THERMODYNAMIC UNCERTAINTY RELATIONS FROM FLUCTUATION THEOREMS

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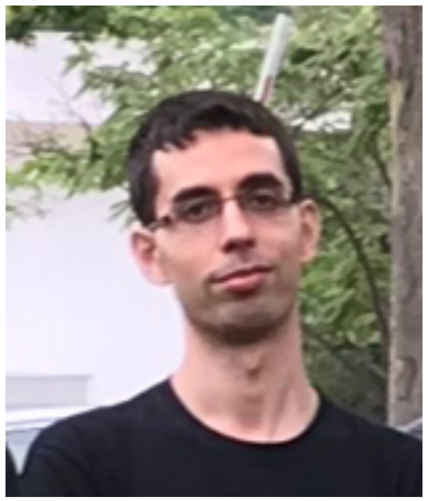
Quarantine Thermo
The interwebs
March 20th, 2020

Quantum thermodynamics
quantum transport
IFUSP

www.fmt.if.usp.br/~gtlandi

Summary



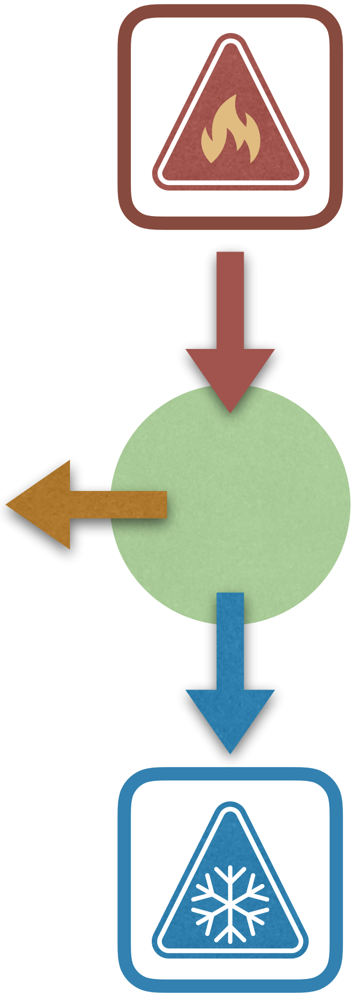
André M. Timpanaro, Giacomo Guarnieri, John Goold, GTL,
"**Thermodynamic uncertainty relations from exchange fluctuation theorems**".
Phys. Rev. Lett. **123**, 090604 (2019) (arXiv 1904.07574)

THE SECOND LAW

- The 1st law puts heat and work on similar footing and says that, in principle, one can be interconverted into the other.

- For a system coupled to two baths, for instance, we have:

$$\frac{dU}{dt} = \dot{Q}_h + \dot{Q}_c + \dot{W}$$



- Not all such processes, however, are actually possible.
  - This is the purpose of the 2nd law.

- The 2nd law deals with entropy.
    - *Entropy, however, does not satisfy a continuity equation.*
- There can be a flow of entropy from the system to the environment, which is given by the famous Clausius expression $\dot{Q}/T$.
- But, in addition, there can also be some entropy which is spontaneously *produced* in the process. The entropy balance equation thus reads

$$\frac{dS}{dt} = \dot{\Sigma} + \frac{\dot{Q}_h}{T_h} + \frac{\dot{Q}_c}{T_c}$$

- The quantity $\dot{\Sigma}$ is called the **entropy production rate.**
- The second law can now be formulated mathematically by the statement

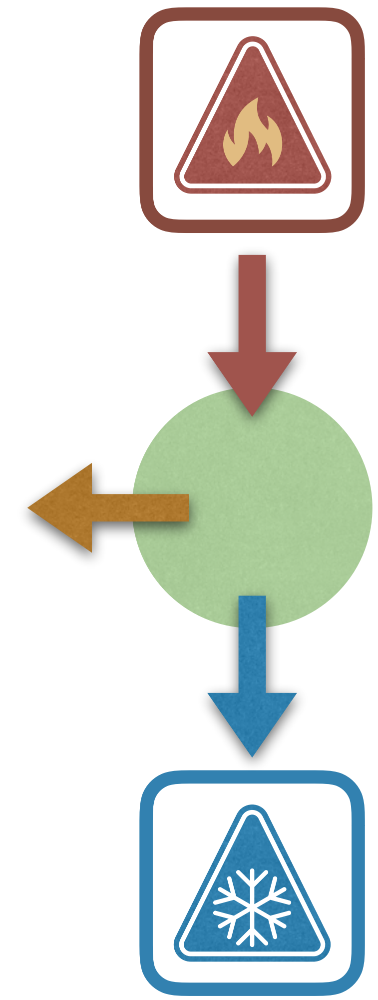
$$\dot{\Sigma} \geq 0$$

Why entropy production matters

- 1st and 2nd laws for a system coupled to two baths:

$$\frac{dU}{dt} = \dot{Q}_h + \dot{Q}_c + \dot{W} = 0$$

$$\frac{dS}{dt} = \dot{\Sigma} + \frac{\dot{Q}_h}{T_h} + \frac{\dot{Q}_c}{T_c} = 0$$



- The efficiency of the engine may then be written as

$$\eta = -\frac{\dot{W}}{\dot{Q}_h} = 1 + \frac{\dot{Q}_c}{\dot{Q}_h} = 1 - \frac{T_c}{T_h} - \frac{T_c}{\dot{Q}_h}\dot{\Sigma}$$

- *Entropy production is therefore the reason the efficiency is smaller than Carnot:*

$$\eta = \eta_C - \frac{T_c}{\dot{Q}_h}\dot{\Sigma}$$

Carnot’s statement of the 2nd law

“The efficiency of a quasi-static or reversible Carnot cycle depends only on the temperatures of the two heat reservoirs, and is the same, whatever the working substance. A Carnot engine operated in this way is the most efficient possible heat engine using those two temperatures.”

Flow of heat

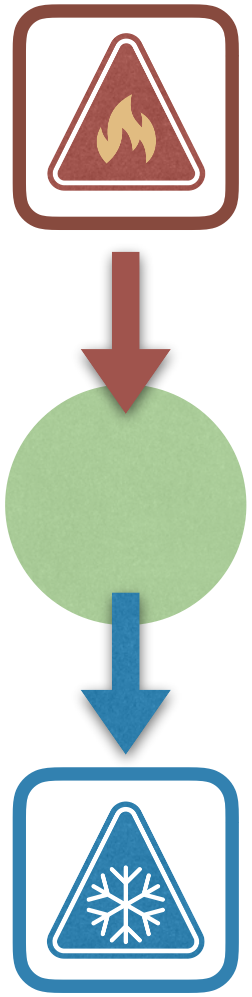
- The 2nd law reads

$$\dot{\Sigma} = -\frac{\dot{Q}_h}{T_h} - \frac{\dot{Q}_c}{T_c} \geq 0$$

- But if there is no work involved, $\dot{Q}_c = -\dot{Q}_h$

$$\therefore \qquad \dot{\Sigma} = \left(\frac{1}{T_c} - \frac{1}{T_h}\right)\dot{Q}_h \geq 0$$

- *Heat flows from hot to cold.*

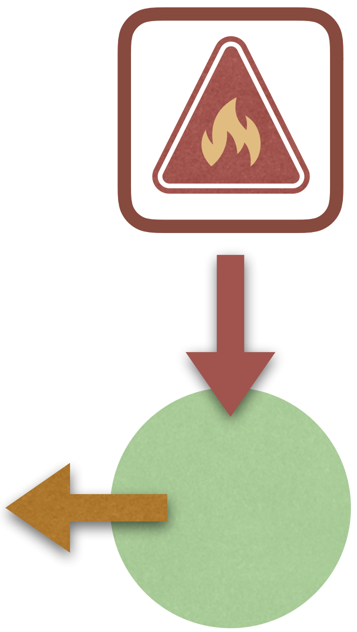


Clausius' statement of the 2nd law

"Heat can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time."

