
THERMODYNAMIC UNCERTAINTY RELATIONS AND THEIR CONNECTION WITH FLUCTUATION THEOREMS

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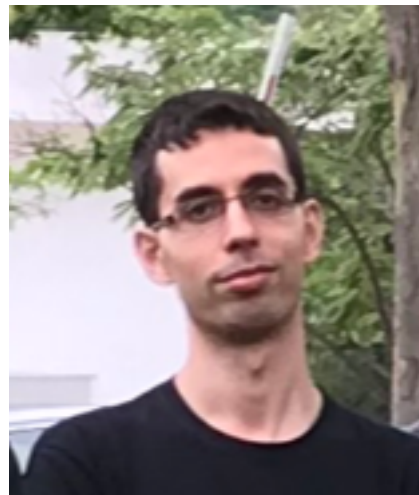
July 23rd, 2019



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summary



- I. Entropy production.
- II. Thermodynamic uncertainty relations (TURs).
- III. TURs and fluctuation theorems.
- IV. Applications to quantum heat engines.
- V. Zubarev Ensemble.
- VI. Battery-charging precision.

arXiv 1902.10428
arXiv 1904.07574

Entropy production $\neq$ entropy

- Entropy does not satisfy a continuity equation:

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

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

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

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

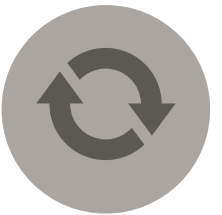
- Example: if there is no work involved,

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

- *Heat flows from hot to cold.*



$\vdots \dot{Q}_h$



$\vdots \dot{Q}_c$

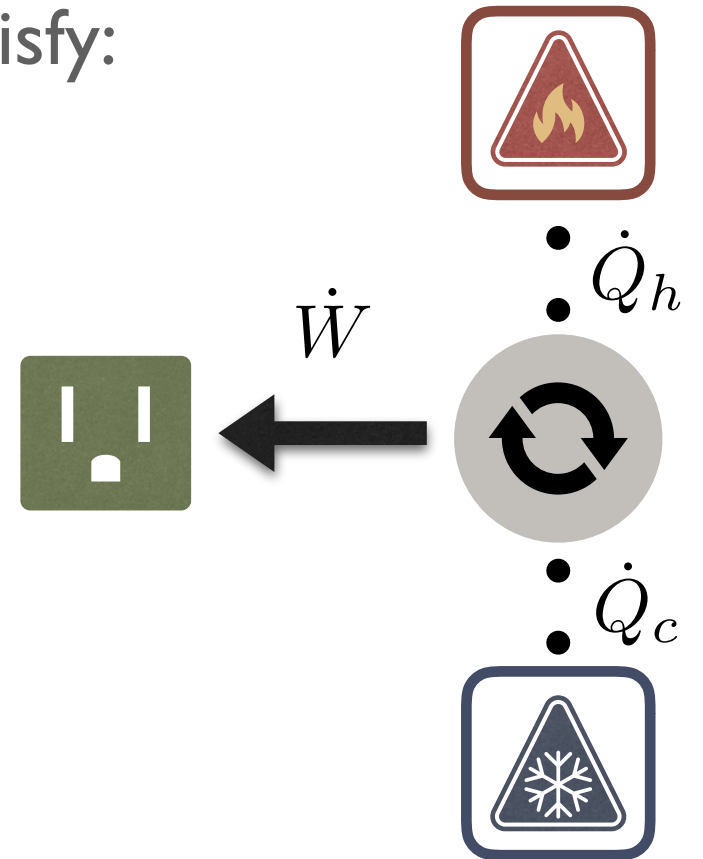


Why entropy production matters

- An engine operating at the steady-state regime will satisfy:

