Nonequilibrium Thermodynamics of Small Systems: Classical and Quantum Aspects

Massimiliano Esposito

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Introduction

Thermodynamics in the 19th century:

Thermodynamics in the 21th century:
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
- Quantum effects (low temperatures)
  - Traditional stochastic descriptions fail
    - Stochastic descriptions taking coherent effects into account are needed

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


Markovian master equation:

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

\[ W_{ij} = \sum_{\nu} W_{ij}^{(\nu)} \]

Energy and Matter currents:

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

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

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 balance:

\[ E = \sum_i \epsilon_i p_i \quad , \quad N = \sum_i n_i p_i \quad , \quad S = \sum_i \left[ -k_b \ln p_i \right] p_i \]

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

Entropy production in the reservoirs:

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

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

Driving reservoirs

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

\[ \dot{Q}^{(\nu)} = I_{E}^{(\nu)} - \mu^{(\nu)} I_{M}^{(\nu)} \]

Slow driving with 1 reservoir:

\[ \dot{S}_i \approx 0 \]

equilibrium thermo

\[ T d_t S = d_t E - \dot{W}_m - \mu d_t N \]
2) Universal Fluctuation Relation

Energy balance: \( \epsilon_{i_1}(\lambda_t) - \epsilon_{i_0}(\lambda_0) = w_m [\Gamma|\lambda] + w_c [\Gamma|\lambda] + \sum_{\nu=1}^{N} (\Delta \epsilon_{\nu} [\Gamma|\lambda] - \mu_{\nu}\Delta n_{\nu} [\Gamma|\lambda]) \)

Particle balance: \( n_{i_1} - n_{i_0} = \sum_{\nu=1}^{N} \Delta n_{\nu} [\Gamma|\lambda] \)

Entropy balance: \( \Delta_i s [\Gamma|\lambda] = \ln \left( \frac{P[\Gamma, \lambda]}{\tilde{P}[\tilde{\Gamma}, \lambda]} \right) = \ln p_{i_0}(0) - \ln p_{i_t}(t) - \sum_{\nu=1}^{N} \beta_{\nu} q_{\nu} [\Gamma|\lambda] \)

Integral fluctuation theorem: \( \langle e^{-\Delta_i s} \rangle = 1 \quad \Rightarrow \quad \langle \Delta_i s \rangle \geq 0 \)
Detailed FT for entropy production

\[
\ln \frac{P(\Delta_i s)}{\tilde{P}(-\Delta_i s)} = \Delta_i s
\]

if \( \Delta_i s [\Gamma|\lambda] = -\tilde{\Delta}_i s [\tilde{\Gamma}|\lambda] \)

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 \( t \to \infty \): Current FT

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

\[
\ln \frac{P(w_m, \{\Delta \epsilon_\nu\}, \{\Delta n_\nu\})}{\tilde{P}(-w_m, \{-\Delta \epsilon_\nu\}, \{-\Delta n_\nu\})} = \beta_1 (w_m - \Delta \Phi_{_1}^{eq}) + \sum_{\nu=2}^{N} (A_\nu^e \Delta \epsilon_\nu + A_\nu^n \Delta n_\nu)
\]

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

\[= \beta_1 - \beta_\nu = \beta_\nu \mu_\nu - \beta_1 \mu_1 \]
Isothermal example: driven junction

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

Setup: 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

...
3) **Finite-time thermodynamics**

a) Steady state energy conversion

- *Thermoelectricity:*

  ![Diagram of thermoelectric effect]

  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:*

  \[ \sigma = J_1 A_1 + J_2 A_2 \geq 0 \]
  \[ \sigma_1 > 0 \quad \sigma_2 < 0 \]
  input \quad output

  \[ \eta = -\frac{\sigma_2}{\sigma_1} = 1 - \frac{\sigma}{\sigma_1} \leq 1 \]
  \[ \mathcal{P} = -\sigma_2 \]
b) Energy conversion in the 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:
\[ \eta^* = \frac{\text{Det}[L] + L_{11}L_{22} - 2\sqrt{\text{Det}[L]L_{11}L_{22}}}{L_{11}L_{22} - \text{Det}[L]} \leq 1 \]

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

Efficiency at maximum power:
\[ \eta^* = \frac{1}{2} - \frac{\text{Det}[L]}{L_{11}L_{22} + \text{Det}[L]} \leq \frac{1}{2} \]
c) Efficiency at maximum power beyond linear regime

