



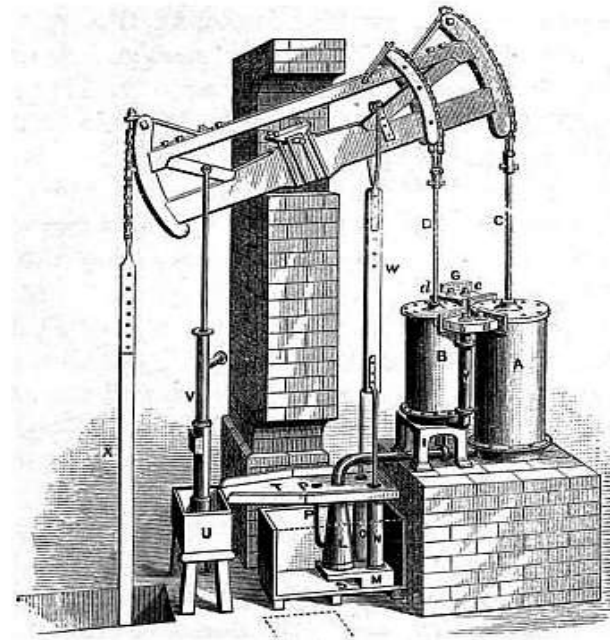
Nonequilibrium Thermodynamics of Small Systems: Classical and Quantum Aspects

Massimiliano Esposito

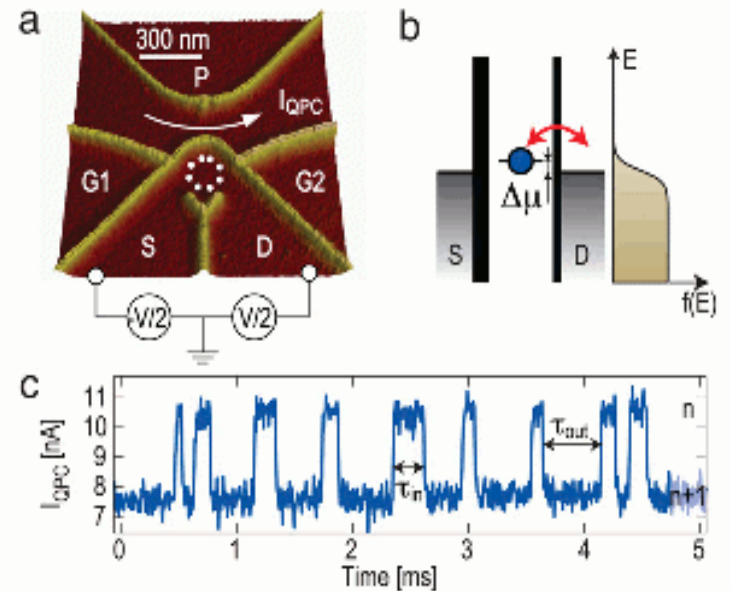
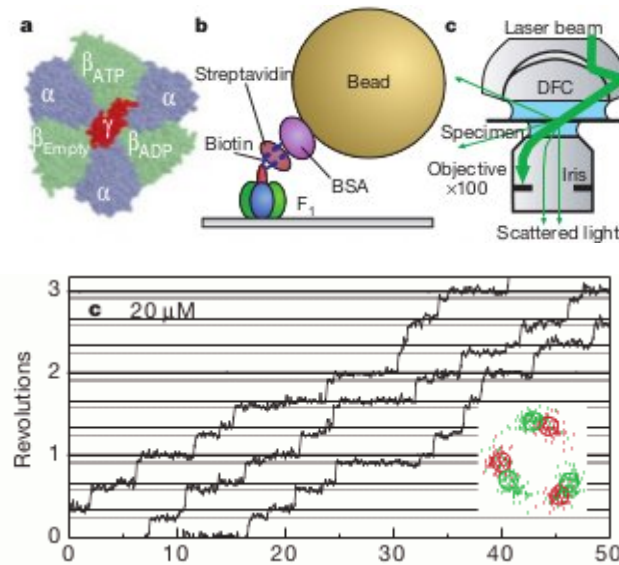
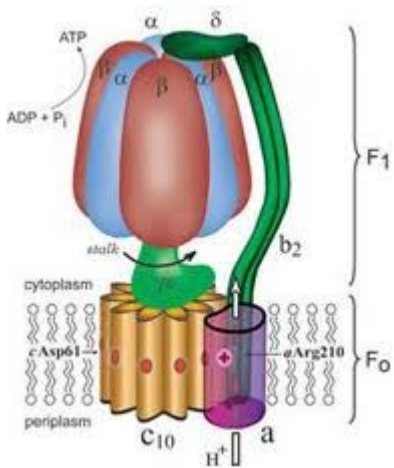
Paris – May 9-11, 2017

Introduction

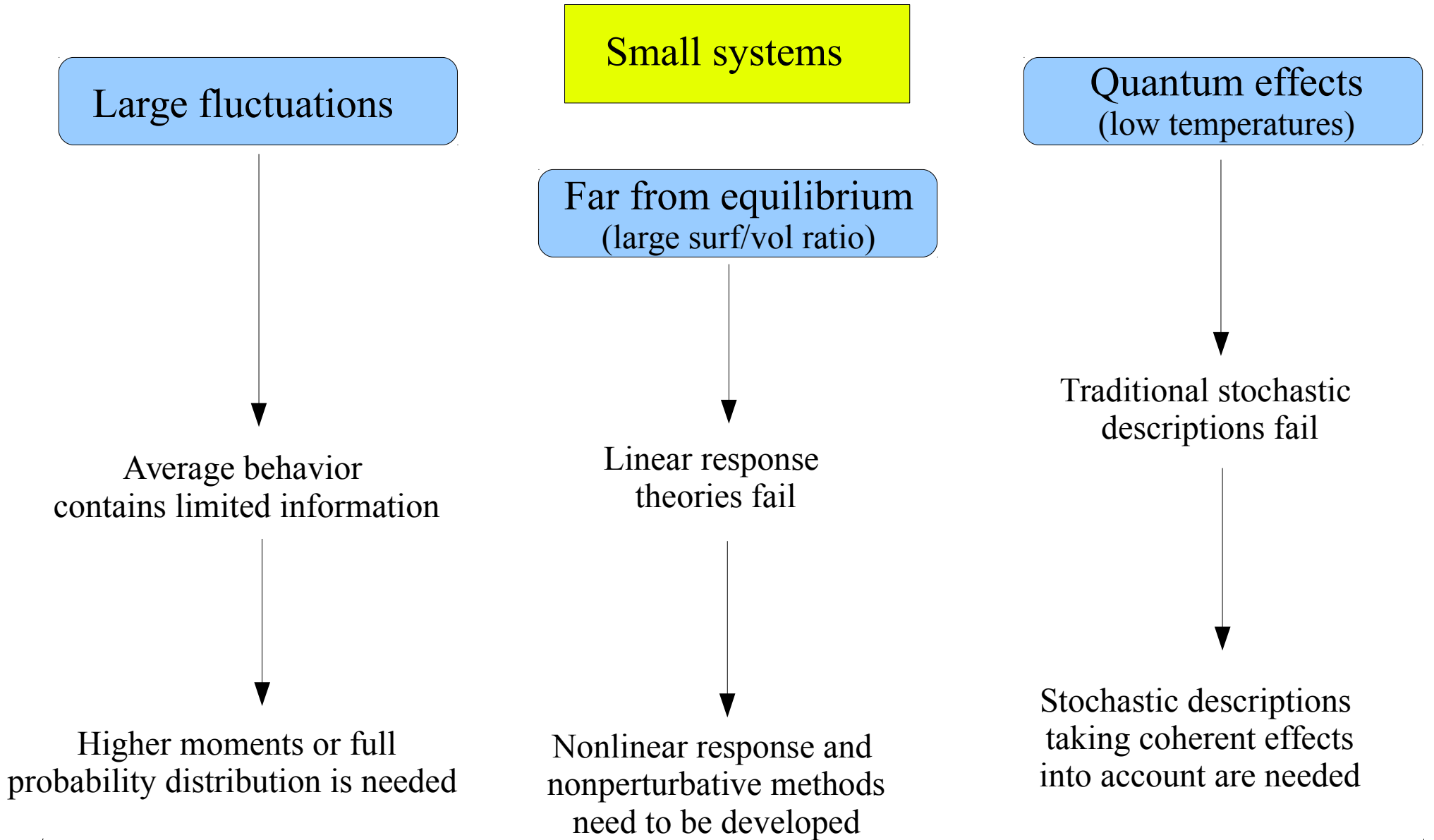
Thermodynamics in the 19th century:



Thermodynamics in the 21st century:



Challenges when dealing with small systems



Stochastic thermodynamics

Outline

Part I: Stochastic Thermodynamics:

From fluctuation theorems to stochastic efficiencies

Part II: Thermodynamics of Information Processing

Part III: Quantum Thermodynamics

Part I: Stochastic Thermodynamics: From fluctuation theorems to stochastic efficiencies

- 1) Stochastic thermodynamics
- 2) Universal fluctuation relation
- 3) Finite-time thermodynamics
- 4) Efficiency fluctuations

1) Stochastic thermodynamics

Esposito and Van den Broeck, Phys. Rev. E **82**, 011143 (2010)

Esposito, Phys. Rev. E **85**, 041125 (2012)

Markovian master equation:

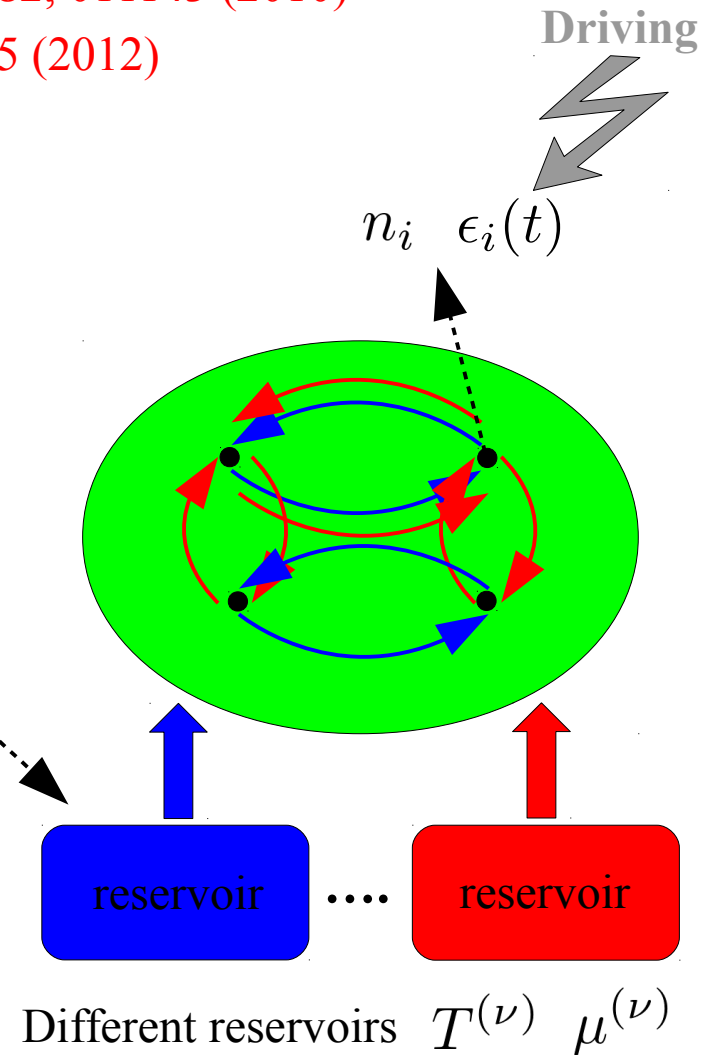
$$d_t p_i = \sum_j W_{ij} p_j = \sum_j (W_{ij} p_j - W_{ji} p_i)$$

$$W_{ij} = \sum_\nu W_{ij}^{(\nu)}$$

$$I_E^{(\nu)} = \sum_{i,j} W_{ij}^{(\nu)} p_j (\epsilon_i - \epsilon_j)$$

$$I_M^{(\nu)} = \sum_{i,j} W_{ij}^{(\nu)} p_j (n_i - n_j)$$

Energy and
Matter currents



Local detailed balance:

$$\frac{W_{ij}^{(\nu)}}{W_{ji}^{(\nu)}} = \exp \left(- \frac{(\epsilon_i - \epsilon_j) - \mu^{(\nu)} (n_i - n_j)}{k_b T^{(\nu)}} \right)$$

| | | |
|-----------------------------|----------------------|--|
| Energy | Particle number | Shannon entropy |
| $E = \sum_i \epsilon_i p_i$ | $N = \sum_i n_i p_i$ | $S = \sum_i \underbrace{[-k_b \ln p_i]}_{s_i} p_i$ |

1st law: Energy balance

$$d_t E = \dot{W}_m + \dot{W}_c + \sum_\nu \dot{Q}^{(\nu)}$$

Particle balance

$$d_t N = \sum_\nu I_M^{(\nu)}$$

2nd law: Entropy balance

$$\dot{S}_i = d_t S - \sum_\nu \frac{\dot{Q}_\nu}{T_\nu} \geq 0$$

Entropy production

Entropy change
in the reservoirs

$$\dot{S}_i = k_b \sum_{\nu, i, j} (W_{ij}^{(\nu)} p_j - W_{ji}^{(\nu)} p_i) \ln \frac{W_{ij}^{(\nu)} p_j}{W_{ji}^{(\nu)} p_i} \geq 0$$

$$\dot{S}_i = 0 \text{ iff } W_{ij}^{(\nu)} p_j = W_{ji}^{(\nu)} p_i \text{ (detailed balance)}$$

Mechanical work

$$\dot{W}_m = \sum_i d_t \epsilon_i p_i$$

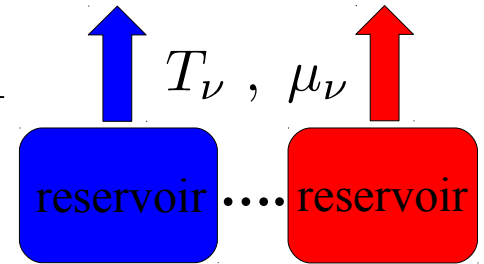
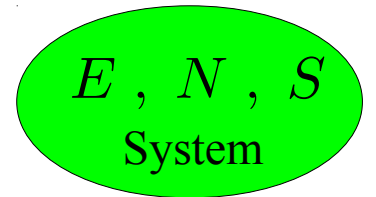
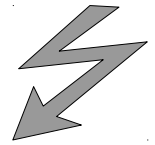
Chemical work

$$\dot{W}_c = \sum_\nu \mu^{(\nu)} I_M^{(\nu)}$$

Heat flow

$$\dot{Q}^{(\nu)} = I_E^{(\nu)} - \mu^{(\nu)} I_M^{(\nu)}$$

Driving



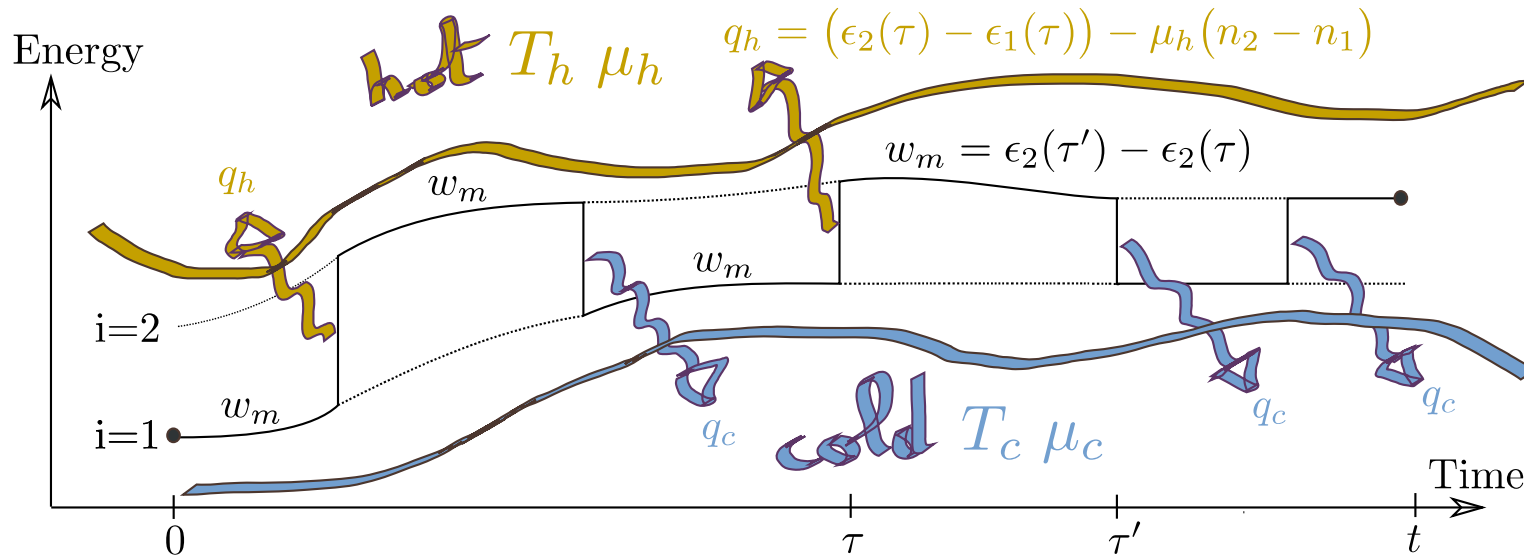
Slow driving with 1 reservoir: $\dot{S}_i \approx 0$



equilibrium thermo

$$T d_t S = d_t E - \dot{W}_m - \mu d_t N \quad 7$$

2) Universal Fluctuation Relation



Energy balance: $\epsilon_{i_t}(\lambda_t) - \epsilon_{i_0}(\lambda_0) = w_m [\Gamma|\lambda] + \underline{w_c [\Gamma|\lambda]} + \underbrace{\sum_{\nu=1}^N (\Delta\epsilon_\nu [\Gamma|\lambda] - \mu_\nu \Delta n_\nu [\Gamma|\lambda])}_{q_\nu [\Gamma|\lambda]}$

