Thermodynamics of Information Processing

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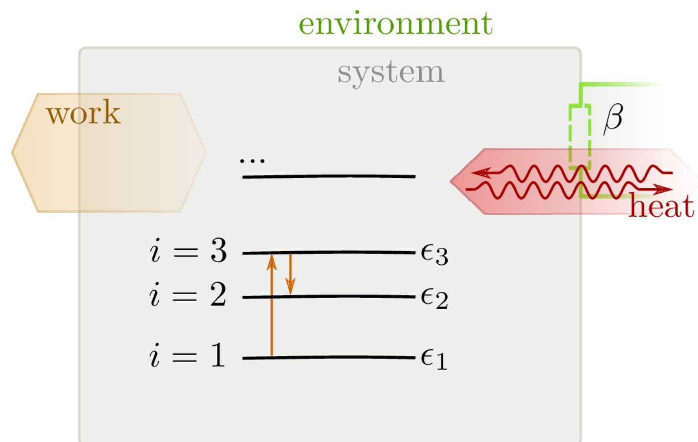
Outline

- Work principle in Stochastic Thermodynamics
- Work principle in Chemical Reaction Networks
    - Homogeneous
    - Reaction-Diffusion
- Conclusions

Stochastic Thermodynamics



Master Equation

$$d_t p_i = \sum_j W_{ij}\, p_j$$

Local Detailed Balance

may depend on time

$$\ln \frac{W_{ij}}{W_{ji}} = -\beta(\epsilon_i - \epsilon_j)$$

0th law: at equilibrium

$$p_i^{eq} = e^{-\beta(\epsilon_i - F^{eq})}$$

Energy: $E = \sum_i \epsilon_i p_i$ Entropy: $S = \sum_i p_i \{-k_B \ln p_i\}$

1st law
Energy Balance

$$d_t E = \underbrace{\boxed{\sum_i d_t \epsilon_i \, p_i}}_{\text{Work } \dot{W}} + \underbrace{\boxed{\sum_i \epsilon_i \, d_t p_i}}_{\text{Heat } \dot{Q}}$$

2nd law
Entropy Balance

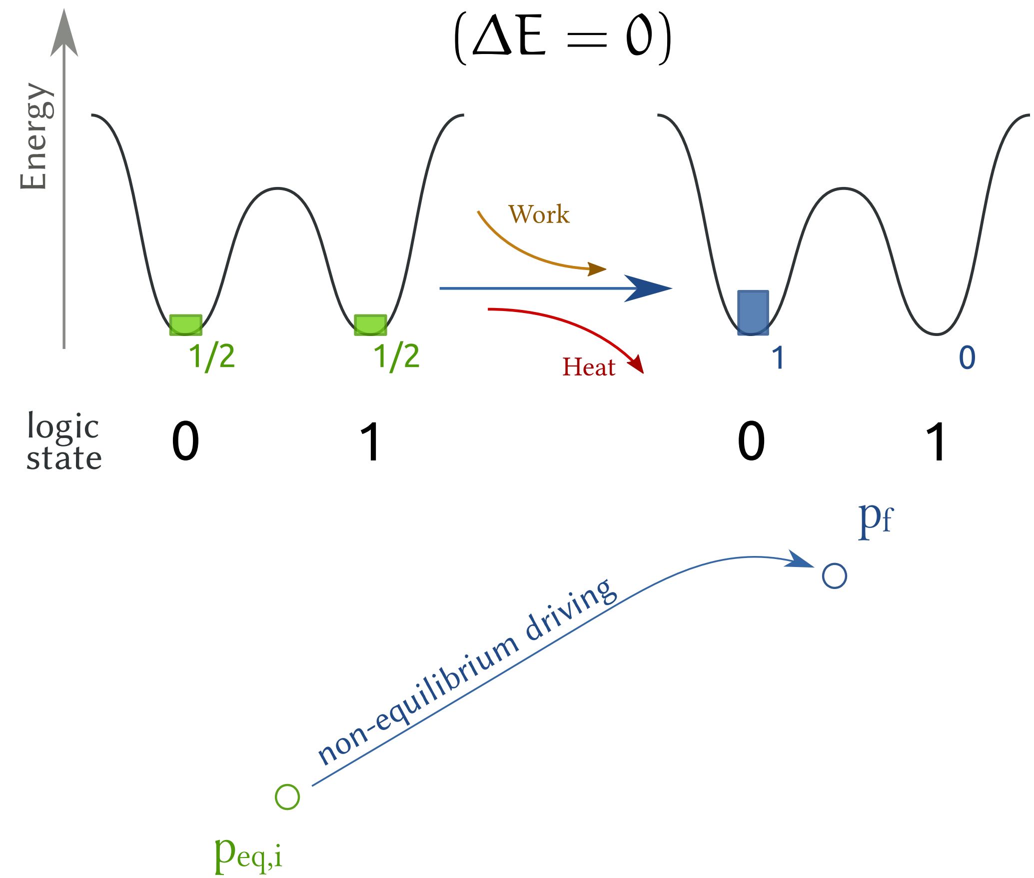
$$\dot{\Sigma} = \underbrace{\boxed{d_t S}}_{\text{Entropy change}} \underbrace{\boxed{-\frac{\dot{Q}}{T}}}_{\text{Entropy change in the reservoir}} \geqslant 0$$

