Université Libre de Bruxelles

Center for Nonlinear Phenomena and Complex Systems

Efficiencies and fluctuations in small out-of-equilibrium devices

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Dresden, March 2011

Challenges when dealing with small systems

Small systems

Large fluctuations

Average behavior
contains limited information

Higher moments or full
probability distribution is needed

Far from equilibrium
(large surf/vol ratio)

Linear response
theories fail

Nonlinear response and
nonperturbative methods
need to be developed

Stochastic thermodynamics

Quantum effects
(low temperatures)

Traditional stochastic
descriptions fail

Stochastic descriptions
taking coherent effects
into account are needed

Esposito, Harbola, Mukamel
Rev. Mod. Phys. **81** 1665 (2009)

Esposito, Lindenberg, Van den Broeck
NJP **12** 013013 (2010)

Outline

I) Introduction to stochastic thermodynamics

- A) Thermodynamics at the level of averages
- B) The trajectory level and fluctuation theorems

II) Efficiency of small devices at maximum power

- A) Steady state devices
- B) Externally driven devices

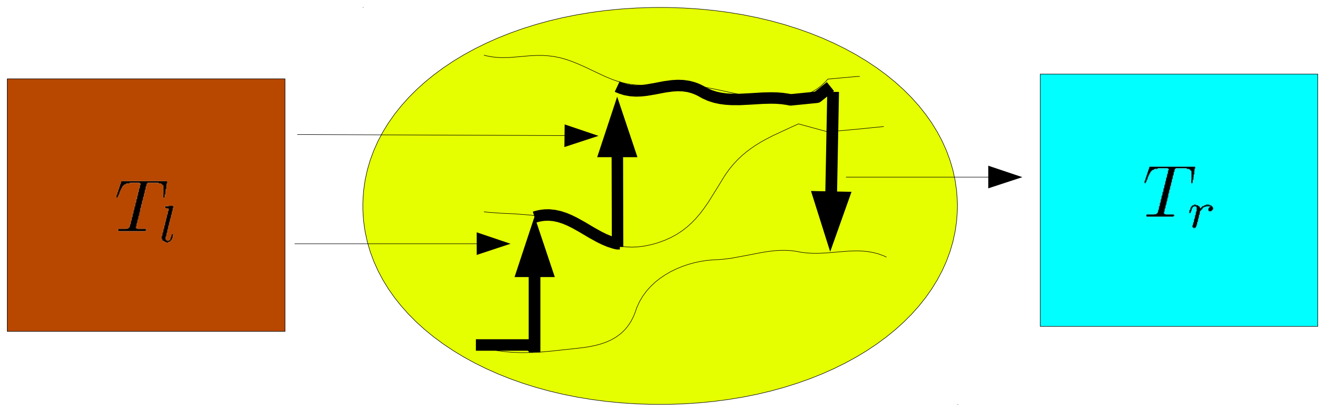
I) Introduction to stochastic thermodynamics:

A) Thermodynamics at the level of averages

Esposito, Harbola, Mukamel, PRE **76** 031132 (2007)

Esposito, Van den Broeck, PRE **82** 011143 & 011144 (2010)

Stochastic dynamics:



Rate matrix

Stochastic master equation

$$\dot{p}_m(t) = \sum_{m',\nu} W^{(\nu)}_{m,m'}(\lambda_t) p_{m'}(t)$$

Reservoir ν at equilibrium
"Local detailed balance"

$$\frac{W^{(\nu)}_{m,m'}(\lambda)}{W^{(\nu)}_{m',m}(\lambda)} = \exp\left(\frac{\epsilon_{m'}(\lambda) - \epsilon_m(\lambda)}{T_\nu}\right)$$

$$k_b = 1$$

Very slow external driving:

$$p_m(t) \approx p^{\mathrm{st}}_m(\lambda_t)$$

First law

System energy: $$U(t)=\sum_m p_m(t)\epsilon_m(\lambda_t)$$

$$\boxed{\dot U(t)=\dot{\mathcal{W}}(t)+\sum_\nu \dot Q^{(\nu)}(t)}$$

Work: $$\sum_m p_m(t)\dot\epsilon_m(\lambda_t)$$

Heat: $$\sum_m \dot p_m(t)\epsilon_m(\lambda_t)$$

Heat from reservoir ν:

$$\dot Q^{(\nu)}(t)=\sum_{m,m'} W^{(\nu)}_{mm'}p_{m'}(t)\big(\epsilon_m(\lambda_t)-\epsilon_{m'}(\lambda_t)\big)$$

Second law

System entropy: $S(t) = -\sum_m p_m(t) \ln p_m(t)$

$$\boxed{\dot{S}(t) = \dot{S}_e(t) + \underset{\geq 0}{\dot{S}_i(t)} = \sum_\nu \frac{\dot{Q}^{(\nu)}(t)}{T_\nu} + \dot{S}_i(t)}$$

Entropy flow:

"Local detailed balance"

$$\dot{S}_e(t) = -\sum_{m,m',\nu} W^{(\nu)}_{m,m'}(\lambda_t) p_{m'}(t) \ln \boxed{\frac{W^{(\nu)}_{m,m'}(\lambda_t)}{W^{(\nu)}_{m',m}(\lambda_t)}} = \sum_\nu \frac{\dot{Q}^{(\nu)}(t)}{T_\nu}$$

