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# THERMODYNAMIC UNCERTAINTY RELATIONS AND THEIR CONNECTION WITH FLUCTUATION THEOREMS

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# Summary

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- I. Entropy production.
- II. Fluctuation theorems (FTs)
- III. Thermodynamic uncertainty relations (TURs).
- IV. TURs from FTs.
- V. Applications to quantum heat engines.

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

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# The 2nd law



# Entropy production

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- In thermodynamics we learn that when a process is done reversibly

$$\Delta S = \frac{Q}{T}$$

- If the process is irreversible, we get Clausius' inequality instead:

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

- We may be write this as

$$\Delta S = \Sigma + \frac{Q}{T}, \quad \Sigma \geq 0$$

- The quantity  $\Sigma$  is called the Entropy Production.

**2nd law:**

$$\Sigma \geq 0$$



# Why entropy production matters

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

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

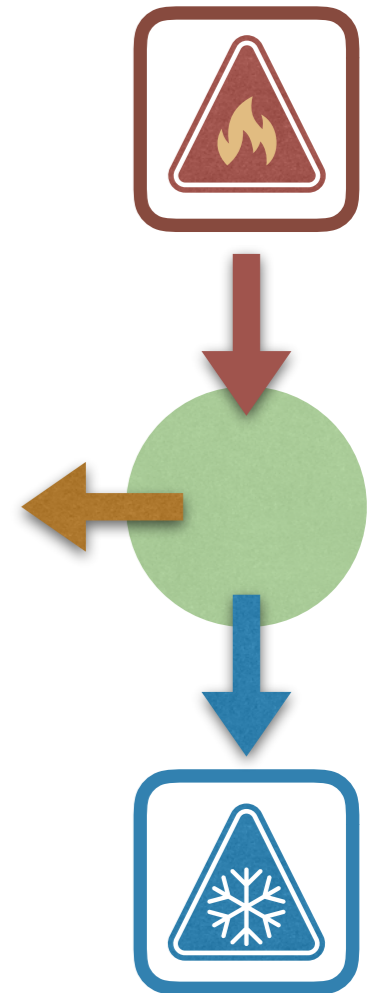
$$\frac{dS}{dt} = \dot{\Sigma} + \frac{\dot{Q}_h}{T_h} + \frac{\dot{Q}_c}{T_c} = 0$$

- 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

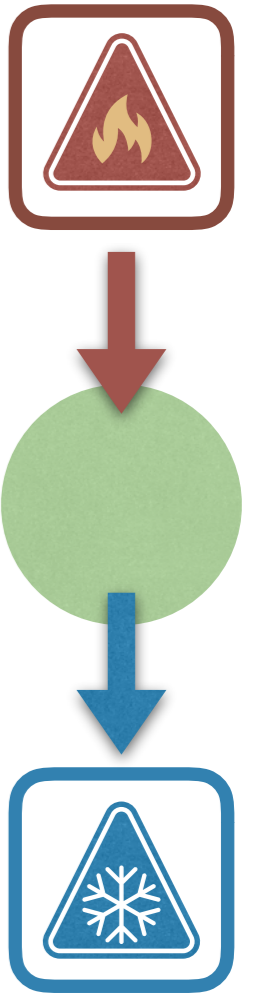
- The 2nd law reads

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

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

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

- *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.”*



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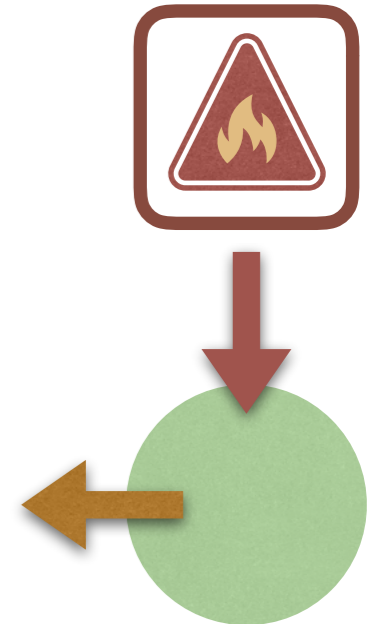
# Work from a single bath

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- 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.
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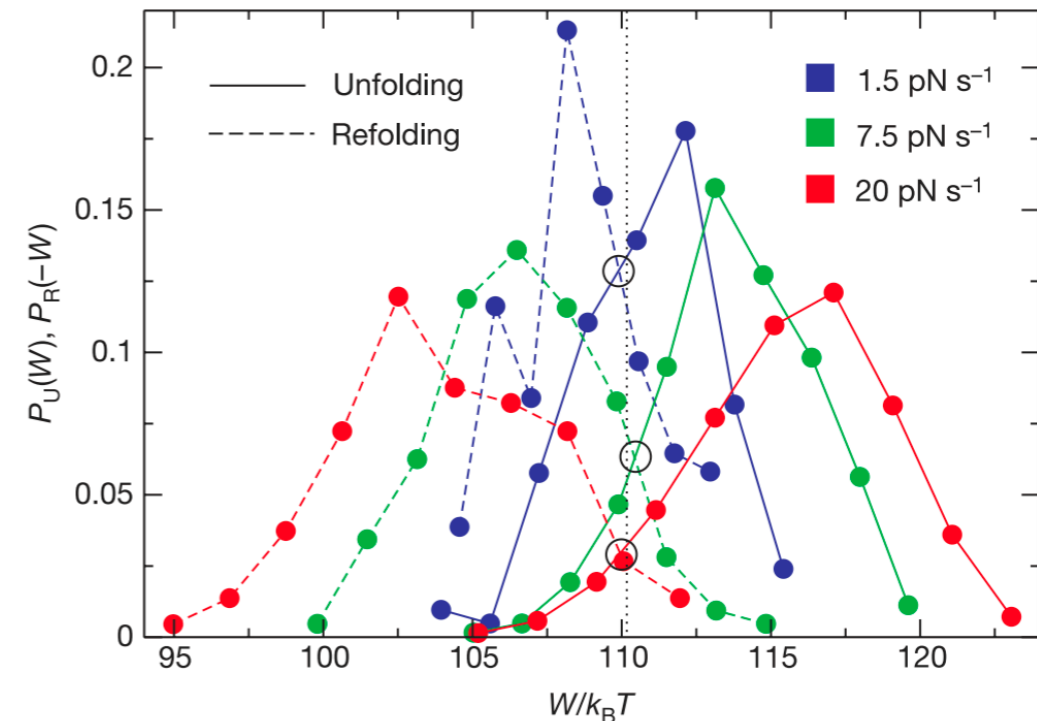