Work from a single bath

- Finally, suppose there is only one bath present:



$$\dot{W} = -\dot{Q}_h$$

$$\dot{\Sigma} = -\frac{\dot{Q}_h}{T_h} = \frac{\dot{W}}{T_h} \geq 0$$

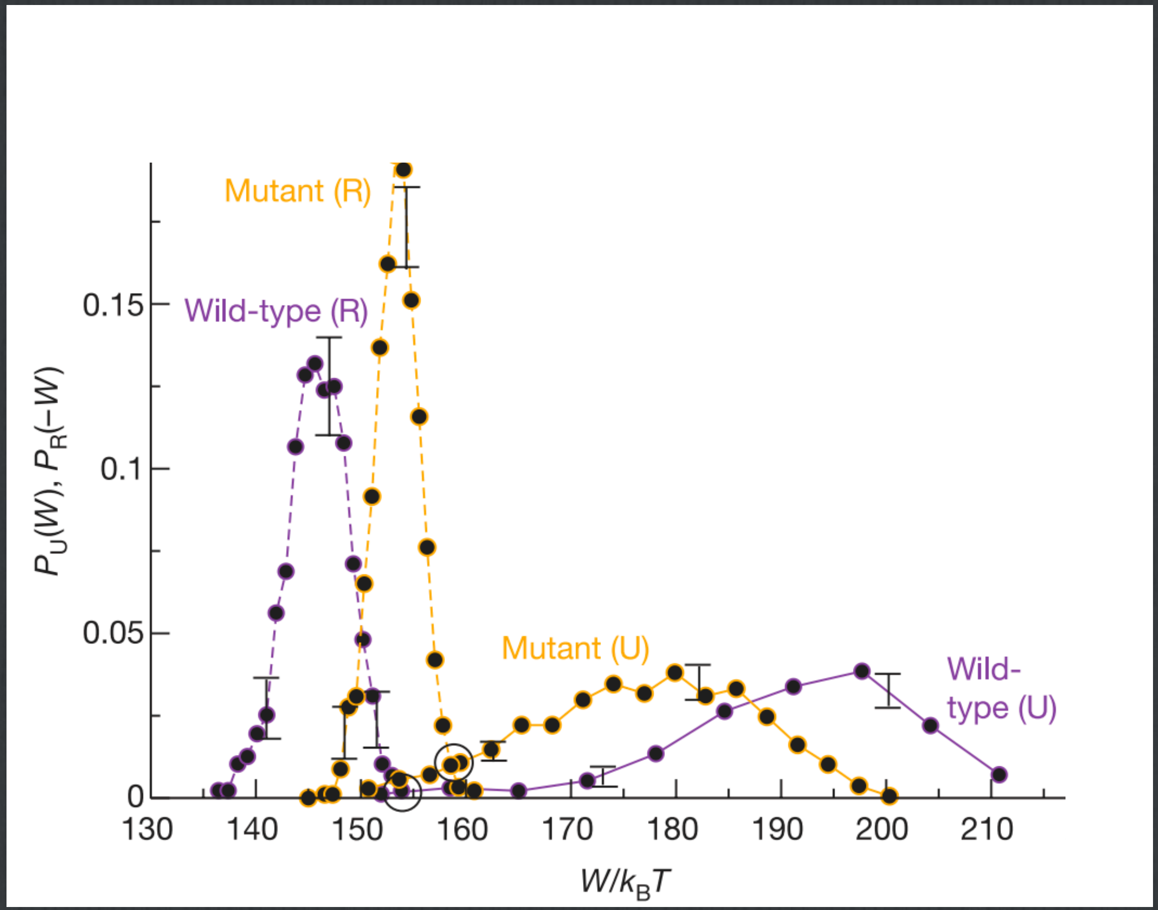
- Positive work (in my definition) means an external agent is *doing* work on the system.

Kelvin-Planck statement of the 2nd law

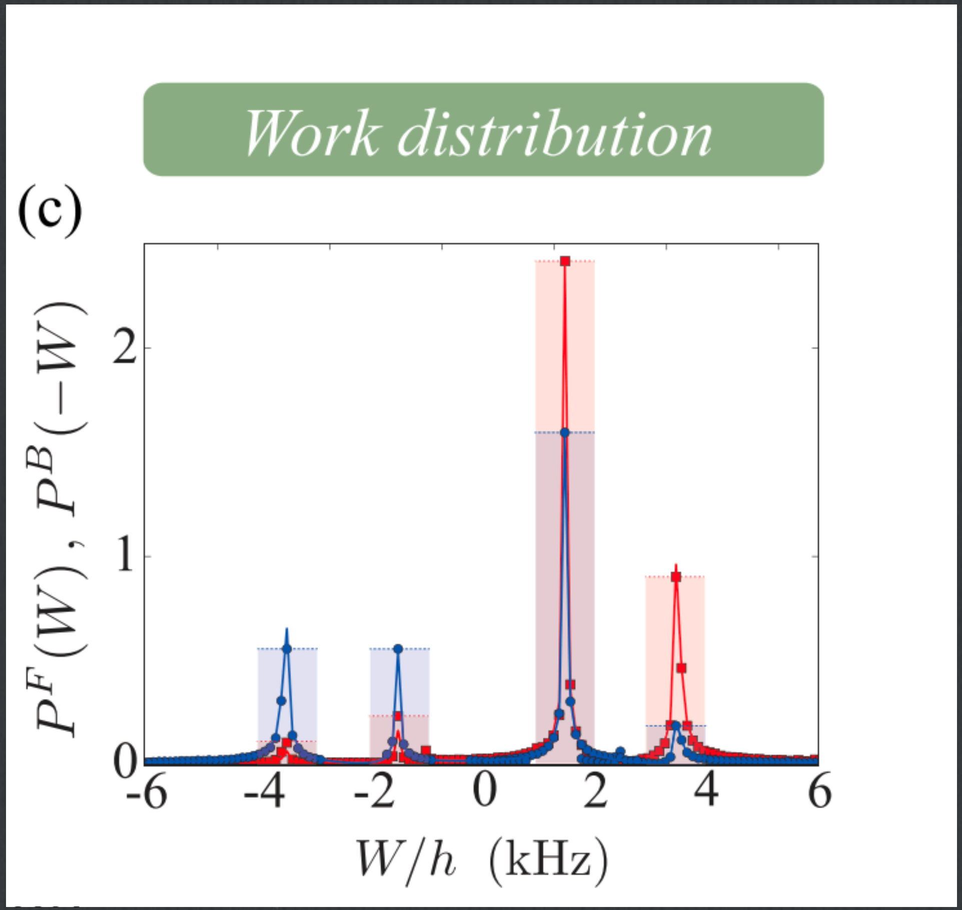
"It is impossible to devise a cyclically operating device, the sole effect of which is to absorb energy in the form of heat from a single thermal reservoir and to deliver an equivalent amount of work."

Thermodynamics at the nanoscale

- **This process requires some work.**
- **But now imagine doing the same with an RNA molecule.**
- **The RNA molecule is constantly fluctuating due to Brownian motion.**
- **Thus, every time we repeat the process, the work required to fold the molecule will be different.**
  - **Work is therefore a** random variable **and we must speak about a** probability of work $P(W)$

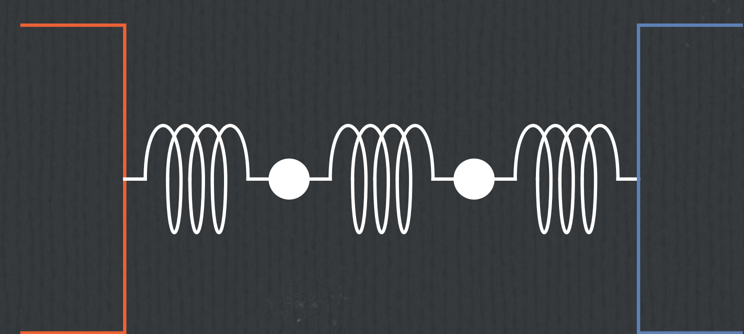


Collin, et. al., Nature, 437 (2005)