Phenomenological models

\[ \eta_{CA} = 1 - \sqrt{1 - \eta_C} \approx \frac{\eta_C}{2} + \frac{\eta_C^2}{8} + \frac{\eta_C^3}{16} + \ldots \]


Linear
(In case of tight coupling)

Nonlinear
(In presence of a left-right symmetry)
Exactly solvable models using stochastic thermodynamics

**Thermoelectric quantum dot**

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

\[ \mathcal{W} = (\mu_l - \mu_r)I_e^- \quad \eta = -\frac{\mathcal{W}}{\dot{Q}_r} \]

\[ \dot{Q}_r = (\varepsilon - \mu_r)I_e^- \]

**Photoelectric nanocell**


\[ \mathcal{W} = (\mu_r - \mu_l)I_e^- \quad \eta = -\frac{\mathcal{W}}{\dot{Q}_s} \]

\[ \dot{Q}_r = (\varepsilon - \mu_r)I_e^- \]

(C) \[ \Gamma_l = \Gamma_r = \Gamma_s = 1 \]

\[ \Gamma_{nr} = 0.1, 1, 10 \]
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


**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

\[ \sigma = \eta C q_h / T + \omega / T \]

\[ \eta = \frac{-\sigma_2}{\sigma_1} = \frac{-\omega}{\eta C q_h} \]

\[ P_t(\sigma_1, \sigma_2) \propto \exp\{-tI(\sigma_1, \sigma_2)\} \]

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

Carnot is the least probable efficiency!!

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

\[ J(\eta) \leq J(1) \]

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: \( \eta^* = \bar{\eta}_{re}{\nu} \)  Consequence of FT!

Carnot efficiency
b) Finite-time efficiency fluctuations


- 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: $P_t(\eta \to \pm\infty) \propto \eta^{-2}$

- 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)  $\phi(\gamma, \lambda) = \int \frac{dE}{2\pi} \ln \left(1 + T(E)\right)$

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

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

The long time results can be generalized:
- to time-asymmetric drivings
- to quantum systems (NEGF approach)

The finite-time behavior:
- Polettini, Verley, Esposito, *Finite-time efficiency fluctuations: Enhancing the most likely value*, PRL 114, 050601 (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: \[ d_t p_i = \sum_j W_{ij} p_j \]

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

0th law

Equilibrium: \[ p_i^{eq} = \exp \left\{ -\frac{(\epsilon_i - F^{eq})}{k_b T} \right\} \]
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

Efficiency:
\[ \eta = \frac{-\Delta S}{-Q/T} = 1 - \frac{\Delta_i S}{-Q/T} \leq 1 \]

Power:
\[ P(Q, t) = \frac{-\Delta S}{t} \]

Accuracy-dissipation trade-offs:
Nonequilibrium state as a resource

Nonequilibrium free energy
\[ F \equiv E - TS \]
\[ F - F^{\text{eq}} = T D(p|p^{\text{eq}}) \geq 0 \]

1\textsuperscript{st} law + 2\textsuperscript{nd} law:
\[ T \Delta_i S = W - \Delta F \geq 0 \]

\[ W_{\text{diss}} \equiv W - \Delta F^{\text{eq}} = T \Delta_i S + T D(p_t|p_t^{\text{eq}}) \geq 0 \]
\[ \geq 0 \]
\[ \geq 0 \]
\[ \geq 0 \]

\[ D(p|p') = k_b \sum_i p_i \ln \frac{p_i}{p_i'} \geq 0 \]
\[ p_i^{\text{eq}} = \exp \left\{ -\frac{(\epsilon_i - F^{\text{eq}})}{k_b T} \right\} \]

Nonequilibrium free energy

Optimal extraction:
\[ x \quad 0 \quad 0 \]

Pure waist:
\[ 0 \quad x \quad 0 \]

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

Second law and Landauer principle far from equilibrium, Esposito and Van den Broeck, EPL 95, 40004 (2011)
2) **Measurement and feedback**

**Phenomenological approach**

\[ p_{i|m}(0) = \frac{p_{im}(0)}{p_m} \quad p_{i|m}(t) = \frac{p_{im}(t)}{p_m} \]