## **Kelvin-Planck statement of the 2nd law**

*“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.”*



# Fluctuation theorems



**Figure 2 | Test of the CFT using an RNA hairpin.** Work distributions for RNA unfolding (continuous lines) and refolding (dashed lines). We plot negative work,  $P_R(-W)$ , for refolding. Statistics: 130 pulls and three molecules ( $r = 1.5 \text{ pN s}^{-1}$ ), 380 pulls and four molecules ( $r = 7.5 \text{ pN s}^{-1}$ ), 700 pulls and three molecules ( $r = 20.0 \text{ pN s}^{-1}$ ), for a total of ten separate experiments. Good reproducibility was obtained among molecules (see Supplementary Fig. S2). Work values were binned into about ten equally spaced intervals. Unfolding and refolding distributions at different speeds show a common crossing around  $\Delta G = 110.3 k_B T$ .

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



# Fluctuation theorems

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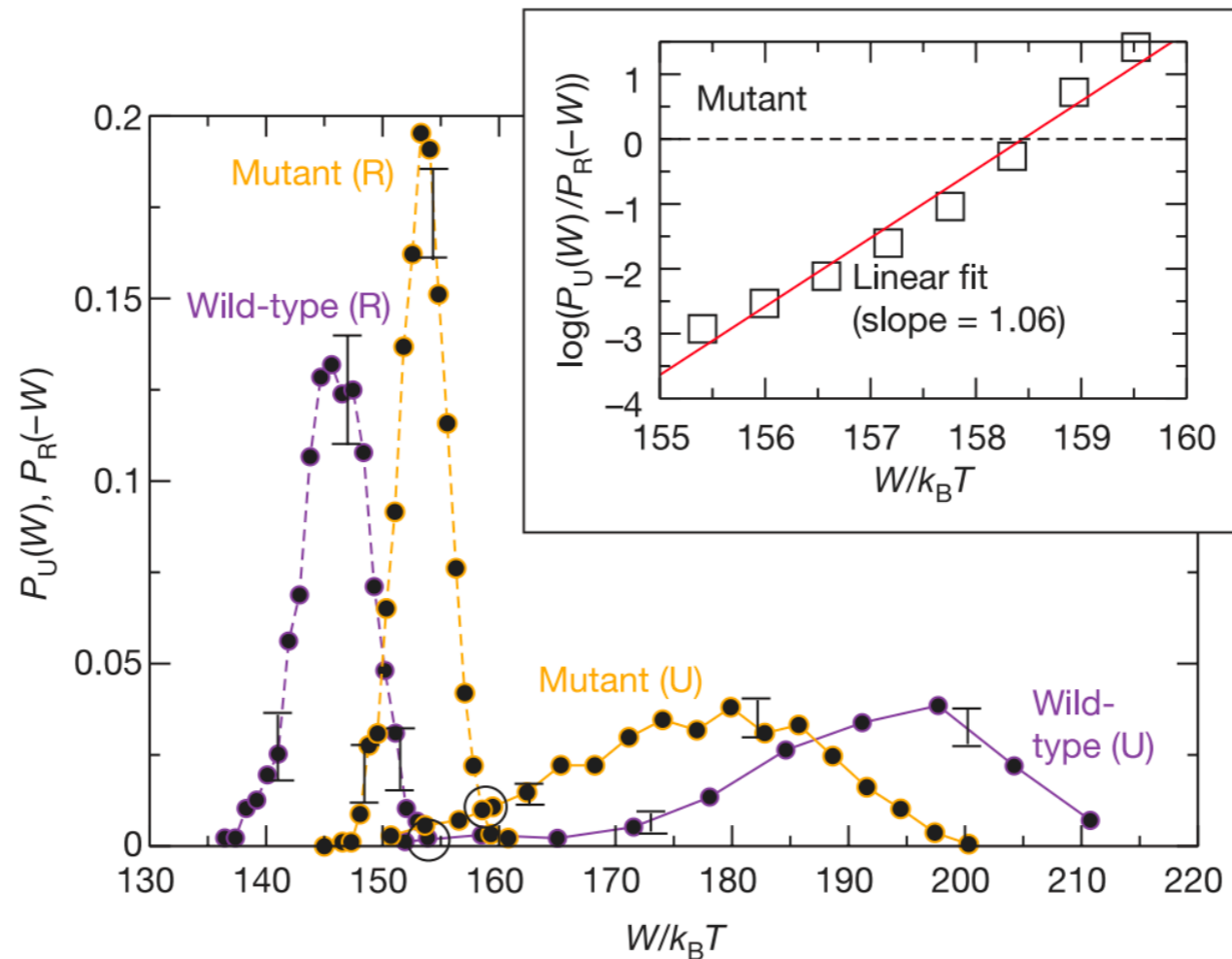
- Fluctuation theorems describe the stochastic behavior of the entropy production:

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

- The most famous one is the Crooks fluctuation theorem:

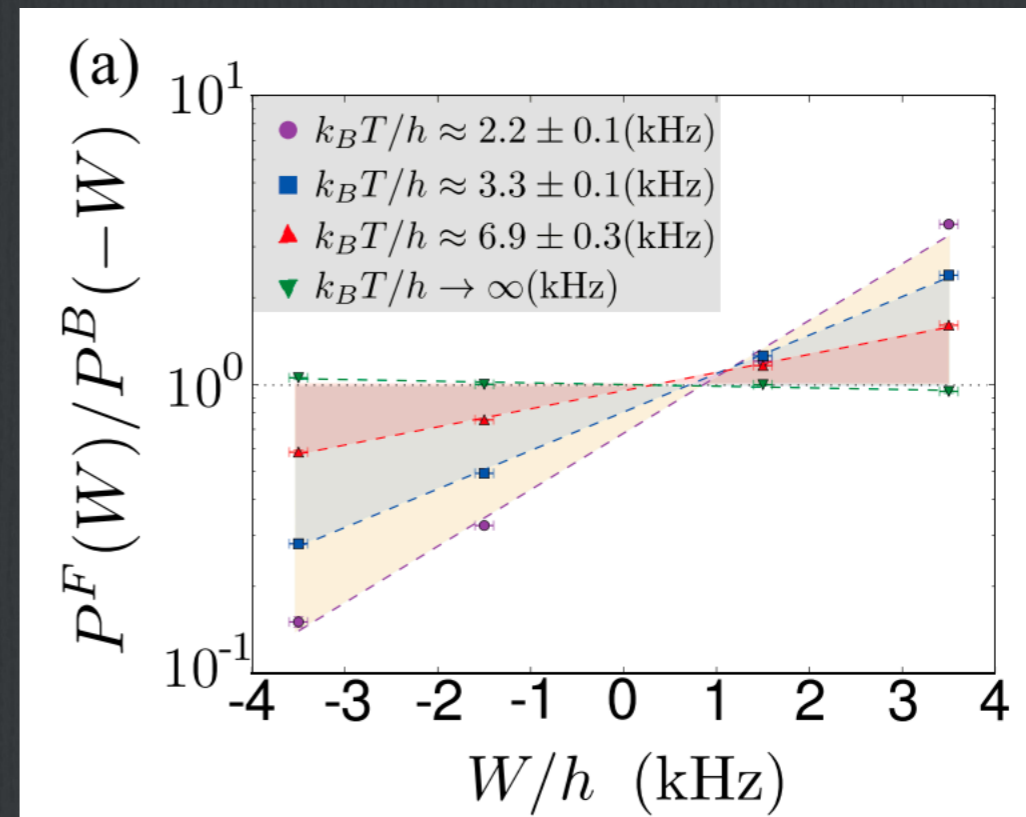
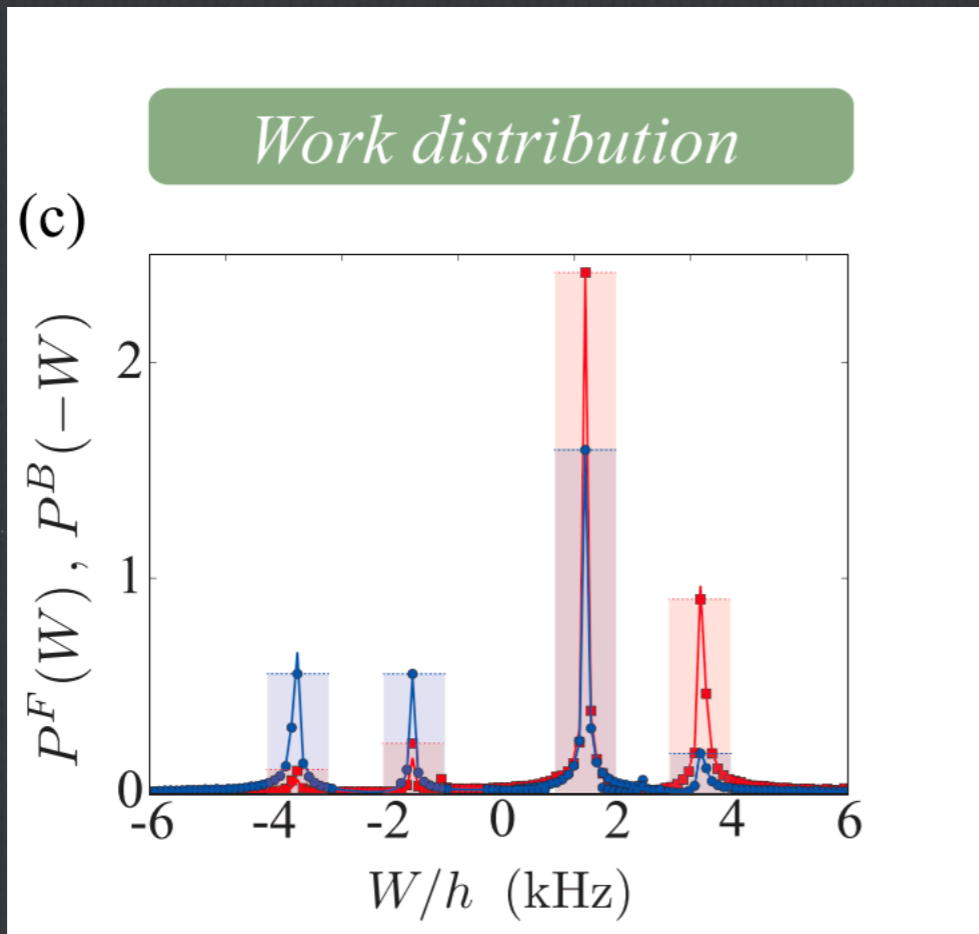
$$\frac{P_F(W)}{P_B(-W)} = e^{\beta(W - \Delta F)}$$





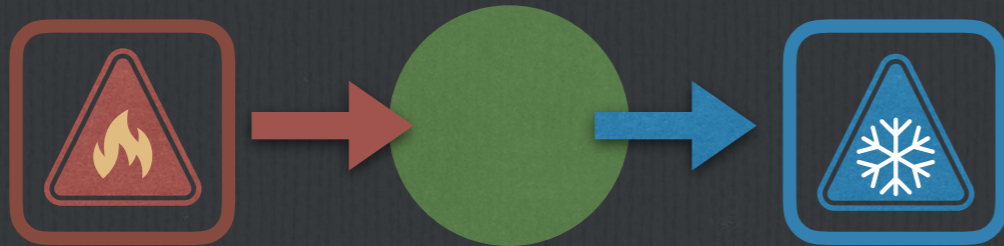
**Figure 3 | Free-energy recovery and test of the CFT for non-gaussian work distributions.** Experiments were carried out on the wild-type and mutant S15 three-helix junction without  $\text{Mg}^{2+}$ . Unfolding (continuous lines) and refolding (dashed lines) work distributions. Statistics: 900 pulls and two molecules (wild type, purple); 1,200 pulls and five molecules (mutant type, orange). Crossings between distributions are indicated by black circles. Work histograms were found to be reproducible among different molecules (error bars indicating the range of variability). Inset, test of the CFT for the mutant. Data have been linearly interpolated between contiguous bins of the unfolding and refolding work distributions.