Particle balance: $n_{i_t} - n_{i_0} = \sum_{\nu=1}^N \Delta n_\nu [\Gamma|\lambda]$

Entropy balance: $\Delta_{i_s} [\Gamma|\lambda] = \ln \frac{P[\Gamma, \lambda]}{\tilde{P}[\bar{\Gamma}, \lambda]} = \underbrace{\ln p_{i_0}(0) - \ln p_{i_t}(t)}_{\Delta s [\Gamma|\lambda]} - \sum_{\nu=1}^N \beta_\nu q_\nu [\Gamma|\lambda]$

Time-reversed driving
Time-reversed trajectory

$\Delta s [\Gamma|\lambda]$ not a physical observable

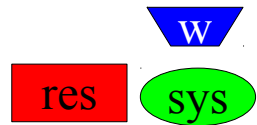
Integral fluctuation theorem: $\langle e^{-\Delta_{i_s}} \rangle = 1 \implies \langle \Delta_{i_s} \rangle \geq 0$

Detailed FT
for entropy production

$$\ln \frac{P(\Delta_{iS})}{\tilde{P}(-\Delta_{iS})} = \Delta_{iS}$$

Involution
if $\Delta_{iS} [\Gamma|\lambda] = -\Delta_{iS} [\tilde{\Gamma}|\lambda]$
Seifert, PRL **95** 040602 (2005)

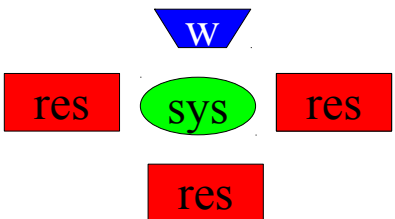
Fluctuation theorem for physical observable?



Driving + 1 reservoir + start at equilibrium: Work FT (Crooks FT)



No driving + multiple reservoirs + longtime limit $t \rightarrow \infty$: Current FT



Driving + multiple reservoirs + start at equilibrium vs reservoir $\nu = 1$:

$$\ln \frac{P(w_m, \{\Delta\epsilon_\nu\}, \{\Delta n_\nu\})}{\tilde{P}(-w_m, \{-\Delta\epsilon_\nu\}, \{-\Delta n_\nu\})} = \beta_1 (w_m - \Delta\Phi_1^{eq}) + \sum_{\nu=2}^N (A_\nu^\epsilon \Delta\epsilon_\nu + A_\nu^n \Delta n_\nu)$$

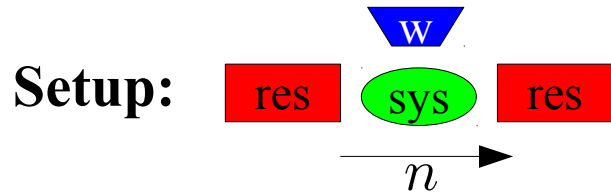
Work FT
Current FT

Bulnes Cuetara, Esposito, Imparato, PRE **89**, 052119 (2014)

$$= \beta_1 - \beta_\nu \quad = \beta_\nu \mu_\nu - \beta_1 \mu_1$$

Isothermal example: driven junction

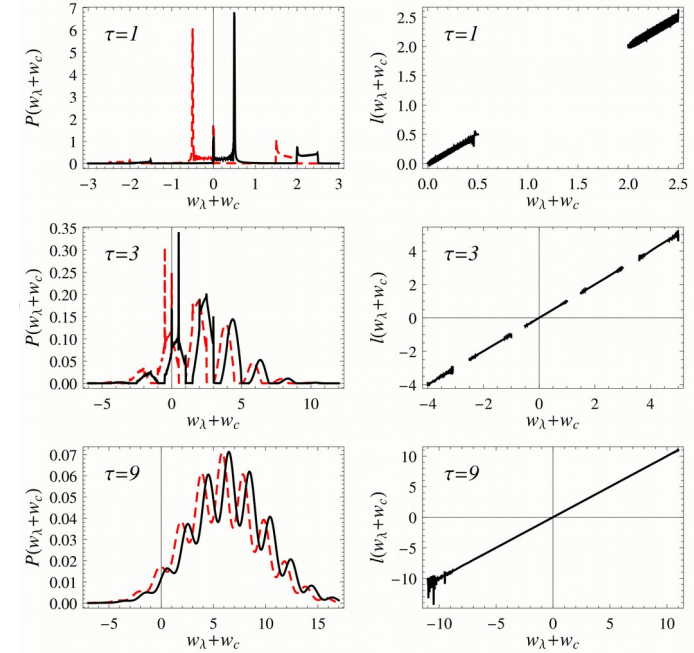
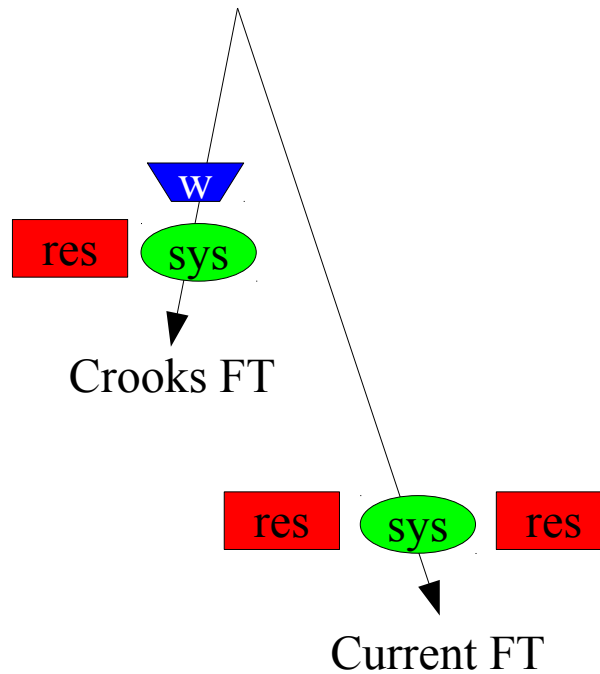
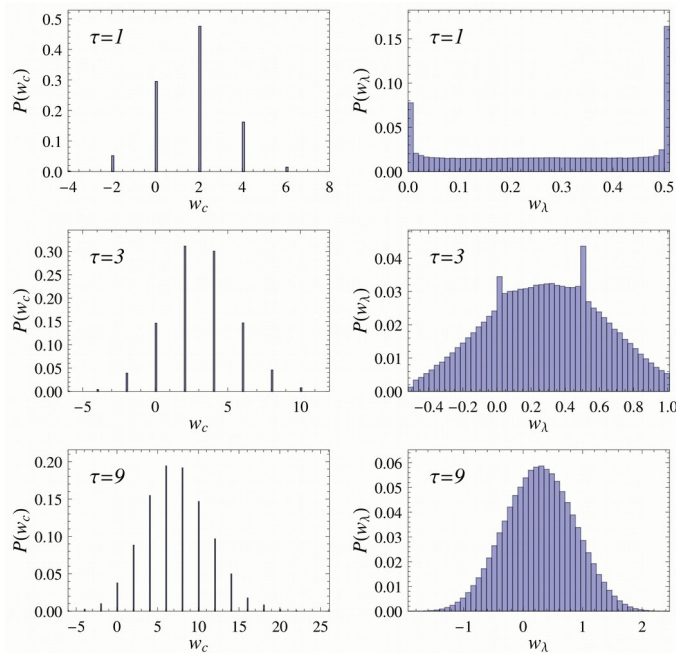
Bulnes Cuetara, Esposito, Imparato, PRE **89**, 052119 (2014)



Initial condition: equilibrium vs a reference reservoir

Mechanical work: w_m Chemical work: $w_c = n\Delta\mu$

$$\frac{P_F(w_m + w_c)}{P_B(-w_m - w_c)} = \frac{P_F(w_m, w_c)}{P_B(-w_m, -w_c)} = \exp\left\{\frac{w_m + w_c - \Delta\Phi_1}{k_B T}\right\}$$



Fluctuation Relation: Synthesis

Fluctuations in small out-of-equilibrium systems satisfy a universal symmetry

Everything can also be done for: - Fokker-Planck dynamics

- Open quantum systems (weak coupling)

FT can be used: to derive Onsager reciprocity relations and generalizations

to derive fluctuation-dissipation relations and generalizations

to check the consistency of a transport theory

to calculate free energy differences

...

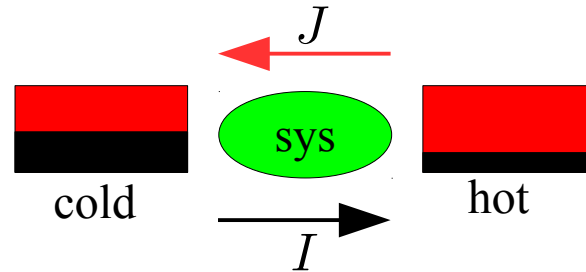
Nonequilibrium fluctuations, fluctuation theorems and counting statistics in quantum systems,
Esposito, Harbola, Mukamel, Rev. Mod. Phys. **81**, 1665 (2009)

Ensemble and Trajectory Thermodynamics: A Brief Introduction,
Van den Broeck and Esposito, Physica A **418**, 6 (2015)

3) Finite-time thermodynamics

a) Steady state energy conversion

● *Thermoelectricity:*



Reservoir entropy change:

$$dS_r = \frac{1}{T_r} dE_r - \mu_r dN_r$$

Entropy production (entropy change in the reservoirs):

$$\sigma = J \left(\frac{1}{T_c} - \frac{1}{T_h} \right) + I \frac{\Delta\mu}{T_c} \geq 0$$

Thermoelectric effect if: $I < 0$

Efficiency: $\eta = \frac{-W}{\eta_C Q_h} \leq 1$

Power: $\mathcal{P} = -I \Delta\mu$

● *General formulation:*

$$\sigma = \underbrace{J_1 A_1}_{\sigma_1 > 0 \text{ input}} + \underbrace{J_2 A_2}_{\sigma_2 < 0 \text{ output}} \geq 0$$

$$\eta = -\frac{\sigma_2}{\sigma_1} = 1 - \frac{\sigma}{\sigma_1} \leq 1$$

$$\mathcal{P} = -\sigma_2$$

b) Energy conversion in the linear regime

Linear regime: $J_1 = L_{11}A_1 + L_{12}A_2 \quad J_2 = L_{21}A_1 + L_{22}A_2$

$$\sigma = L_{11}A_1^2 + 2L_{12}A_1A_2 + L_{22}A_2^2 \geq 0$$

Maximum efficiency: $\partial_{A_2}\eta = 0$ $\eta^* = \frac{\text{Det}[L] + L_{11}L_{22} - 2\sqrt{\text{Det}[L]L_{11}L_{22}}}{L_{11}L_{22} - \text{Det}[L]} \leq 1$

Maximum is reached at *tight coupling*: $\text{Det}[L] = 0$ vanishing power!
 $(J_1 \propto J_2)$ $\mathcal{P} \rightarrow 0$

Efficiency at maximum power: $\partial_{A_2}\mathcal{P} = 0$ $\eta^* = \frac{1}{2} - \frac{\text{Det}[L]}{L_{11}L_{22} + \text{Det}[L]} \leq \frac{1}{2}$

c) Efficiency at maximum power beyond linear regime

Phenomenological models

I. I. Novikov & P. Chambadal (1957).

F. Curzon and B. Ahlborn, *Am. J. Phys.* **43**, 22 (1975).

$$\eta_{CA} = 1 - \sqrt{1 - \eta_C} \approx \eta_C/2 + \eta_C^2/8 + \eta_C^3/16 + \dots$$

Linear
(In case of tight coupling)

Van den Broeck, *Phys. Rev. Lett.* **95**, 190602, (2005)

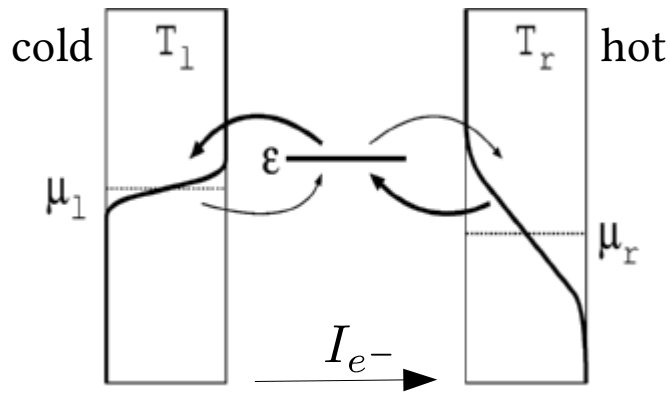
Nonlinear
(In presence of a left-right symmetry)

Esposito, Lindenberg, Van den Broeck, *Phys. Rev. Lett.* **102**, 130602 (2009)

Exactly solvable models using stochastic thermodynamics

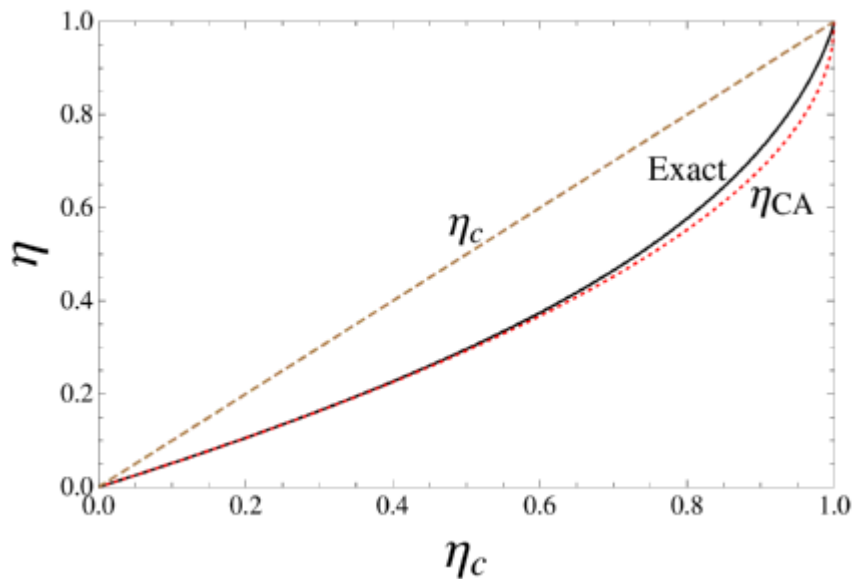
Thermoelectric quantum dot

Esposito, Lindenberg, Van den Broeck,
EPL **85**, 60010 (2009)