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

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



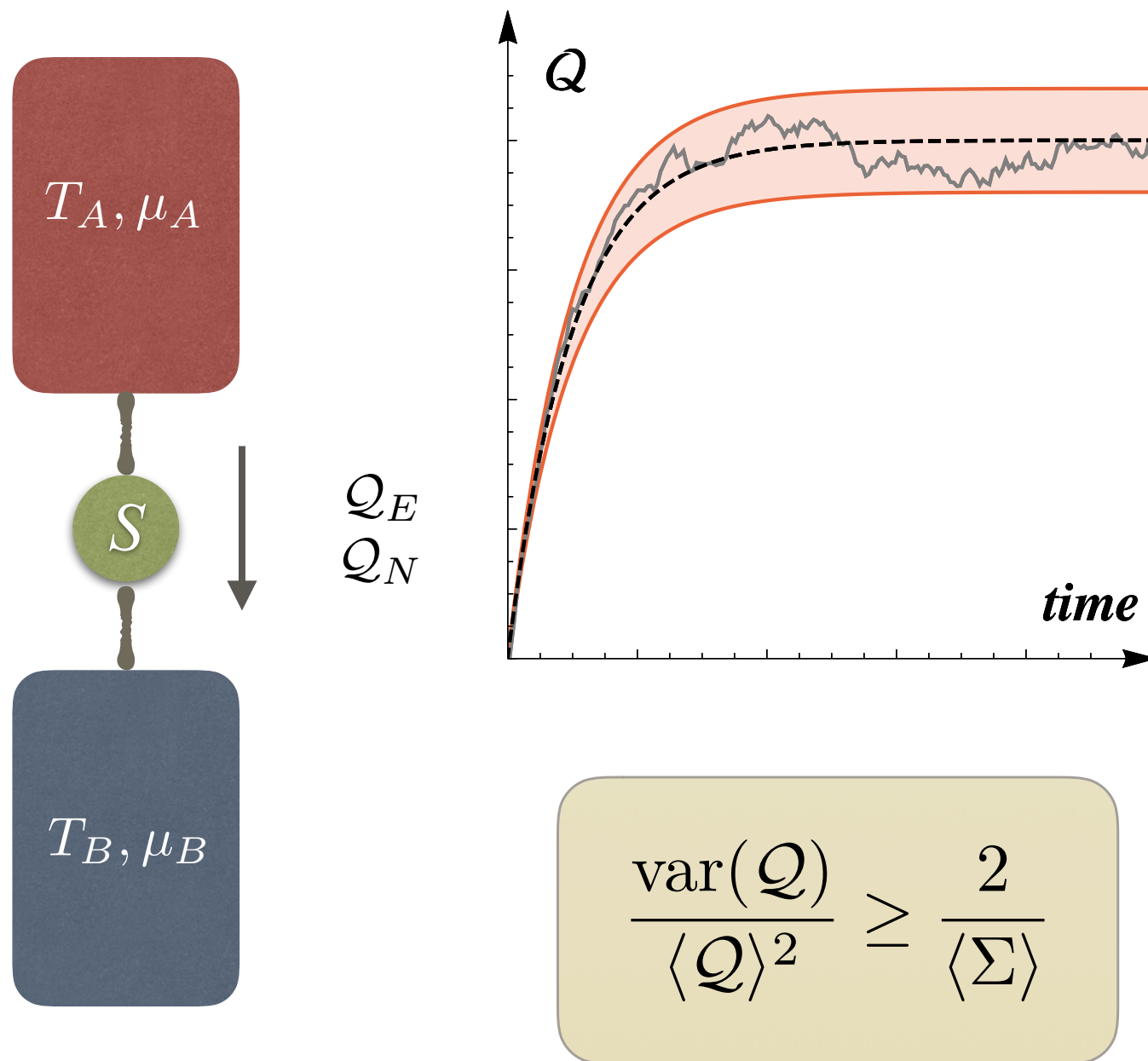
- The efficiency of the engine may then be written as

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

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

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

Thermodynamic Uncertainty Relations (TURs)



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

A. C. Barato, U. Seifert, "Thermodynamic Uncertainty Relation for Biomolecular Processes", *Physical Review Letters*, **114**, 158101 (2015)

Implications for mesoscopic engines

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

$$\frac{\text{var}P}{\langle P \rangle^2} \geq \frac{2}{\langle \dot{\Sigma} \rangle}$$

- But $\langle \dot{\Sigma} \rangle = \frac{\langle \dot{Q}_h \rangle}{T_c} (\eta_C - \eta)$, which gives

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

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

$$\text{var}P \geq 2T_c \langle P \rangle \frac{\eta}{\eta_C - \eta}$$

Violations of the TUR in the quantum regime

- The classical TUR can be violated in quantum transport problems.

