_\nu\}|\gamma_S(0))\delta(w-\int_0^\tau \dot{\lambda}\partial_\lambda H_S dt),$$

and the complete joint distribution

$$P(w,\{q_\nu\},\gamma_S(\tau),\gamma_S(0)) := \sum_{\{\gamma_S\}} \mathcal{P}_S(\gamma_S;\{q_\nu\})\delta(w-\int_0^\tau \dot{\lambda}\partial_\lambda H_S dt).$$

- The differential fluctuation theorems

$$\frac{\tilde{P}(-w,\{-q_\nu\},\tilde{\gamma}_S(\tau)|\tilde{\gamma}_S(0))}{P(w,\{q_\nu\},\gamma_S(\tau)|\gamma_S(0))} = e^{\sum_\nu \beta_\nu q_\nu},$$

$$\frac{\tilde{P}(-w,\{-q_\nu\},\tilde{\gamma}_S(\tau),\tilde{\gamma}_S(0))}{P(w,\{q_\nu\},\gamma_S(\tau),\gamma_S(0))} = e^{-\beta_S[w-\Delta F_S]+\sum_\nu(\beta_\nu-\beta_S)q_\nu}.$$

Generalized Jarzynski equality and Crooks relation

- When there are more than one heat reservoirs, the marginal distribution of work or heat does not satisfy any fluctuation theorem, but the joint distribution of work and heat does

- Integrate over the initial and final phase-space points, the joint distribution of work and heat is

$$P(w,\{q_\nu\}) := \iint d\gamma_S(\tau)d\gamma_S(0)P(w,\{q_\nu\},\gamma_S(\tau),\gamma_S(0)).$$

- The generalized Crooks relation

Y. Murashita, M. Esposito, Phys. Rev. E. 94, 062148 (2016)

P. S. Pal, S. Lahiri, and A. M. Jayannavar, Phys. Rev. E 95, 042124 (2017).

$$\frac{\tilde{P}(-w,\{-q_\nu\})}{P(w,\{q_\nu\})} = e^{-\beta_S[w-\Delta F_S]+\sum_\nu(\beta_\nu-\beta_S)q_\nu}.$$

- The integral fluctuation theorem of work and heat

Jinfu Chen and **HTQ**, Phys. Rev. E 107, 024135 (2023)

$$\left\langle e^{-\beta_S w+\sum_\nu(\beta_\nu-\beta_S)q_\nu}\right\rangle = e^{-\beta_S \Delta F_S}.$$

The unification of fluctuation theorems and the second law

Microreversibility $\tilde{\mathcal{P}}(\tilde{\Gamma}|\tilde{\Gamma}(0)) = \mathcal{P}(\Gamma|\Gamma(0))$ Eq. (4)

↓ *coarse graining bath trajectory*

Detailed FTs $$\frac{\tilde{\mathcal{P}}_S(\tilde{\gamma}_S;\{-q_\nu\}|\tilde{\gamma}_S(0))}{\mathcal{P}_S(\gamma_S;\{q_\nu\}|\gamma_S(0))} = e^{\sum_\nu \beta_\nu q_\nu}$$ Eq. (6)

↓ *for initial equilibrium system state* $\pi^{\mathrm{i}}_S(\gamma_S(0))$

$$\frac{\tilde{\mathcal{P}}_S(\tilde{\gamma}_S;\{-q_\nu\})}{\mathcal{P}_S(\gamma_S;\{q_\nu\})} = e^{-\beta_S[w(\gamma_S)-\Delta F_S]+\sum_\nu(\beta_\nu-\beta_S)q_\nu}$$ Eq. (8)

↓ *coarse graining system trajectory*

Differential FTs $$\frac{\tilde{P}(-w,\{-q_\nu\},\tilde{\gamma}_S(\tau)|\tilde{\gamma}_S(0))}{P(w,\{q_\nu\},\gamma_S(\tau)|\gamma_S(0))} = e^{\sum_\nu \beta_\nu q_\nu}$$ Eq. (9)

$$\frac{\tilde{P}(-w,\{-q_\nu\},\tilde{\gamma}_S(\tau),\tilde{\gamma}_S(0))}{P(w,\{q_\nu\},\gamma_S(\tau),\gamma_S(0))} = e^{-\beta_S[w-\Delta F_S]+\sum_\nu(\beta_\nu-\beta_S)q_\nu}$$ Eq. (10)