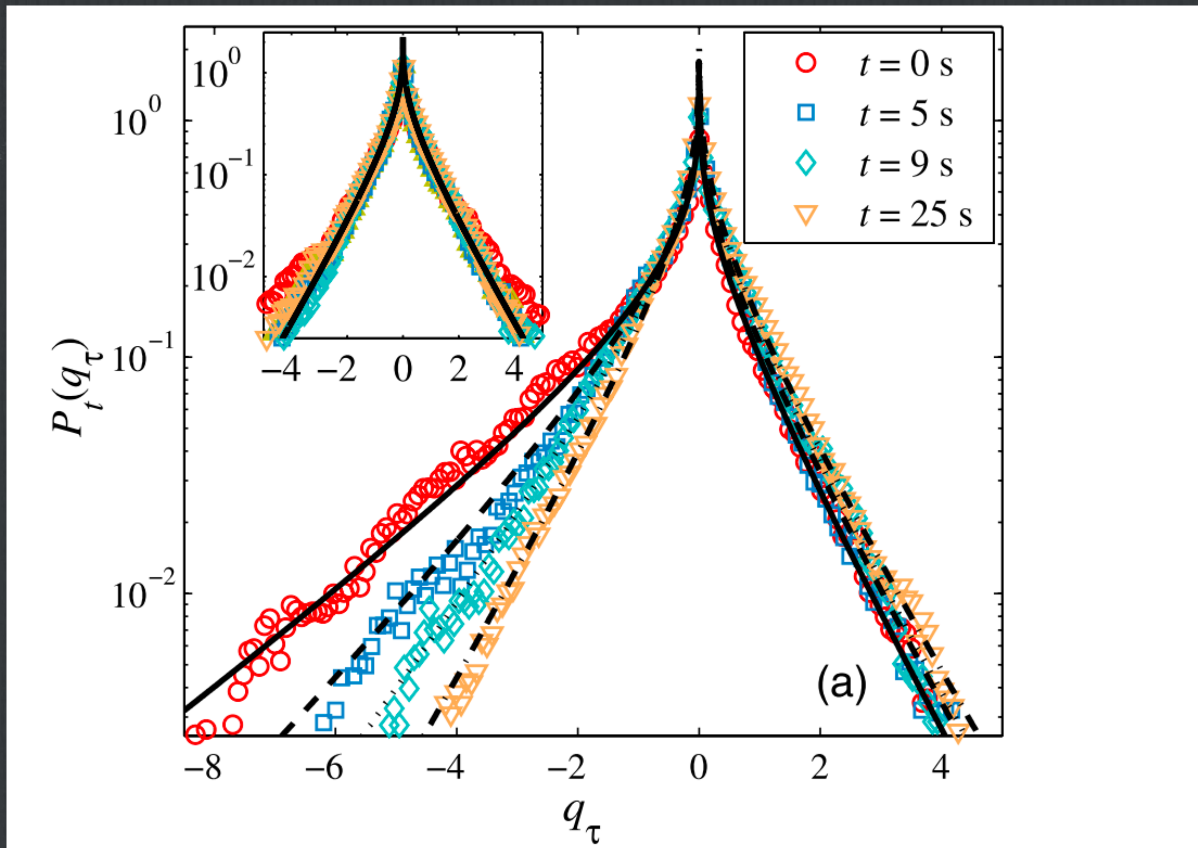


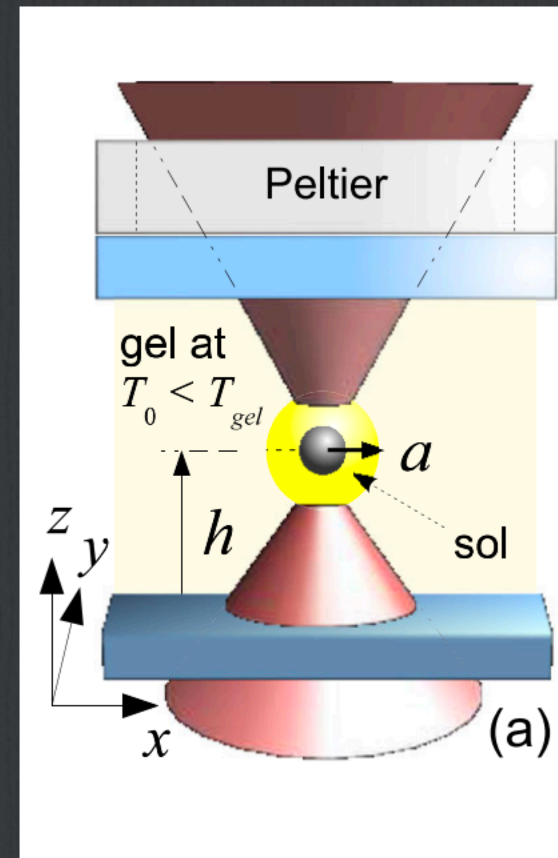
Batalhão, et. al., Phys. Rev. Lett. 113 (2014).

- The exact same thing happens for heat.
- The heat exchanged between two buckets of water practically does not fluctuate.
    - But the heat exchanged between two harmonic oscillators does.

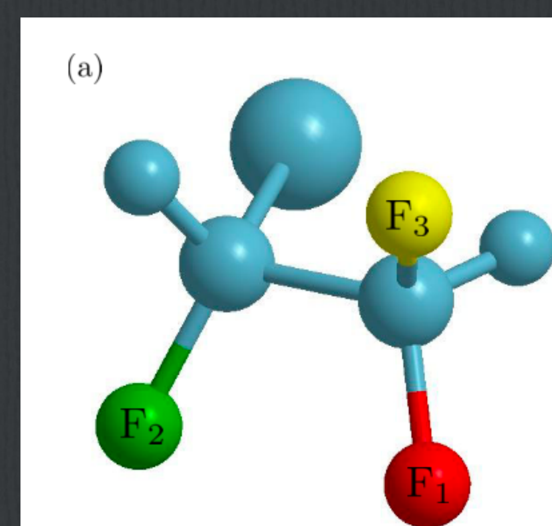


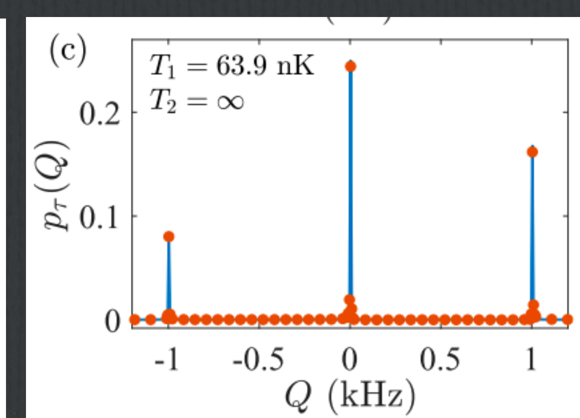
- Heat will therefore also be described by a prob. dist. $P(Q)$





J. R. Gomes-Solano, et. al., Phys. Rev. Lett. 106, 200602 (2011)





S. Pal et. al, Phys. Rev. A. 100, 042119 (2019)

Consequences of microscopic fluctuations

Fluctuation theorems

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

Thermodynamic Uncertainty Relations

$$\frac{\mathrm{var}(\Sigma)^2}{\mathbb{E}(\Sigma)^2} \geq \frac{2}{\mathbb{E}(\Sigma)}$$

Fluctuation theorems

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

Fluctuation theorems

- The probability distributions of thermodynamic quantities cannot be arbitrary,
  - They must satisfy a special symmetry known as a Fluctuation Theorem:

Work (Jarzynski-Crooks)

$$\frac{P_F(W)}{P_B(-W)} = e^{\beta(W-\Delta F)}$$

Heat (Jarzynski-Wójcik)

$$\frac{P(Q)}{P(-Q)} = e^{(\beta_c-\beta_h)Q}$$

- In the case of work, we have a forward and a backward process (fold and unfold).
- For heat, $P_B = P_F$

- The two can be written in a unified way in terms of the entropy production.

Work: $\Sigma = \beta(W - \Delta F)$

$$\frac{P_F(W)}{P_B(-W)} = e^{\beta(W-\Delta F)}$$

then

$$\frac{P_F(\Sigma)}{P_B(-\Sigma)} = e^{\Sigma}$$

Heat: $\Sigma = (\beta_c - \beta_h)Q$

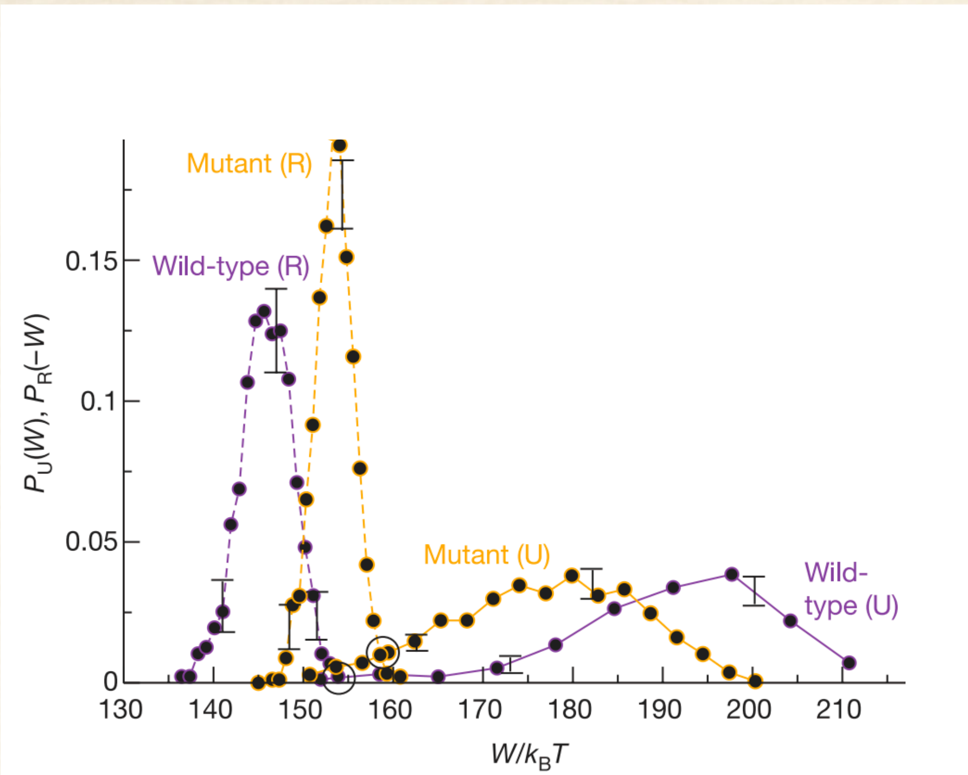
$$\frac{P(Q)}{P(-Q)} = e^{(\beta_c-\beta_h)Q}$$