We have recently shown that close to linear response the bound is 1/2 looser:

$$\frac{\text{var}(Q)}{\langle Q \rangle^2} \geq \frac{1}{\langle \Sigma \rangle}$$

- This has been observed in quantum transport experiments.
- A violation of the TUR could be exploited to increase the output power.

G. Guarnieri, G. T. Landi, S. R. Clark, J. Goold, arXiv 1902.10428

K. Ptaszyński, K. *Phys. Rev. B*, **98**, 085425 (2018)

B. Agarwalla, D. Segal, *Phys. Rev. B.*, **98**, 155438 (2018)

Connection with fluctuation theorems

A. M. Timpanaro, G. Guarnieri, J. Goold, G. T. Landi “Thermodynamic uncertainty relations from exchange fluctuation theorems”, arXiv 1904.07574

Fluctuation theorems

- 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:

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

- Jarzynski-Wójcik Exchange Fluctuation Theorem
(Phys. Rev. Lett. 92, 230602 (2004))

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

**Stronger
symmetry!**

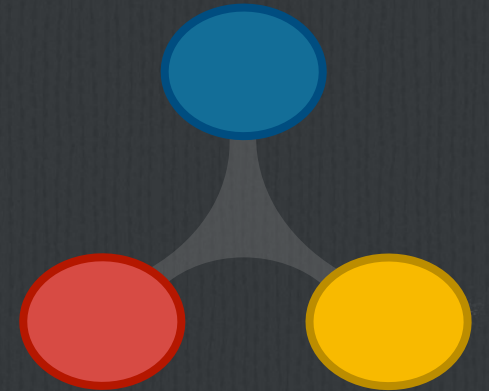
T_A

T_B

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:

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

$$\delta \beta \mu = \beta_1 \mu_1 - \beta_2 \mu_2$$

- 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

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

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

□ For fixed
can attain

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 $x \tanh(x)$.

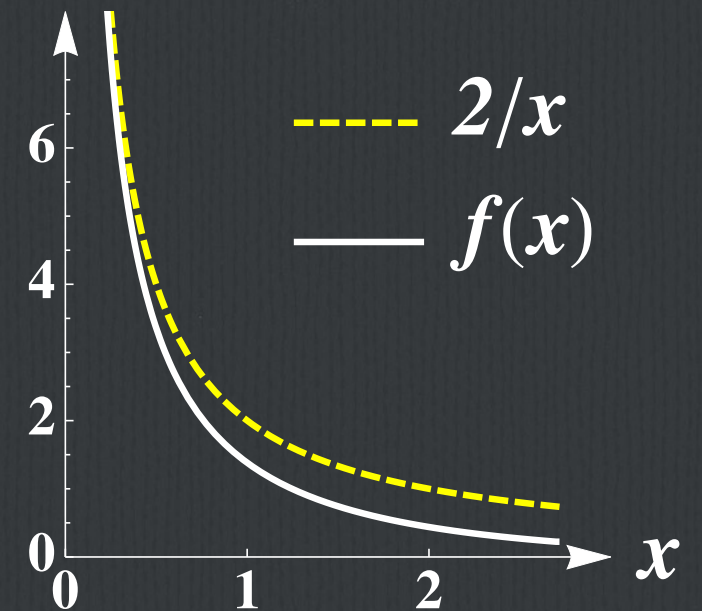
variance that Z

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

□ **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** $z^T \left(C - f q q^T \right) z \geq 0$