↙ *integrating over* $\gamma_S(0)$, w, $\{q_\nu\}$

Generalized Hummer-Szabo relation Eq. (12)

$$\left\langle e^{-\beta_S[w-\Delta F_S]+\sum_\nu(\beta_\nu-\beta_S)q_\nu}\right\rangle\Big|_{\gamma_S(\tau)} = \frac{\tilde{\pi}^{\mathrm{i}}_S(\tilde{\gamma}_S(0))}{\rho^{\mathrm{f}}_S(\gamma_S(\tau))}$$

↓ *integrating over* $\gamma_S(0)$, $\gamma_S(\tau)$

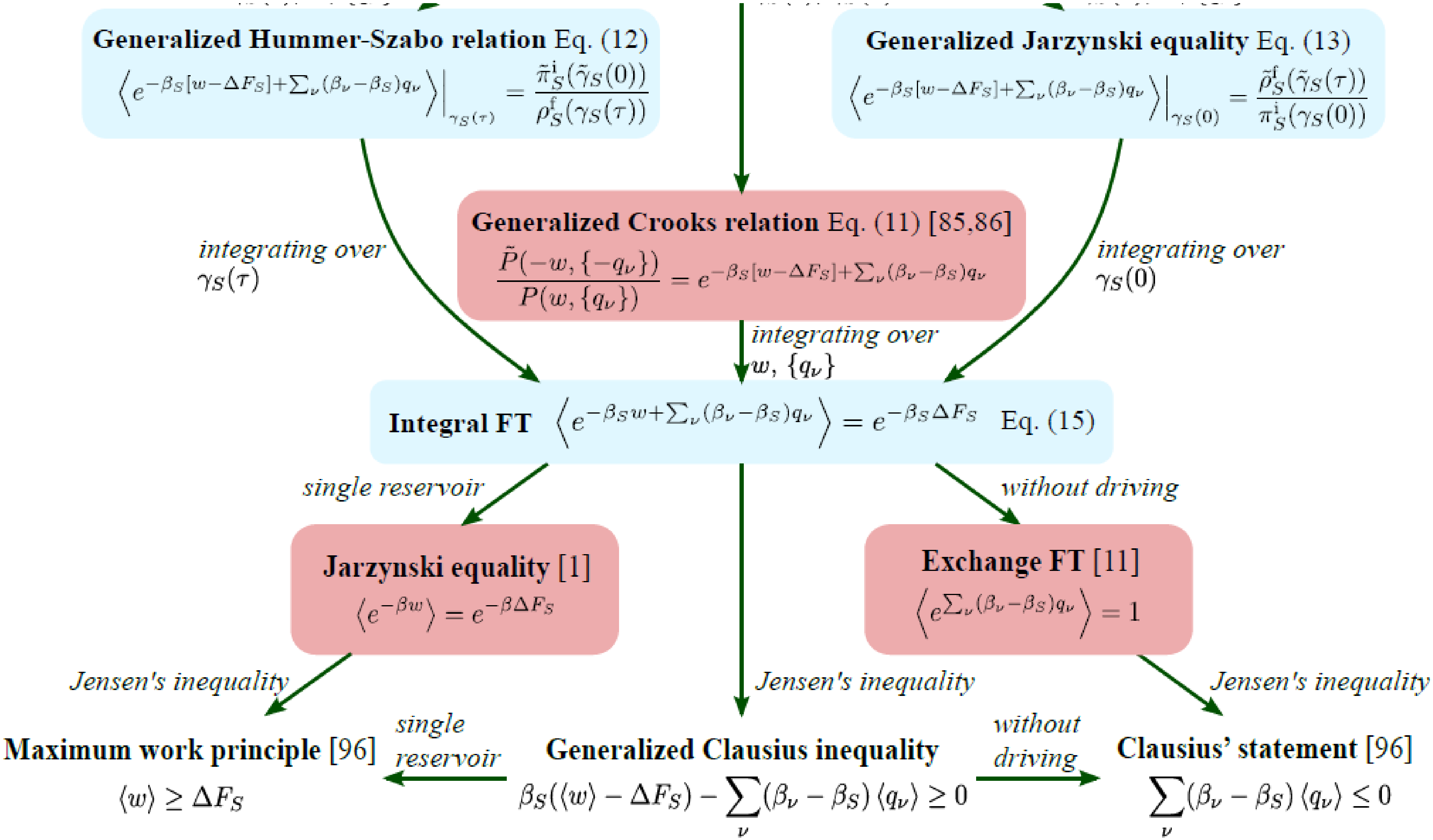
↘ *integrating over* $\gamma_S(\tau)$, w, $\{q_\nu\}$