then

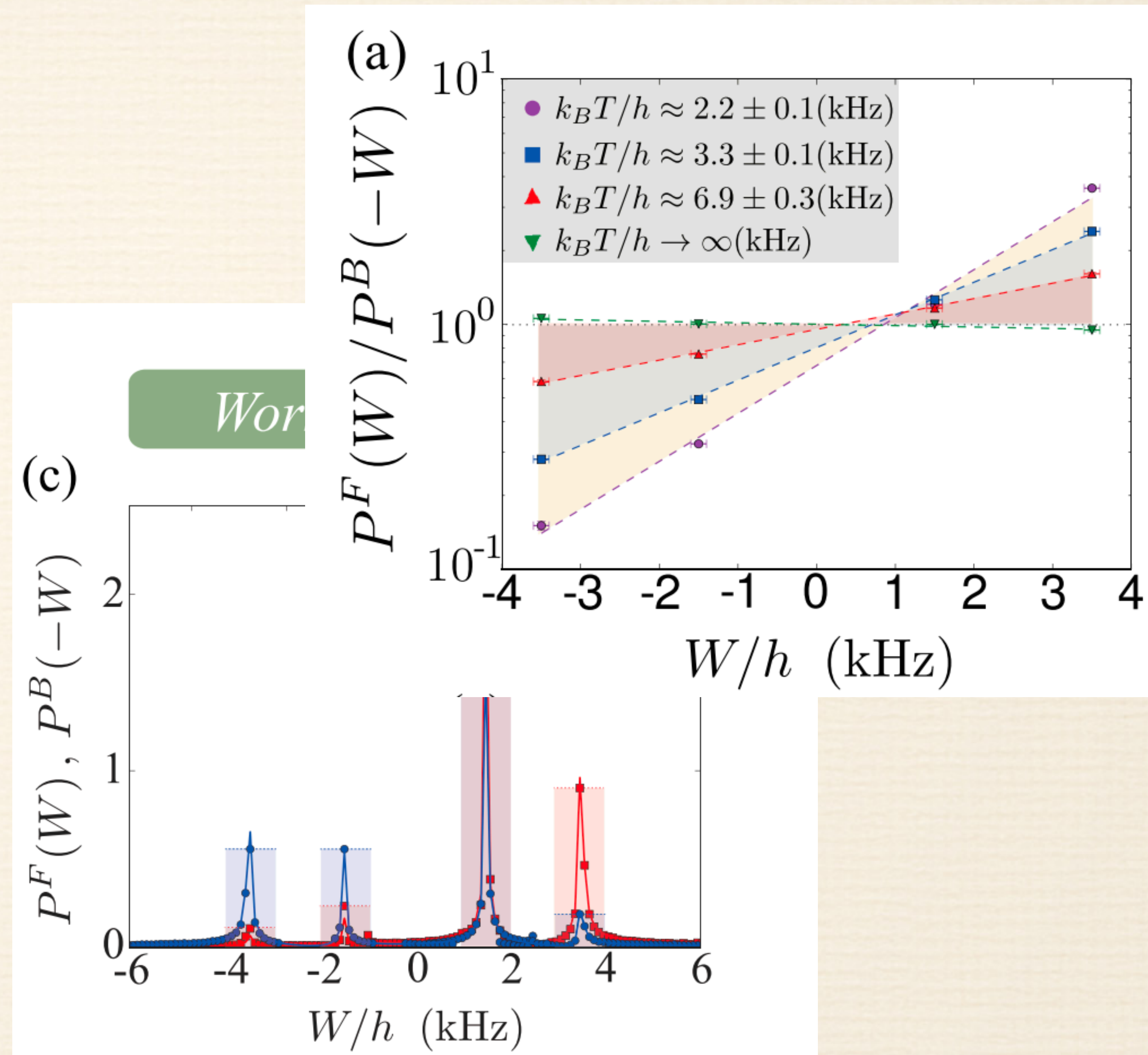
$$\frac{P(\Sigma)}{P(-\Sigma)} = e^{\Sigma}$$

- The case of heat is called an Exchange FT (EFT).
- It is stronger because it represents a symmetry for the *same* distribution.
  - (Sometimes this happens for work too. But depends on the problem)

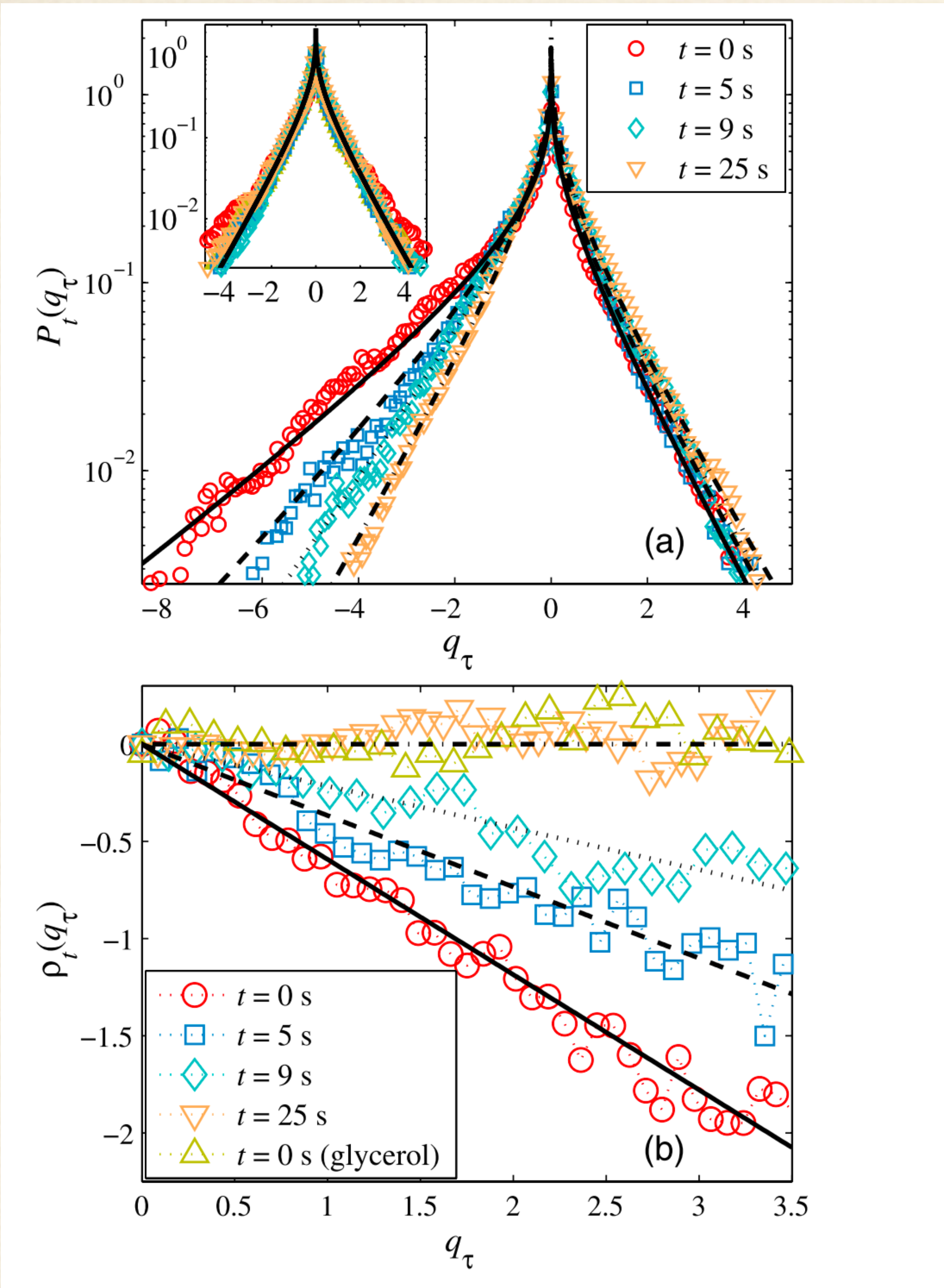
Experimental confirmation

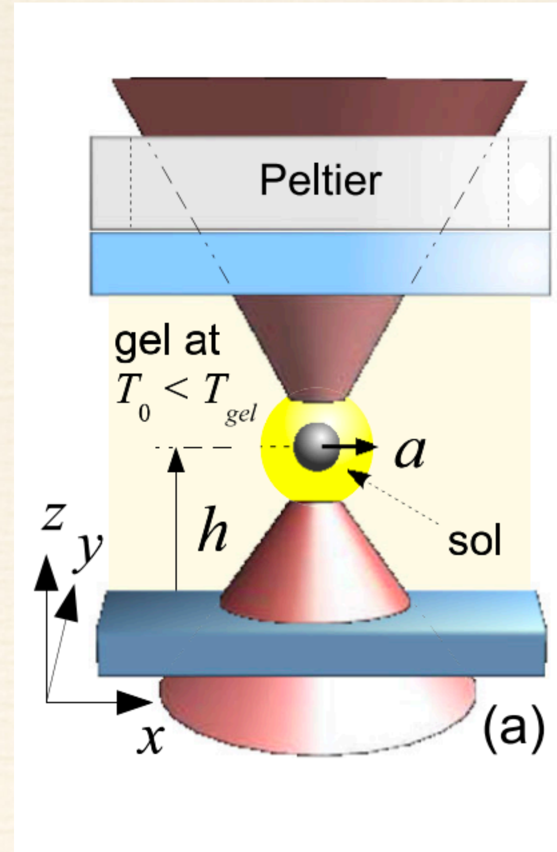


Collin, et. al., Nature, 437 (2005)



Batalhão, et. al., Phys. Rev. Lett. 113 (2014).



