Non-adiabaticity and irreversible entropy production

F. Plastina

Università della Calabria

After lots of work discussions with:

N. Lo Gullo and A. Alecce

F. Galve and R. Zambrini

G. Francica, T.J.G. Apollaro, G. Falcone

Università della Calabria

Outline:

1. Thermodynamic transformations
2. Isothermal process: Irreversible work
3. Adiabatic process: Inner friction
4. Entropy production
5. Use of a non-equilibrium reference state
6. Conclusions

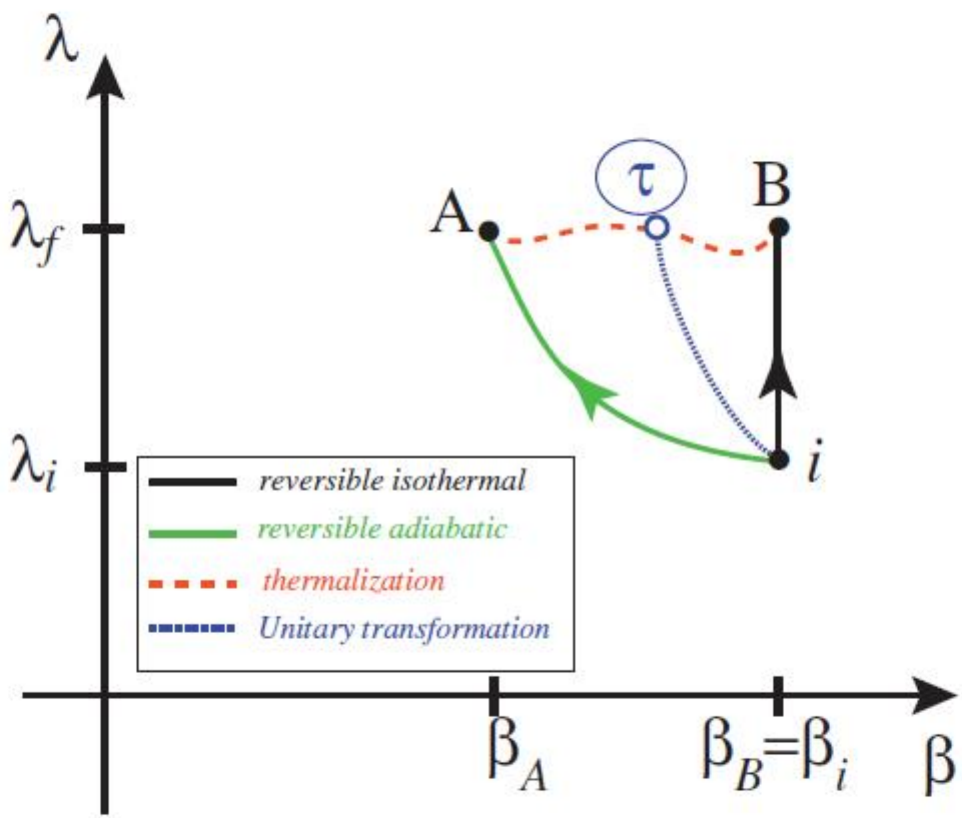
based on: F.P. et al., PRL 113, 260601 (2014)

Setting the stage: Thermodynamic transformation

Work parameter $\lambda(t)$ **:** $\lambda(t=0)=\lambda_i \longrightarrow \lambda(\tau)=\lambda_f$

Closed quantum system :

the Hamiltonian $H[\lambda(t)]$ generates the evolution $U(\tau,0)$



Initial (equilibrium) state

$$\rho_i = e^{-\beta_i H_i}/Z[\lambda_i,\beta_i]$$

final state

$$\rho_\tau = U(\tau,0)\rho_i U^\dagger(\tau,0)$$

Work and Jarzynski relation

Probability density for the work done on the system:

$$p(w) = \sum_{n,m} P_n^{(i)} \, P_{n\to m}^{(\tau)} \, \delta(w - \varepsilon_m^{(f)} + \varepsilon_n^{(i)})$$

with $P_n^{(i)} = Z_i^{-1} e^{-\beta_i \varepsilon_n^{(i)}}$ and $P_{n\to m}^{(\tau)} = \left| \left\langle \varepsilon_m^{(f)} \right| U(\tau,0) \left| \varepsilon_n^{(i)} \right\rangle \right|^2$