$$C - f q q^T \geq 0$$

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

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

$$\mathcal{C} - f\mathbf{q}\mathbf{q}^T \geq 0$$

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

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

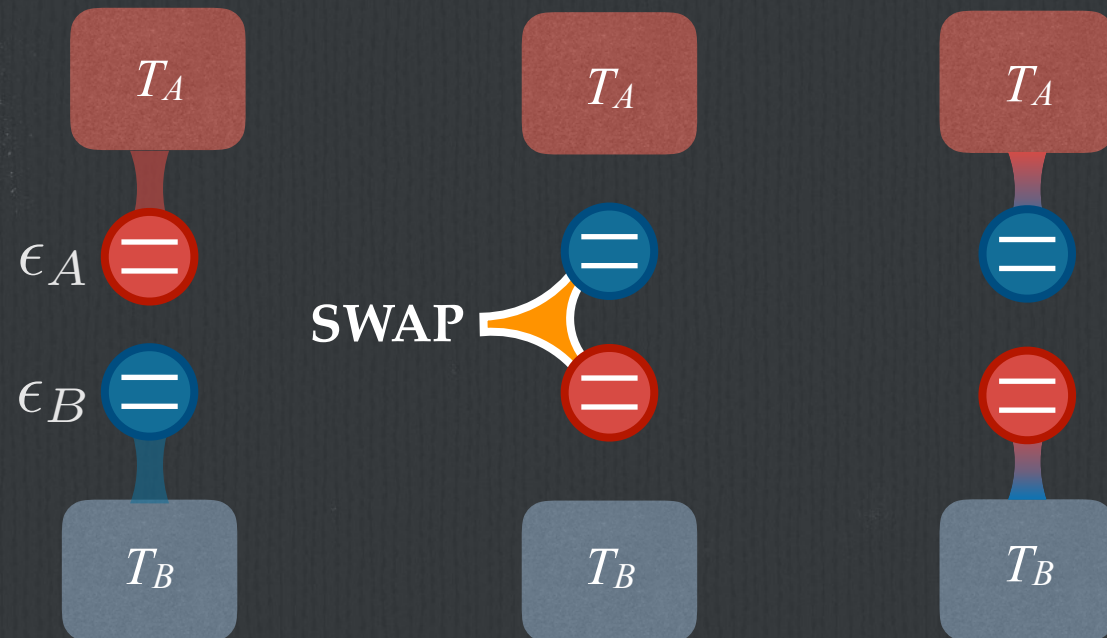
- Whence:

$$fq_iq_j - M_{ij} \leq C_{ij} \leq fq_iq_j + M_{ij}, \quad M_{ij} = \sqrt{(\text{var}(\mathcal{Q}_i) - fq_i^2)(\text{var}(\mathcal{Q}_j) - fq_j^2)}$$

- Particularly interesting are the signs of the covariance:

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

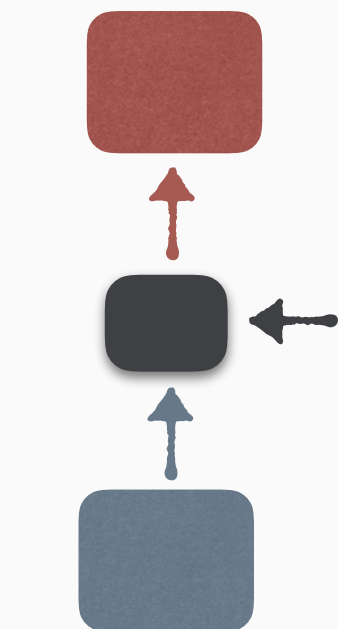
SWAP engine



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

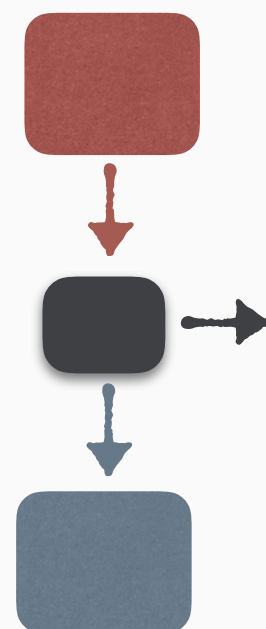
$$\langle Q_c \rangle = -\epsilon_B (f_A - f_B) \quad f_i = \frac{1}{e^{\beta_i \epsilon_i} + 1}$$