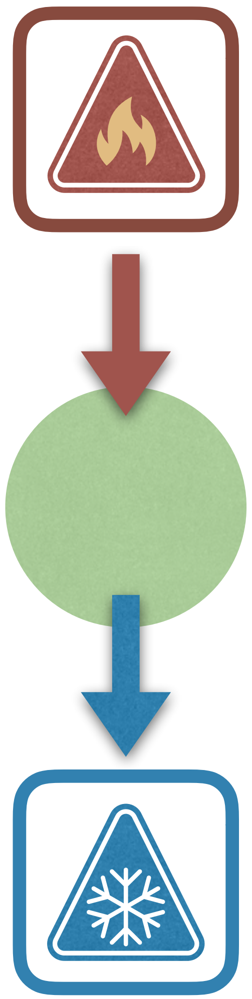


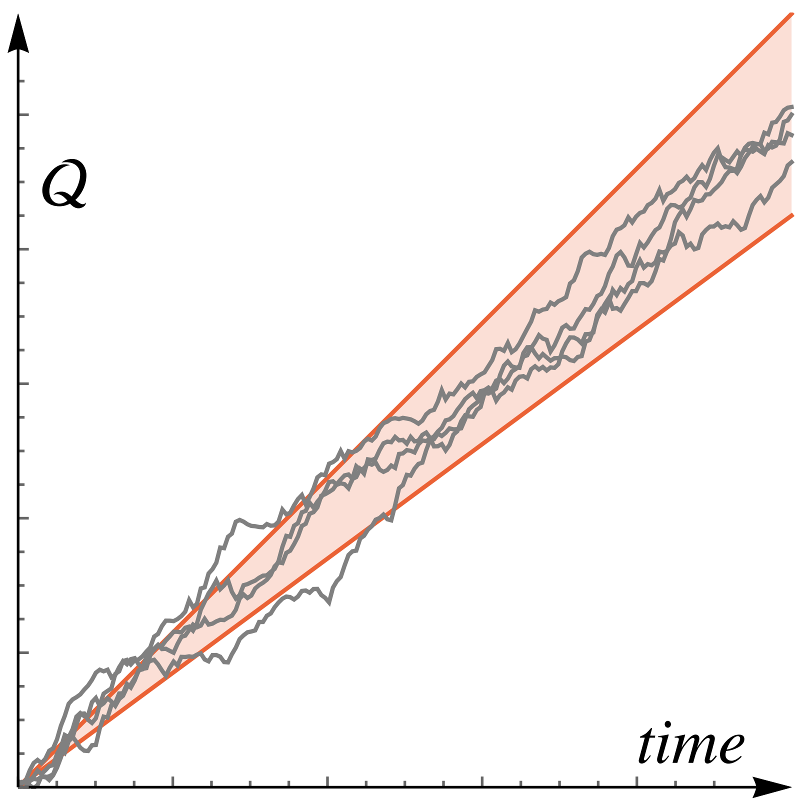
J. R. Gomes-Solano, et. al., Phys. Rev. Lett. 106, 200602 (2011)

Thermodynamic Uncertainty Relations

$$\frac{\mathrm{var}(\Sigma)^2}{\mathbb{E}(\Sigma)^2} \geq \frac{2}{\mathbb{E}(\Sigma)}$$

Thermodynamic Uncertainty Relations (TURs)





$$\frac{\mathrm{var}(\dot{Q})}{\mathbb{E}(\dot{Q})^2} \geq \frac{2}{\mathbb{E}(\dot{\Sigma})}$$

$$\Sigma = \delta\beta\, Q \ \text{(in the simplest case)}$$

- Simple, elegant and powerful.
- Counterintuitive: To reduce the fluctuations, the process should be *more irreversible.*

- Derived only for the steady-state of classical Markov chains.
- Can be violated in many relevant scenarios (e.g. thermoelectrics).

A. C. Barato, U. Seifert, *Physical Review Letters*, **114**, 158101 (2015)

Implications for mesoscopic engines

- In an autonomous engine the output power is $\dot{W}$
- The TUR in this case then reads

$$\frac{\mathrm{var}(\dot{W})}{\mathbb{E}(\dot{W})^2} \geq \frac{2}{\mathbb{E}(\dot{\Sigma})}$$

- From our previously derived result:

$$\eta = \eta_C - \frac{T_c}{\dot{Q}_h}\dot{\Sigma} \quad \to \quad \mathbb{E}(\dot{\Sigma}) = \frac{\mathbb{E}(\dot{Q}_h)}{T_c}(\eta_C - \eta)$$

- Thus:

$$\frac{\mathrm{var}(\dot{W})}{\mathbb{E}(\dot{W})^2} \geq \frac{2T_c}{\mathbb{E}(\dot{Q}_c)}\frac{1}{\eta_C - \eta}$$

P. Pietzonka and U. Seifert, *Phys. Rev. Lett.*, **120**, 190602 (2017)

- Thus:

$$\frac{\mathrm{var}(\dot{W})}{\mathbb{E}(\dot{W})^2} \geq \frac{2T_c}{\mathbb{E}(\dot{Q}_c)} \frac{1}{\eta_C - \eta}$$

- Finally, we note that $\eta = \dfrac{\mathbb{E}(\dot{W})}{\mathbb{E}(\dot{Q})}$, so that

$$\mathrm{var}(\dot{W}) \geq 2T_c |\mathbb{E}(\dot{W})| \frac{\eta}{\eta_C - \eta}$$

- If you wish to operate the engine close to Carnot efficiency, you pay the price that the fluctuations may become very large.

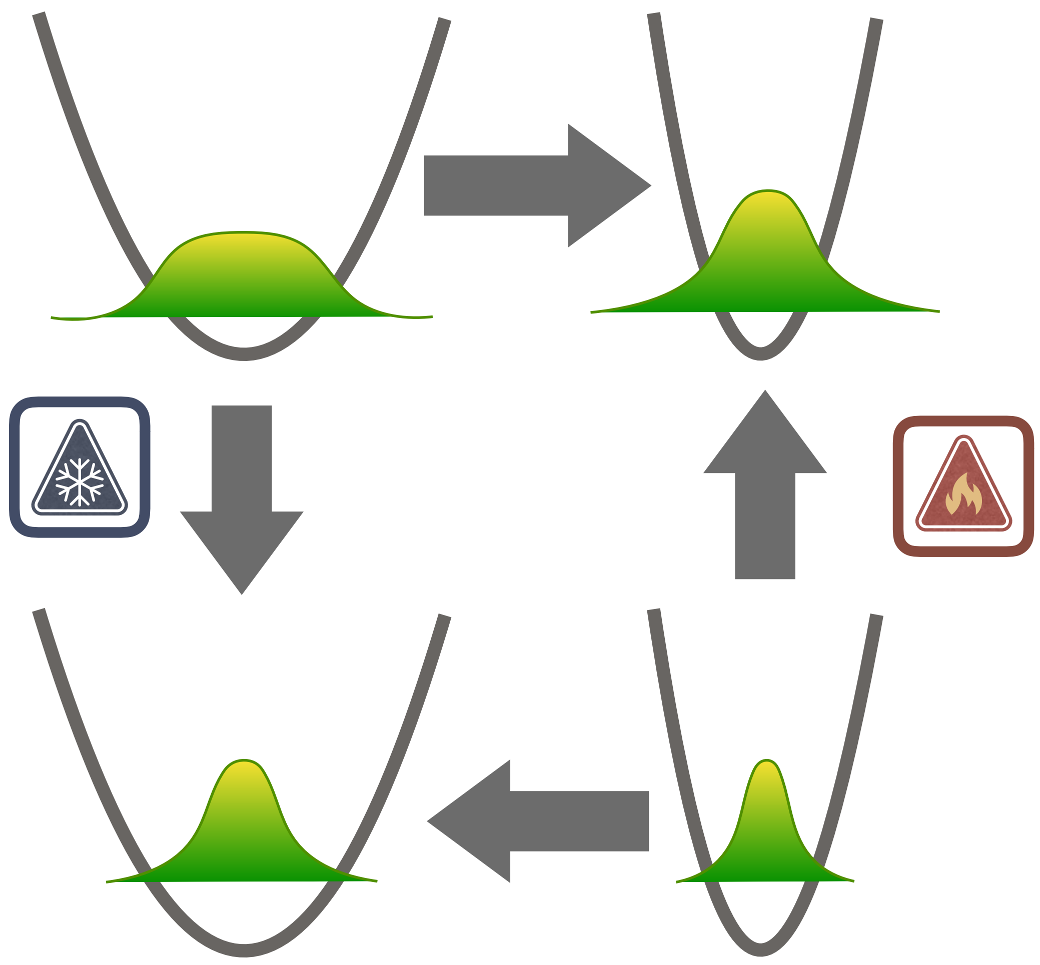
  - To curb fluctuations, the engine should be operated irreversibly!