Generalized Jarzynski equality Eq. (13)

$$\left\langle e^{-\beta_S[w-\Delta F_S]+\sum_\nu(\beta_\nu-\beta_S)q_\nu}\right\rangle\Big|_{\gamma_S(0)} = \frac{\tilde{\rho}^{\mathrm{f}}_S(\tilde{\gamma}_S(\tau))}{\pi^{\mathrm{i}}_S(\gamma_S(0))}$$

Jinfu Chen and **HTQ**, Phys. Rev. E 107, 024135 (2023)

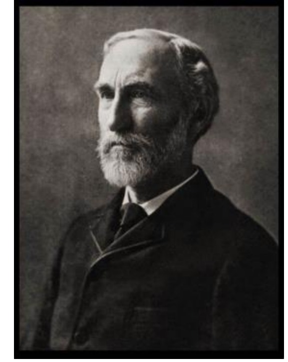
The unification of fluctuation theorems and the second law



Jinfu Chen and **HTQ**, Phys. Rev. E 107, 024135 (2023)

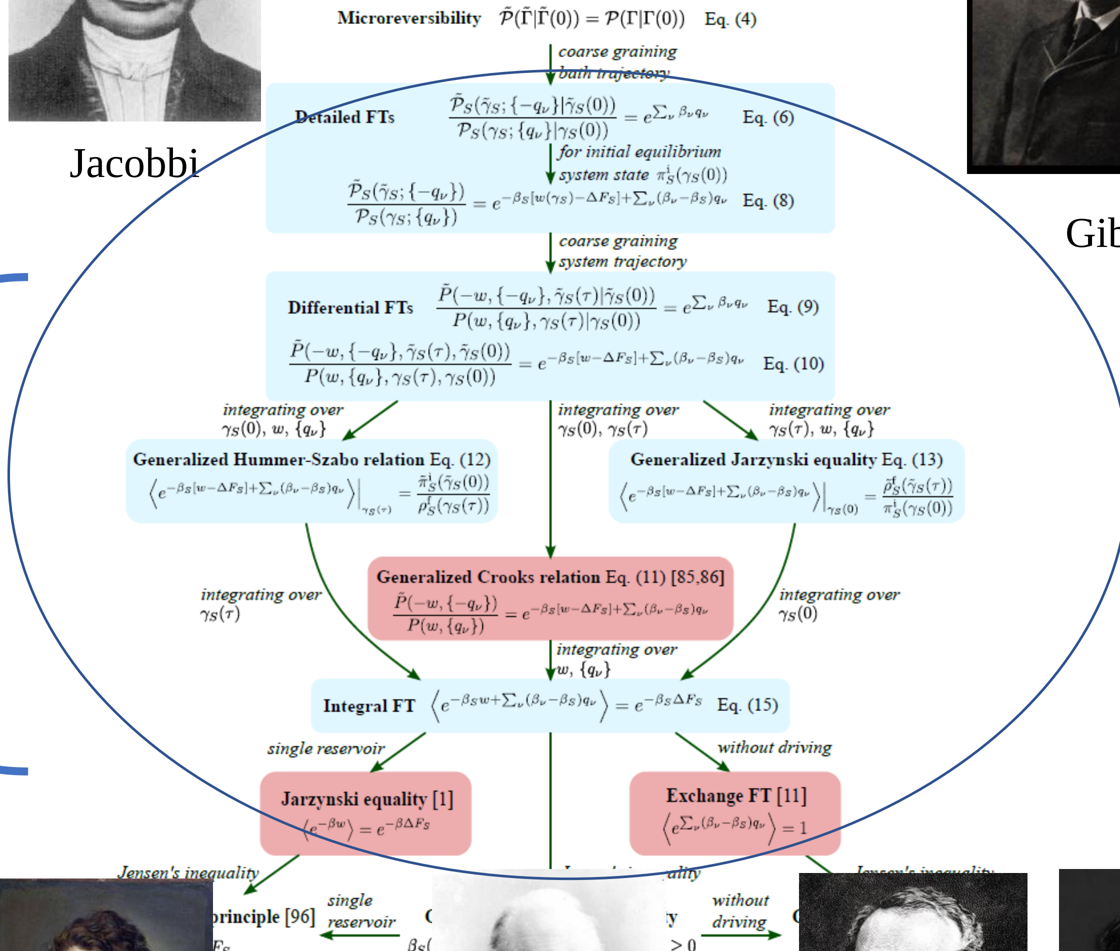
Liouville

Jacobbi

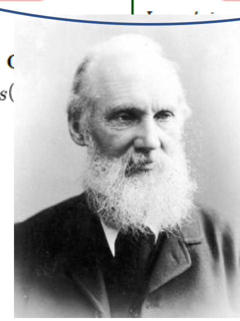


Gibbs

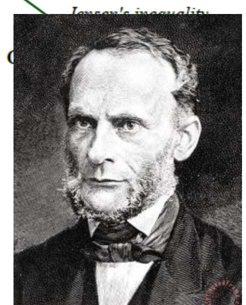
What Carnot, Kelvin, Clausius, Planck do not know about the second law



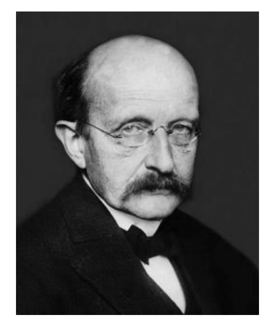
Carnot



Kelvin



Clausius



Planck

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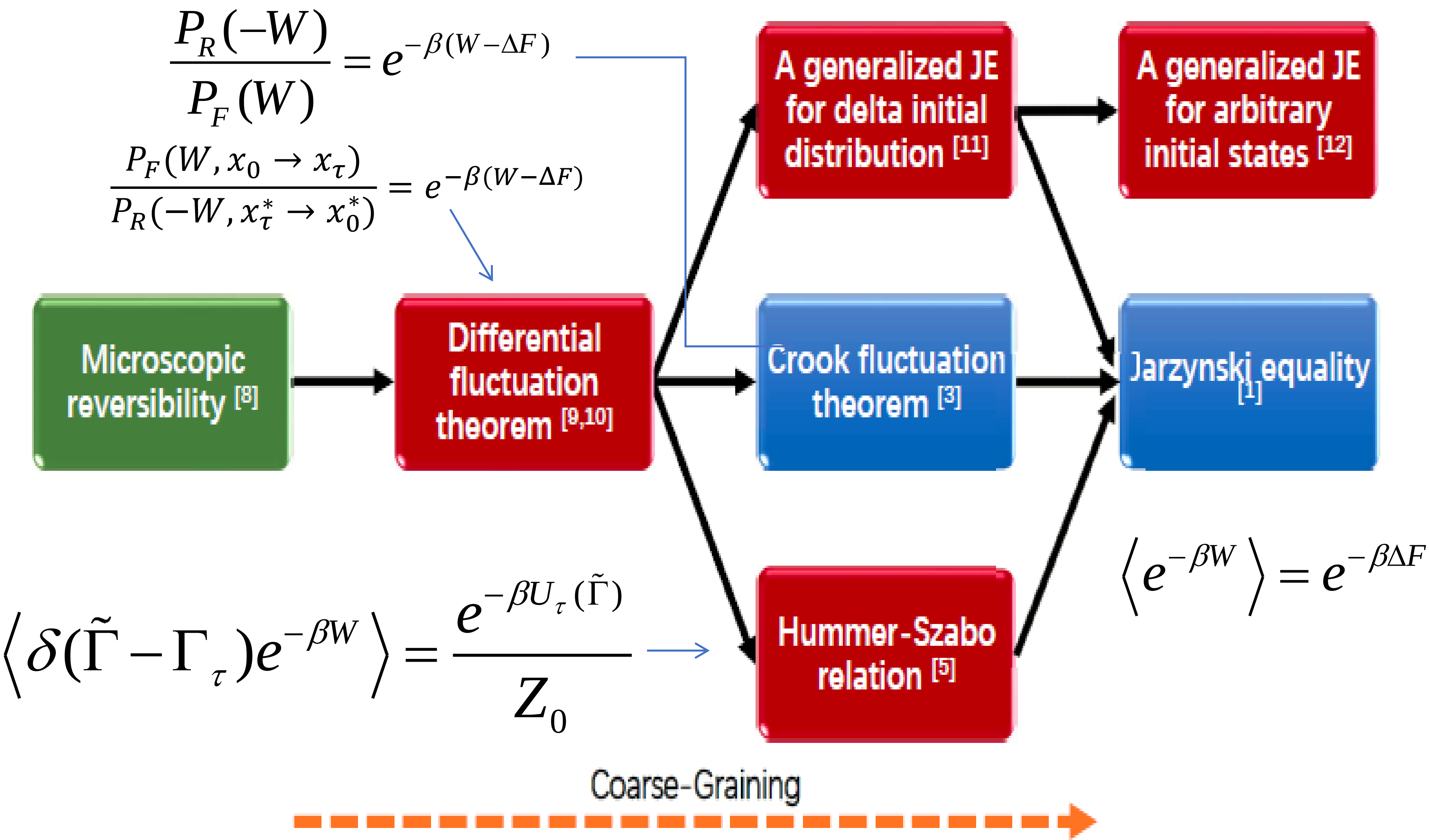
Hierarchy of fluctuation theorems “one reservoir”