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



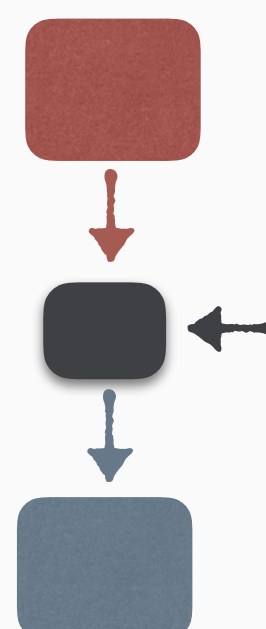
Refrigerator

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



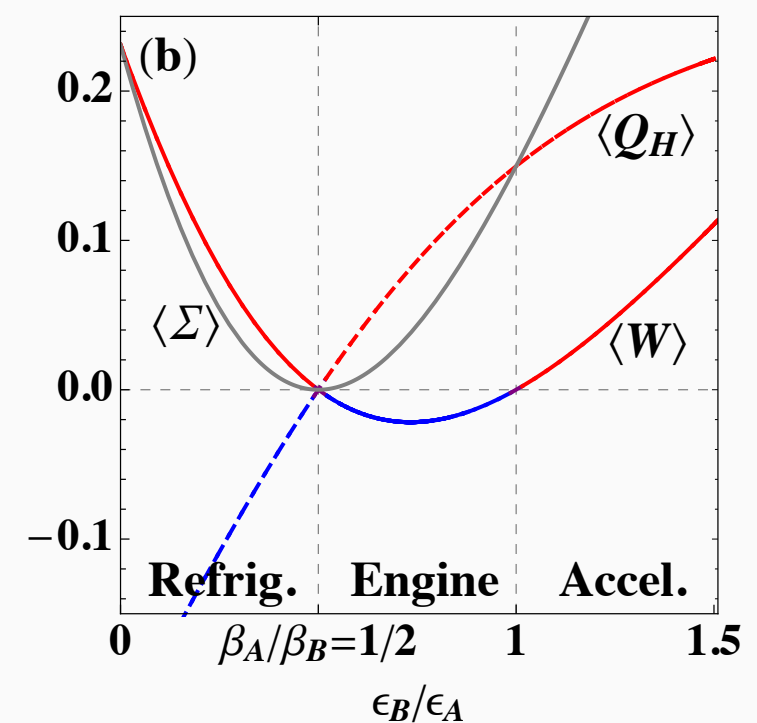
Engine

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