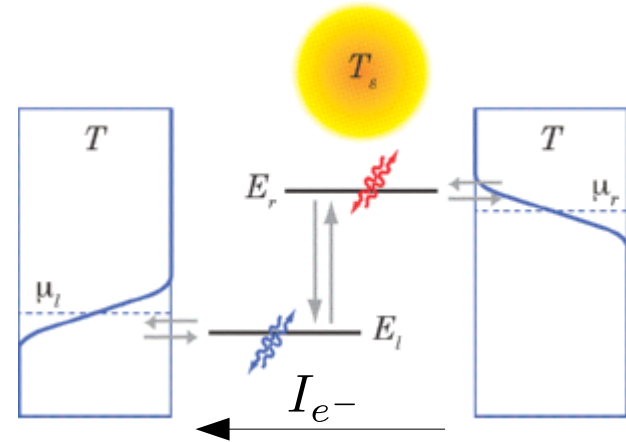
$$\dot{W} = (\mu_l - \mu_r)I_{e^-} \quad \eta = \frac{-\dot{W}}{\dot{Q}_r}$$

$$\dot{Q}_r = (\varepsilon - \mu_r)I_{e^-}$$

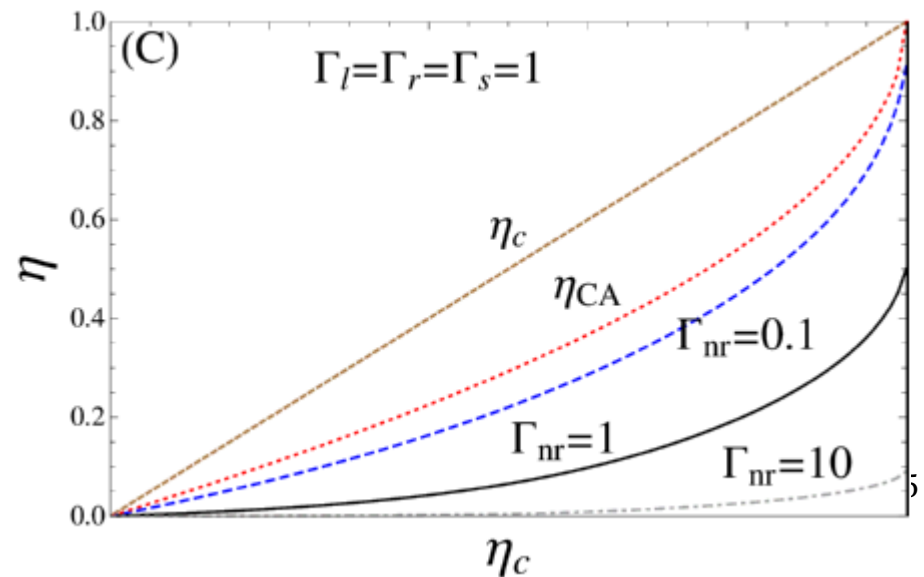


Photoelectric nanocell

Rutten, Esposito, Cleuren,
Phys. Rev. B **80**, 235122 (2009)



$$\dot{W} = (\mu_r - \mu_l)I_{e^-} \quad \eta = \frac{-\dot{W}}{\dot{Q}_s}$$



Finite-Time Thermodynamics: Synthesis

Stochastic thermodynamics naturally combines kinetics and thermodynamics



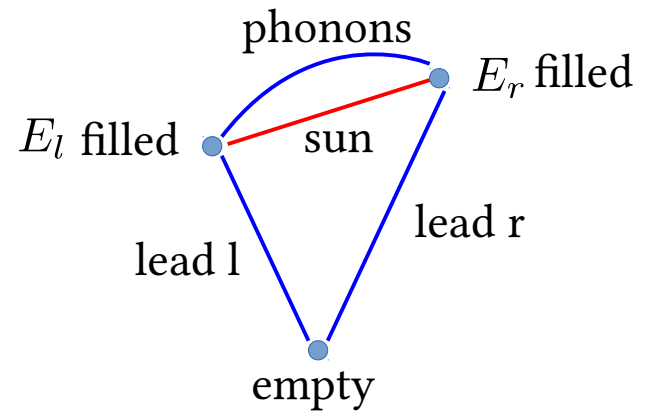
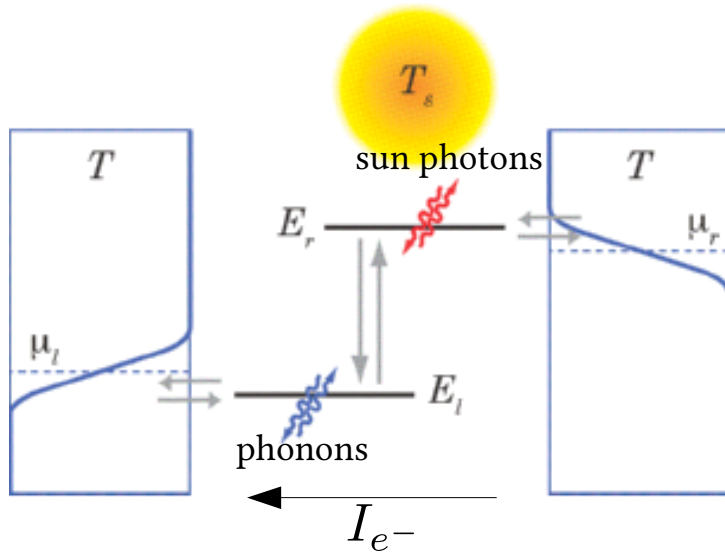
Powerful formalism to study energy transduction at the nanoscale

It allows to:

- Unambiguously define thermodynamic efficiencies (connected to EP)
- Distinguish the system specific features from the universal ones
- View very different devices (bio., chem., meso.) from the same global perspective
- ...

4) Efficiency fluctuations

Verley, Esposito, Willaert, Van den Broeck, *The unlikely Carnot efficiency*, Nature Communications 5, 4721 (2014)



Ensemble averaged description:

$$\langle w \rangle = (\mu_r - \mu_l) \langle I_{e^-} \rangle$$

$$\langle q_h \rangle = (E_r - E_l) \langle I_{ph}^{sun} \rangle$$

$$T \langle \sigma \rangle = \langle w \rangle + \eta_C \langle q_h \rangle \geq 0$$

$$\bar{\eta} = \frac{-\langle w \rangle}{\eta_C \langle q_h \rangle} \leq 1$$

At the trajectory level:

$$T \sigma = w + \eta_C q_h$$

$$\eta = \frac{-w}{\eta_C q_h}$$

Fluctuation theorem: $\frac{P(\sigma)}{P(-\sigma)} = \exp \sigma$

What can we say about $P(\eta)$?

a) Long time efficiency fluctuations

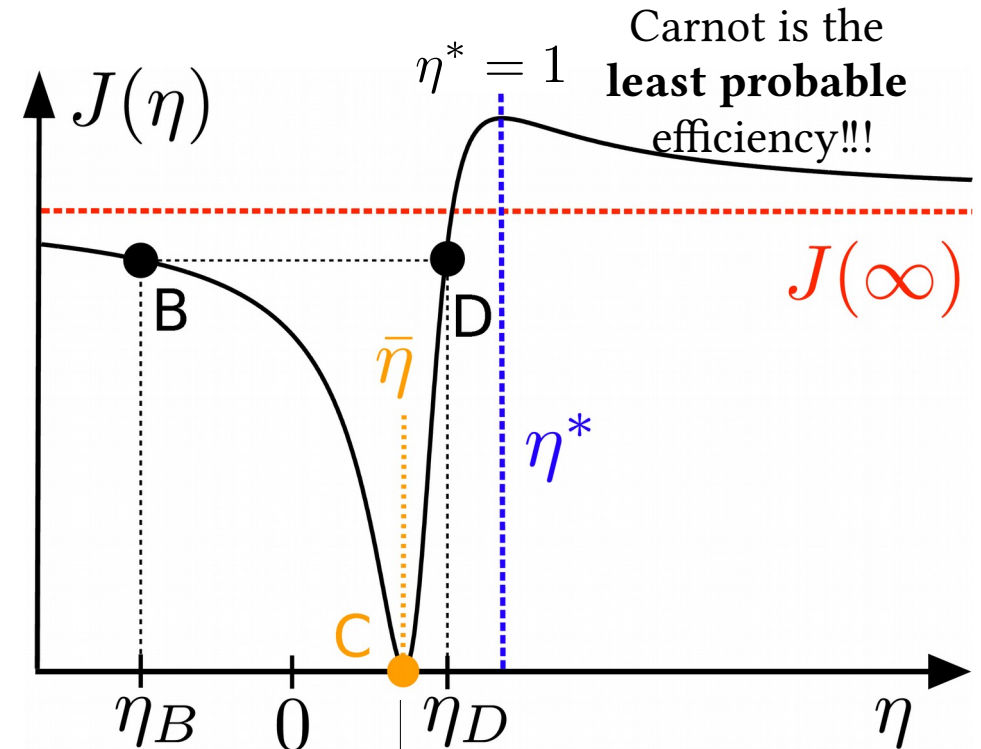
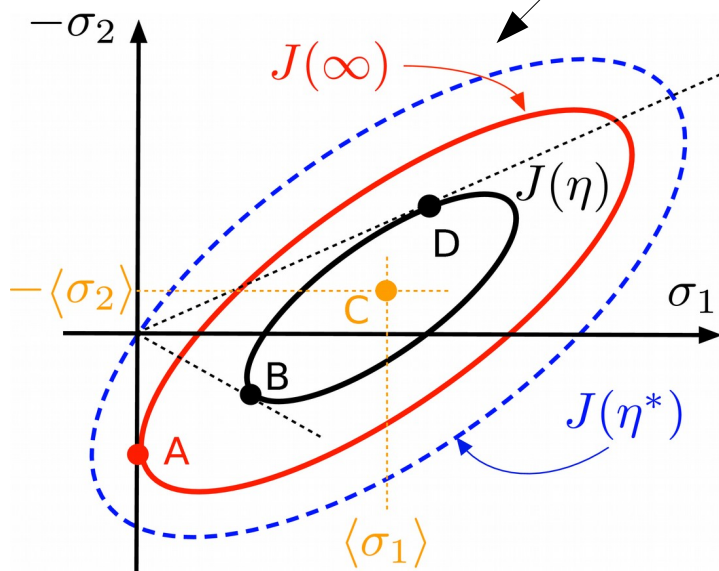
$$\sigma = \eta_C q_h / T + w / T$$

$$\eta = \frac{-\sigma_2}{\sigma_1} = \frac{-w}{\eta_C q_h}$$

$$P_t(\eta) \asymp \exp\{-tJ(\eta)\}$$

$$J(\eta) = \min_{\sigma_1} I(\sigma_1, -\eta\sigma_1)$$

$$P_t(\sigma_1, \sigma_2) \asymp \exp\{-tI(\sigma_1, \sigma_2)\}$$



Carnot is the **least probable** efficiency!!!

FT: $J(1) = I(0, 0)$

$\rightarrow J(\eta) \leq J(1)$

Macroscopic efficiency is the **most probable** efficiency

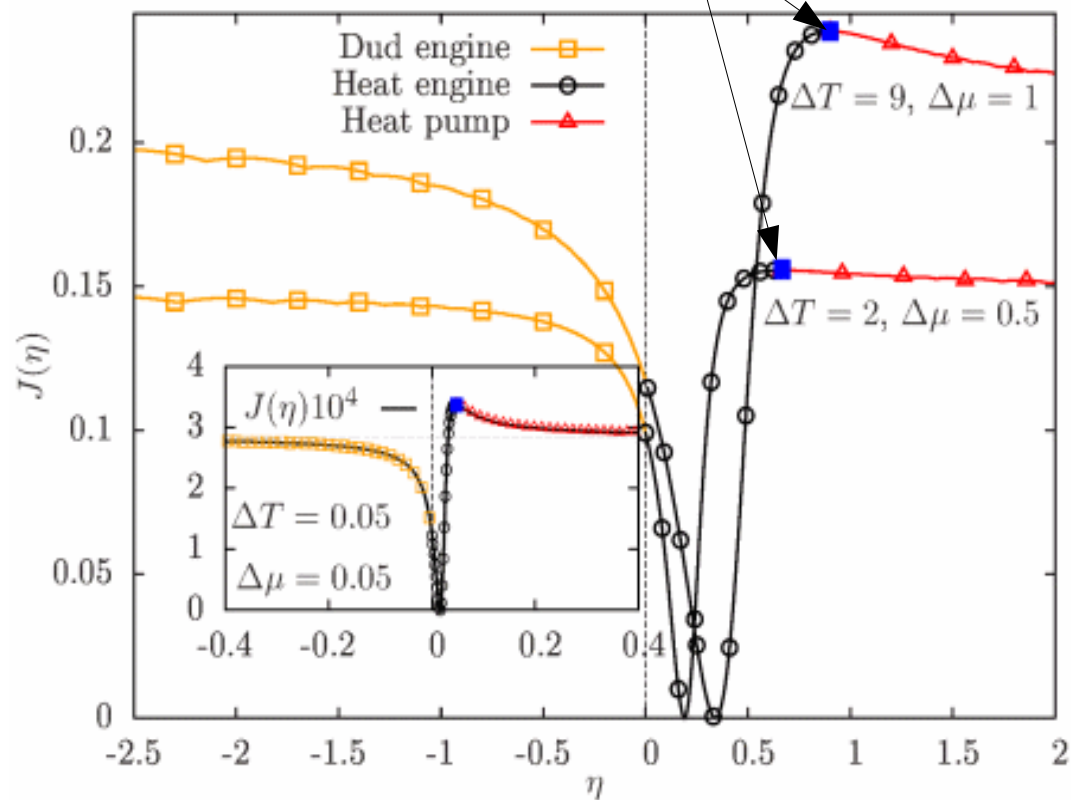
$$\bar{\eta} = \frac{-\langle \sigma_2 \rangle}{\langle \sigma_1 \rangle} \leq 1$$

The least likely efficiency is the Carnot efficiency:

$$\eta^* = \bar{\eta}_{rev}$$

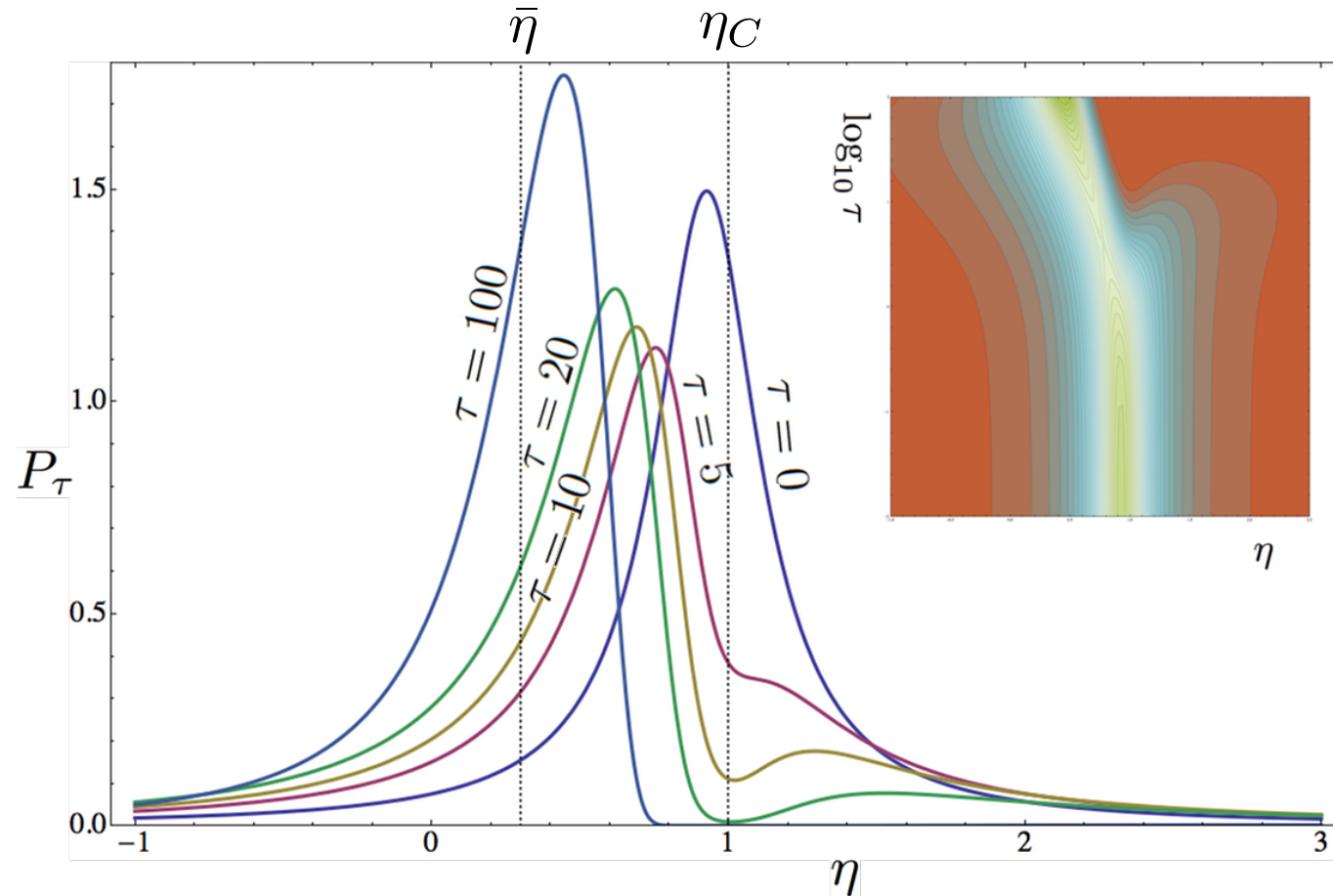
Consequence of FT!