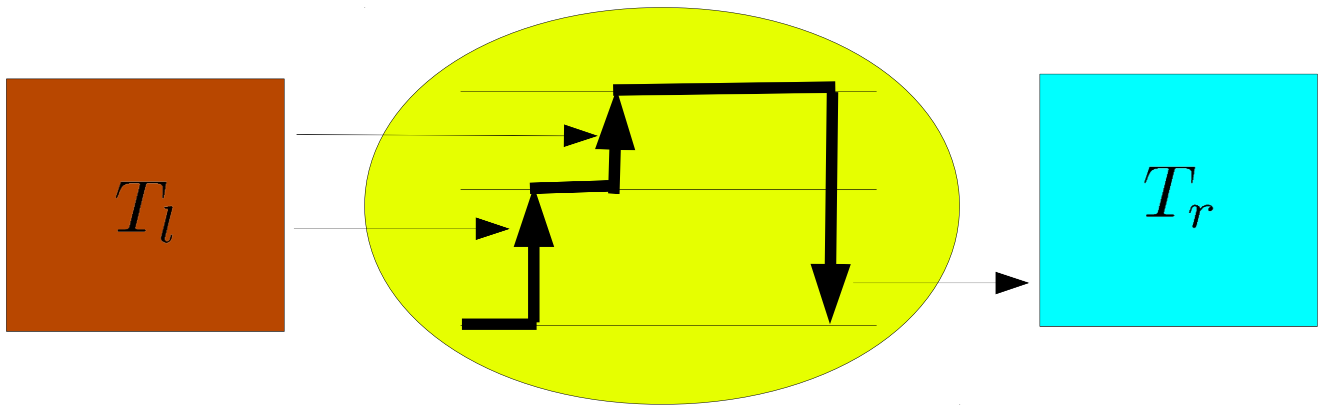
$$= \frac{\epsilon_{m'}(\lambda) - \epsilon_m(\lambda)}{T_\nu}$$

Entropy production:

$$\dot{S}_i(t) = \sum_{m,m',\nu} W^{(\nu)}_{m,m'}(\lambda_t) p_{m'}(t) \ln \boxed{\frac{W^{(\nu)}_{m,m'}(\lambda_t) p_{m'}(t)}{W^{(\nu)}_{m',m}(\lambda_t) p_m(t)}} \geq 0$$

Measures the breaking of detailed balance

Equilibrium and nonequilibrium steady state:



- If all the reservoirs have the same thermodynamic properties $T_c = T_h = T$

the stationary distribution satisfies detailed balance (equilibrium)

$$W^{(\nu)}_{m,m'}(\lambda) p^{\rm st}_{m'}(\lambda) = W^{(\nu)}_{m',m}(\lambda) p^{\rm st}_{m}(\lambda)$$

$$\Longrightarrow \quad \dot{S}_i(t) = 0$$

$$p^{\rm st}_m(\lambda) = p^{\rm eq}_m(\lambda) = \frac{\exp\big(-\epsilon_m(\lambda)/T\big)}{Z(\lambda)}$$

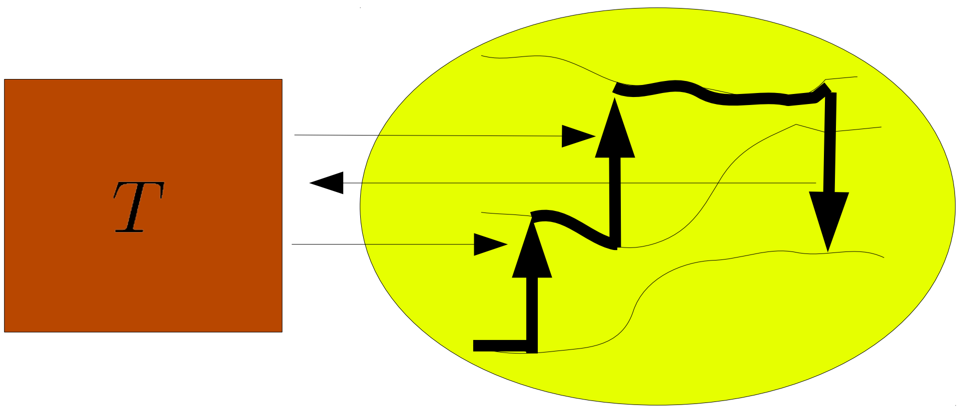
- If the reservoirs have different thermodynamic properties $T_c \neq T_h$

the stationary distribution breaks detailed balance

$$W^{(\nu)}_{m,m'}(\lambda) p^{\rm st}_{m'}(\lambda) \neq W^{(\nu)}_{m',m}(\lambda) p^{\rm st}_{m}(\lambda) \quad \Longrightarrow \quad \dot{S}_i(t) > 0$$

Externally driven system (single reservoir):

$$\dot{S}(t) = \dot{S}_e(t) + \dot{S}_i(t) = \frac{\dot{Q}(t)}{T} + \dot{S}_i(t)$$



For a slow transformation (reversible transformation):

$$p_m(t) \approx p_m^{\mathrm{eq}}(\lambda_t)$$

$$W_{m,m'}(\lambda_t) p_{m'}^{\mathrm{eq}}(\lambda_t) \approx W_{m',m}(\lambda_t) p_m^{\mathrm{eq}}(\lambda_t)$$

$$\Rightarrow$$

$$\int_0^t d\tau \dot{S}_i(\tau) \approx 0$$

$$\int_0^t d\tau \frac{\dot{Q}(\tau)}{T} \approx S(t) - S(0)$$

Thermodynamics emerges at the level of averages from an underlying stochastic dynamics

What did we gain?