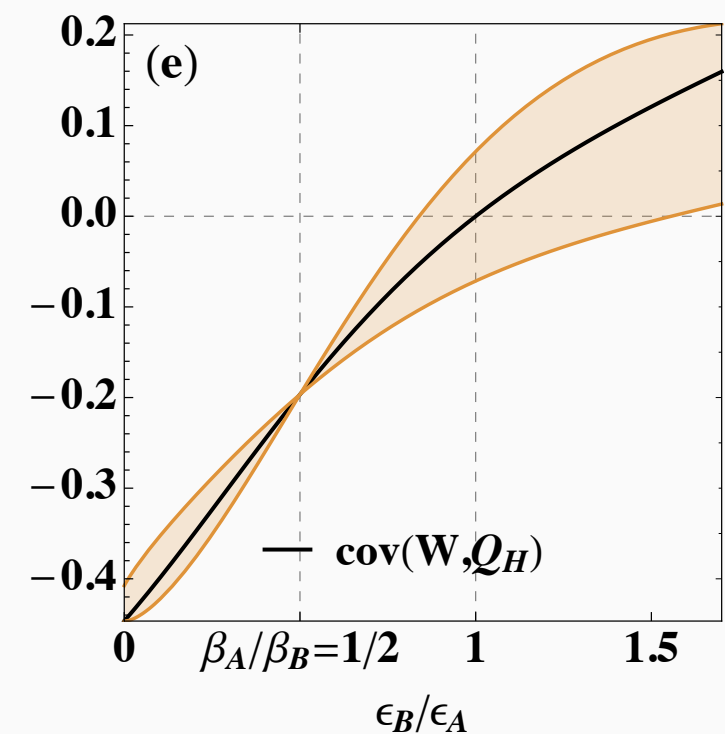
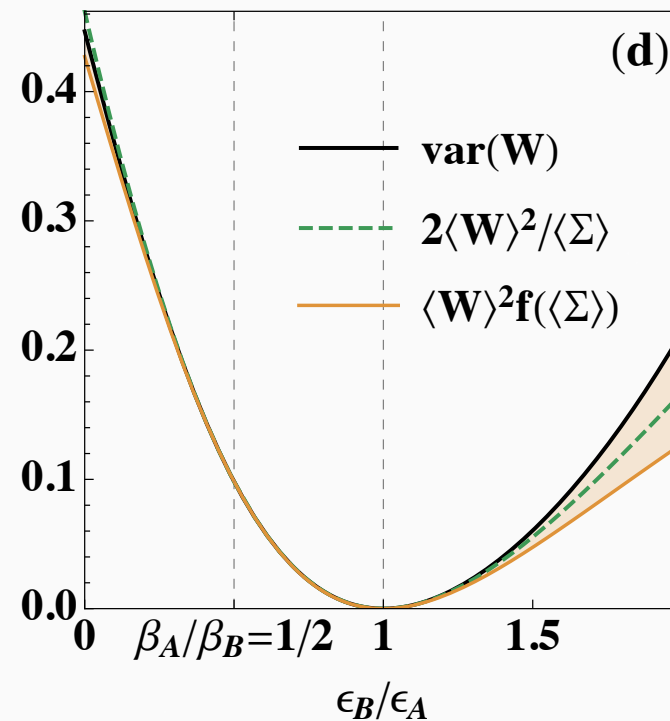
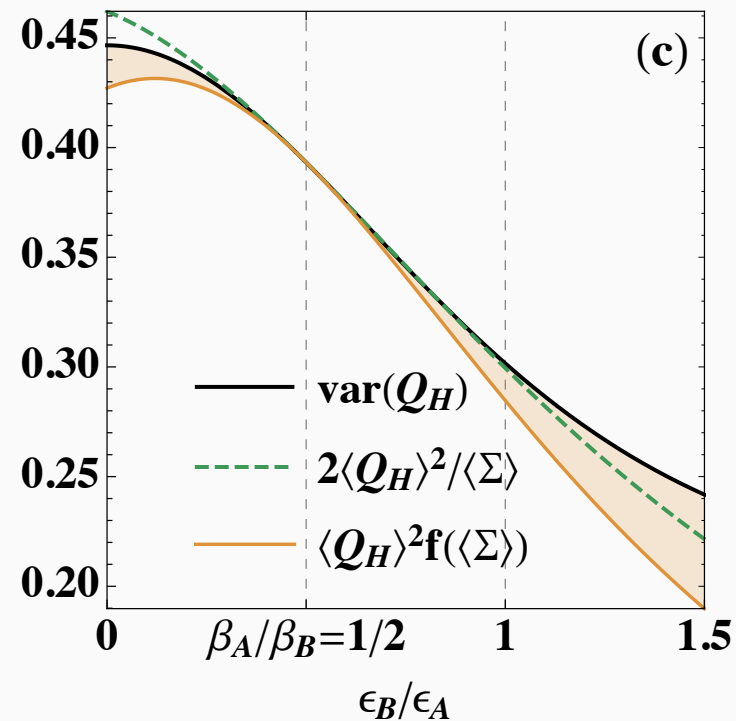
Heat pump

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



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



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