Carnot efficiency



b) Finite-time efficiency fluctuations

Polettini, Verley, Esposito, *Finite-time efficiency fluctuations: Enhancing the most likely value*, PRL **114**, 050601 (2015)



- At $\tau = 0$: Lorentzian with max $\eta_0 = -L_{12}f_1/(L_{22}f_2) : 1 \geq \eta_0 \geq \bar{\eta}$
- After critical time, the distribution becomes bimodal:
 - local min goes to $\eta_C = 1$
 - local max goes to infinity
 - global max goes to $\bar{\eta}$
- $P_t(\eta < 1) = P_t(\sigma > 0)$ and $P_t(\eta > 1) = P_t(\sigma < 0)$
- The distribution has no moments: $P_t(\eta \rightarrow \pm\infty) \propto \eta^{-2}$
- Tight coupling: no efficiency fluctuations $P_t(\eta) = \delta(\eta - \eta_C)$

c) Long-time efficiency fluctuations in quantum systems

Esposito, Ochoa, Galperin, Efficiency fluctuation in quantum thermoelectric devices, PRB **91**, 115717 (2015)

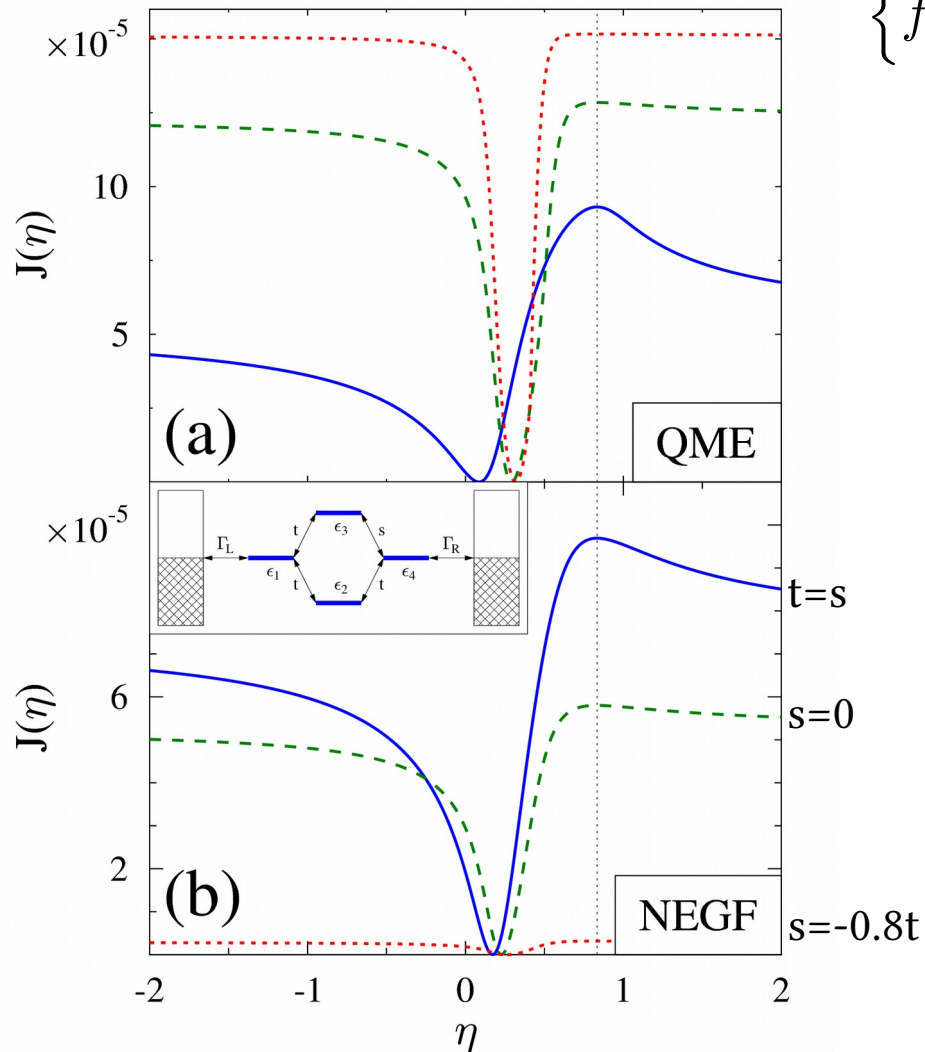
Cumulant GF (heat & work) $\phi(\gamma, \lambda) = \int \frac{dE}{2\pi} \ln \left(1 + T(E) \right.$

$$\left. \left\{ f_L(E)[1 - f_R(E)][e^{-([E-\mu_R]\lambda - [\mu_L - \mu_R]\gamma)} - 1] + f_R(E)[1 - f_L(E)][e^{+([E-\mu_R]\lambda - [\mu_L - \mu_R]\gamma)} - 1] \right\} \right)$$

Fluctuation relation

$$\phi(\gamma, \lambda) = \phi\left(-\frac{1}{T_L} - \gamma, \frac{1}{T_R} - \frac{1}{T_L} - \lambda\right)$$

$$J(\eta) = -\min_{\gamma_2} \phi(\gamma_2 \eta, \gamma_2)$$



Efficiency fluctuations: Synthesis

Finite-time thermodynamics at the fluctuating level



Accurate characterization of energy transduction at the nanoscale

- Experimental verification: *Martinez, Roldan, Dinis, Petrov, Parrondo, Rica, Brownian Carnot engine, Nature Physics DOI: 10.1038/NPHYS3518 (2015)*
Proesmans, Dreher, Gavrilov, Bechhoefer, Van den Broeck, Brownian duet: A novel tale of thermodynamic efficiency, Phys. Rev. X 6, 041010 (2016)
- The long time results can be generalized:
 - to time-asymmetric drivings
Verley, Willaert, Van den Broeck, Esposito, Universal theory of efficiency fluctuations, PRE 90, 052145 (2014)
Gingrich, Rotskoff, Vaikuntanathan, and Geissler, Efficiency and Large Deviations in Time-Asymmetric Stochastic Heat Engines, NJP 16, 102003 (2014)
 - to quantum systems (NEGF approach)
Esposito, Ochoa, Galperin, Efficiency fluctuation in quantum thermoelectric devices, PRB 91, 115717 (2015)
Agarwalla, Jiang, Segal, Full counting statistics of vibrationally-assisted electronic conduction: transport and fluctuations of the thermoelectric efficiency, PRB 92, 245418 (2015)
- The finite-time behavior:
Polettini, Verley, Esposito, Finite-time efficiency fluctuations: Enhancing the most likely value, PRL 114, 050601 (2015)
Proesman, Cleuren, Van den Broeck, Stochastic efficiency for effusion as a thermal engine, EPL 109, 20004 (2015)
Jiang, Agarwalla, Segal, Efficiency Statistics and Bounds for Systems with Broken Time-Reversal Symmetry, PRL 115, 040601 (2015)

Part II: Thermodynamics of Information Processing

1) Stochastic thermodynamics

- Nonequilibrium thermodynamics
- Landauer principle
- Nonequilibrium state as a resource

2) Measurement and feedback

- Szilard engine
- Erasure with feedback

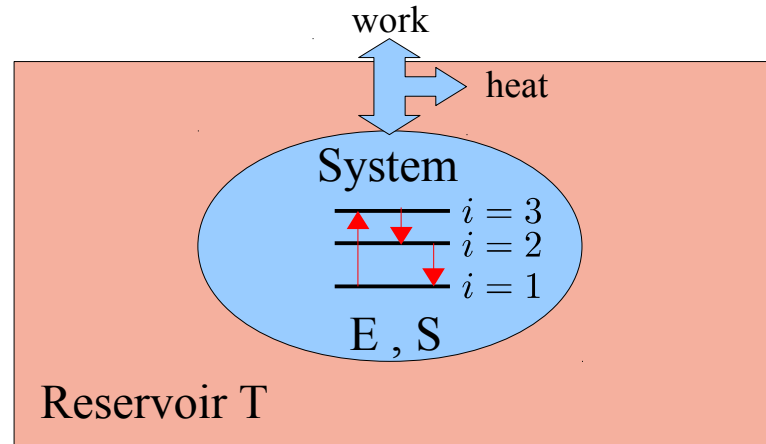
3) Bipartite perspective

- Nonautonomous (measurement and feedback)
- Autonomous (information flow)

4) Conclusions and perspectives

1) Stochastic Thermodynamics

Open system dynamics



Master equation:
$$d_t p_i = \sum_j W_{ij} p_j$$
 may depend on time

Local detailed balance:
$$\ln \frac{W_{ij}}{W_{ji}} = -\frac{(\epsilon_i - \epsilon_j)}{k_b T}$$

0th law Equilibrium:
$$p_i^{\text{eq}} = \exp \left\{ -\frac{(\epsilon_i - F^{\text{eq}})}{k_b T} \right\}$$

Nonequilibrium Thermodynamics

Energy: $E = \sum_i \epsilon_i p_i$

Entropy: $S = \sum_i [-k_b \ln p_i] p_i$

1st law

$$d_t E = \sum_i d_t \epsilon_i p_i + \sum_i \epsilon_i d_t p_i$$

Energy change

Work \dot{W}

Heat \dot{Q}

2nd law

$$\dot{S}_i = d_t S - \frac{\dot{Q}}{T} \geq 0$$

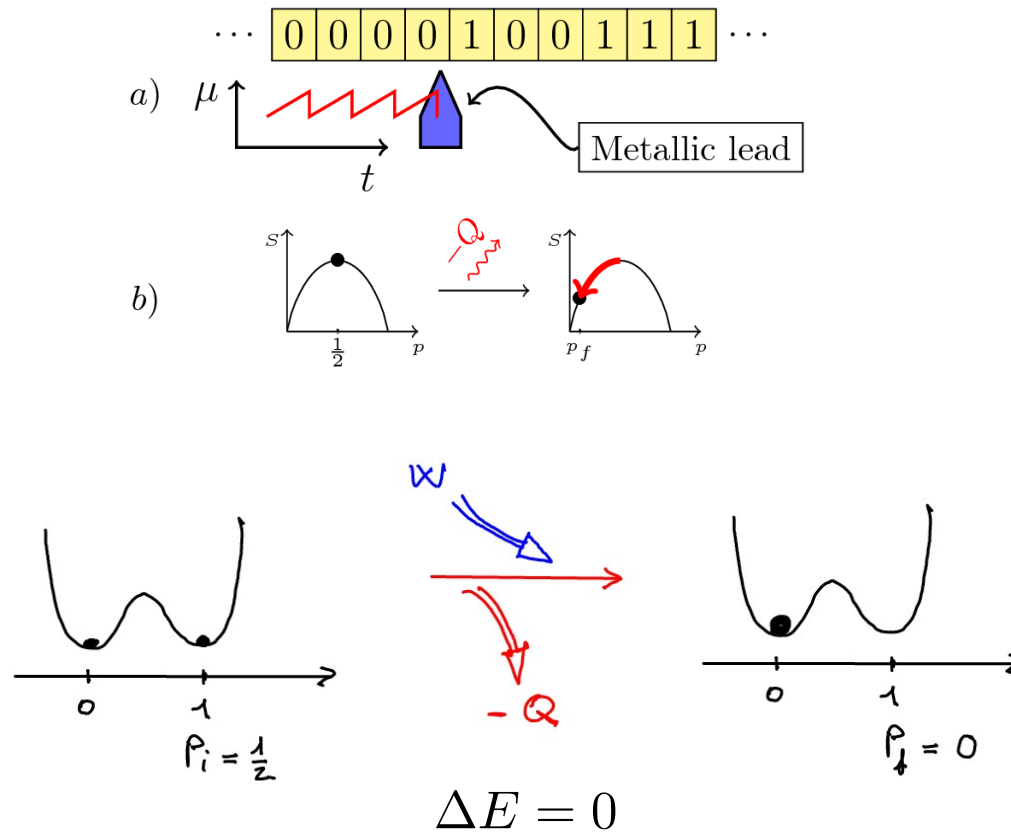
Entropy production

Entropy change

Entropy change in the reservoir

$$\dot{S}_i = k_b \sum_{i,j} (W_{ij} p_j - W_{ji} p_i) \ln \frac{W_{ij} p_j}{W_{ji} p_i} \geq 0$$

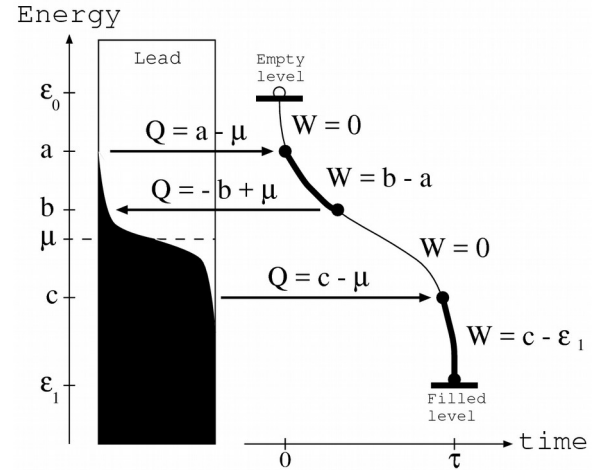
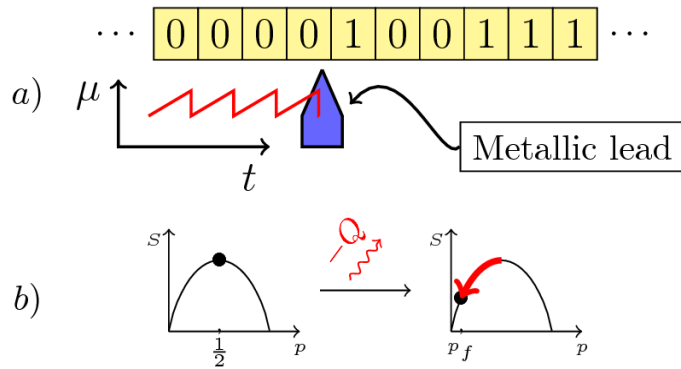
Landauer principle



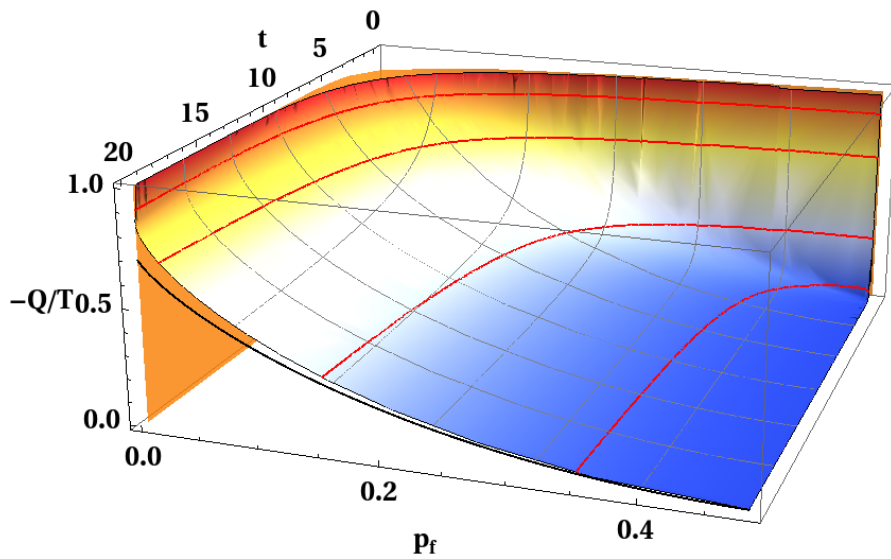
Heat expelled: $-Q \geq -T\Delta S = TS_i - TS_f = k_b T \ln 2$