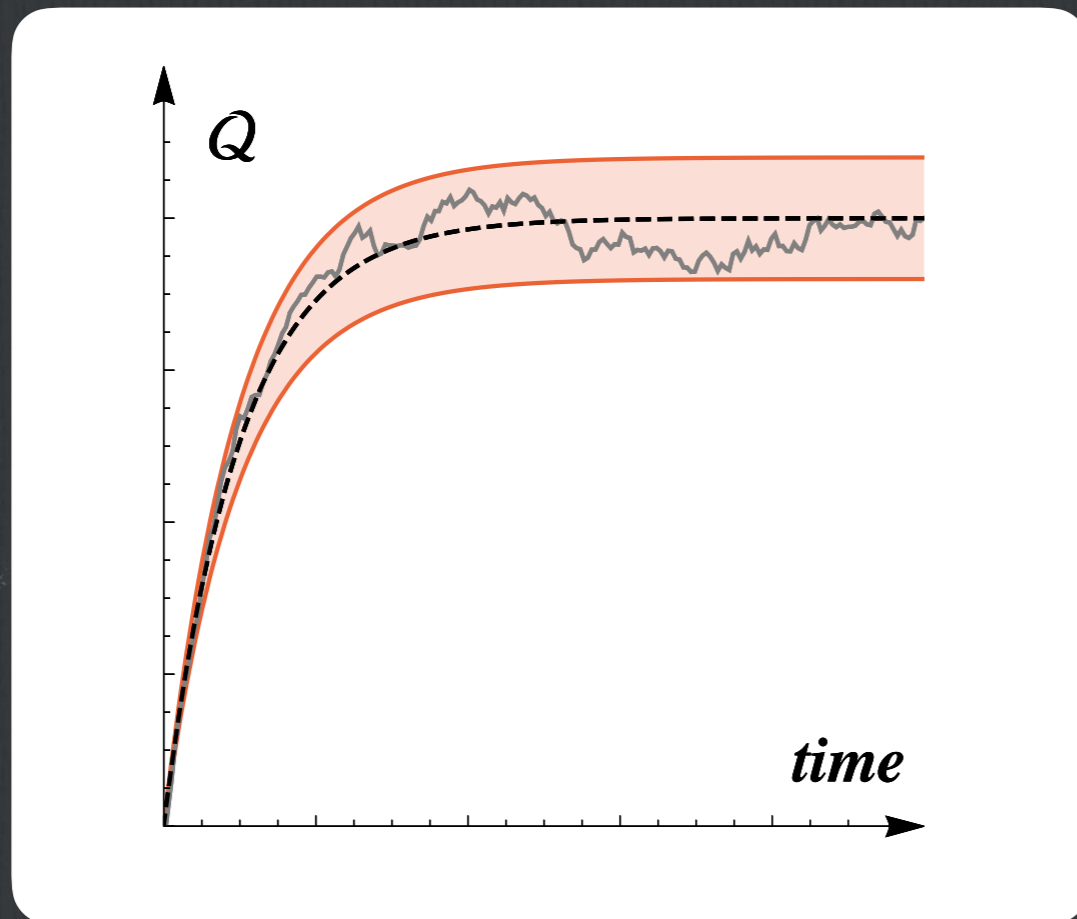




# Exchange fluctuation theorem



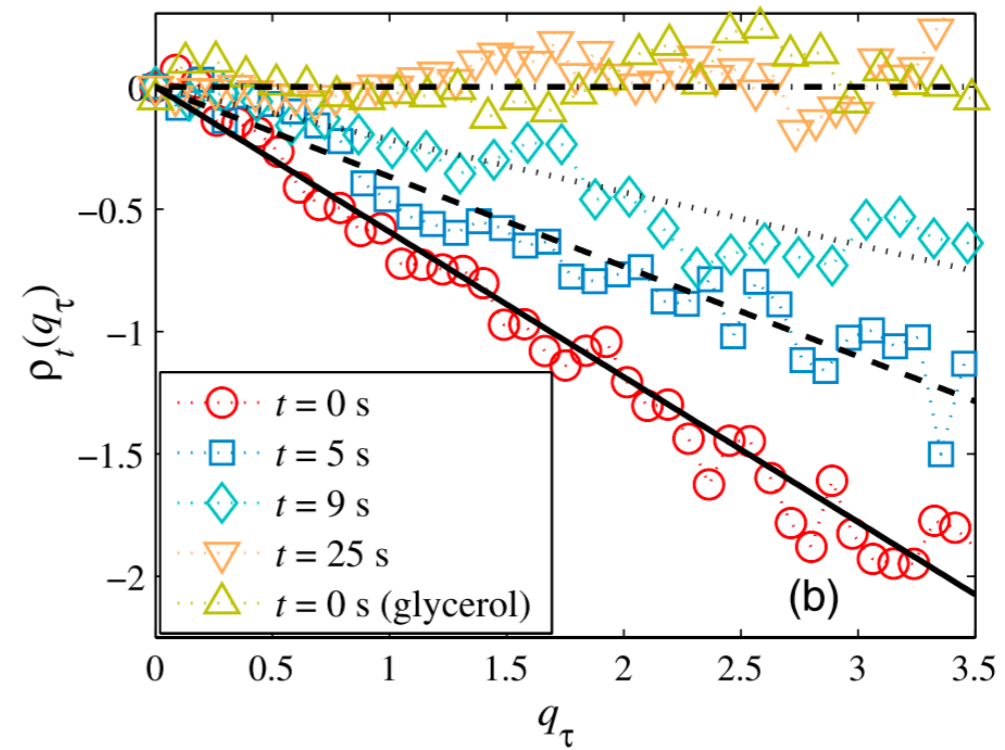
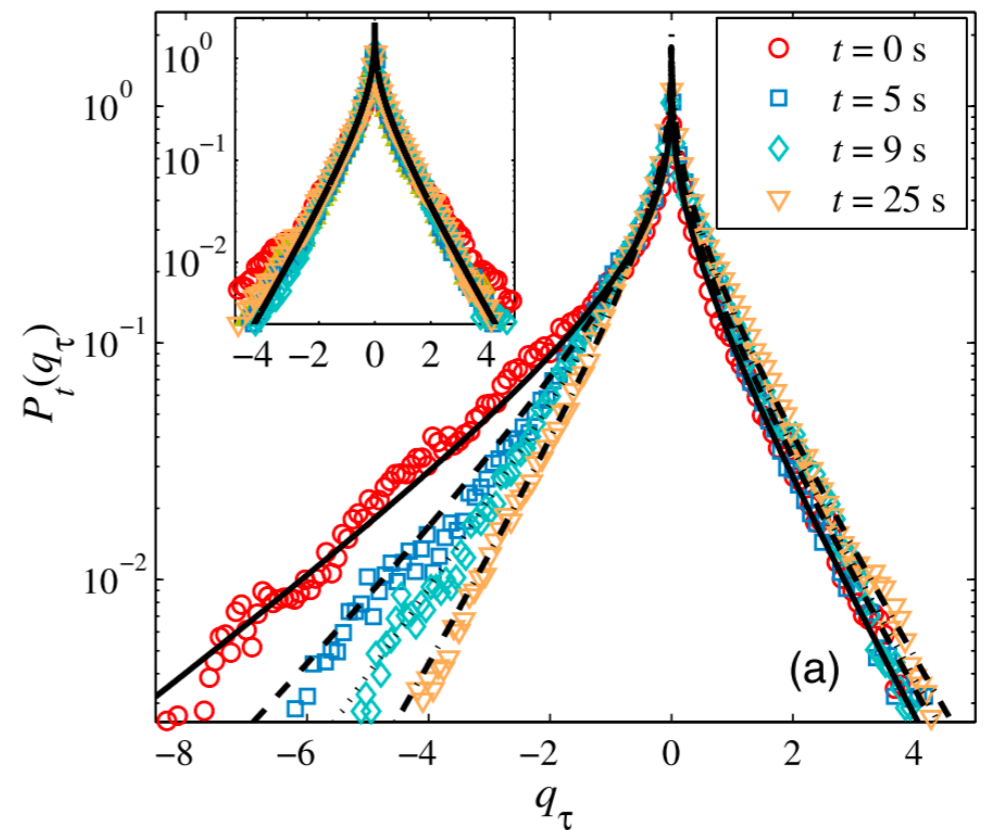
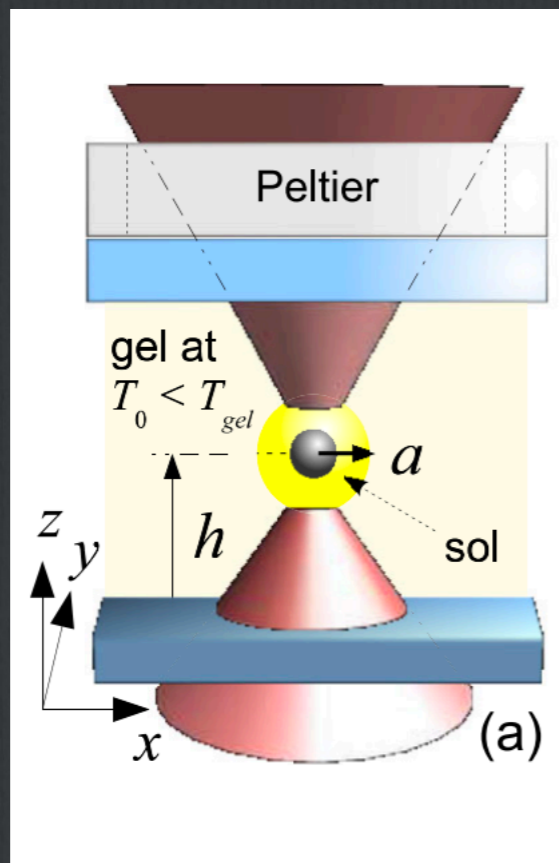
- The heat exchange between two bodies satisfies a stronger fluctuation theorem