**Measurement**

\[
\delta F_{\text{meas}} = \sum_m p_m F^m - F = TS - T \sum_m p_m S^m = TD(p_{i,m} | p_{i} p_m) \geq 0 \]

**Feedback**

\[
T \Delta_i S^m = W^m - \Delta F^m \geq 0 \]

\[
\sum_m p_m \]

\[
W - (F_t - F_0) \geq T(I_t - I_0) \geq -TI_0 \]

without feedback \[ \geq 0 \]
Ex1: Szilard engine

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

$S_L^L = k_b \ln \frac{V}{2}$

$S_R^R = k_b \ln \frac{V}{2}$

$p_L = 1/2$

$p_R = 1/2$

$S_0 = k_b \ln V$

$S_t = k_b \ln V$

Measurement

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

Feedback

$W = -k_b T \ln 2$
Ex2: Erasure with feedback in finite time

Finite-time erasing of information stored in fermionic bits, Diana, Bagci, Esposito, Phys. Rev. E 85, 041125 (2012)
3) Bipartite perspective

Non-autonomous systems (measurement and feedback)

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

\[ \Delta E_{XY} = \Delta E_X + \Delta E_Y \]
\[ \Delta F_{XY} = \Delta F_X + \Delta F_Y - T \Delta I \]

Measurement
\[ \Delta E_X = 0 \]
\[ \Delta E_Y = \Delta S_Y = 0 \]

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

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: \( d_t I = 0 \)

\[ \dot{\mathcal{I}} = \dot{I}^X = -\dot{I}^Y \]

\[ \dot{S}_i^X = \dot{S}_r^X - \dot{\mathcal{I}} \geq 0 \]

\[ \dot{S}_i^Y = \dot{S}_r^Y + \dot{\mathcal{I}} \geq 0 \]


At steady state see also Hartich, Barato, Seifert, JSM P02016 (2014)
Ex: Two coupled quantum dots

\[ \dot{S}_i = -J_e \frac{\Delta \mu}{T} + J(C) \left( \frac{U}{T_D} - \frac{U}{T} \right) \geq 0 \]

\[ J_e = J(C_Y^0) + J(C_Y^1) \]

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

\[ \dot{S}_i^X = J(C) \left[ \frac{U}{T_D} - \mathcal{F}^I(C) \right] \geq 0 \]

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

Maxwell demon limit: \( U \to 0 \quad T_D \to 0 \quad U/T_D = \text{Cte} \)

*Thermodynamics of a physical model implementing a Maxwell demon, Strasberg, Schaller, Brandes, Esposito, Phys. Rev. Lett. 110, 040601 (2013)*
Thermodynamics with continuous information flow, Horowitz and Esposito, Phys. Rev. X 4, 031015 (2014)
4) Conclusions and perspectives


- 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
  - Jun, Gavrilo, Bechhoefer, PRL 113, 190601 (2014)

- 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

1\textsuperscript{st} law: \[ d_t E = \dot{W} + \dot{Q} \]

2\textsuperscript{nd} 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

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

\[ \rho_{XY}(0) = \rho_X(0)\rho_Y(0) \quad \rho_{XY}(\tau) = U_\tau \rho_X(0)\rho_Y(0)U_\tau^\dagger \]

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

\[ I_{X:Y}(t) \equiv S_X(t) + S_Y(t) - S_{XY}(t) \quad S_{XY}(t) \equiv -\text{tr}_{XY}\{\rho_{XY}(t)\ln \rho_{XY}(t)\} \]

\[ = \Delta S_X(\tau) + \Delta S_Y(\tau) = D[\rho_{XY}(t)||\rho_X(t)\rho_Y(t)] \geq 0 \]
System X – Reservoir R

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

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

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

1\textsuperscript{st} law:
\[ d_t E_X(t) = \dot{W}(t) + \dot{Q}(t) \]
\[ \begin{cases} 
\dot{W}(t) = d_t E_{XY}(t) \\
\dot{Q}(t) \equiv -\text{tr}_R \{H_R d_t \rho_R(t)\} 
\end{cases} \]

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

[Esposito, Lindenberg, & Van den Broeck, NJP 12, 013013 (2010)]
Ideal reservoir

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

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

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

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

Summary: \begin{align*}
1^{\text{st}}, 2^{\text{nd}} \text{ law, strong coupling} \\
\text{no } 0^{\text{th}} \text{ law, } \Sigma \geq 0 \text{ but not } \dot{\Sigma}
\end{align*}
3) Born-Markov-Secular QME

\[ H_{\text{tot}}(t) = H_X(t) + H_R + \sum_{k} A_k \otimes B_k \]