Work needed: $W = -Q = k_b T \ln 2$

Optimal erasure in finite time



Accuracy-dissipation trade-offs:

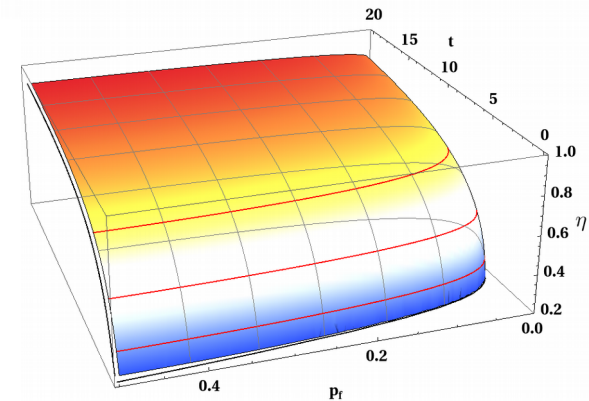
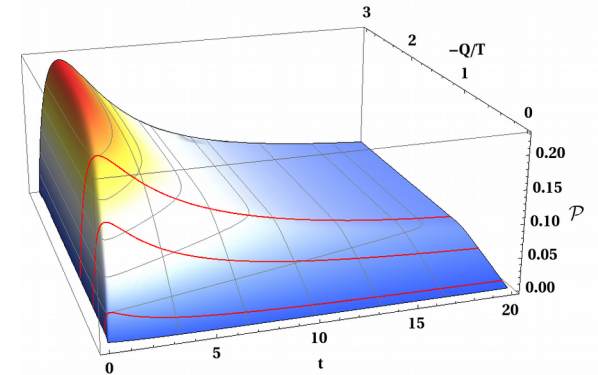


Power:

$$\mathcal{P}(Q, t) = \frac{-\Delta S}{t}$$

Efficiency:

$$\eta = \frac{-\Delta S}{-Q/T} = 1 - \frac{\Delta_i S}{-Q/T} \leq 1$$



Nonequilibrium state as a resource

Nonequilibrium free energy

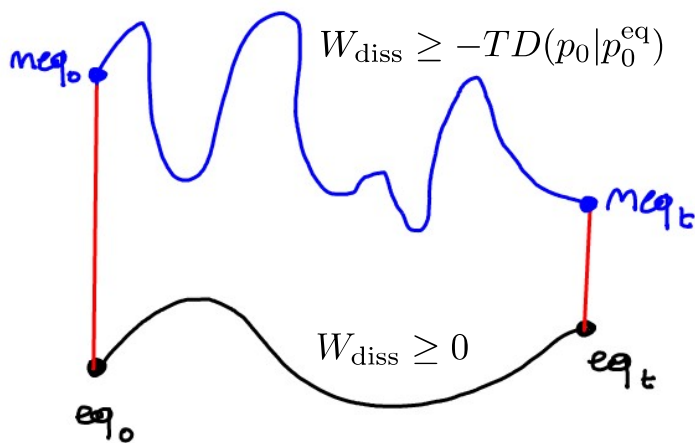
$$F \equiv E - TS$$

$$F - F^{\text{eq}} = TD(p|p^{\text{eq}}) \geq 0$$

$$\left\{ \begin{array}{l} D(p|p') \equiv k_b \sum_i p_i \ln \frac{p_i}{p'_i} \geq 0 \\ p_i^{\text{eq}} = \exp \left\{ -\frac{(\epsilon_i - F^{\text{eq}})}{k_b T} \right\} \end{array} \right.$$

$$1^{\text{st}} \text{ law} + 2^{\text{nd}} \text{ law} : \quad T\Delta_i S = W - \Delta F \geq 0$$

$$W_{\text{diss}} \equiv \underbrace{W - \Delta F^{\text{eq}}}_{\substack{\text{if eq. to eq.} \\ \geq 0}} = \underbrace{T\Delta_i S}_{\geq 0} + \underbrace{TD(p_t|p_t^{\text{eq}})}_{\geq 0} - \underbrace{TD(p_0|p_0^{\text{eq}})}_{\geq 0}$$



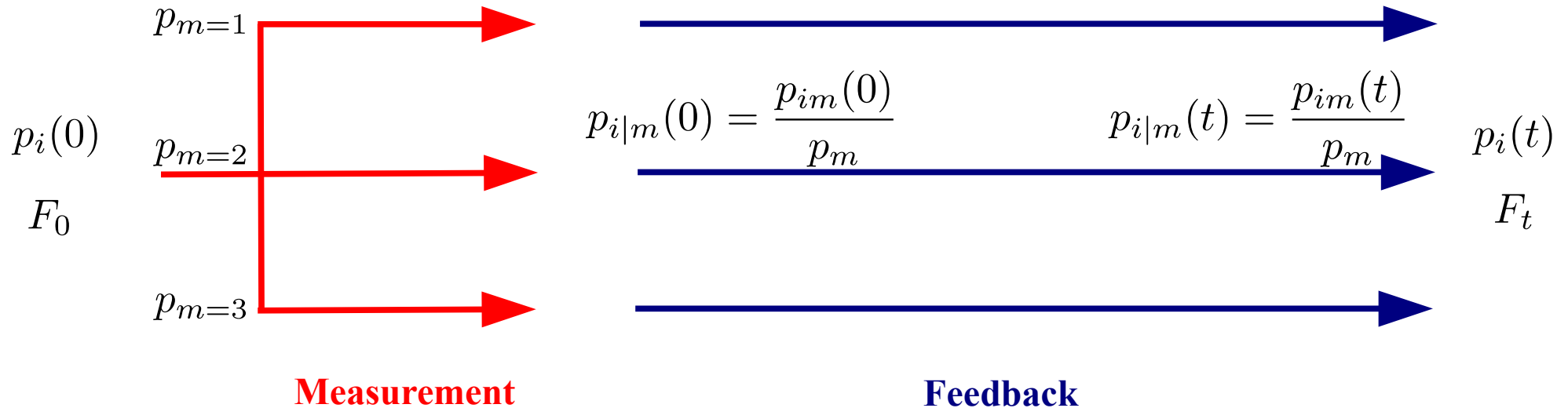
$$TD(p_0|p_0^{\text{eq}}) = -W_{\text{diss}} + T\Delta_i S + TD(p_t|p_t^{\text{eq}})$$

Pure waist: 0 x 0

Optimal extraction: x 0 0

2) Measurement and feedback

Phenomenological approach



$$\begin{aligned}
 \delta F_{\text{meas}} &= \sum_m p_m F^{|m} - F \\
 &= TS - T \sum_m p_m S^{|m} \\
 &= TD(p_{i,m} | p_i p_m) \geq 0 \\
 &\quad \underbrace{\hspace{10em}}_{\equiv I} \\
 &\quad \text{Mutual Information}
 \end{aligned}$$

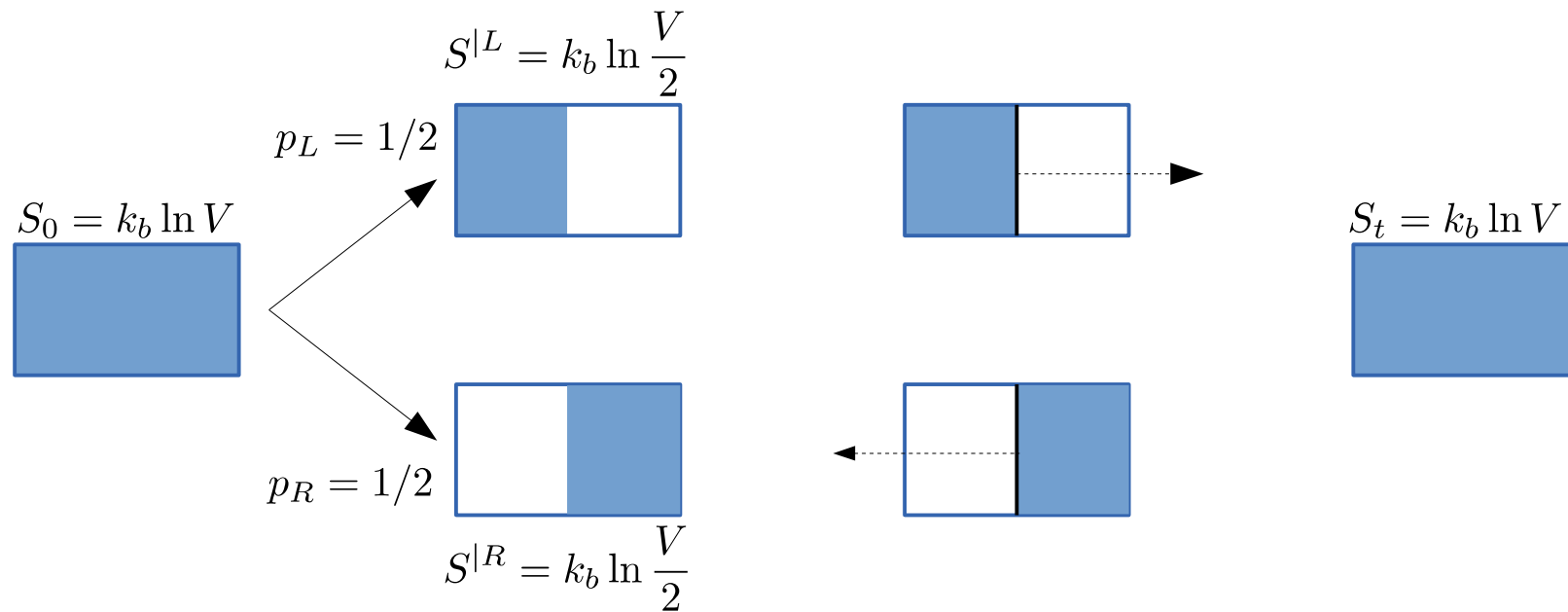
$$T \Delta_i S^{|m} = W^{|m} - \Delta F^{|m} \geq 0$$

$$\sum_m p_m \cdot$$

$$\underbrace{W - (F_t - F_0)}_{\text{without feedback}} \geq T(I_t - I_0) \geq -T I_0 \geq 0$$

Ex1: Szilard engine

Energy plays no role: $\Delta F = -T \Delta S$



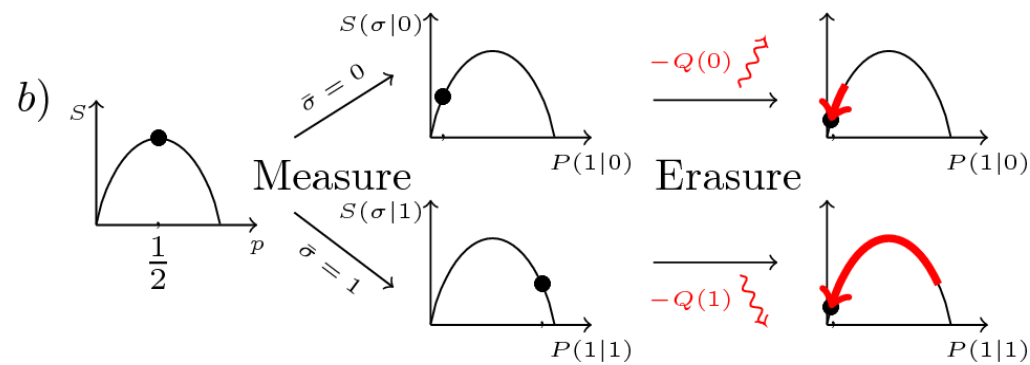
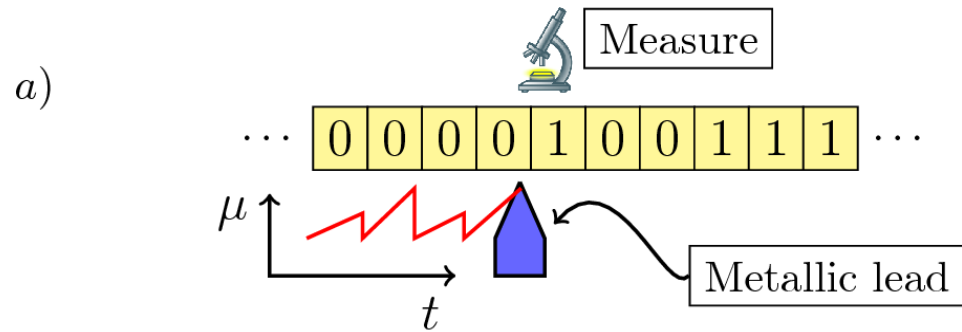
Measurement

$$\delta F_{\text{meas}} = TI = k_b T \ln 2$$

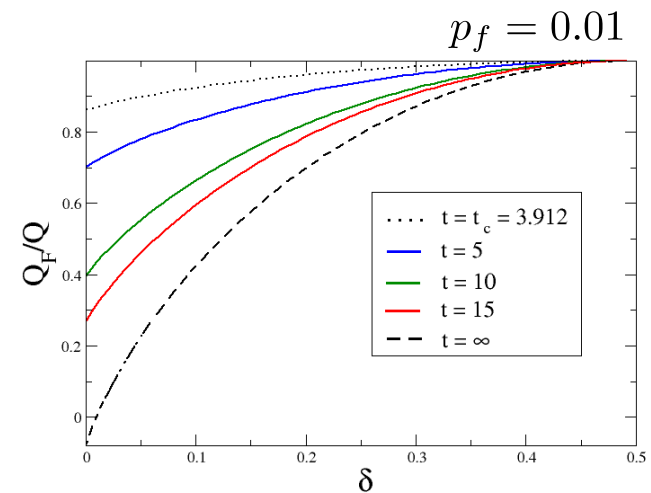
Feedback

$$W = -k_b T \ln 2$$

Ex2: Erasure with feedback in finite time

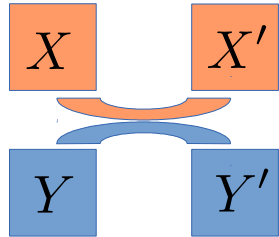


$$T(S_t - S_0) - Q \geq T(I_t - I_0) \geq -T I_0$$



3) Bipartite perspective

Non-autonomous systems (measurement and feedback)



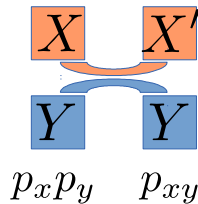
Mutual Information $I \equiv S_X + S_Y - S_{XY} = D(p_{xy}|p_x p_y) \geq 0$

$$\Delta E_{XY} = \Delta E_X + \Delta E_Y$$

$$\Delta F_{XY} = \Delta F_X + \Delta F_Y - T\Delta I$$

$$T\Delta_i S = W - \Delta F_X - \Delta F_Y - T\Delta I \geq 0$$

Measurement



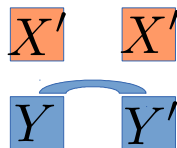
$$\Delta E_X = 0$$

$$\Delta E_Y = \Delta S_Y = 0$$

$$W_{\text{meas}} - \Delta F_X \geq T I$$

Perfect measurement
 $p_{xy} = p_y \delta_{xy}$
 $I = S_X = S_Y = S_{XY}$
 $W_{\text{meas}} \geq 0$

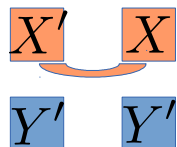
Feedback



$$\Delta E_X = \Delta S_X = 0$$

$$W_{\text{feed}} - \Delta F_Y \geq T\Delta I \geq -T I$$

Resetting memory



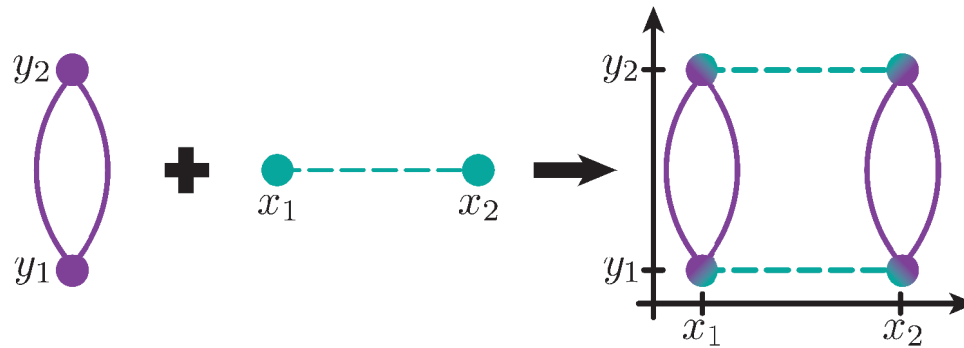
$$\Delta E_Y = \Delta S_Y = 0$$

$$W_{\text{reset}} + \Delta F_X \geq 0$$

$$W_{\text{meas}} + W_{\text{feed}} - \Delta F_X - \Delta F_Y \geq 0$$

$$W_{\text{meas}} + W_{\text{reset}} \geq T I$$

Autonomous systems (continuous information flow)