  - Goes against everything we learn in undergraduate thermodynamics 🤯

P. Pietzonka and U. Seifert, *Phys. Rev. Lett.*, **120**, 190602 (2017)

Implications for mesoscopic autonomous heat engines

- In an autonomous engine the output power is defined by $P = \dot{W}$
- Thermal Machines: Otto Cycle



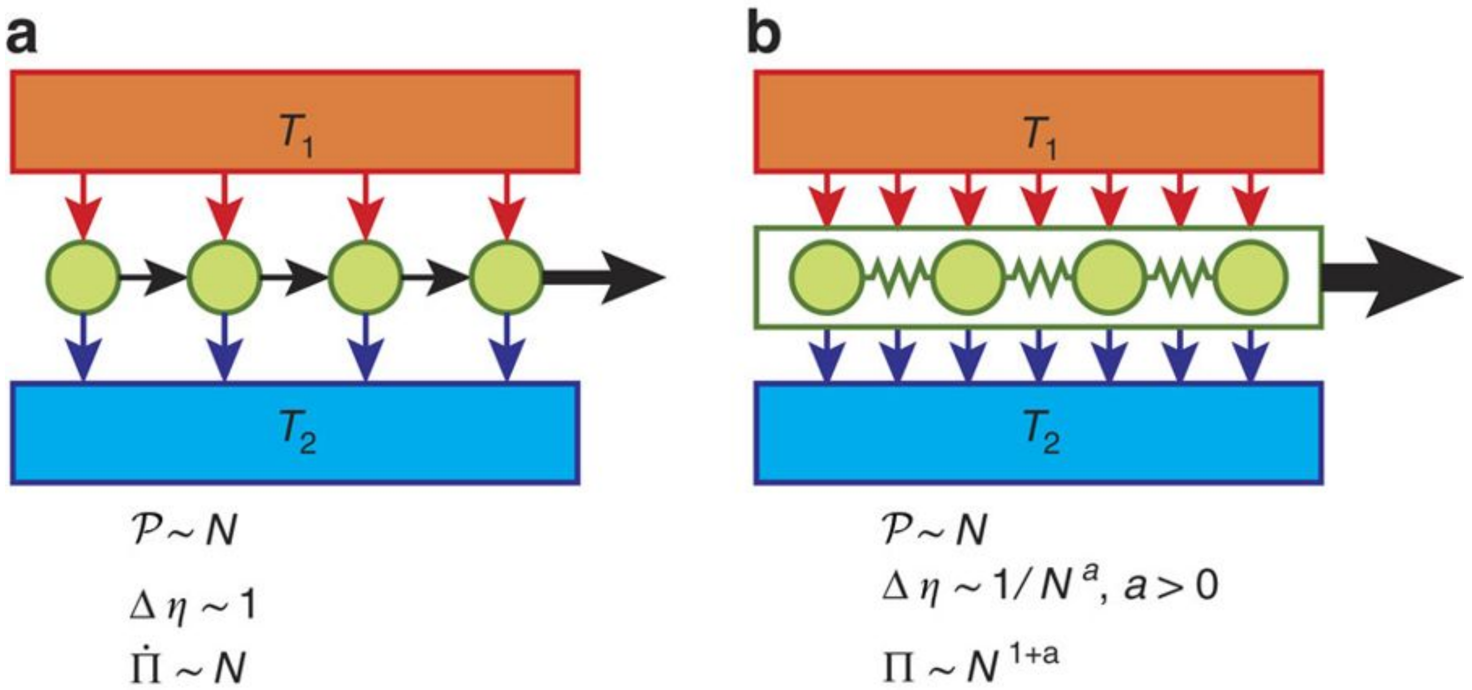
$$\eta = \eta_c \quad \text{if} \quad \mathbb{E}(\dot{\Sigma}) = 0$$

$$\Rightarrow \quad P = 0$$

- Carnot efficiency achievable only at the expense of zero power

Implications for mesoscopic autonomous heat engines

- However…



Campisi and Fazio 'The power of a critical engine'. Nat. Comms. 7, 11895 (2016).

"We focus on quantum Otto engines and show that when the working substance is at the verge of a second order phase transition diverging energy fluctuations can enable approaching the Carnot point without sacrificing power."

TURs explain: To approach Carnot efficiency at a finite power one must pay with diverging fluctuations!

nature physics

PERSPECTIVE

https://doi.org/10.1038/s41567-019-0702-6

Thermodynamic uncertainty relations constrain non-equilibrium fluctuations

Jordan M. Horowitz[1,2,3] and Todd R. Gingrich[4]

Experimental study of the thermodynamic uncertainty relation

Soham Pal,[1] Sushant Saryal,[1] D. Segal,[2,3] T. S. Mahesh,[1] and Bijay Kumar Agarwalla[1,*]

1912.08391

Thermodynamic uncertainty relation in atomic-scale quantum conductors

Hava Meira Friedman,[1] Bijay K. Agarwalla,[2] Ofir Shein-Lumbroso,[3] Oren Tal,[3] and Dvira Segal[1,4,*]

2002.00284

TUR from FTs

André M. Timpanaro, Giacomo Guarnieri, John Goold, GTL,
"**Thermodynamic uncertainty relations from exchange fluctuation theorems**".
Phys. Rev. Lett. **123**, 090604 (2019) (arXiv 1904.07574)

EXCHANGE FLUCTUATION THEOREM

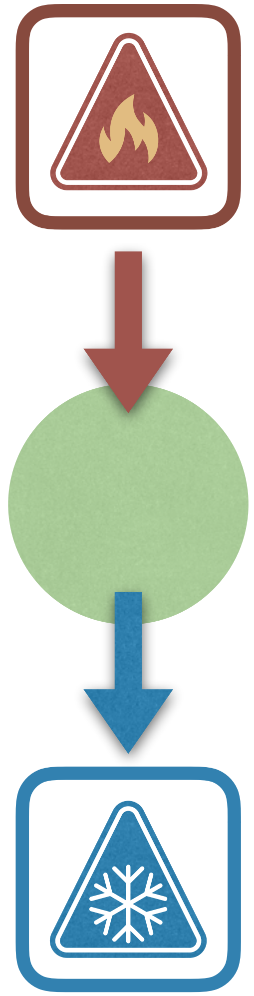
- Fluctuation theorems for thermodynamic processes usually have the form

$$\frac{P_F(\Sigma)}{P_B(-\Sigma)} = e^{\Sigma}$$

- e.g. Crooks theorem for work: $\Sigma = \beta(W - \Delta F)$
- FTs, however, compare a *forward* with a *backward* process.
- In some systems, both coincide. These are called *Exchange FTs:*

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

- This is *much stronger*: it is a symmetry on a single probability distribution.
- Example: direct heat exchange: $\Sigma = \delta\beta Q$



- We consider a system satisfying an exch[ange] fluctuation theorem.

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

- We proved the following theorem:

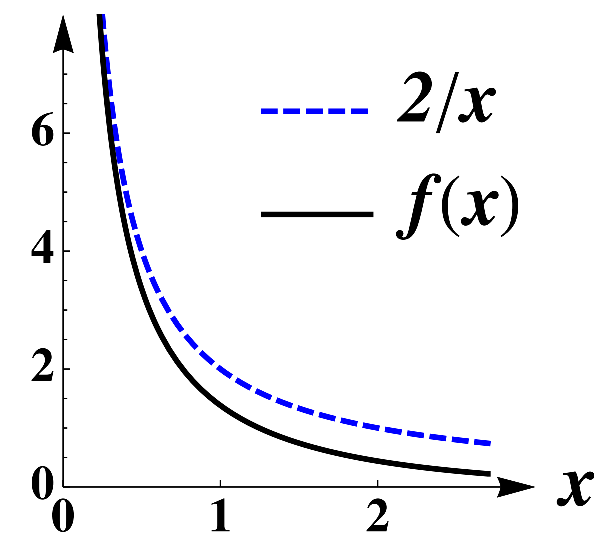
Theorem (*"TUR de force"*). *For fixed finite $\mathbb{E}(\Sigma)$, the probability distribution $P(\Sigma)$ satisfying $P(\Sigma)/P(-\Sigma) = e^{\Sigma}$, with the smallest possible variance (the minimal distribution) is*

$$P_{min}(\Sigma) = \frac{1}{2\cosh(a/2)}\left\{e^{a/2}\delta(\Sigma - a) + e^{-a/2}\delta(\Sigma + a)\right\},$$

where the value of a is fixed by $\mathbb{E}(\Sigma) = a\tanh(a/2)$. For this distribution

$$\mathrm{Var}(\Sigma)_{min} = \mathbb{E}(\Sigma)^2 f(\mathbb{E}(\Sigma)),$$

where $f(x) = csch^2(g(x/2))$, $csch(x)$ is the hyperbolic cosecant and $g(x)$ is the function inverse of $x\tanh(x)$.



For any other distribution we must then have:

$$\frac{\mathrm{var}(\Sigma)}{\mathbb{E}(\Sigma)^2} \geq f(\mathbb{E}(\Sigma))$$

TUR de force IS TIGHT

- Our TUR is the tighest (saturable) bound for this scenario.
- And we know which thermodynamic process saturates it.
- This is relevant because, around the same time, similar papers appeared.
  - But all derived a looser bound with

$$f(x) = \frac{2}{e^x - 1}$$

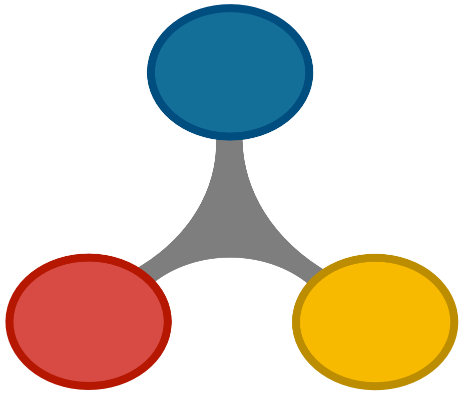
- This bound, however, is never tight.

Hasegawa & Vu 1902.06376.
Proesman & Horowitz 1902.07008.
Potts & Samuelsoon 1904.04913.