Effective dynamics

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

\[ \mathcal{L}_\beta(t)\rho(t) = \sum_\omega \sum_{k,\ell} \gamma_{k\ell}(\omega) \left( A_\ell(\omega)\rho(t)A_k^\dagger(\omega) - \frac{1}{2}\{A_k^\dagger(\omega)A_\ell(\omega), \rho(t)\} \right) \]

\[ A_k(\omega) \equiv \sum_{\epsilon - \epsilon' = \omega} \Pi_\epsilon A_k \Pi_{\epsilon'} \quad \gamma_{k\ell}(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \text{tr}_R\{B_k(t)B_\ell(0)\rho_\beta^R\} \]

Local detailed balance: \[ \gamma_{k\ell}(-\omega) = e^{-\beta \omega} \gamma_{\ell k}(\omega) \]

\[ \mathcal{L}_\beta(t)\rho_X^\beta(t) = 0, \quad \rho_X^\beta(t) = \frac{e^{-\beta H_X(t)}}{Z_X(t)} \]
Thermodynamics

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

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

1\textsuperscript{st} law \[ d_t E_X(t) = \dot{W}(t) + \dot{Q}(t) \]

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

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

2\textsuperscript{nd} law \[ \dot{\Sigma}(t) = d_t S_X(t) - \beta \dot{Q}(t) \]

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

Summary:\[
\left\{ \begin{array}{c}
0\textsuperscript{th}, 1\textsuperscript{st}, 2\textsuperscript{nd} \text{ law, } \dot{\Sigma} \geq 0 \text{ , slow trsf. } \dot{\Sigma} \approx 0 \\
\text{but weak coupling}
\end{array} \right\}
\]
4) A Landau-Zener approach

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

Prob. diabatic transition:

\[ R_i = \exp \left\{ -\pi \frac{\delta_i^2}{(2\hbar \dot{\epsilon}_i)} \right\} \]

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

Validity: \[ \Delta t_i^+ > t_i^{lz} \quad \Delta \epsilon_i^+ > \delta_i \quad \rightarrow \quad \Delta \epsilon_i^+ > \sqrt{\hbar \dot{\epsilon}_i}, \delta_i \]

[Barra & Esposito, PRE 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

\[ \frac{M_i^+}{M_i^-} = e^{-\beta (\varepsilon_i - \mu)} \]

Exact vs stochastic dynamics

[Barra & Esposito, PRE 93, 062118 (2016)]
First law \( \Delta E_{i+} = E_{i+1} - E_i = W_{i+} + Q_{i+} \)

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

\[
W_{i+} = W_{i+}^m + W_{i+}^c \left\{ \begin{array}{l}
W_{i+}^m = (\varepsilon_{i+1} - \varepsilon_i)p_{i+1} \\
W_{i+}^c = \mu(p_{i+1} - p_i)
\end{array} \right.
\]

Second law \( \Delta S_{i+} = S_{i+1} - S_i = \Sigma_{i+} + Q_{i+}/T \)

\[
S_i = -k_B p_i \ln p_i - k_B (1 - p_i) \ln (1 - p_i)
\]

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

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

\[ W^m_{i+} - \Delta \Omega^\text{eq}_{i+} \]

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

at crossing

**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 \( i \to i+1 \): \[ W^\text{diss}_{i+} = k_B T D(f_i|f_{i+1}) \]

Reversibility only occurs if:

\( \Delta \varepsilon, \delta, \dot{\varepsilon} \to 0 \)

\( \Delta \varepsilon > \delta \gg \sqrt{\hbar \dot{\varepsilon}} \)

\[ \Sigma_{i+}, W^\text{diss}_{i+} \sim \Delta \varepsilon^2 \]

[Barra & Esposito, PRE 93, 062118 (2016)]
\[ \Sigma_{i+} = \frac{W_{i+}^{\text{diss}}}{T} - k_B D(p_{i+1}|f_{i+1}) + k_B D(p_i|f_i) \geq 0 \]

**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

\[
\frac{P(w^m)}{\tilde{P}(-w^m)} = \exp \left\{ \beta \left( w^m - \Delta \Omega^{eq} \right) \right\}
\]