Fluctuation relation

$$\left\langle e^{-\beta_i w} \right\rangle = e^{-\beta_i \Delta F}$$

where $\Delta F = F[\lambda_f, \beta_B] - F[\lambda_i, \beta_i]$

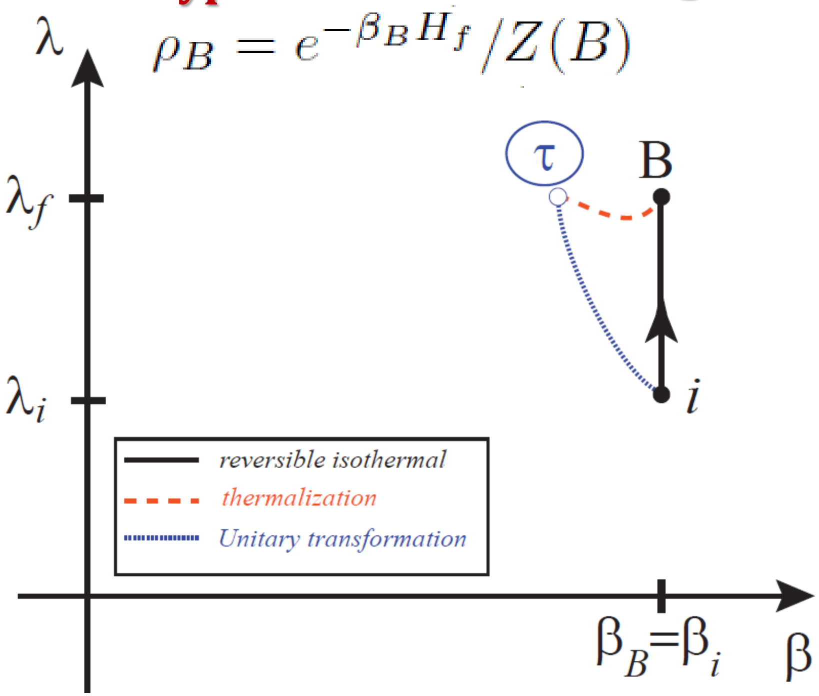
Irreversible Work

$$\langle e^{-\beta_i w} \rangle = e^{-\beta_i \Delta F} \quad \Longrightarrow \quad \langle w_{irr} \rangle = \langle w \rangle - \Delta F \geq 0$$

Loosely speaking, the irreversible work gives a measure of the irreversibility.

Hypothetical final state @ B:

$$\rho_B = e^{-\beta_B H_f}/Z(B)$$



Relation with the relative entropy

$$\langle w_{irr} \rangle = \frac{1}{\beta_B} D(\rho_\tau || \rho_B)$$

S. Deffner and E. Lutz, PRL10

Thermalization

$$\langle w_{irr} \rangle = T_B(S_B - S_i) - \langle Q^{th}_{\tau \to B} \rangle$$

where $\langle Q^{th}_{\tau \to B} \rangle = \mathrm{tr}\{(\rho_B - \rho_\tau) H_f\}$