EXTENSION TO MULTIPLE CHARGES

- We can also generalize our framework to Exchange FTs involving multiple charges:

$$\frac{P(\mathcal{Q}_1,\ldots,\mathcal{Q}_n)}{P(-\mathcal{Q}_1,\ldots,-\mathcal{Q}_n)} = e^{\sum_i A_i \mathcal{Q}_i}$$



- The entropy production in this case is $\Sigma = \sum_i A_i \mathcal{Q}_i$

- ex: heat engine FT:

$$\frac{P(Q_h, W)}{P(-Q_h, -W)} = e^{(\beta_h-\beta_c)Q_h+\beta_c W}$$

- In this case we obtain the matrix bound

$$\mathcal{C} - f(\mathbb{E}(\Sigma))\boldsymbol{q}\boldsymbol{q}^{\mathrm{T}} \geq 0$$

$$q_i = \mathbb{E}(\mathcal{Q}_i)$$

$$\mathcal{C}_{ij} = \mathrm{cov}(\mathcal{Q}_i, \mathcal{Q}_j)$$

M. Campisi, J. Pekola, R. Fazio, NJP, **17**, 035012 (2015)

$$\mathcal{C} - f(\mathbb{E}(\Sigma))\boldsymbol{q}\boldsymbol{q}^{\mathrm{T}} \geq 0$$

$$q_i = \mathbb{E}(\mathcal{Q}_i)$$

$$\mathcal{C}_{ij} = \mathrm{cov}(\mathcal{Q}_i, \mathcal{Q}_j)$$

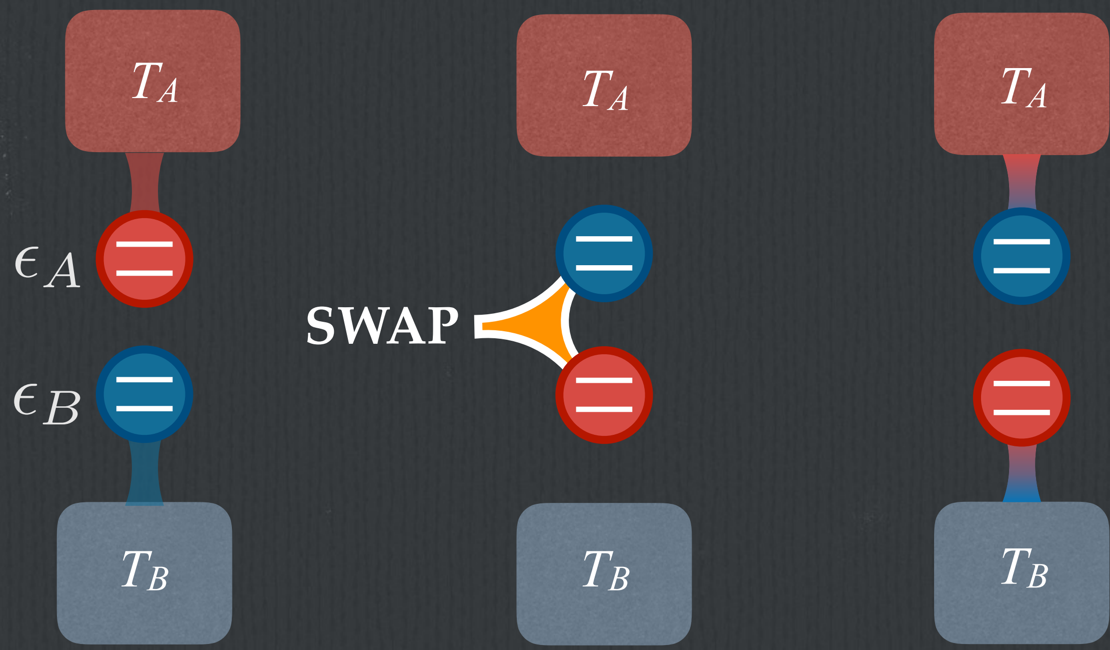
- This says that the matrix above is positive semi-definite.
- As a consequence, all diagonal entries must be positive, which implies an individual TUR for each charge:

$$\frac{\mathrm{var}(\mathcal{Q}_i)}{\mathbb{E}(\mathcal{Q}_i)^2} \geq f(\mathbb{E}(\Sigma))$$

- In addition, it also places a restriction on the *sign* on the covariances:

$$\frac{\mathbb{E}(\mathcal{Q}_i)^2}{\mathrm{var}(\mathcal{Q}_i)} + \frac{\mathbb{E}(\mathcal{Q}_j)^2}{\mathrm{var}(\mathcal{Q}_j)} \geq \frac{1}{f(\mathbb{E}(\Sigma))} \quad \to \quad \mathrm{sign}(C_{ij}) = \mathrm{sign}(\mathbb{E}(\mathcal{Q}_i)\mathbb{E}(\mathcal{Q}_j))$$

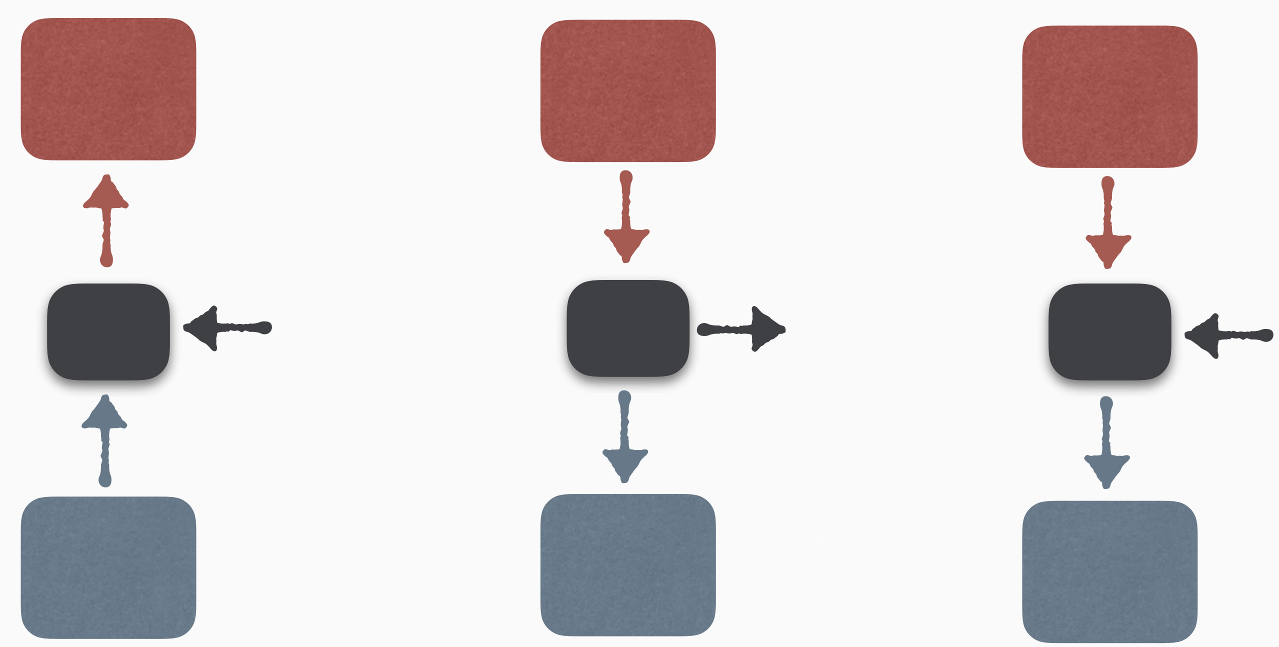
SWAP engine



$$\langle Q_h \rangle = \epsilon_A (f_A - f_B)$$

$$\langle Q_c \rangle = -\epsilon_B (f_A - f_B) \qquad f_i = \frac{1}{e^{\beta_i \epsilon_i} + 1}$$

$$\langle W \rangle = -(\epsilon_A - \epsilon_B)(f_A - f_B)$$



Refrigerator

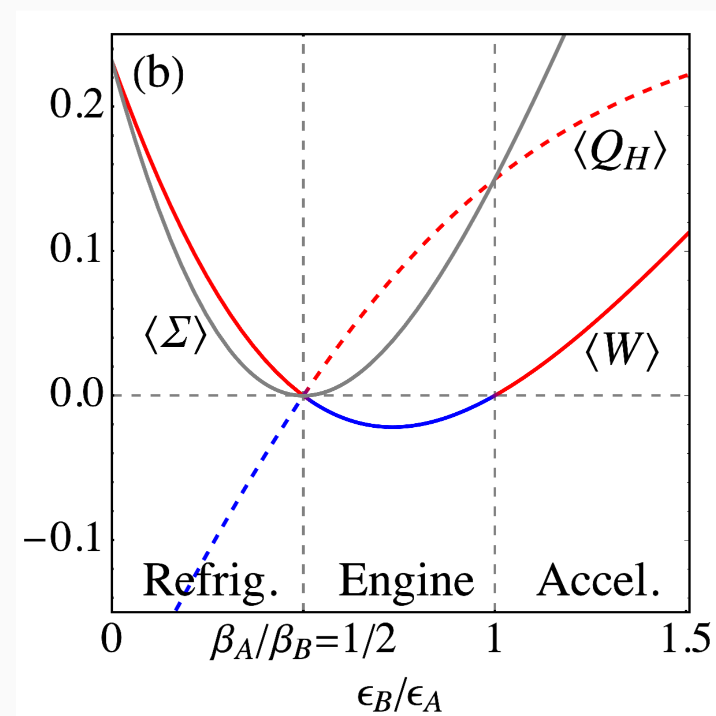
$$\frac{\epsilon_B}{\epsilon_A} < \frac{\beta_A}{\beta_B}$$