Time scales

Finite time thermodynamics

Efficiency at maximum power

Optimal work extraction

Fluctuations

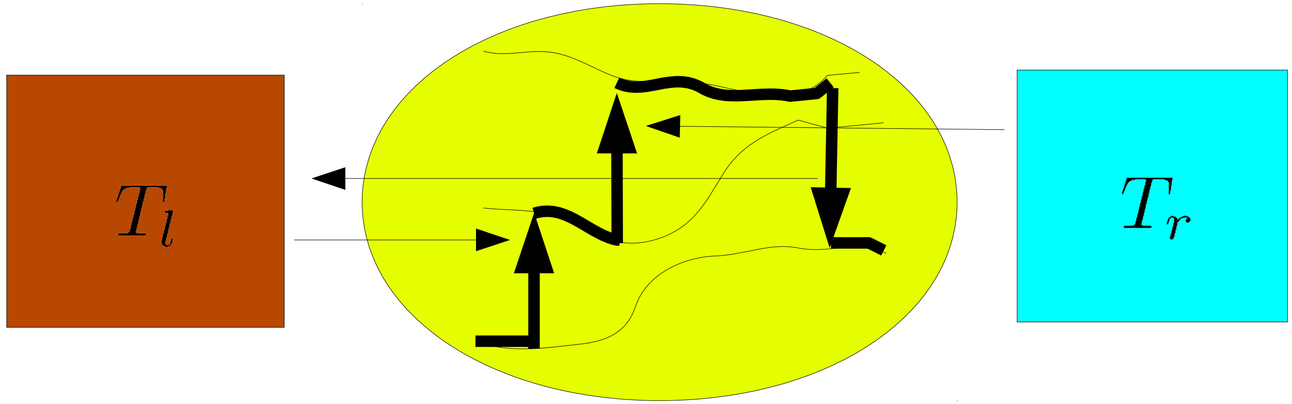
Trajectory level thermodynamics

Fluctuation theorems

I) Introduction to stochastic thermodynamics:

B) The trajectory level and Fluctuation Theorems

Thermodynamics at the trajectory level:



First Law: $$\boxed{\Delta U[\mathbf{m}] = W[\mathbf{m}] + \sum_{\nu} Q^{(\nu)}[\mathbf{m}]} = \epsilon_{m_N}(\lambda_T) - \epsilon_{m_0}(\lambda_0)$$

$$W[\mathbf{m}] = \sum_{j=1}^{N+1} \left(\epsilon_{m_{j-1}}(\lambda_{\tau_j}) - \epsilon_{m_{j-1}}(\lambda_{\tau_{j-1}})\right)$$

$$Q^{(\nu)}[\mathbf{m}] = \sum_{j=1}^{N} \delta_{Kr}(\nu - \nu_j)\left(\epsilon_{m_{j-1}}(\lambda_{\tau_j}) - \epsilon_{m_j}(\lambda_{\tau_j})\right)$$

Second Law: $$\boxed{\Delta S[\mathbf{m}] = \Delta S_i[\mathbf{m}] + \Delta S_e[\mathbf{m}]} = \ln \frac{p_{m_0}(0)}{p_{m_N}(T)}$$

$$\Delta S_i[\mathbf{m}] = \ln \mathcal{P}_{\mathbf{m}} / \bar{\mathcal{P}}_{\bar{\mathbf{m}}}$$

$$\Delta S_e[\mathbf{m}] = \sum_{j=1}^{N} \ln \frac{W^{(\nu_j)}_{m_j, m_{j-1}}(\lambda_{\tau_j})}{W^{(\nu_j)}_{m_{j-1}, m_j}(\lambda_{\tau_j})} = \sum_{j=1}^{N} \frac{\epsilon_{m_{j-1}}(\lambda_{\tau_j}) - \epsilon_{m_j}(\lambda_{\tau_j})}{T_{\nu_j}}$$

Fluctuation theorems

Entropy production: $$\langle \Delta_i S \rangle = \sum_{\mathbf{m}} \mathcal{P}[\mathbf{m}] \log \frac{\mathcal{P}[\mathbf{m}]}{\bar{\mathcal{P}}[\bar{\mathbf{m}}]} \geq 0$$

Seifert PRL **95** 040602 (2005)

Fluctuation theorem: $$\boxed{\frac{P(\Delta_i S)}{\bar{P}(-\Delta_i S)} = \mathrm{e}^{\Delta_i S}}$$

Symmetry relations between nonlinear coefficients

Andrieux, Gaspard JSM P02006

Work FT:

$$\frac{P(\mathcal{W})}{\bar{P}(-\mathcal{W})} = \exp\left(\frac{\mathcal{W} - \Delta F}{kT}\right)$$

Jarzynski PRL **78** 2690 (1997)

Crooks J.Stat.Phys. **90** 1481 (1998)
& PRE **60** 2721 (1999)

Current FT:

$$\frac{P(I)}{P(-I)} \overset{t\to\infty}{\sim} \exp\left(\frac{eV}{k_b T} I t\right)$$

Andrieux, Gaspard JSTAT P01011 (2006)

Esposito, Harbola, Mukamel PRB **75** 155316 (2007)

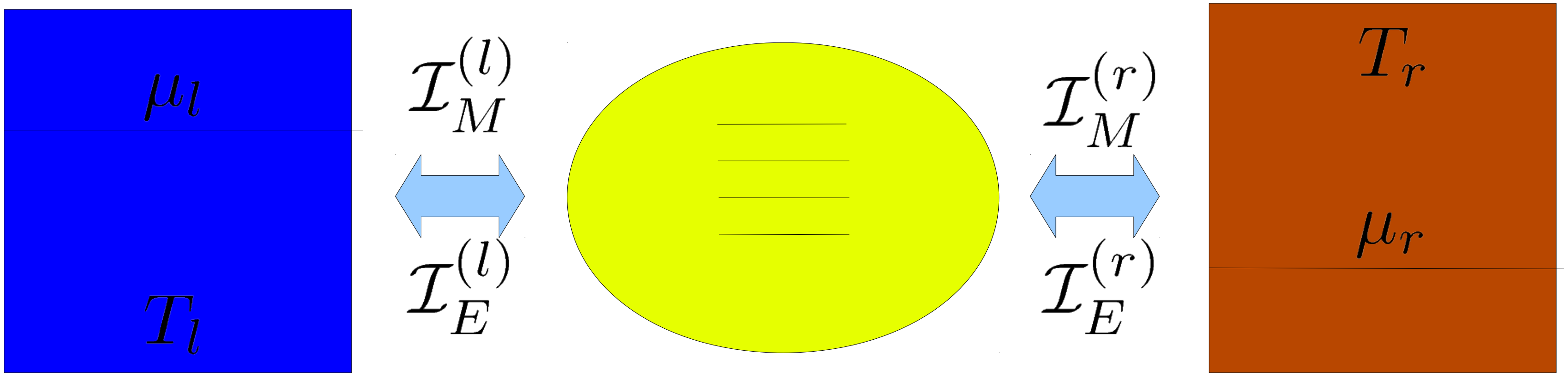
General formulation: Esposito, Van den Broeck, PRL **104** 090601 (2010)