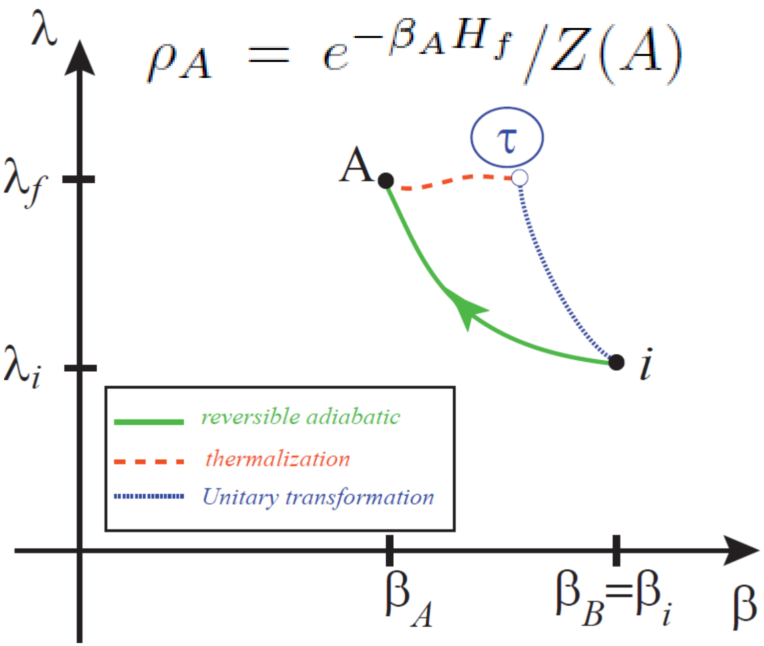
Adiabatic Transformation (reversible and quasi-static !)

Define Point A by the relation: $P_m^{(i)} = P_m^{(A)}$ **(*)**

(*)
This is possible iff all of the energy gaps scale by the same ratio β_i/β_A

Hypothetical final state @ A:

$$\rho_A = e^{-\beta_A H_f}/Z(A)$$



Work in the ideal case

$$\langle w_{i\to A}\rangle = \mathcal{U}_A - \mathcal{U}_i \equiv \sum_m P_m^{(i)}(\varepsilon_m^{(f)} - \varepsilon_m^{(i)})$$

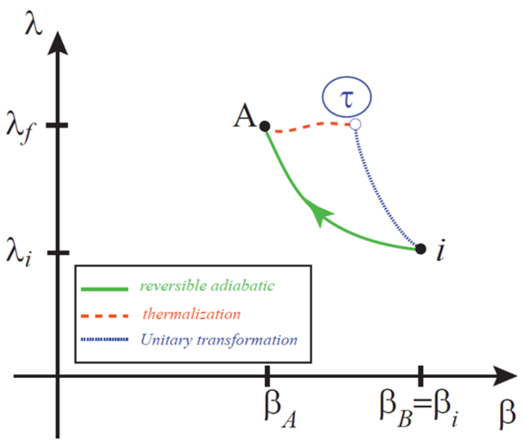
Inner friction

$$\langle w_{fric}\rangle = \langle w\rangle - \langle w_{i\to A}\rangle$$

Inner friction

- due to unwanted transitions one would typically associate with heat.

Indeed, it is the heat the system would release in thermalizing towards A :



Performing an adiabatic transformation in a finite time, the amount of work that `gets lost' is larger when the system is brought far and far away from equilibrium.

Thermalization

$$\langle w_{fric} \rangle \equiv - \langle Q^{th}_{\tau \to A} \rangle$$

Relation with the relative entropy

$$\langle w_{fric} \rangle = \frac{1}{\beta_A} D(\rho_\tau || \rho_A)$$

Relation with the Bures angle

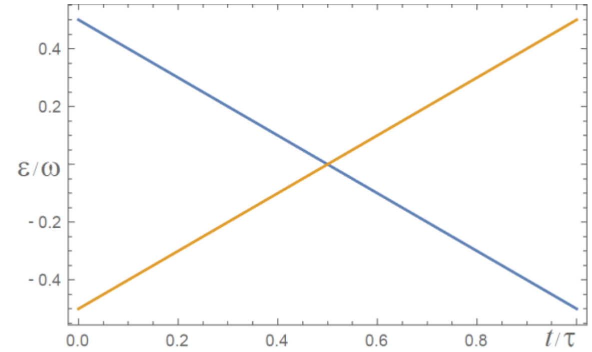
$$\beta_A \langle w_{fric} \rangle \geq \frac{8}{\pi^2} \mathcal{L}^2(\rho_\tau, \rho_A)$$