Engine

$$\frac{\beta_A}{\beta_B} < \frac{\epsilon_B}{\epsilon_A} < 1$$

Accelerator

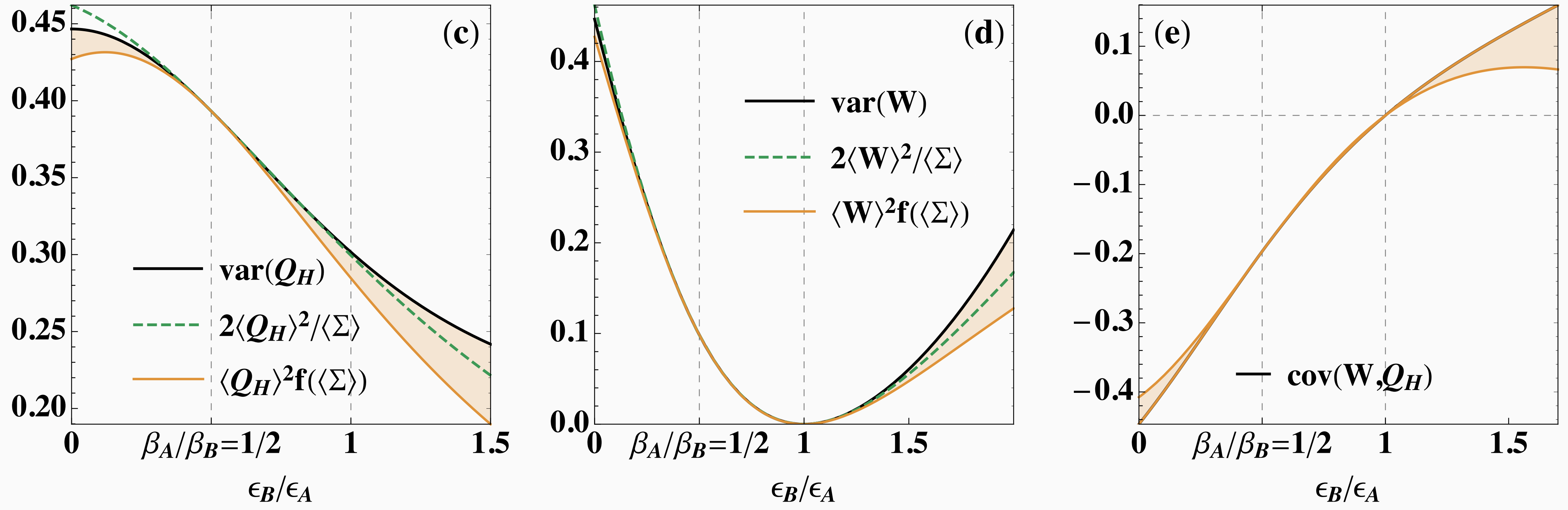
$$1 < \frac{\epsilon_B}{\epsilon_A}$$



M. Campisi, J. Pekola, R. Fazio, NJP, 17, 035012 (2015)

SWAP engine

$$\frac{P(Q_H, W)}{P(-Q_H, -W)} = e^{(\beta_B - \beta_A)Q_H + \beta_B W}$$



EXPERIM

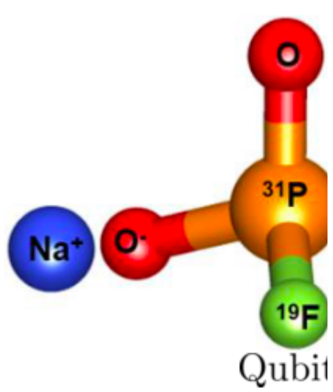
- The above r… y.

Experim… relation

Soham Pal,[1] … Agarwalla[1,*]

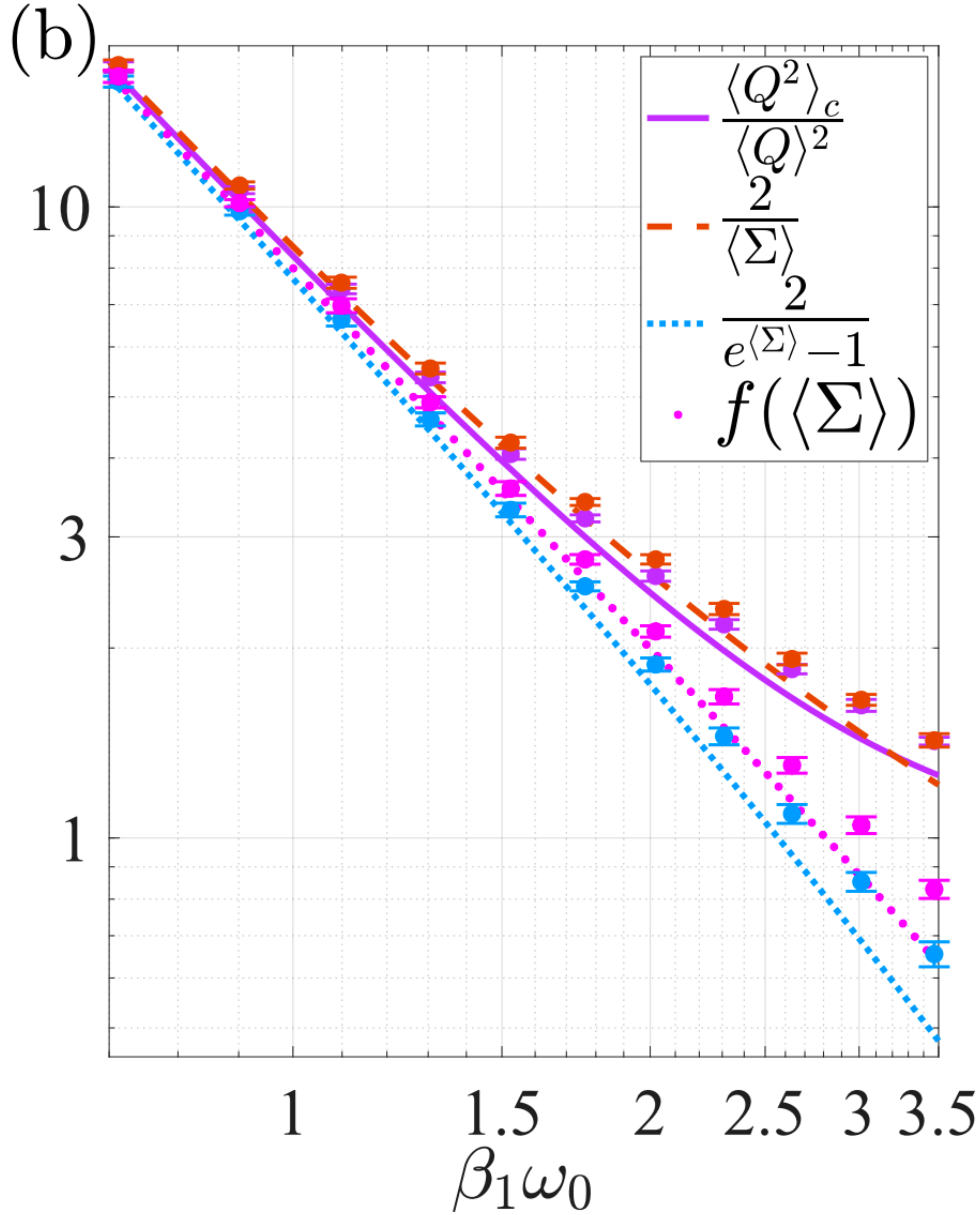
1912.08391

(a)



Sodium fluoro…

(b)



ACHIEVABILITY OF THE OPTIMAL PROCESS

Theorem (*"TUR de force"*). *For fixed finite* $\mathbb{E}(\Sigma)$*, the probability distribution* $P(\Sigma)$ *satisfying* $P(\Sigma)/P(-\Sigma) = e^{\Sigma}$*, with the smallest possible variance (the minimal distribution) is*

$$P_{min}(\Sigma) = \frac{1}{2\cosh(a/2)}\left\{e^{a/2}\delta(\Sigma - a) + e^{-a/2}\delta(\Sigma + a)\right\},$$

where the value of a *is fixed by* $\mathbb{E}(\Sigma) = a\tanh(a/2)$*. For this distribution*

$$\mathrm{Var}(\Sigma)_{min} = \mathbb{E}(\Sigma)^2 f(\mathbb{E}(\Sigma)),$$

where $f(x) = csch^2(g(x/2))$*,* $csch(x)$ *is the hyperbolic cosecant and* $g(x)$ *is the function inverse of* $x\tanh(x)$*.*

The *minimal process* is one which has only 2 points in the support.

But is this achievable in practice?

i.e., is the bound saturable?

Conclusions

Acknowledgements:
FAPESP, Heraeus foundation

- In this talk I discussed how TURs can be viewed as a consequence of Fluctuation Theorems.

- I believe that this is important because:

  a. It sheds light on the phy

  b. Shows that FTs not only
  additional constraints o

  c. Introduces the idea of a
  optimizes a given therm

Quantum thermodynamics
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www.fmt.if.usp.br/~gtlandi