Review: Esposito, Harbola, Mukamel, Rev. Mod. Phys. **81** 1665 (2009)

II) Efficiency at maximum power

A) Steady state devices

Efficiency of heat-matter transport



$$\dot{p}_i(t) = \sum_{\substack{j,\nu \\ (\nu = l, r)}} W_{ij}^{(\nu)} p_j(t) \qquad \frac{W_{ji}^{(\nu)}}{W_{ij}^{(\nu)}} = \exp\left\{\beta_\nu\left[(\epsilon_i - \epsilon_j) - \mu_\nu(N_i - N_j)\right]\right\}$$

Heat: $\dot{\mathcal{Q}}^{(\nu)}(t) = \mathcal{I}_E^{(\nu)}(t) - \mu_\nu \mathcal{I}_M^{(\nu)}(t)$

Power: $\mathcal{P} = -\dot{\mathcal{W}} = \sum_\nu \dot{\mathcal{Q}}^{(\nu)}(t) = -(\mu_r - \mu_l)\mathcal{I}_M$

Steady state: $\dot{p}_i = 0 \implies \dot{S} = 0 \, , \; \dot{U} = 0 \, , \; \mathcal{I}_{M,E}^{(r)} = -\mathcal{I}_{M,E}^{(l)} = \mathcal{I}_{M,E}$

Entropy production: $$\boxed{\dot{S}_i = -\dot{S}_e = \mathcal{F}_E \mathcal{I}_E + \mathcal{F}_M \mathcal{I}_M \geq 0}$$

Fluxes: $\mathcal{I}_E,\ \mathcal{I}_M$

Forces: $\mathcal{F}_E = \frac{1}{T_l} - \frac{1}{T_r},\quad \mathcal{F}_M = (-\frac{\mu_l}{T_l}) - (-\frac{\mu_r}{T_r})$

Efficiency: $$\boxed{\eta = \frac{-\mathcal{W}}{\mathcal{Q}^{(r)}} = \frac{-\dot{\mathcal{W}}}{\dot{\mathcal{Q}}^{(r)}} = \frac{\mu_r - \mu_l}{\mu_r - \mathcal{I}_E/\mathcal{I}_M}}$$

Tight coupling: $$\mathcal{I} \equiv \boxed{\mathcal{I}_E = \varepsilon \mathcal{I}_M}$$

constant

$\Rightarrow$

$$\dot{S}_i = \mathcal{F}\mathcal{I}$$

Collapse of forces

$$\mathcal{F} = \mathcal{F}_M + \varepsilon \mathcal{F}_E$$

$$\eta = \frac{\mu_l - \mu_r}{\varepsilon - \mu_r}$$

Current independent

Efficiency at equilibrium: $\boxed{\eta \leq \eta_c = 1 - \frac{T_l}{T_r}}$ Carnot efficiency

tight coupling $=$

But $\mathcal{P} \to 0$ zero power!

Efficiency at maximum power:

- *Phenomenologically:*

I. I. Novikov & P. Chambadal (1957) ; F. Curzon and B. Ahlborn, Am. J. Phys. **43**, 22 (1975).

$$\eta_{CA} = 1 - \sqrt{1 - \eta_c} \approx \eta_c/2 + \eta_c^2/8 + 6\eta_c^3/96 + \ldots$$

- *Not too far from equilibrium:* $\boxed{\eta^* \leq \eta_c/2 + \eta_c^2/8}$

tight coupling $=$

Linear

Nonlinear
(in presence of a
left-right symmetry)

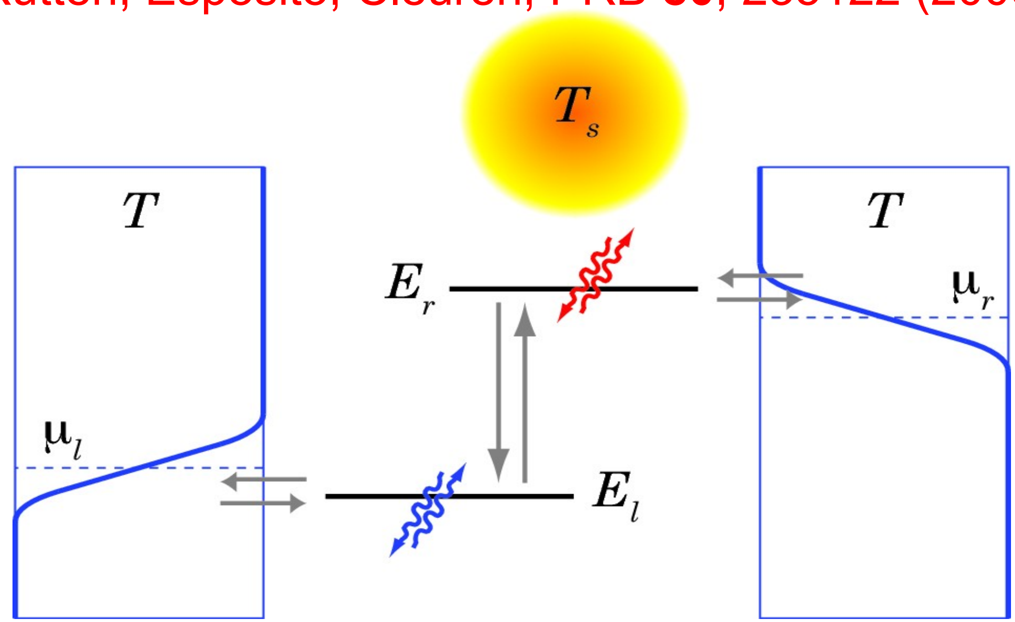
Van den Broeck, PRL **95**, 190602 (2005)