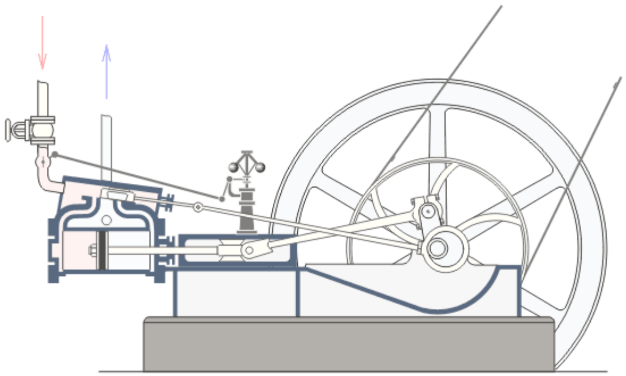


Z. Gong, **HTQ**, Phys. Rev. E 92, 012131 (2015)

T. M. Hoang, …, **HTQ**, T. Li, Phys. Rev. Lett. 120, 080602 (2018)

Application I: $\left\langle e^{-\beta_S w+\sum_\nu(\beta_\nu-\beta_S)q_\nu}\right\rangle = e^{-\beta_S \Delta F_S}.$

Heat engine: alternatively in contact with two heat baths



$$\left\langle e^{-\beta_S w+(\beta_C-\beta_S)q_C+(\beta_H-\beta_S)q_H}\right\rangle = 1$$

$= 0$ First law

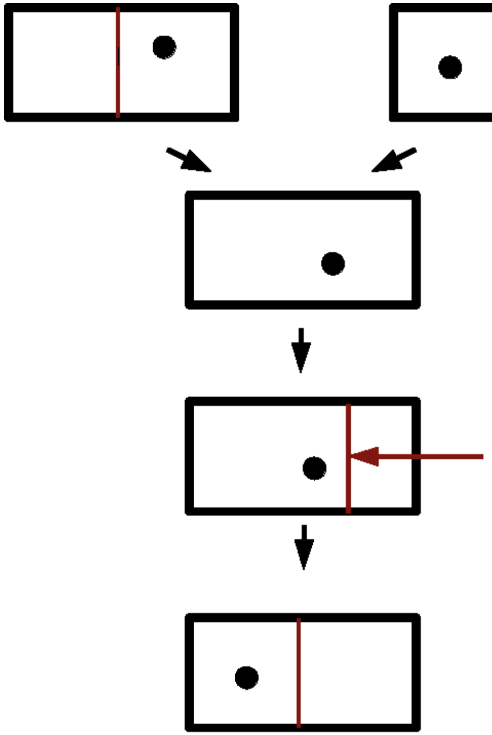
$$\Rightarrow \quad -\beta_S\left(\langle w\rangle + \langle q_C\rangle + \langle q_H\rangle\right) + \beta_C\langle q_C\rangle + \beta_H\langle q_H\rangle \le 0$$

$$\Rightarrow \quad \eta = 1 + \frac{\langle q_C\rangle}{\langle q_H\rangle} \le 1 - \frac{\beta_H}{\beta_C}$$