$$\frac{P(Q)}{P(-Q)} = e^{\delta\beta Q}$$

- Here it's the same  $P(Q)$  that appears on the numerator and denominator.



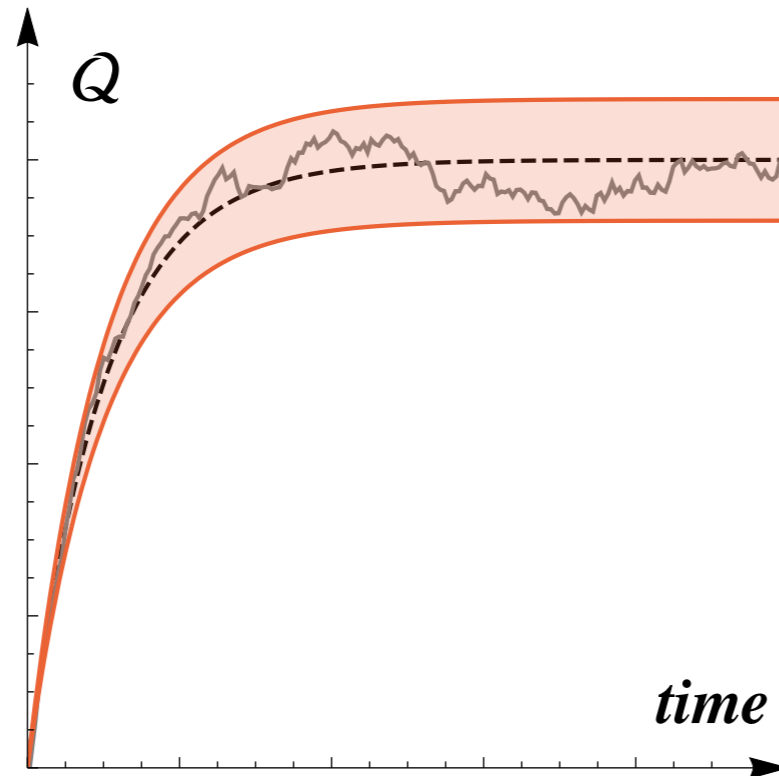
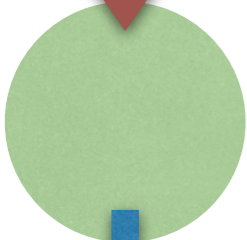




# **Thermodynamic Uncertainty Relations**



# Thermodynamic Uncertainty Relations (TURs)



- Proved for classical Markov processes.
- Physical origins are rather obscure.
- Regimes of validity?
- Quantum effects?

$$\frac{\text{var}(Q)}{\langle Q \rangle^2} \geq \frac{2}{\langle \Sigma \rangle}$$



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# Implications for mesoscopic engines

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

$$\frac{\text{var}(\dot{W})}{\langle \dot{W} \rangle^2} \geq \frac{2}{\langle \dot{\Sigma} \rangle}$$