Esposito, Lindenberg, Van den Broeck, PRL **102**, 130602 (2009)

- *Far from equilibrium:* Everything is possible Seifert, PRL **106**, 020601 (2011)

Photoelectric nanocell

Rutten, Esposito, Cleuren, PRB **80**, 235122 (2009)



$$P = (\mu_r - \mu_l)J$$

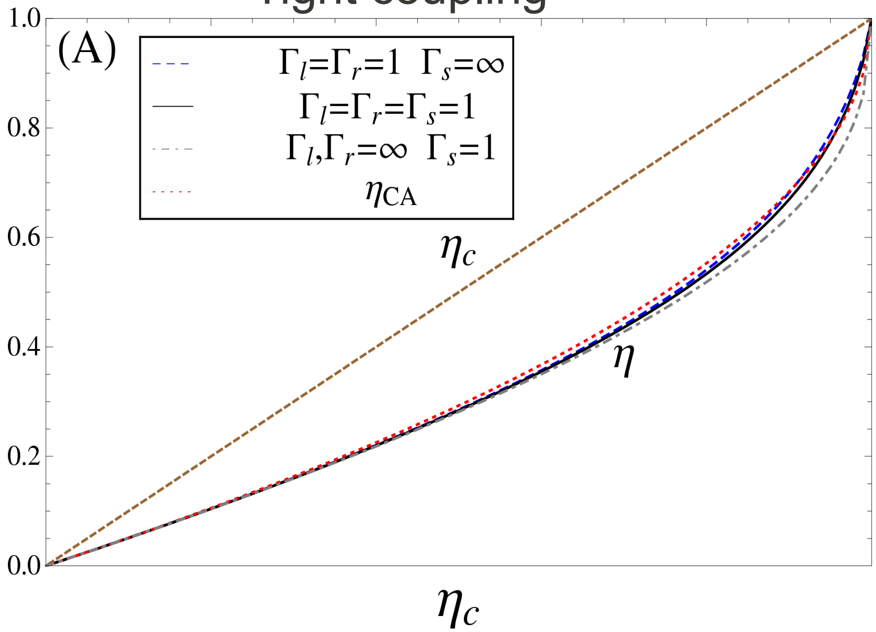
$$J = k_{l0}p_0 - k_{0l}p_l.$$

$$P = \dot{Q}_l + \dot{Q}_r + \dot{Q}_{nr} + \dot{Q}_s$$

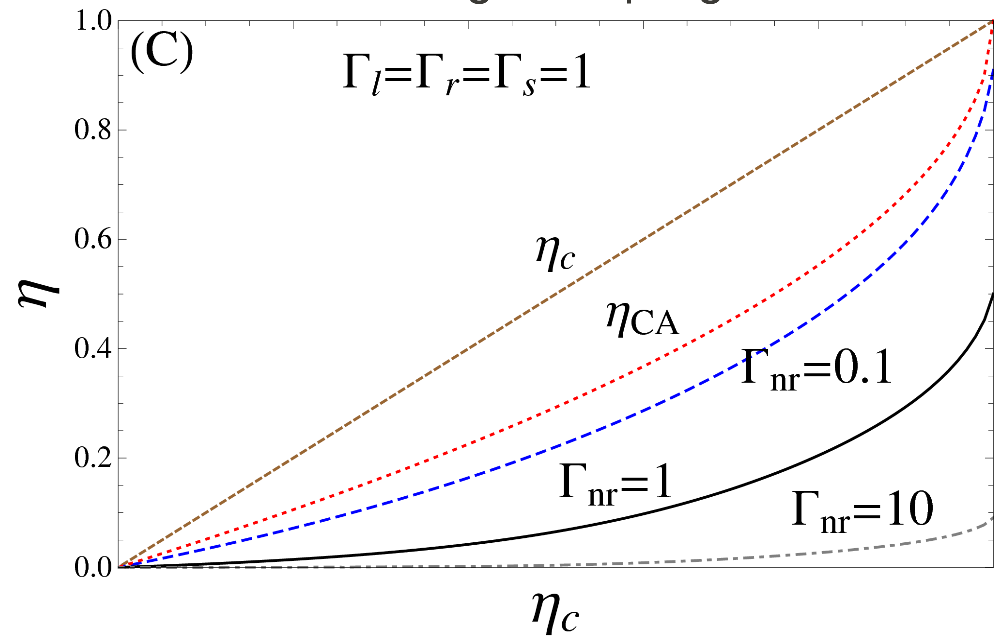
$$\eta = \frac{P}{\dot{Q}_s}$$

Maximum power vs x_l x_r x_s

Tight coupling



No tight coupling



II) Efficiency at maximum power

B) Externally driven devices

Finite-time Carnot cycle

Weak Dissipation regime

$$Q_h = T_h \left(\Delta S - \frac{\Sigma_h}{\tau_h} + \dots \right) \qquad Q_c = T_c \left(-\Delta S - \frac{\Sigma_c}{\tau_c} + \dots \right)$$

Esposito, Kawai, Lindenberg, Van den Broeck, PRL **105** 150603 (2010)

Maximize power vs τ_c and τ_h :

$$\boxed{\eta^* = \frac{\eta_C \left(1 + \sqrt{\frac{T_c \Sigma_c}{T_h \Sigma_h}}\right)}{\left(1 + \sqrt{\frac{T_c \Sigma_c}{T_h \Sigma_h}}\right)^2 + \frac{T_c}{T_h}\left(1 - \frac{\Sigma_c}{\Sigma_h}\right)}}$$

$$\left(\frac{\tau_c}{\tau_h} = \sqrt{\frac{T_c \Sigma_c}{T_h \Sigma_h}}\right)$$