N. A. Sinitsyn, J. Phys. A: Math. Theor. 44, 405001 (2011).

Application II:

$$\left\langle e^{-\beta_S w+\sum_\nu(\beta_\nu-\beta_S)q_\nu}\right\rangle = e^{-\beta_S \Delta F_S}.$$



Information erasure when the temperature of the environment is different from that of the bit

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A Brownian particle coupled to multiple reservoirs

- The Langevin equation

$$\dot{x} = \frac{\partial H_S}{\partial p}$$

$$\dot{p} = -\frac{\partial H_S}{\partial x} + \sum_\nu \left[\xi_\nu(t) - \kappa_\nu m \dot{x}\right],$$

κ_ν : friction coefficient

β_ν : inverse temperature

$$H_S = \frac{p^2}{2m} + \mathcal{U}$$

Fluctuation-dissipation relation: $\langle \xi_\mu(t) \xi_\nu(t') \rangle = \frac{2\kappa_\nu m}{\beta_\nu} \delta_{\mu\nu} \delta(t - t').$

- The stochastic dynamics is equivalently described by the Fokker-Planck equation

H. A. Kramers, Physica 7, 284 (1940)

$$\frac{\partial \rho}{\partial t} = \mathscr{L}[\rho] + \sum_\nu \mathscr{D}_\nu[\rho],$$

deterministic dissipative

$$\mathscr{L}[\rho] = -\frac{\partial}{\partial x}\left(\frac{p}{m}\rho\right) + \frac{\partial}{\partial p}\left(\frac{\partial \mathcal{U}}{\partial x}\rho\right)$$

$$\mathscr{D}_\nu[\rho] = \frac{\partial}{\partial p}\left(\kappa_\nu p \rho + \frac{\kappa_\nu m}{\beta_\nu}\frac{\partial \rho}{\partial p}\right)$$

Joint statistics of work and heat

- The characteristic function of work and heat

$$\chi^{w,\{q_\nu\}}(s,\{u_\nu\}) := \left\langle \exp[i(sw + \sum_\nu u_\nu q_\nu)] \right\rangle$$

$$= \iint_{-\infty}^{\infty} \eta(x,p,\tau)dxdp.$$

- η is governed by the Feynman-Kac equation

$$\frac{\partial \eta}{\partial t} = \mathscr{L}[\eta] + \sum_\nu e^{iu_\nu H_S} \mathscr{D}_\nu \left[e^{-iu_\nu H_S}\eta\right] + is\dot{\lambda}\frac{\partial \mathcal{U}}{\partial \lambda}\eta,$$

with the initial condition $\eta(x,p,0) = \rho(x,p,0) = \frac{e^{-\beta_S H_S(x,p,\lambda(0))}}{Z_S^{\mathrm{i}}(\beta_S)}.$

Jinfu Chen and **HTQ**, Phys. Rev. E 107, 024135 (2023)

Verification of the fluctuation theorem

- The integral fluctuation theorem can be rewritten into

$$\chi^{w,\{q_\nu\}}(i\beta_S, \{i(\beta_S - \beta_\nu)\}) = e^{-\beta_S \Delta F_S}.$$