- From our previously derived result:

$$\eta = \eta_C - \frac{T_c}{\dot{Q}_h} \dot{\Sigma} \quad \rightarrow \quad \langle \dot{\Sigma} \rangle = \frac{\langle \dot{Q}_h \rangle}{T_c} (\eta_C - \eta)$$

- Thus:

$$\frac{\text{var}(\dot{W})}{\langle \dot{W} \rangle^2} \geq \frac{2T_c}{\langle \dot{Q}_h \rangle} \frac{1}{\eta_C - \eta}$$

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- Thus:

$$\frac{\text{var}(\dot{W})}{\langle \dot{W} \rangle^2} \geq \frac{2T_c}{\langle \dot{Q}_h \rangle} \frac{1}{\eta_C - \eta}$$

- Finally, we note that  $\eta = -\frac{\langle \dot{W} \rangle}{\langle \dot{Q}_h \rangle}$ . Whence

$$\text{var}(\dot{W}) \geq 2T_c |\langle \dot{W} \rangle| \frac{\eta}{\eta_C - \eta}$$

- If you wish to operate the engine close to Carnot efficiency, you pay the price that the fluctuations may become very large.
  - To reduce fluctuations, the engine should be operated irreversibly!



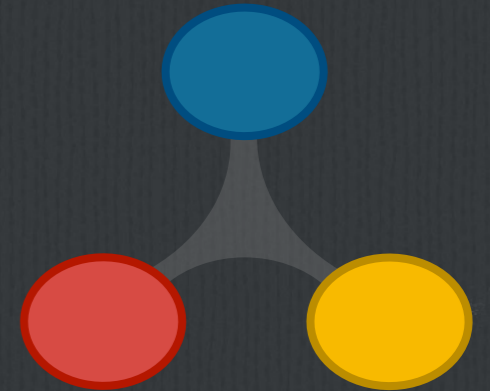
# TURs from FTs



# Extension to multiple charges

- Can be generalized to an arbitrary number of systems and an arbitrary number of currents:

$$\frac{P(Q_1, \dots, Q_n)}{P(-Q_1, \dots, -Q_n)} = e^{\sum_i A_i Q_i}$$



- e.g.: two systems, but with particle and energy flow:

$$\frac{P(\Delta E_1, \Delta E_2, \Delta N_1)}{P(-\Delta E_1, -\Delta E_2, -\Delta N_1)} = e^{\beta_1 \Delta E_1 + \beta_2 \Delta E_2 + \delta \beta \mu \Delta N_1} \quad \delta \beta \mu = \beta_1 \mu_1 - \beta_2 \mu_2$$

- In general  $\Delta E_1 \neq -\Delta E_2$ : this means there is work involved; e.g.,

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



# TUR de force

□ Our main

□ Consider

□ For fixed  
can attain

**Theorem** (“TUR de force”). For fixed finite  $\langle \Sigma \rangle$  and  $\langle Z \rangle$ , the probability distribution  $P(\Sigma, Z)$  satisfying  $P(\Sigma, Z)/P(-\Sigma, -Z) = e^\Sigma$ , with the smallest possible variance (the minimal distribution) is the distribution

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

where the values of  $a$  and  $b$  are fixed by  $\langle \Sigma \rangle = a \tanh(a/2)$  and  $\langle Z \rangle = b \tanh(a/2)$ . For this distribution

$$\text{Var}(Z)_{min} = \langle Z \rangle^2 f(\langle \Sigma \rangle), \quad (2)$$

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

variance that Z

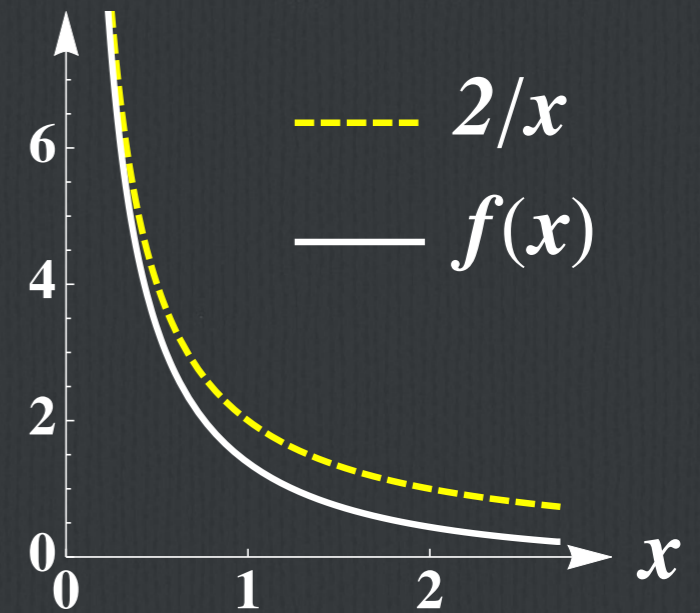


- As a consequence, for any other distribution, one must have

$$\text{var}(Z) \geq \langle Z \rangle^2 f(\langle \Sigma \rangle)$$

- ✓ This is the *tightest* (saturable) bound possible for this scenario.
- ✓ And we know which distribution saturates this bound.
- Similar papers appeared at the same time, but all deriving a looser bound (which is thus never tight):

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



Hasegawa & Vu 1902.06376.

Proesman & Horowitz 1902.07008.

Potts & Samuelsoon 1904.04913.



□ **Consider now a general TUR**  $\frac{P(Q_1, \dots, Q_n)}{P(-Q_1, \dots, -Q_n)} = e^{\sum_i A_i Q_i}$

□ **Define**  $\Sigma = \sum_i A_i Q_i$        $Z = \sum_i z_i Q_i, \quad \forall z_i$

□ **Then**  $\frac{P(\Sigma, Z)}{P(-\Sigma, -Z)} = e^{\Sigma} \implies \text{var}(Z) \geq \langle Z \rangle^2 f(\langle \Sigma \rangle)$

□ **But**  $\langle Z \rangle = \sum_i z_i q_i, \quad q_i = \langle Q_i \rangle$

$\text{var}(Z) = \sum_{ij} C_{ij} z_i z_j, \quad C_{ij} = \text{cov}(Q_i, Q_j)$

□ **Thus**  $z^T (C - fqq^T) z \geq 0$

$C - fqq^T \geq 0$



- When a matrix is positive semi-definite, all the diagonal entries must be non-negative:

$$\frac{\text{var}(Q_i)}{\langle Q_i \rangle^2} \geq f(\langle \Sigma \rangle)$$

$$C - fqq^T \geq 0$$

- With our framework, we can also go further and say something about the covariances.