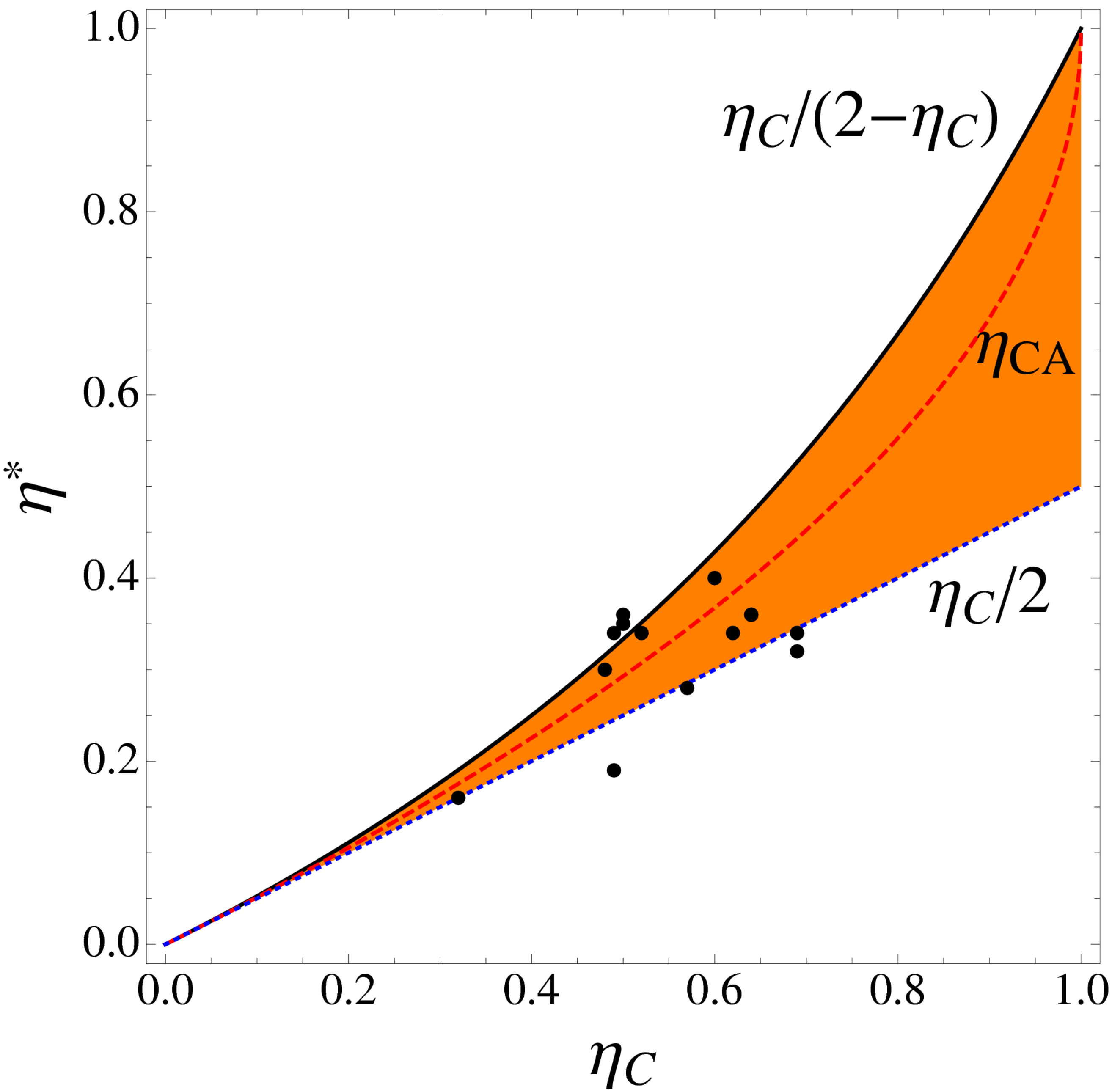
$$(\Sigma_c/\Sigma_h \to \infty) \quad \boxed{\frac{\eta_C}{2} \equiv \eta_- \leq \eta^* \leq \eta_+ \equiv \frac{\eta_C}{2 - \eta_C}} \quad (\Sigma_c/\Sigma_h \to 0)$$