- The solution to $s = i\beta_S$ and $u_\nu = i(\beta_S - \beta_\nu)$ is

$$\eta(x,p,t) = \frac{e^{-\beta_S H(x,p,\lambda(t))}}{Z_S^{\mathrm{i}}(\beta_S)},$$

since

$$\mathscr{L}[\eta] = 0$$

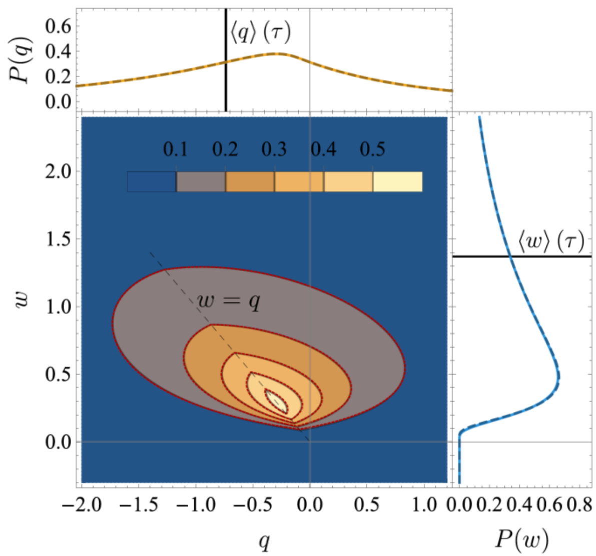
$$e^{-(\beta_S-\beta_\nu)H_S}\mathscr{D}_\nu\left[e^{(\beta_S-\beta_\nu)H_S}\eta\right] = 0$$

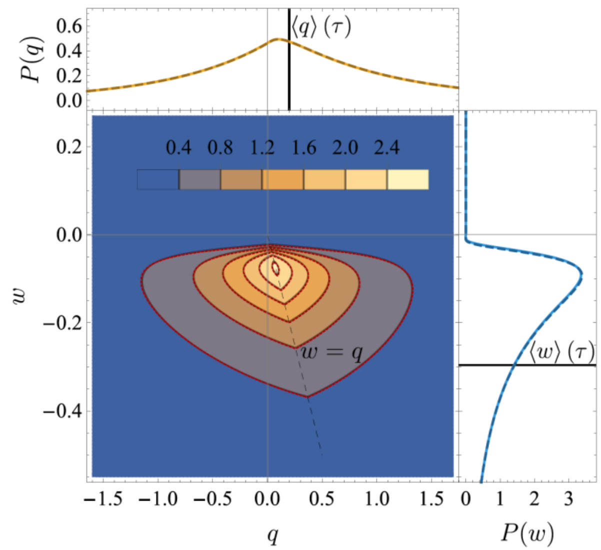
$$\frac{\partial \eta}{\partial t} = -\beta_S \dot{\lambda}\frac{\partial \mathcal{U}}{\partial \lambda}\eta = \mathrm{r.\ h.\ s.}$$

Jinfu Chen and **HTQ**, Phys. Rev. E 107, 024135 (2023)

Join distribution of work and heat

- The joint distribution of work and heat $P(w,q)$ is the inverse Fourier transform of the characteristic function.
- The fluctuation theorems can be verified with the results of $P(w,q)$.
- Breathing harmonic oscillator $H_S = \frac{p^2}{2m} + \frac{1}{2}m\lambda(t)^2x^2$





$\beta = \beta_S = 1$
$t = \tau = 20$

Red contours: analytical
Black contours: numerical

Underdamped compression

Protocol: $\lambda(t) = e^{0.05t}$
$\kappa = 0.1$

Overdamped expansion

Protocol: $\lambda(t) = 1/\sqrt{1+0.05t}$
$\kappa = 10$

D. S. P. Salazar, Phys. Rev. E. 101, 030101 (2020)
C. Kwon, J. D. Noh, H. Park, Phys. Rev. E. 88, 062102 (2013)

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Summary

- We find a hierarchical structure of fluctuation theorems. All fluctuation theorems concerning work and heat can be unified into a single framework.
- When there are more than one heat reservoirs, the marginal distribution of work or heat does not satisfy any fluctuation theorems, but the joint distribution does
- A general method to calculate the joint statistics of work and heat via the Feynman-Kac equation.
- Quantum version is similar with slight difference

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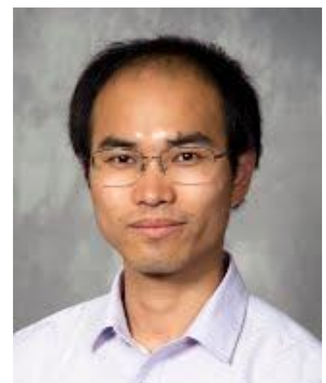
Zongping Gong



Tongcang Li

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