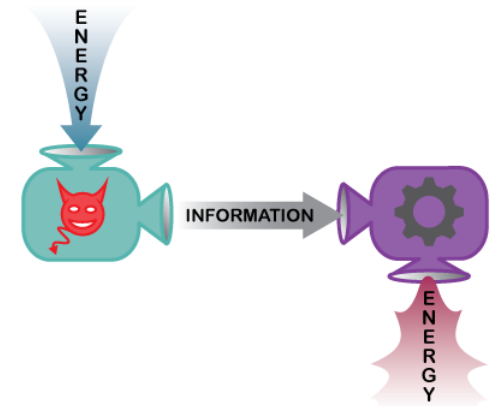


$$I = \sum_{x,y} p(x,y) \ln \frac{p(x,y)}{p(x)p(y)} \geq 0, \quad d_t I = \dot{I}^X + \dot{I}^Y$$

$$\dot{S}_i = \dot{S}_i^X + \dot{S}_i^Y$$

$$\dot{S}_i^X = d_t S^X + \dot{S}_r^X - \dot{I}^X \geq 0$$

$$\dot{S}_i^Y = d_t S^Y + \dot{S}_r^Y - \dot{I}^Y \geq 0$$



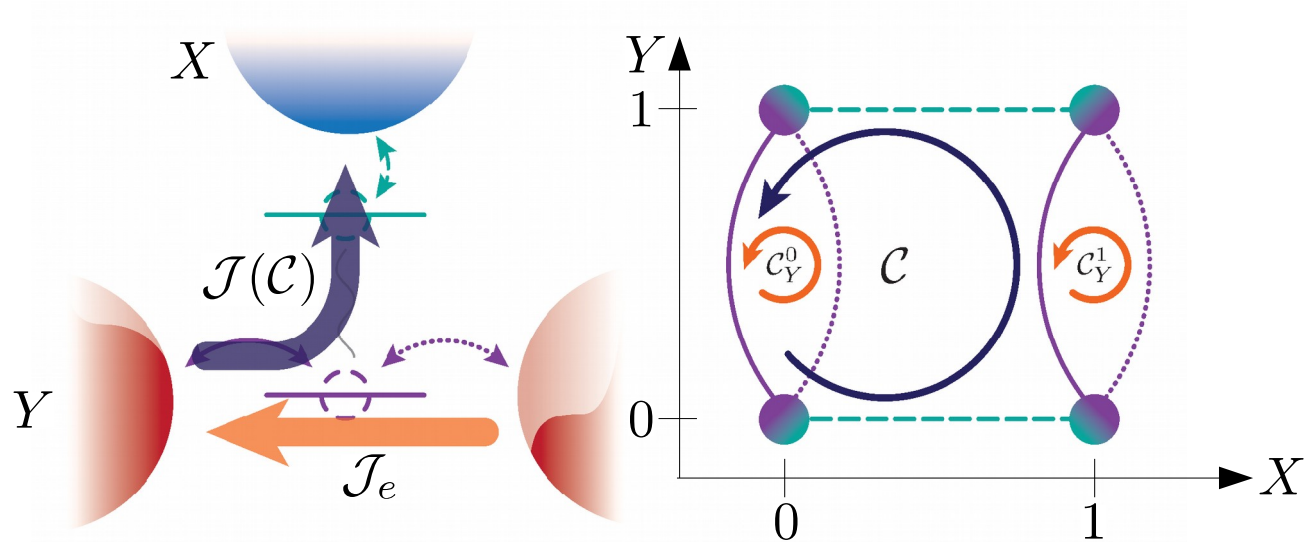
Steady state: $d_t I = 0$

$$\dot{I} = \dot{I}^X = -\dot{I}^Y$$

$$\dot{S}_i^X = \dot{S}_r^X - \dot{I} \geq 0$$

$$\dot{S}_i^Y = \dot{S}_r^Y + \dot{I} \geq 0$$

Ex: Two coupled quantum dots



$$\dot{S}_i = -\mathcal{J}_e \frac{\Delta\mu}{T} + \mathcal{J}(\mathcal{C}) \left(\frac{U}{T_D} - \frac{U}{T} \right) \geq 0 \quad \mathcal{J}_e = \mathcal{J}(\mathcal{C}_Y^0) + \mathcal{J}(\mathcal{C}_Y^1)$$

$$\dot{I} = \mathcal{J} \mathcal{F}^I > 0 \quad \text{where} \quad \mathcal{F}^I(\mathcal{C}) = \ln \frac{p(x=1|y=0)p(x=0|y=1)}{p(x=1|y=1)p(x=0|y=0)}$$

$$\dot{S}_i^X = \mathcal{J}(\mathcal{C}) \left[\frac{U}{T_D} - \mathcal{F}^I(\mathcal{C}) \right] \geq 0 \quad \dot{S}_i^Y = -\mathcal{J}_e \frac{\Delta\mu}{T} + \mathcal{J}(\mathcal{C}) \left[\mathcal{F}^I(\mathcal{C}) - \frac{U}{T} \right] \geq 0$$

Maxwell demon limit: $U \rightarrow 0$ $T_D \rightarrow 0$ $U/T_D = \text{Cte}$

4) Conclusions and perspectives

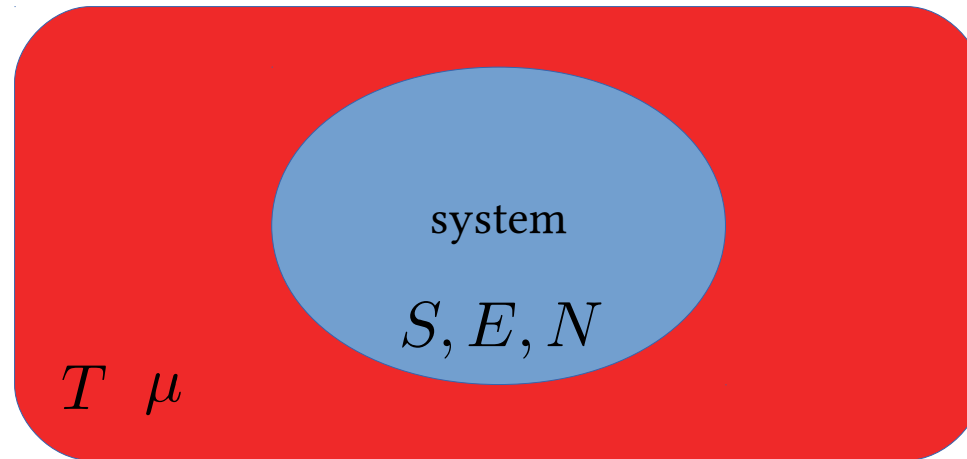
Thermodynamics of information, Parrondo, Horowitz, Sagawa, Nature Physics **11**, 131 (2015)

- Many other approaches Esposito and Schaller, EPL **99**, 30003 (2012)
Mandal, Jarzynski, PNAS **109**, 11641 (2012)
Barato, Seifert, PRL **112** 09061 (2014)
Horowitz, Sandberg, NJP **16**, 125007 (2012)
- Experiments Toyabe & al., Nature Physics **6**, 988 (2010)
Bérut & al., Nature **483**, 187 (2012)
Jun, Gavrilov, Bechhoefer, PRL **113**, 190601 (2014)
Koski & al. PRL **115**, 260602 (2015)
- Biology (sensing, proofreading, chemotaxis, chemical computing...)

Part III: Quantum Thermodynamics

- 1) Phenomenological thermodynamics
- 2) A Hamiltonian formulation
- 3) Born-Markov-Secular Quantum Master Equation (QME)
- 4) Landau-Zener QME
- 5) Repeated interactions
- 6) More...

1) Phenomenological Nonequilibrium Thermodynamics



Zeroth law: System dynamics with an equilibrium

1st law:
$$d_t E = \dot{W} + \dot{Q}$$

2nd law:
$$\dot{\Sigma} = d_t S - \frac{\dot{Q}}{T} \geq 0$$

↓
Entropy production
(dissipation)

Slow transformation

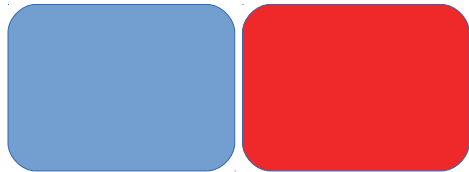
$$d_t S \approx \frac{\dot{Q}}{T}$$

2) Hamiltonian formulation

System X – System Y

$$H_{\text{tot}}(t) = H_X(t) + H_Y(t) + H_{XY}(t)$$

$$\rho_{XY}(0) = \rho_X(0)\rho_Y(0)$$



$$\rho_{XY}(\tau) = U_\tau \rho_X(0)\rho_Y(0)U_\tau^\dagger$$



$$d_t E_{XY}(t) = \text{tr}_{XY} \{ \rho_{XY}(t) d_t H_{\text{tot}}(t) \} \equiv \dot{W}(t)$$

$$\begin{aligned} I_{X:Y}(t) &\equiv S_X(t) + S_Y(t) - S_{XY}(t) & S_{XY}(t) &\equiv -\text{tr}_{XY} \{ \rho_{XY}(t) \ln \rho_{XY}(t) \} \\ &= \Delta S_X(\tau) + \Delta S_Y(\tau) = D[\rho_{XY}(t) || \rho_X(t)\rho_Y(t)] \geq 0 \end{aligned}$$

System X – Reservoir R

$$H_{\text{tot}}(t) = H_X(t) + H_R + H_{XR}(t)$$

Assumption: $\rho_{XR}(0) = \rho_X(0)\rho_\beta^R$ $\rho_\beta^R \equiv \frac{e^{-\beta H_R}}{Z_R}$

$$E_X(t) \equiv \text{tr}_{XR}\{[H_X(t) + H_{XR}(t)]\rho_{XR}(t)\}$$

1st law: $d_t E_X(t) = \dot{W}(t) + \dot{Q}(t)$ $\left\{ \begin{array}{l} \dot{W}(t) = d_t E_{XY}(t) \\ \dot{Q}(t) \equiv -\text{tr}_R \{H_R d_t \rho_R(t)\} \end{array} \right.$

2nd law: $\Sigma(\tau) \equiv \Delta S_X(\tau) - \beta Q(\tau) = D[\rho_{XR}(\tau) || \rho_X(\tau)\rho_\beta^R]$
 $= D[\rho_R(\tau) || \rho_\beta^R] + I_{X:R}(\tau) \geq 0$

Ideal reservoir

Another identity: $TD[\rho_R(\tau)||\rho_\beta^R] = -Q(\tau) - T\Delta S_R(\tau) \geq 0$

$$\rho_R(\tau) = \rho_\beta^R + \epsilon\sigma_R \quad D[\rho_R(\tau)||\rho_\beta^R] = \mathcal{O}(\epsilon^2)$$



$$\Delta S_R(\tau) = -\beta Q(\tau)$$

$$\Sigma(\tau) = I_{X:R}(\tau)$$

Summary:

{ 1st, 2nd law, strong coupling
no 0th law, $\Sigma \geq 0$ but not $\dot{\Sigma}$

3) Born-Markov-Secular QME

$$H_{\text{tot}}(t) = H_X \underset{\text{slow}}{\circledast}(t) + H_R + \sum_k \underset{\text{weak}}{\circledast} A_k \otimes B_k$$

Effective dynamics

$$d_t \rho_X(t) = -i[H_X(t), \rho_X(t)] + \mathcal{L}_\beta(t) \rho_X(t) \equiv \mathcal{L}_X(t) \rho_X(t),$$

$$\mathcal{L}_\beta(t) \rho(t) = \sum_\omega \sum_{k,l} \gamma_{kl}(\omega) \left(A_l(\omega) \rho(t) A_k^\dagger(\omega) - \frac{1}{2} \{ A_k^\dagger(\omega) A_l(\omega), \rho(t) \} \right)$$

$$A_k(\omega) \equiv \sum_{\epsilon - \epsilon' = \omega} \Pi_\epsilon A_k \Pi_{\epsilon'} \quad \gamma_{kl}(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \text{tr}_R \{ B_k(t) B_l(0) \rho_\beta^R \}$$

Local detailed balance: $\gamma_{kl}(-\omega) = e^{-\beta\omega} \gamma_{lk}(\omega)$

$$\mathcal{L}_\beta(t) \rho_\beta^X(t) = 0, \quad \rho_\beta^X(t) = \frac{e^{-\beta H_X(t)}}{Z_X(t)}$$

Thermodynamics

$$\text{Energy: } E_X(t) = -\text{tr}_X \{H_X(t)\rho_X(t)\}$$

$$\text{Entropy: } S_X(t) = -\text{tr}_X \{\rho_X(t) \ln \rho_X(t)\}$$

$$1^{\text{st}} \text{ law} \quad d_t E_X(t) = \dot{W}(t) + \dot{Q}(t)$$

$$\dot{W}(t) = \text{tr}_X \{\rho_X(t) d_t H_X(t)\}$$

$$\dot{Q}(t) = \text{tr}_X \{H_X(t) d_t \rho_X(t)\} = \text{tr}_X \{H_X(t) \mathcal{L}_X(t) \rho_X(t)\}$$

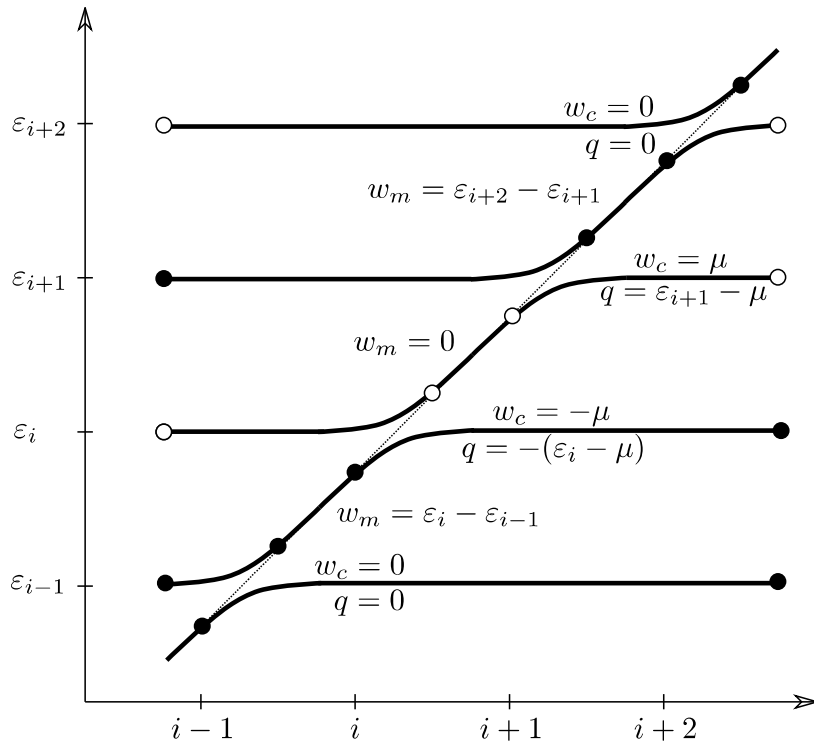
$$2^{\text{nd}} \text{ law} \quad \dot{\Sigma}(t) = d_t S_X(t) - \beta \dot{Q}(t)$$

$$= -\text{tr} \{[\mathcal{L}_X(t) \rho_X(t)] [\ln \rho_X(t) - \ln \rho_\beta^X(t)]\} \geq 0$$

Summary: $\left\{ \begin{array}{l} 0^{\text{th}}, 1^{\text{st}}, 2^{\text{nd}} \text{ law, } \dot{\Sigma} \geq 0, \text{ slow trsf. } \dot{\Sigma} \approx 0 \\ \text{but weak coupling} \end{array} \right.$