Curzon-Ahlborn in the symmetric dissipation: $(\Sigma_h = \Sigma_c)$

$$\eta^* = \eta_{CA} = 1 - \sqrt{\frac{T_c}{T_h}} = 1 - \sqrt{1 - \eta_C}$$

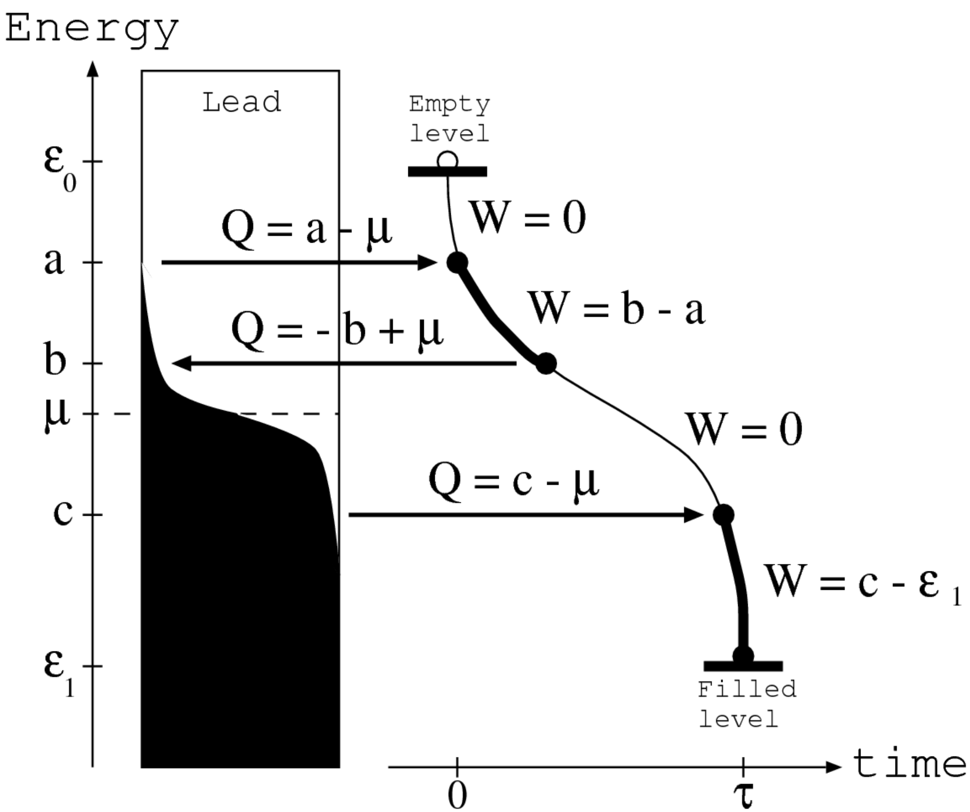
Expansion in η_C :

$$\eta^* = \frac{\eta_C}{2} + \frac{\eta_C^2}{4 + 4\sqrt{\Sigma_c/\Sigma_h}} + \mathcal{O}(\eta_C^3)$$



$\eta_C/(2-\eta_C)$
η_{CA}
$\eta_C/2$
η^*
η_C
0.0
0.2
0.4
0.6
0.8
1.0

Optimal work extraction (driven quantum dot)



$p(t)$ is the dot occupation probability

$$\dot{p}(t) = -\omega_1(t)p(t) + \omega_2(t)[1 - p(t)]$$

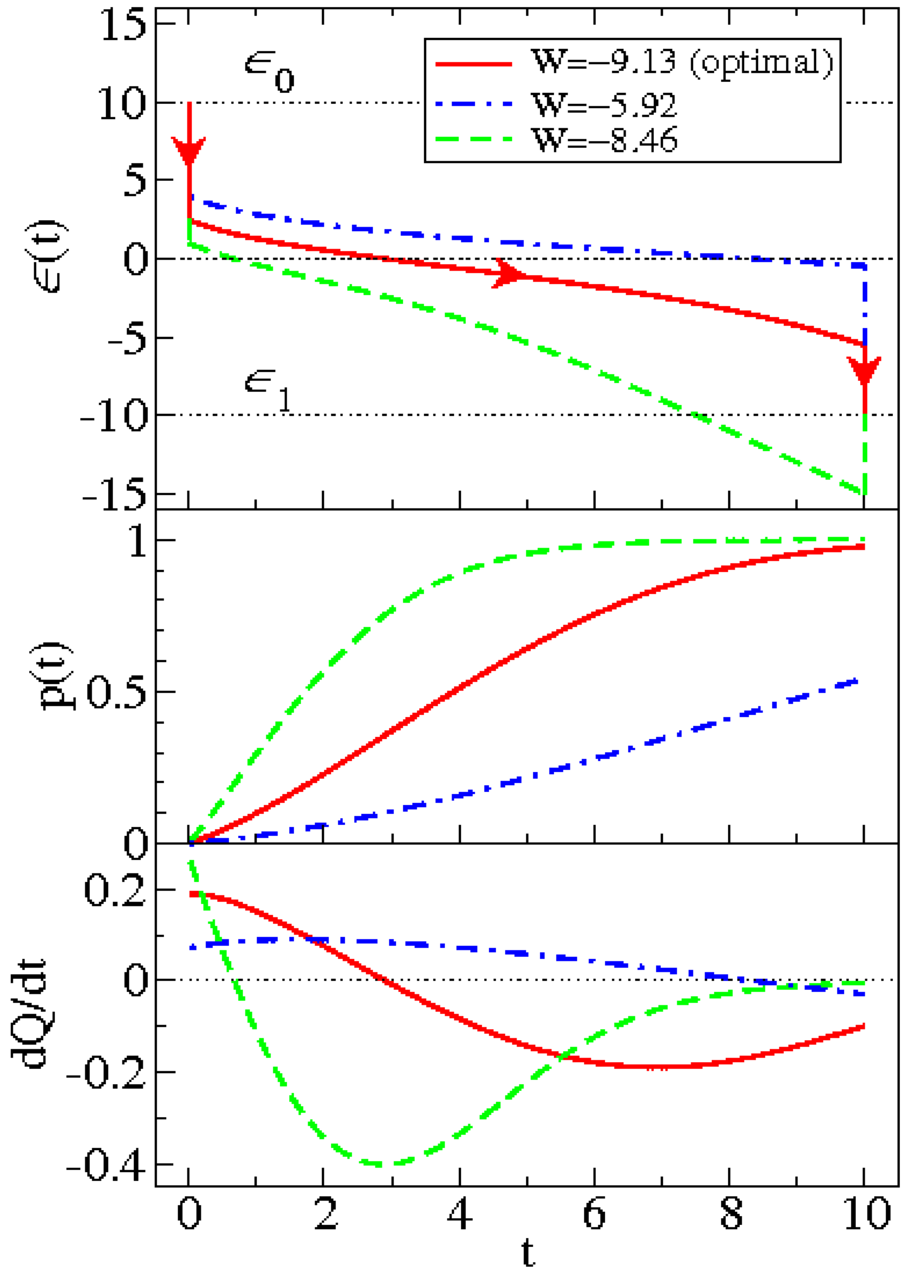
$$\omega_1 = \frac{C}{\mathrm{e}^{-\beta[\varepsilon(t) - \mu(t)]} + 1}$$