an example with negative temperature

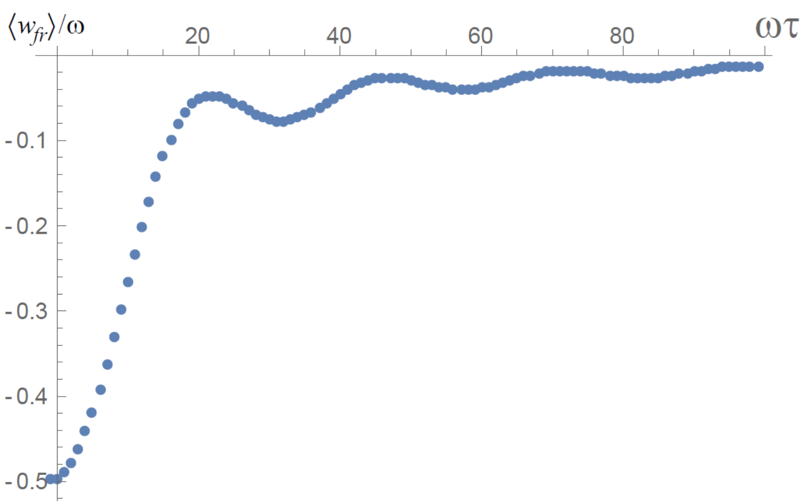
Consider a qubit in a t-dependent slowly rotating magnetic field

$$H = \omega(h_x \sigma_x + h_z \sigma_z)$$

$$h_x = \left(\frac{1}{2} - \frac{t}{\tau}\right)\cos\left(\frac{\pi}{2}\frac{t}{\tau}\right), \quad h_z = \left(\frac{1}{2} - \frac{t}{\tau}\right)\sin\left(\frac{\pi}{2}\frac{t}{\tau}\right)$$



$\beta_A < 0$ if a level crossing is present



$\langle w_{fric} \rangle < 0$ **!**

Entropy production

Relation with the irreversible work :

$$\langle w_{irr}\rangle - \langle w_{fric}\rangle = (\mathcal{U}_A - \mathcal{U}_B) - T_i(S_A - S_B)$$

Link with the entropy production

Ideal case:

$$S_i = S_A \quad \Rightarrow \quad \beta_A \mathcal{U}_A - \beta_i \mathcal{U}_i = \beta_A F_A - \beta_i F_i$$

Actual case:

we can build the **stochastic variable** $s = \beta_A \varepsilon_m^{(f)} - \beta_i \varepsilon_n^{(i)}$

with **prob. density:**

$$p(s) = \sum_{n,m} P_n^{(i)}\, P_{n\to m}^{(\tau)}\, \delta(s - \beta_A \varepsilon_m^{(f)} + \beta_i \varepsilon_n^{(i)})$$

and **average value:**

$$\langle s\rangle = \beta_A \,\mathrm{tr}\,\{\rho_\tau H_f\} - \beta_i \mathcal{U}_i$$

Notice that, in the ideal case :

$$\langle s\rangle = \beta_A \mathcal{U}_A - \beta_i \mathcal{U}_i = \beta_A F_A - \beta_i F_i$$

Inner friction ⟺ irreversible entropy

fluctuation relation:

$$\langle e^{-s} \rangle = \sum_{n,m} P_n^{(i)} \, P_{n\to m}^{(\tau)} \, e^{-(\beta_A \varepsilon_m^{(f)} - \beta_i \varepsilon_n^{(i)})} = $$
$$= \frac{Z_A}{Z_i} \equiv e^{-(\beta_A F_A - \beta_i F_i)}$$

Entropy production

$$\langle \sigma \rangle := \langle s \rangle - (\beta_A F_A - \beta_i F_i) \geq 0$$

=

Inner friction

$$\langle \sigma \rangle \equiv \beta_A \langle w_{fric} \rangle \equiv D(\rho_\tau || \rho_A)$$

!