4) A Landau-Zener approach

$$H(t) = \epsilon_t c^\dagger c + \sum_{i=1}^L \epsilon_i c_i^\dagger c_i + \gamma \sum_{i=1}^L (c^\dagger c_i + c_i^\dagger c)$$



Prob. diabatic transition:

$$R_i = \exp \left\{ -\pi \delta_i^2 / (2\hbar \dot{\epsilon}_i) \right\}$$

$$t_i^{\text{LZ}} = \sqrt{\hbar / \dot{\epsilon}_i} \max[1, \sqrt{\delta_i^2 / (\hbar \dot{\epsilon}_i)}]$$

Validity: $\Delta t_{i+} > t_i^{\text{LZ}}$ $\Delta \epsilon_{i+} > \delta_i$ \longrightarrow $\Delta \epsilon_{i+} > \sqrt{\hbar \dot{\epsilon}_i}, \delta_i$

[Barra & Esposito, PRL **93**, 062118 (2016)]

Effective dynamics

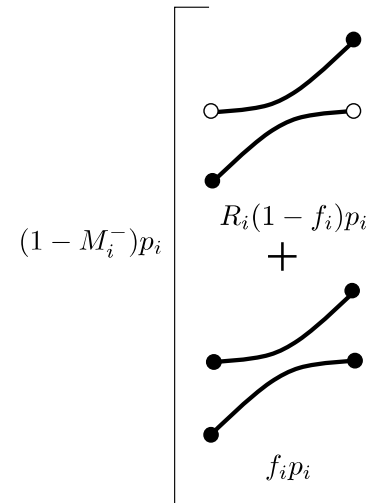
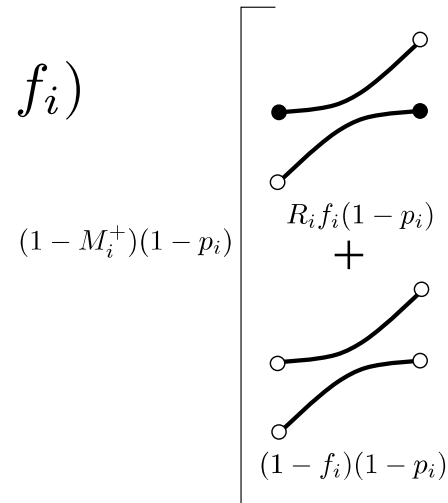
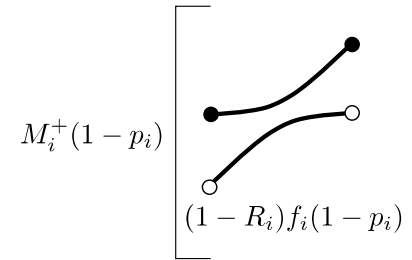
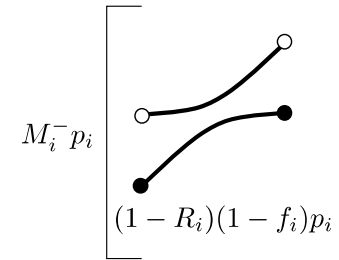
Master equation

$$p_{i+1} = (1 - M_i^-)p_i + M_i^+(1 - p_i)$$

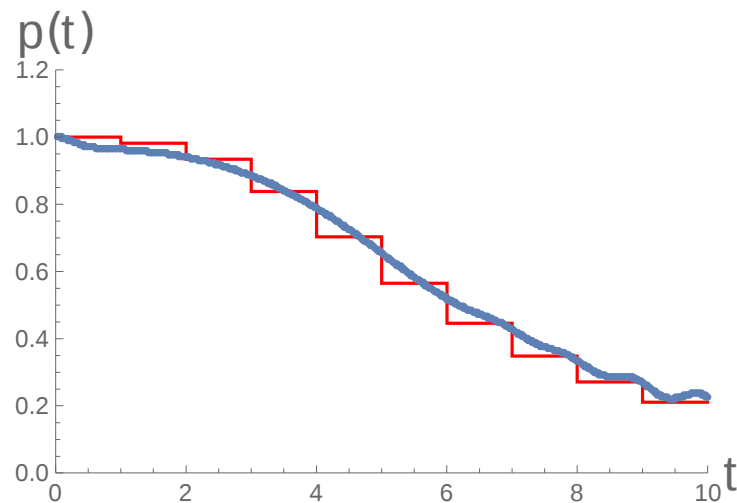
$$M_i^+ = (1 - R_i)f_i \quad M_i^- = (1 - R_i)(1 - f_i)$$

Local detailed balance

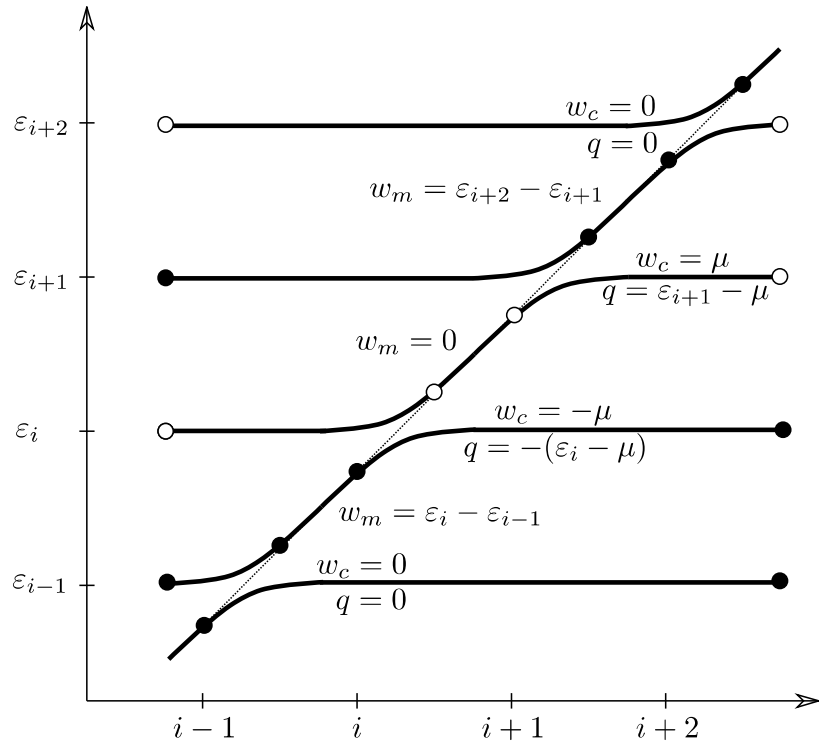
$$M_i^+ / M_i^- = e^{-\beta(\varepsilon_i - \mu)}$$



Exact vs stochastic dynamics



Thermodynamics



$$1^{\text{st}} \text{ law } \Delta E_{i+} = E_{i+1} - E_i = W_{i+} + Q_{i+}$$

$$N_i = p_i \quad E_i = \varepsilon_i p_i \quad Q_{i+} = (\varepsilon_i - \mu)(p_{i+1} - p_i)$$

$$W_{i+} = W_{i+}^{\text{m}} + W_{i+}^{\text{c}} \quad \begin{cases} W_{i+}^{\text{m}} = (\varepsilon_{i+1} - \varepsilon_i)p_{i+1} \\ W_{i+}^{\text{c}} = \mu(p_{i+1} - p_i) \end{cases}$$

$$2^{\text{nd}} \text{ law } \Delta S_{i+} = S_{i+1} - S_i = \Sigma_{i+} + Q_{i+}/T$$

$$S_i = -k_B p_i \ln p_i - k_B (1 - p_i) \ln(1 - p_i)$$

$$\Sigma_{i+} = k_B M_i^+ (1 - p_i) \ln \frac{M_i^+ (1 - p_i)}{M_i^- p_i} + k_B M_i^- p_i \ln \frac{M_i^- p_i}{M_i^+ (1 - p_i)} - k_B D(p_{i+1}|p_i) \geq 0$$

between crossing

$$\underbrace{W_{i+}^m - \Delta\Omega_{i+}^{\text{eq}}}_{\text{at crossing}} = \frac{W_{i+}^{\text{diss}}}{T} - k_B D(p_{i+1}|f_{i+1}) + k_B D(p_i|f_i) \geq 0$$

QM adiabatic regime (slow driving)

$$p_i = f_{i-1} \quad p_{i+1} = f_i$$

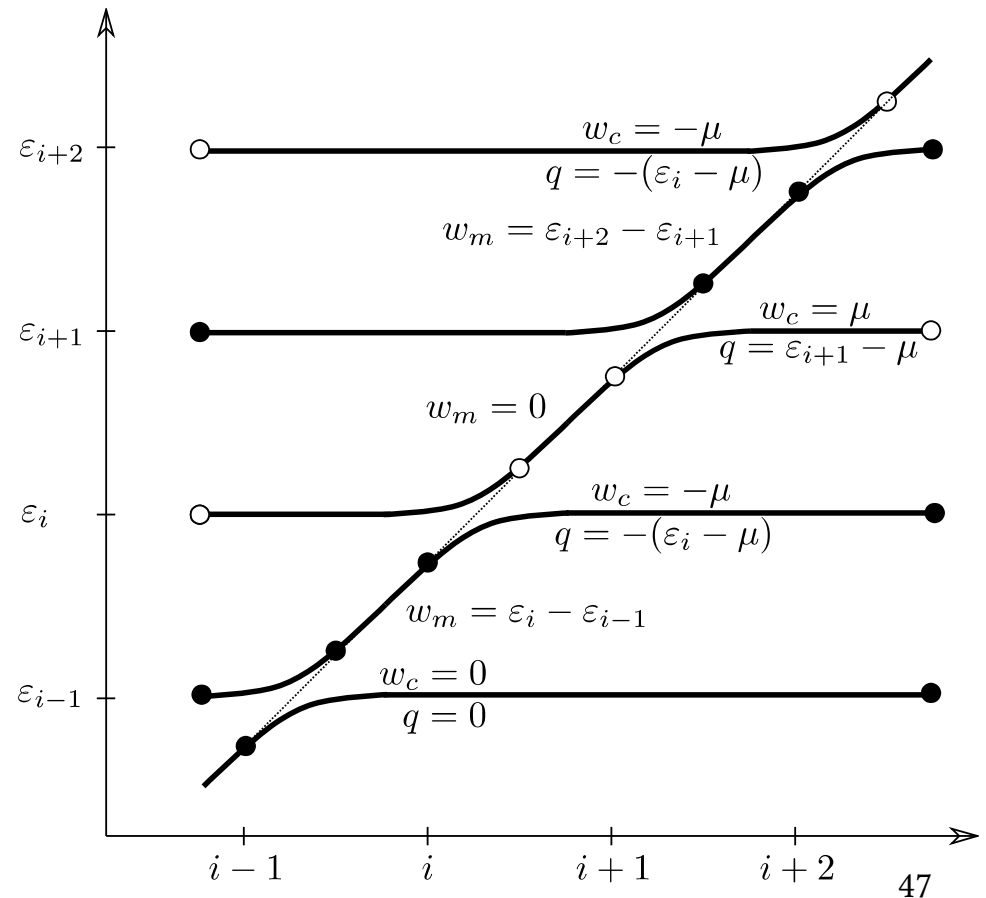
At the crossing: $\Sigma_{i+} = k_B D(f_{i-1}|f_i)$

From $i \rightarrow i+1$: $W_{i+}^{\text{diss}} = k_B T D(f_i|f_{i+1})$

Reversibility only occurs if:

$$\Delta\epsilon, \delta, \dot{\epsilon} \rightarrow 0$$

$$\Delta\epsilon > \delta \gg \sqrt{\hbar\dot{\epsilon}} \quad \Sigma_{i+}, W_{i+}^{\text{diss}} \sim \Delta\epsilon^2$$



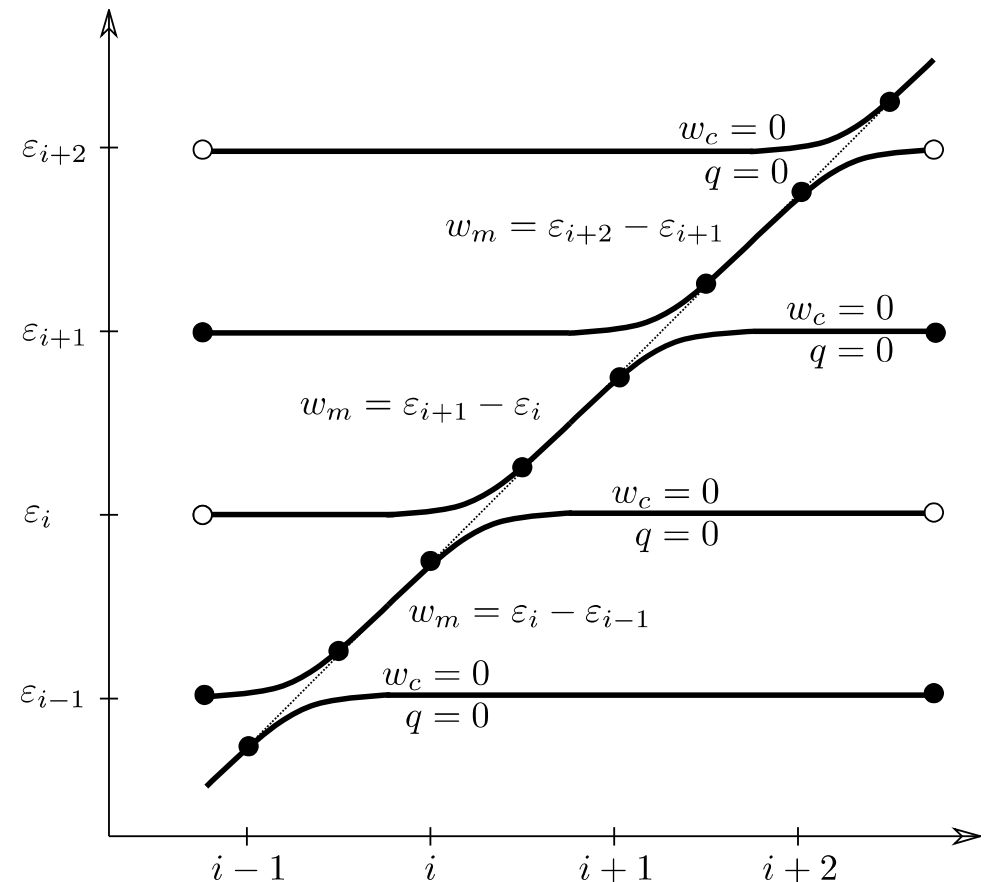
$$\Sigma_{i+} = \frac{W_{i+}^{\text{diss}}}{T} - k_B D(p_{i+1}|f_{i+1}) + k_B D(p_i|f_i) \geq 0$$