$$\omega_2 = \frac{C}{\mathrm{e}^{+\beta[\varepsilon(t) - \mu(t)]} + 1}$$

$$\boxed{E(t)} = U(t) - \mu N(t) = \boxed{\epsilon(t)p(t)}$$

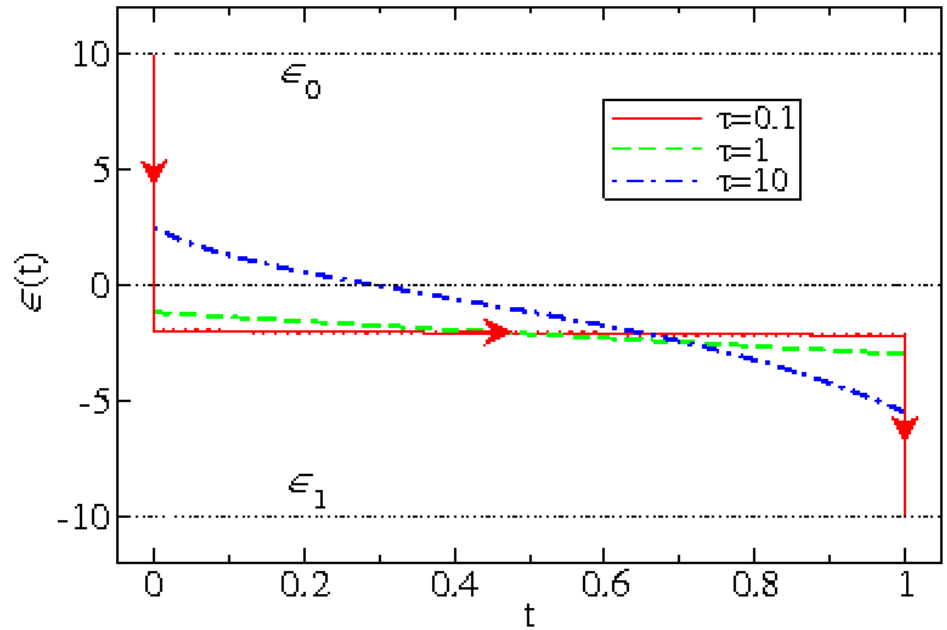
$$U(t) = \varepsilon(t)p(t), \quad N(t) = p(t)$$

$$\boxed{\begin{aligned} \dot{\mathcal{W}} &= \dot{\epsilon}p \\ \dot{\mathcal{Q}} &= \epsilon\dot{p} \end{aligned}}$$



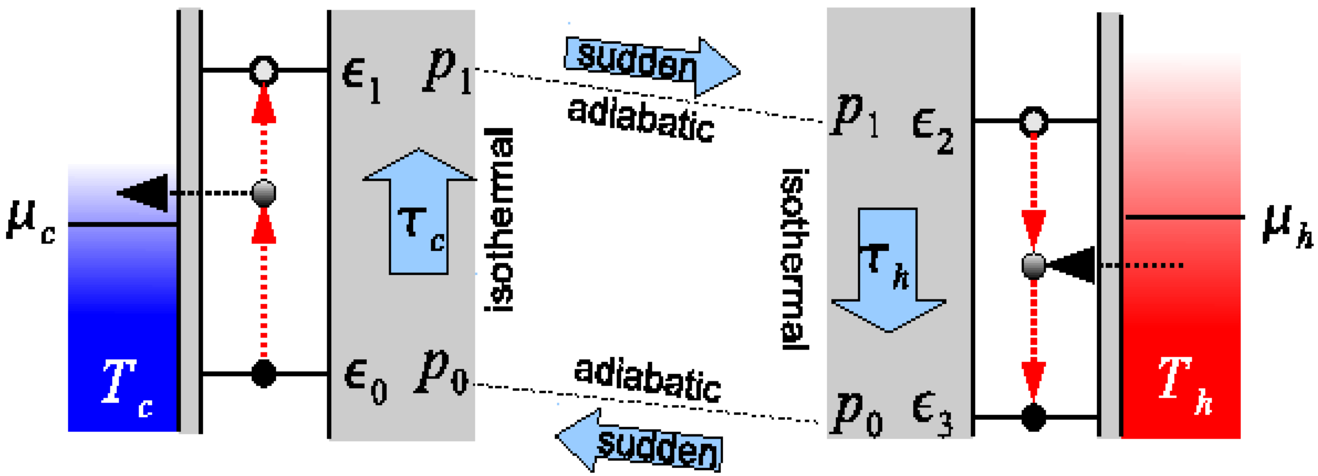
Esposito, Kawai, Lindenberg, Van den Broeck , EPL **89**, 20003 (2010).

The optimal protocol contains an initial and final jump!



Efficiency of the finite-time Carnot cycle

Esposito, Kawai, Lindenberg, Van den Broeck,
Phys. Rev. E **81**, 041106 (2010).



In the low dissipation regime efficiency at maximum power:

$$\eta^* = \frac{\eta_C \left(1 + \sqrt{\dfrac{T_c C_c}{T_h C_h}}\right)}{\left(1 + \sqrt{\dfrac{T_c C_c}{T_h C_h}}\right)^2 + \dfrac{T_c}{T_h}\left(1 - \dfrac{C_c}{C_h}\right)}$$

Conclusions

- Stochastic thermodynamics is a natural and powerful tool to study small systems:

- It can be used to study finite time thermodynamics

  - Efficiencies: Tight coupling and Curzon-Ahlborn efficiency

  - Optimal work extraction: jumps in the protocol

- It can be used to study fluctuations around average behaviors

  - Fluctuation theorems, ...

- Further directions: quantum effects, feedbacks and information...

Collaborators:

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Bart Cleuren & Bob Cleuren, University of Hasselt, Belgium.

Ryoichi Kawai, University of Alabama at Birmingham, USA.