Cumulants of the entropy

The cumulants of the **stochastic variable s**

$$C_1 = \langle s \rangle$$

$$C_2 = \langle s^2 \rangle - \langle s \rangle^2$$

$$C_3 = \langle s^3 \rangle - 3 \langle s^2 \rangle \langle s \rangle + 2 \langle s \rangle^3$$

....

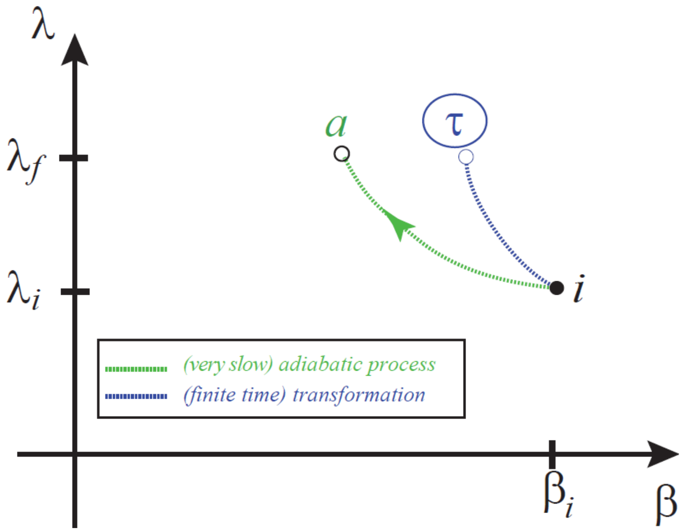
obey the relation

$$-(\beta_A F_A - \beta_i F_i) = \sum_{n=1} \frac{(-1)^n}{n!} C_n$$

Then, the average entropy production is :

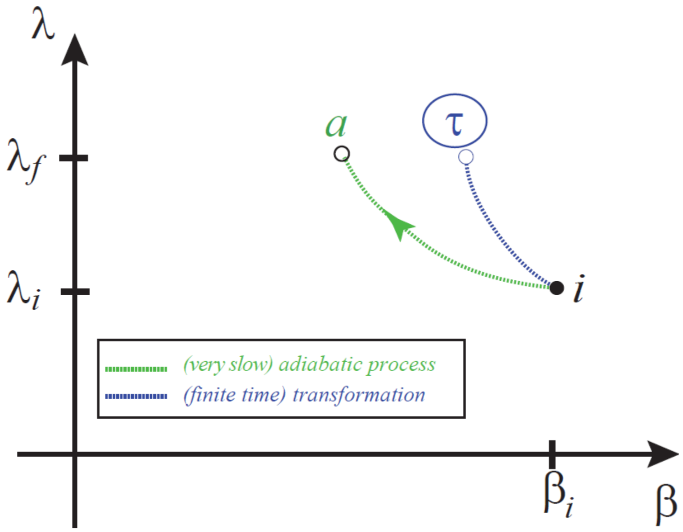
$$\langle \sigma \rangle = \beta_A \langle w_{fric} \rangle = \frac{C_2}{2} - \frac{C_3}{6} + \dots ,$$

What if A is not an equilibrium state ?



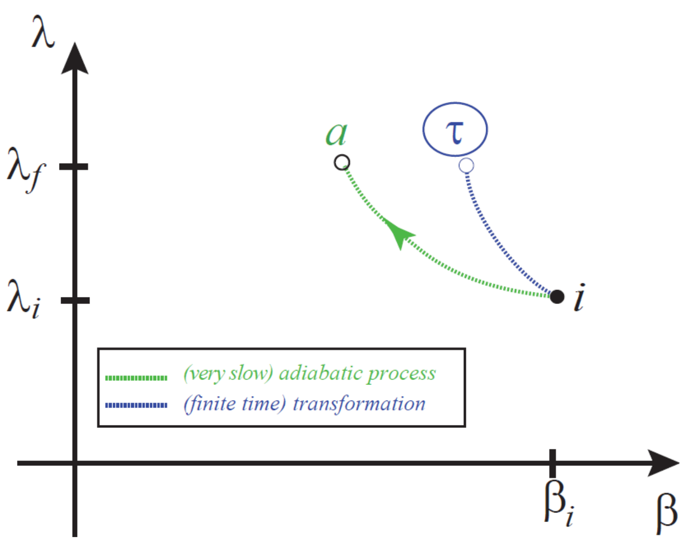
$$\langle \sigma \rangle = \beta_A(\langle w \rangle - \langle w_{i\to A} \rangle)$$