System initially at equilibrium

Full system: two point measurement approach

\[
\Delta \Omega^{eq}
\]

vs

System: stochastic trajectory approach

[Barra & Esposito, PRE 93, 062118 (2016)]
QM diabatic regime: continuous limit

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

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

\[ d_i = 1 / \Delta \varepsilon_i \quad \Delta t_{i+} = 1 / (\dot{\varepsilon}_i d_i) \]

\[ d_t p = w^+ (1 - p) - w^- p \]

\[ w^+ = \frac{\pi \delta^2 (\epsilon_t) d(\epsilon_t)}{2\hbar} f(\epsilon_t) \quad w^- = \frac{\pi \delta^2 (\epsilon_t) d(\epsilon_t)}{2\hbar} (1 - f(\epsilon_t)) \]

Pauli master equation with Fermi golden rule rates

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

Exact identities

\[ \Delta E_X = \Delta E_U + \Delta E_S = W + Q \]
\[ \Sigma = \Delta S_S + \Delta S_U - I_{S:U}(\tau) - \beta Q \geq 0 \]

\[ \Delta S_X \]

\[ \Delta E_{SU} \equiv \lim_{\epsilon \searrow 0} \int_{-\epsilon}^{\tau - \epsilon} dt \frac{dE_X(t)}{dt} = \Delta E_S + \Delta E_U \]

\[ W \equiv \lim_{\epsilon \searrow 0} \int_{-\epsilon}^{\tau - \epsilon} dt \dot{W}(t) = W_X + W_{sw} \]
\[ Q \equiv \lim_{\epsilon \searrow 0} \int_{-\epsilon}^{\tau - \epsilon} dt \dot{Q}(t) \]

\[
\begin{align*}
W_X &= \int_{0}^{\tau} dt tr_X \{ \rho_X(t) d_t H_S(t) \} \\
&\quad + \lim_{\epsilon \searrow 0} \int_{\epsilon}^{\tau - \epsilon} dt' tr_X \{ \rho_X(t) d_t V_{SU}(t) \} \\
W_{sw} &= tr_X \{ V_{SU}(0) \rho_X(0) - V_{SU}(\tau') \rho_X(\tau') \}
\end{align*}
\]

[Strasberg, Schaller, Brandes & Esposito, PRX 7, 021003 (2017)]
1\textsuperscript{st} law \[ \Delta E_S = W + Q - \Delta E_U \]

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

[Strasberg, Schaller, Brandes & Esposito, PRX 7, 021003 (2017)]
Repeated interaction QME

Effective dynamics

Effect of a kick: \[ U = e^{-iV_{SU}} \]

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

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

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

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

[Strasberg, Schaller, Brandes & Esposito, PRX 7, 021003 (2017)]
Thermodynamics

$1^{\text{st}}$ law

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

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

$$\dot{W}_{SU} = \gamma \text{tr}_{SU}\{[H_S(t) + H_U][U \rho_S(t) \rho U U^\dagger - \rho_S(t) \rho U]\}$$

$$= \gamma \text{tr}_S\{H_S(t)(J_S - 1) \rho_S(t)\} + \gamma \text{tr}_U\{H_U(J_U - 1) \rho_U\}$$

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

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

$2^{\text{nd}}$ law

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

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

thermodynamics cannot always be deduced from dynamics alone

[Strasberg, Schaller, Brandes & Esposito, PRX 7, 021003 (2017)]
Units entropy changes

Approach 1:

\[ \rho_U(t) = \mathcal{J}_U \rho_U \]
\[ d_t S_U(t) = \gamma (-\operatorname{tr}_U \{ (\mathcal{J}_U \rho_U) \ln(\mathcal{J}_U \rho_U) \} + \operatorname{tr}_U \{ \rho_U \ln \rho_U \}) \]

Approach 2: \text{Fraction of units which interacted} \quad d_t n_t = \gamma N

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

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

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

Thermal units \quad \rho_U = \rho_{\beta'}^U \quad \begin{cases} 
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{cases}

[Strasberg, Schaller, Brandes & Esposito, PRX 7, 021003 (2017)]
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 $N \to \infty$ and $t \to \infty$

- Chemical Reaction Networks (Stochastic & Deterministic)
  Toward energy and information processing in biology

Thank you