- If G is psd, any 2x2 sub-matrix must also be psd:  $-\sqrt{G_{ii}G_{jj}} \leq G_{ij} \leq \sqrt{G_{ii}G_{jj}}$

- Whence:

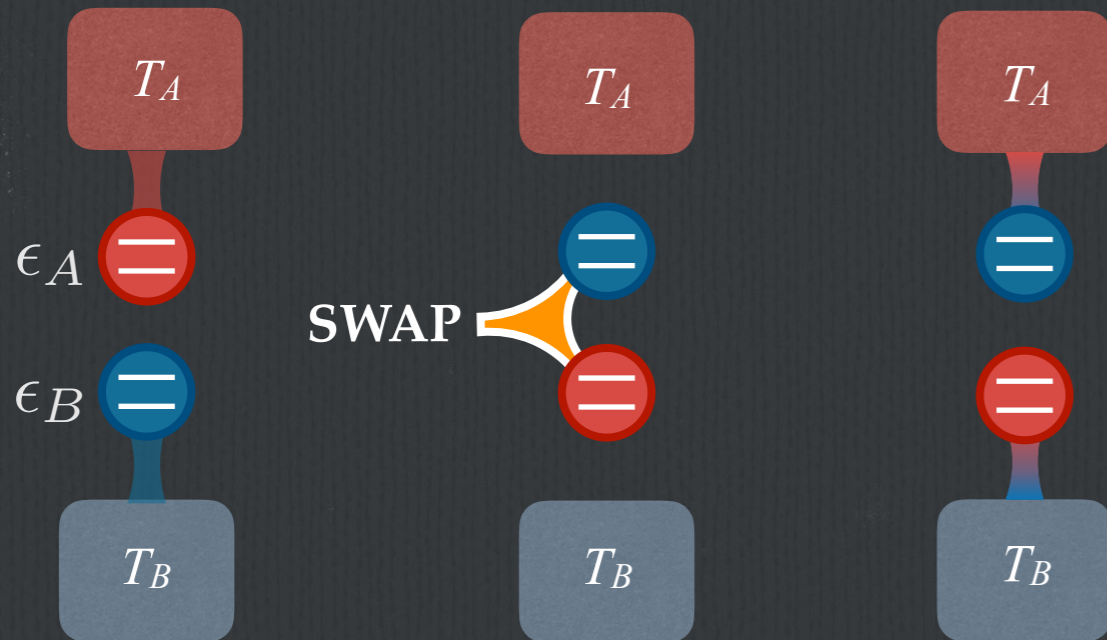
$$fq_iq_j - M_{ij} \leq C_{ij} \leq fq_iq_j + M_{ij}, \quad M_{ij} = \sqrt{(\text{var}(Q_i) - fq_i^2)(\text{var}(Q_j) - fq_j^2)}$$

- Particularly interesting are the signs of the covariance:

$$\frac{q_i^2}{\text{var}(Q_i)} + \frac{q_j^2}{\text{var}(Q_j)} \geq \frac{1}{f(\langle \Sigma \rangle)} \implies \text{sign}(C_{ij}) = \text{sign}(q_iq_j)$$



# SWAP engine

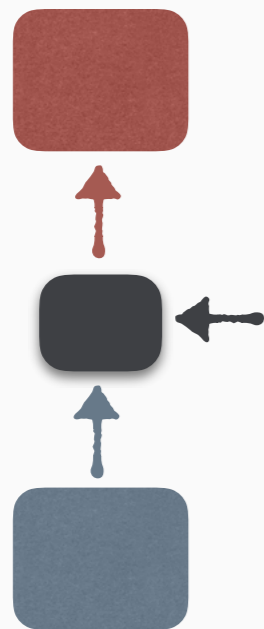


$$\langle Q_h \rangle = \epsilon_A (f_A - f_B)$$

$$\langle Q_c \rangle = -\epsilon_B (f_A - f_B)$$

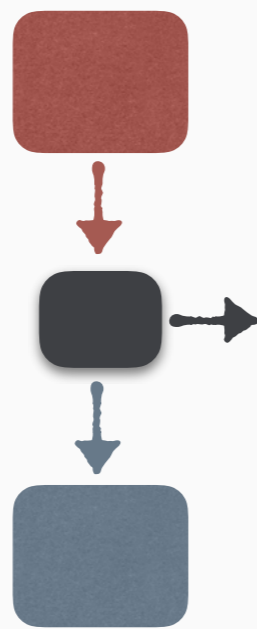
$$\langle W \rangle = -(\epsilon_A - \epsilon_B)(f_A - f_B)$$