What if A is not an equilibrium state ?



$$\langle \sigma \rangle = \beta_A(\langle w \rangle - \langle w_{i\to A} \rangle)$$

What if A is not an equilibrium state ?



$$\langle\sigma\rangle = \beta_A(\langle w\rangle - \langle w_{i\to A}\rangle)$$

(non-equilibrium) adiabatic reference state:

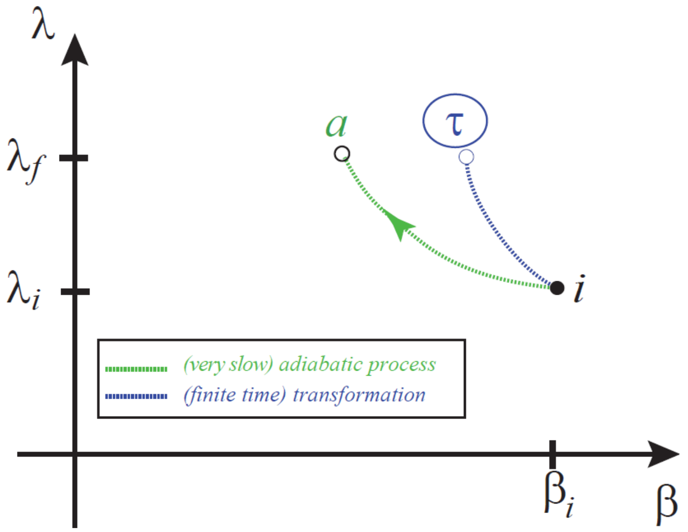
$$\rho_a = \sum_n P_n^{(i)} \left|\varepsilon_n^{(f)}\right\rangle \left\langle \varepsilon_n^{(f)}\right|$$

Entropy production :

$$P(\sigma) = \sum_{n,m} P_n^{(i)} P_{n\to m}^{(\tau)} \, \delta\left(\sigma - \sigma_{mn}\right)$$

$$\sigma_{mn} = \beta_A \varepsilon_m^{(f)} - \beta_i \varepsilon_n^{(i)} - (\beta_A F_A - \beta_i F_i) = \beta_i \left(\varepsilon_m^{(i)} - \varepsilon_m^{(i)}\right)$$

What if A is not an equilibrium state ?



$$\langle \sigma \rangle = \beta_A (\langle w \rangle - \langle w_{i \to A} \rangle)$$

(non-equilibrium) adiabatic reference state:

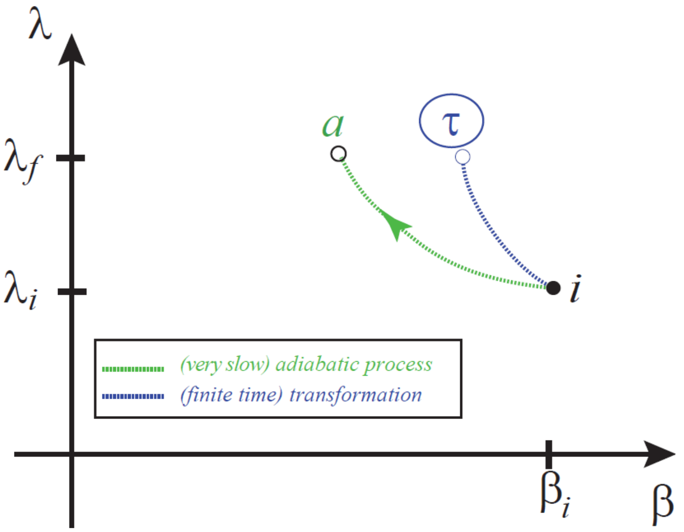
$$\rho_a = \sum_n P_n^{(i)} \left| \varepsilon_n^{(f)} \right\rangle \left\langle \varepsilon_n^{(f)} \right|$$