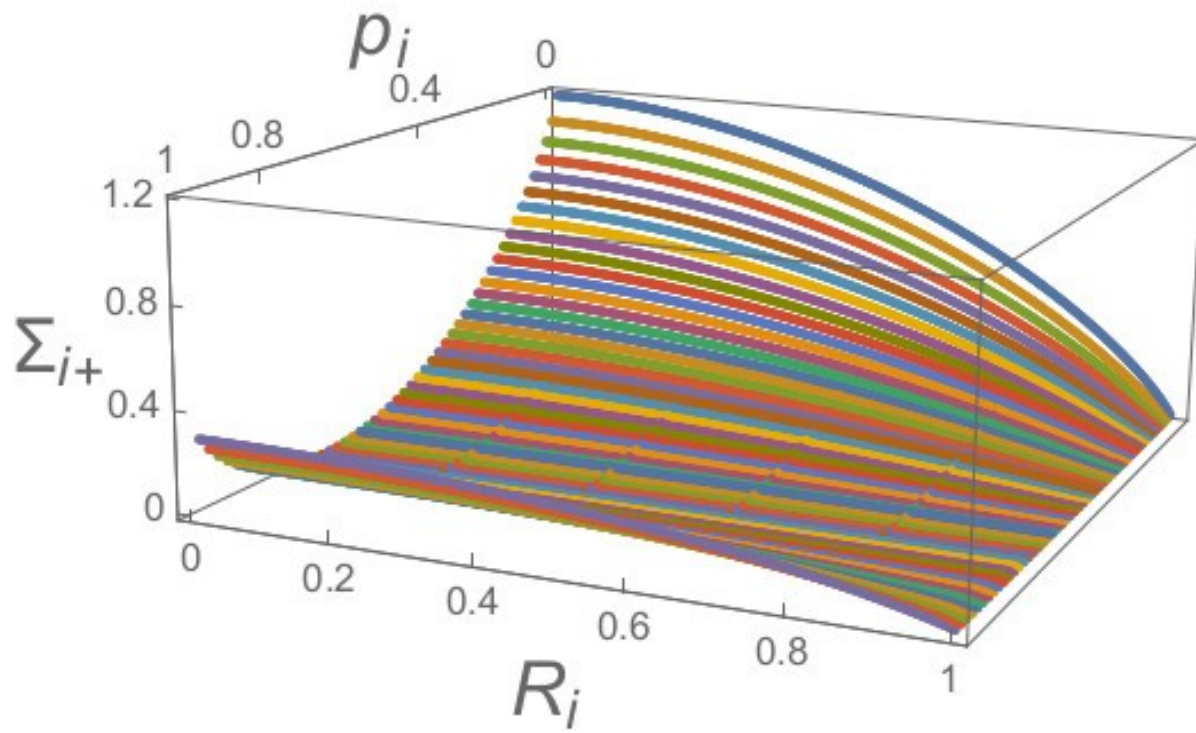
QM diabatic regime (fast driving)

$$p_i = p_1$$

$$\Sigma = \Delta S = Q = 0$$

$$W^{\text{diss}} = k_B T \sum_i (D(p_1|f_{i+1}) - D(p_1|f_i))$$





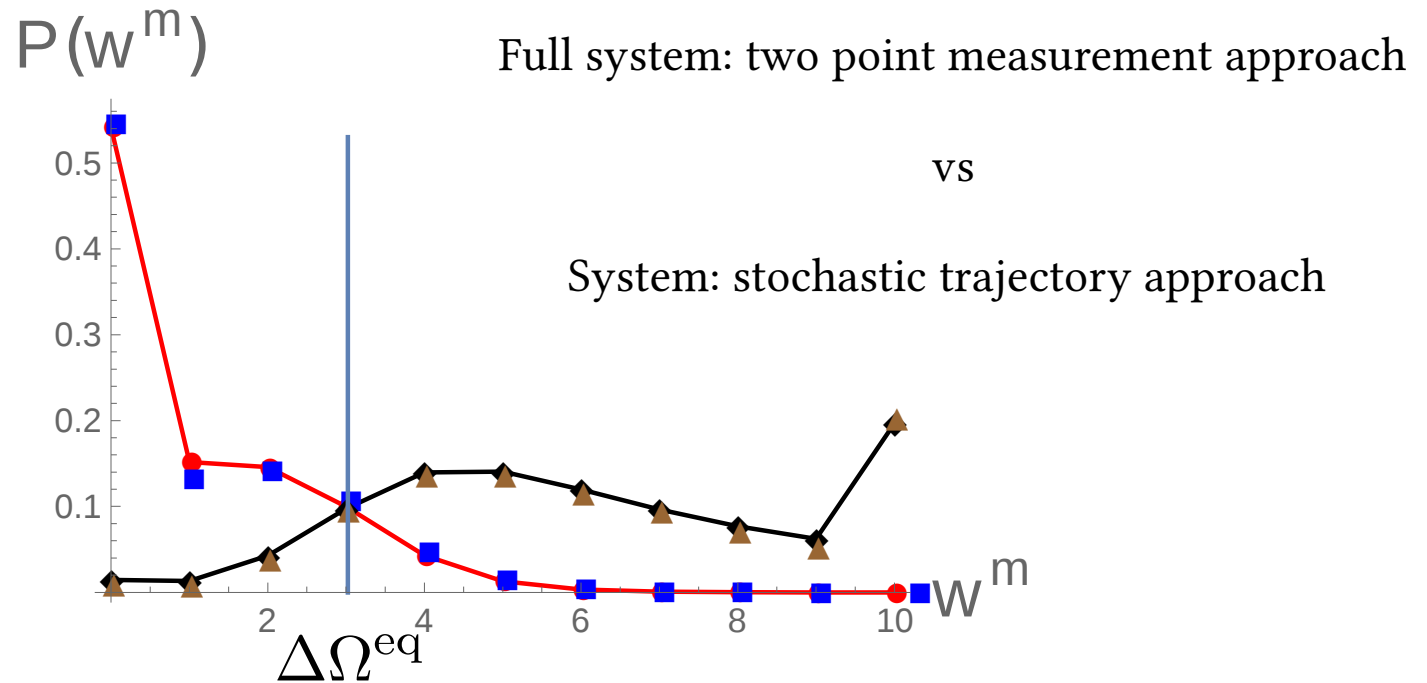
[Barra & Esposito, PRE 93, 062118 (2016)]

Work fluctuations

Jarzynski and Crooks fluctuation relation

System initially
at equilibrium

$$\frac{P(w^m)}{\tilde{P}(-w^m)} = \exp \{ \beta (w^m - \Delta\Omega^{\text{eq}}) \}$$



QM diabatic regime: continuous limit

$$\Delta\varepsilon > \sqrt{\hbar\dot{\varepsilon}} > \delta \qquad R \approx 1 - \frac{\delta^2}{\hbar\dot{\varepsilon}} \frac{\pi}{2}$$

$$(p_{i+1} - p_i)/\Delta t_{i+} = (f_i - p_i)(1 - R_i)/\Delta t_{i+}$$

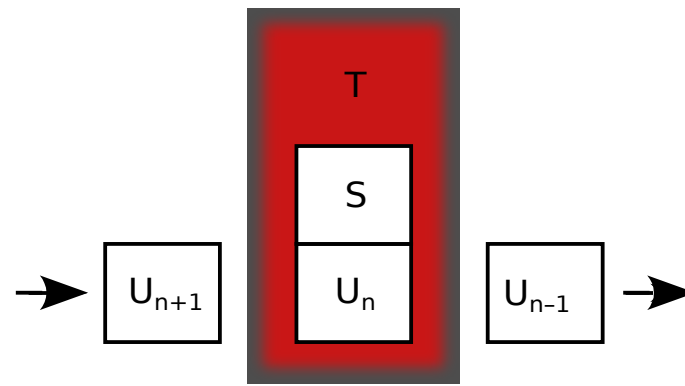
$$d_i = 1/\Delta\varepsilon_i \qquad \Delta t_{i+} = 1/(\dot{\varepsilon}_i d_i)$$



$$d_t p = w^+(1 - p) - w^- p$$

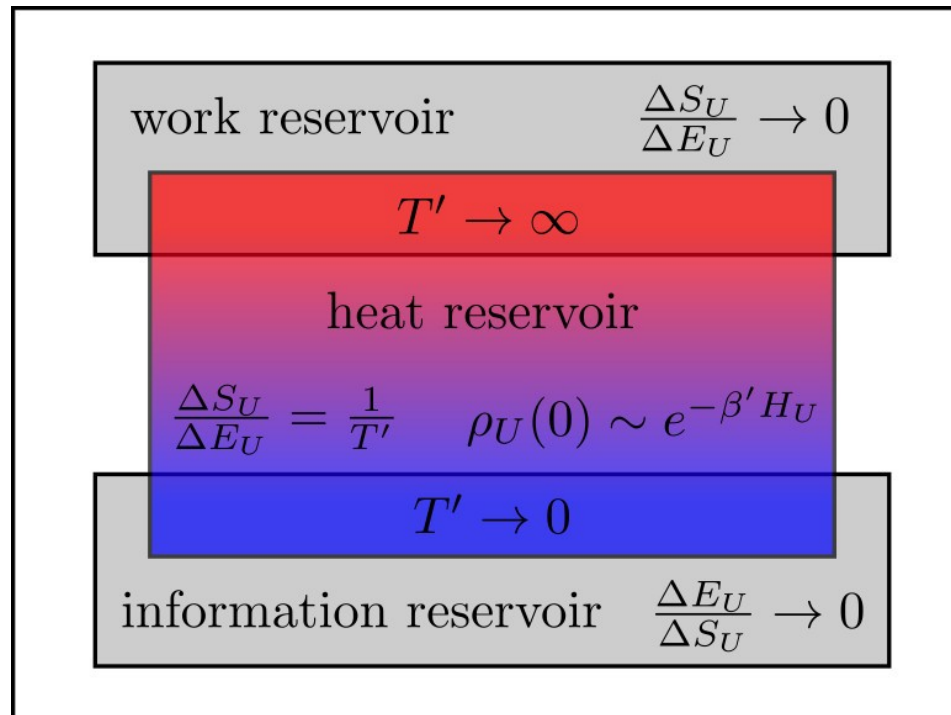
$$w^+ = \frac{\pi\delta^2(\varepsilon_t)d(\varepsilon_t)}{2\hbar} f(\varepsilon_t) \qquad w^- = \frac{\pi\delta^2(\varepsilon_t)d(\varepsilon_t)}{2\hbar} (1 - f(\varepsilon_t))$$

Pauli master equation with Fermi golden rule rates

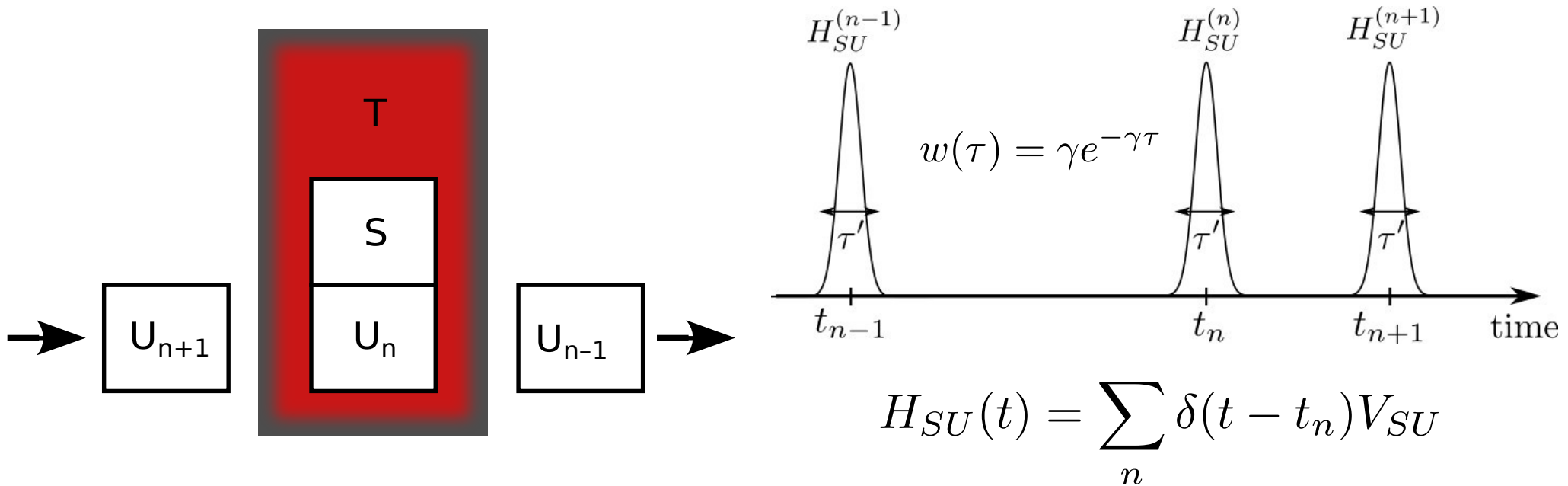


1st law
$$\Delta E_S = W + Q - \Delta E_U$$

2nd law
$$\Sigma_S \equiv \Delta S_S + \Delta S_U - \beta Q \geq I_{S:U}(\tau) \geq 0$$



Repeated interaction QME



Effective dynamics

Effect of a kick: $U = e^{-iV_{SU}}$

$$\mathcal{J}_S \rho_S(t) \equiv \text{tr}_U \{ U \rho_S(t) \otimes \rho_U U^\dagger \}$$

$$\mathcal{J}_U \rho_U \equiv \text{tr}_S \{ U \rho_S(t) \otimes \rho_U U^\dagger \}$$

$$d_t \rho_S(t) = -i[H_S(t), \rho_S(t)] + \mathcal{L}_\beta \rho_S(t) + \mathcal{L}_{\text{new}} \rho_S(t)$$

$$\mathcal{L}_{\text{new}} \rho_S(t) \equiv \gamma(\mathcal{J}_S - 1)\rho_S(t)$$

Thermodynamics

1st law
$$d_t E_S(t) = \dot{W}_S(t) + \dot{W}_{SU}(t) + \dot{Q}(t) - d_t E_U(t)$$

$$\dot{W}_S = \text{tr}_S \{ \rho_S(t) d_t H_S(t) \}$$

$$\begin{aligned} \dot{W}_{SU} &= \gamma \text{tr}_{SU} \{ [H_S(t) + H_U] [U \rho_S(t) \rho_U U^\dagger - \rho_S(t) \rho_U] \} \\ &= \gamma \text{tr}_S \{ H_S(t) (\mathcal{J}_S - 1) \rho_S(t) \} + \gamma \text{tr}_U \{ H_U (\mathcal{J}_U - 1) \rho_U \} \end{aligned}$$

$$\dot{Q}(t) = \text{tr}_S \{ H_S(t) \mathcal{L}_\beta \rho_S(t) \}$$

$$d_t E_U(t) = \gamma \text{tr}_U \{ H_U (\mathcal{J}_U - 1) \rho_U \}$$

2nd law
$$\dot{\Sigma}_S(t) = d_t S_S(t) + d_t S_U(t) - \beta \dot{Q} \geq 0$$

$$\neq -\text{tr} \{ [\mathcal{L}_0 \rho_S(t)] [\ln \rho_S(t) - \ln \rho_\beta^S(t)] \} - \text{tr} \{ [\mathcal{L}_{\text{new}} \rho_S(t)] [\ln \rho_S(t) - \ln \bar{\rho}_{\text{new}}] \}$$

thermodynamics cannot always be deduced from dynamics alone

Units entropy changes

Approach 1:

$$\rho_U(t) = \mathcal{J}_U \rho_U$$

$$d_t S_U(t) = \gamma(-\text{tr}_U \{(\mathcal{J}_U \rho_U) \ln(\mathcal{J}_U \rho_U)\} + \text{tr}_U \{\rho_U \ln \rho_U\})$$

Approach 2:

Fraction of units which interacted $d_t n_t = \gamma N$

$$\bar{\rho}_U(t) = \frac{n_t}{N} \mathcal{J}_U \rho_U + \frac{N - n_t}{N} \rho_U$$

$$d_t \bar{S}_U(t) = -d_t \text{tr}_U \{\bar{\rho}_U(t) \ln \bar{\rho}_U(t)\} = -\gamma \text{tr}_U \{[(\mathcal{J}_U - 1)\rho_U] \ln \rho_U\}$$

Different by $d_t \bar{S}_U(t) - d_t S_U(t) = \gamma D(\mathcal{J}_U \rho_U \| \rho_U)$ “mixing” contribution

Thermal units $\rho_U = \rho_{\beta'}^U$ $\left\{ \begin{array}{l} d_t S_U(t) = \beta' d_t E_U(t) - \gamma D(\mathcal{J}_U \rho_{\beta'}^U \| \rho_{\beta'}^U) \\ d_t \bar{S}_U(t) = \beta' d_t \bar{E}_U(t) \quad \text{ideal reservoir} \end{array} \right.$

More...

Quantum master equation including degenerate states:

[Bulnes-Cuetara, Esposito & Schaller, *Entropy* **18**, 447 (2016)]

Fast periodic driving using master equation and Floquet theory:

[Bulnes-Cuetara, Engel & Esposito, *NJP* **18**, 447 (2016)]

Strong coupling using polaron transformation and quantum master equation:

[Krause, Brandes, Esposito & Schaller, *JCP* **142**, 134106 (2015)]

[Schaller, Krause, Brandes & Esposito, *NJP* **15**, 033032 (2013)]

Strong coupling using Nonequilibrium Green's functions:

[Esposito, Ochoa & Galperin, *PRL* **114**, 080602 (2015)]

[Esposito, Ochoa & Galperin, *PRB* **92**, 235440 (2015)]

Strong coupling (classical) using time scale separation:

[Strasberg & Esposito, *arxiv:1703.05098*]

[Esposito, *Phys. Rev. E* **85**, 041125 (2012)]

Perspectives

- Stochastic thermodynamics in the thermodynamic limit



Interplays between $N \rightarrow \infty$ and $t \rightarrow \infty$

- Chemical Reaction Networks (Stochastic & Deterministic)



Toward energy and information processing in biology

Thank you