$$f_i = \frac{1}{e^{\beta_i \epsilon_i} + 1}$$



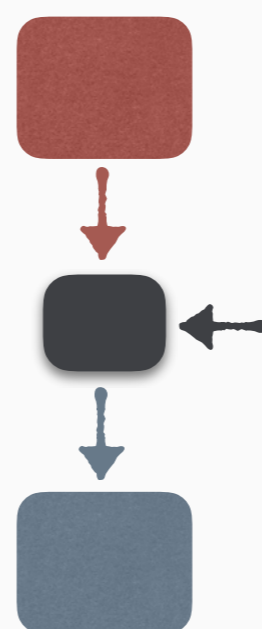
**Refrigerator**

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



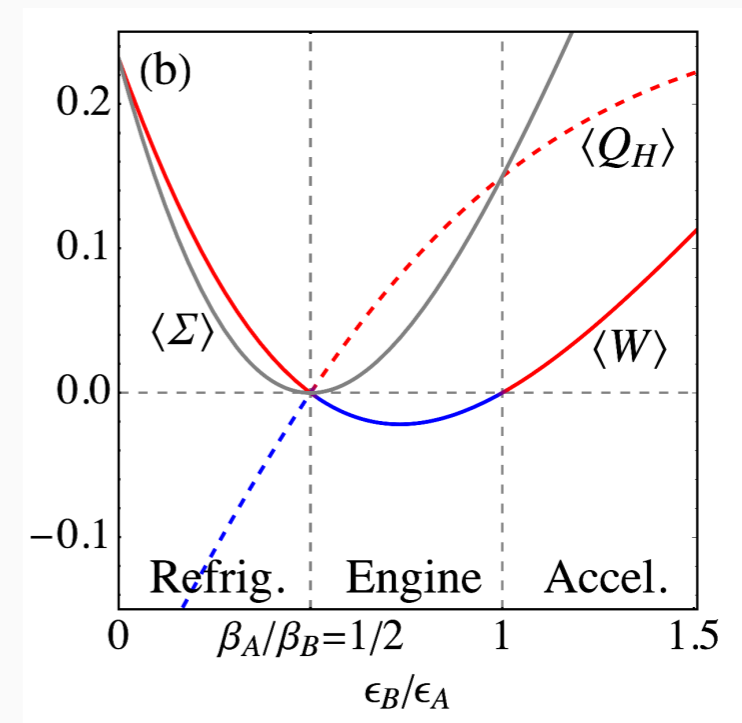
**Engine**

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



**Accelerator**

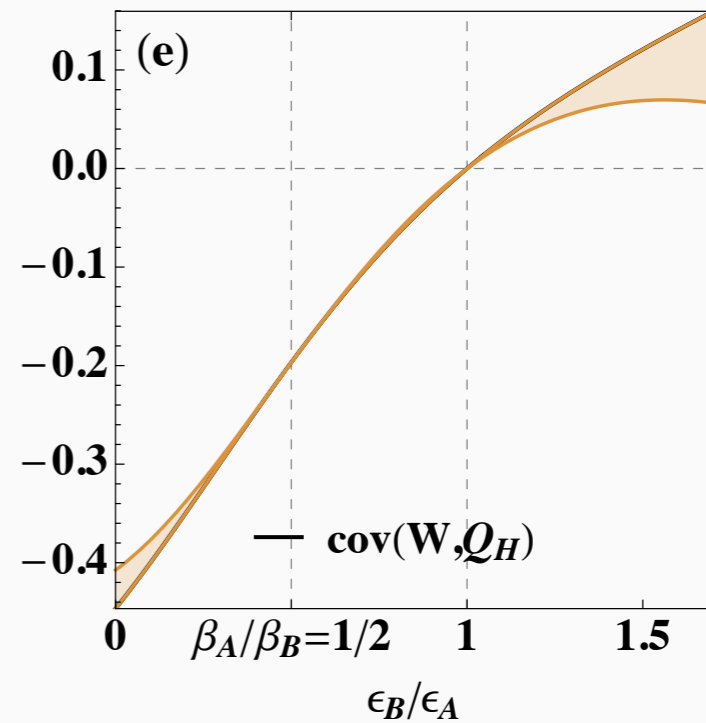
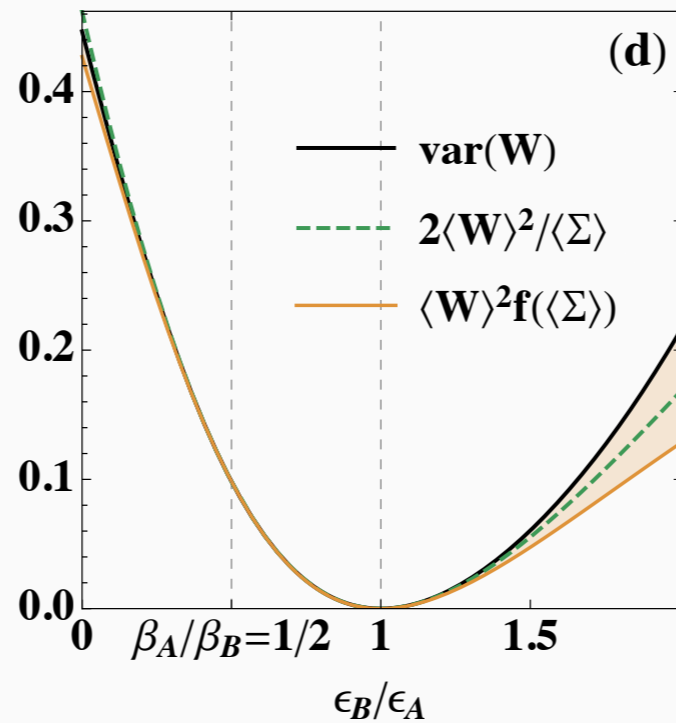
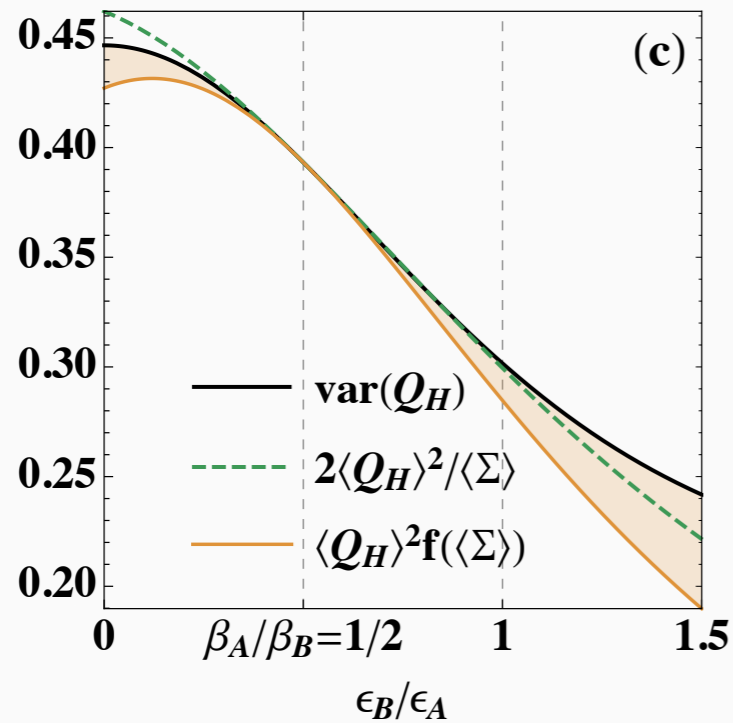
$$1 < \frac{\epsilon_B}{\epsilon_A}$$





# SWAP engine

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





# Conclusions

Acknowledgements:  
IFUSP, FAPESP, CNPq

- TURs: simple but with enormous predictive power.
- A dynamical TUR can be derived as a *consequence* of Fluctuation Theorems.
- Our TUR is matrix valued:
  - Bounds all variances;
  - as well as covariances.
- It is the tightest bound possible. And we know which distribution saturates it.



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