Entropy production :

$$P(\sigma) = \sum_{n,m} P_n^{(i)} P_{n \to m}^{(\tau)} \delta \left(\sigma - \sigma_{mn} \right)$$

$$\sigma_{mn} = \beta_A \varepsilon_m^{(f)} - \beta_i \varepsilon_n^{(i)} - (\beta_A F_A - \beta_i F_i) = \beta_i \left(\varepsilon_m^{(i)} - \varepsilon_m^{(i)} \right)$$

What if A is not an equilibrium state ?



$$\langle \sigma \rangle = \beta_A (\langle w \rangle - \langle w_{i \to A} \rangle)$$

(non-equilibrium) adiabatic reference state:

$$\rho_a = \sum_n P_n^{(i)} \left| \varepsilon_n^{(f)} \right\rangle \left\langle \varepsilon_n^{(f)} \right|$$

Entropy production :

$$P(\sigma) = \sum_{n,m} P_n^{(i)} P_{n \to m}^{(\tau)} \delta\left(\sigma - \sigma_{mn}\right)$$

$$\sigma_{mn} = \beta_A \varepsilon_m^{(f)} - \beta_i \varepsilon_n^{(i)} - (\beta_A F_A - \beta_i F_i) = \beta_i \left(\varepsilon_m^{(i)} - \varepsilon_m^{(i)} \right)$$

Crook's like relation

$$P(\sigma) = P_{back}(-\sigma)\, e^{\sigma}$$

under micro-reversibility assumption

Entropy production – general case

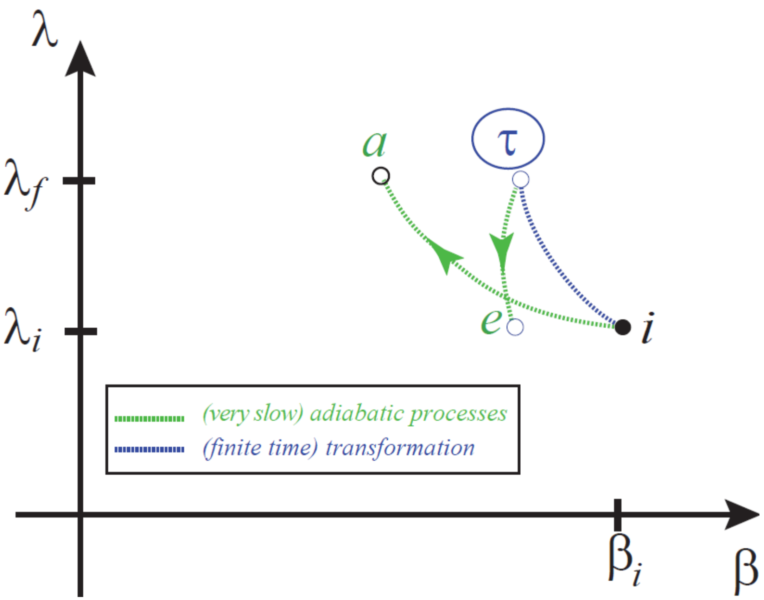
1. fluctuation relation:

$$\langle e^{-\sigma} \rangle = 1$$

2. Expression as a relative entropy :

$$\langle \sigma \rangle = D(\rho_\tau || \rho_a)$$

3. connection with work:



3.1 $$\langle \sigma \rangle = \beta_i \left(\langle w_{i \to \tau} \rangle + \langle w_{\tau \to e} \rangle \right)$$

3.2 $$\mathrm{cov}\{\sigma, w\} = \beta_i \frac{\mathrm{var}\{w_{i \to \tau}\} - \mathrm{var}\{w_{\tau \to e}\}}{2} + \frac{\mathrm{var}\{\sigma\}}{2\beta_i}$$

Summary :

- ☑ inner friction in terms or relative entropy
- ☑ relation with heat exchange during thermalization
- ☑ fluctuation relation and entropy production