Entropy production

$$\dot{\Sigma} = k_B \sum_{i,j} \left(W_{ij} p_j - W_{ji} p_i \right) \ln \frac{W_{ij} p_j}{W_{ji} p_i} \geqslant 0$$

[Van den Broeck & Esposito, *Physica A* **418**, 6 (2015)]

Landauer's Principle

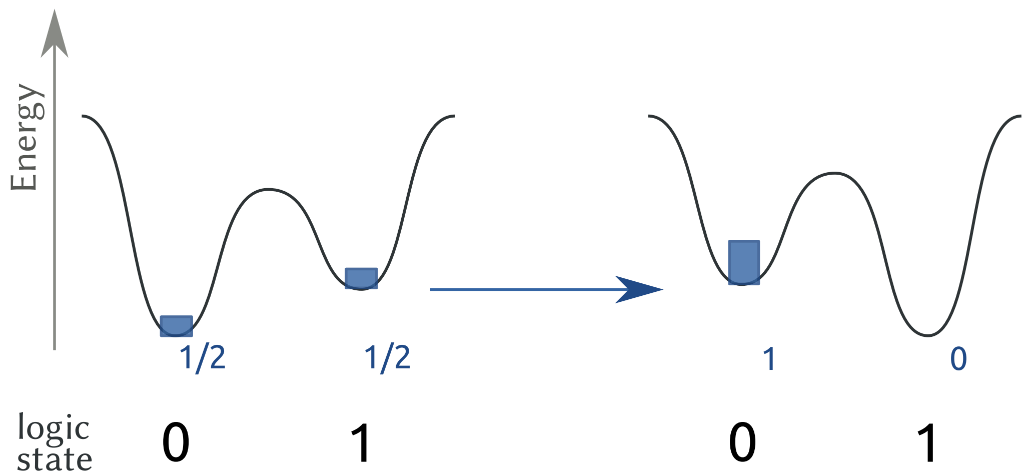


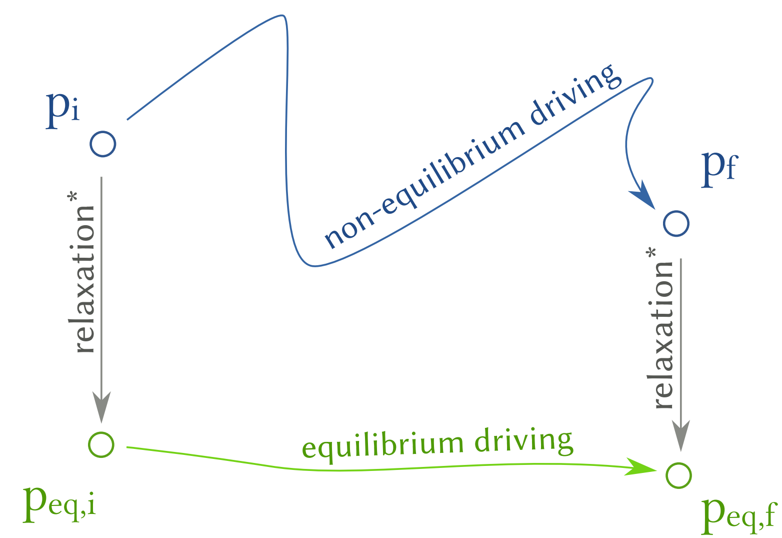
$$W = -Q \geqslant T(S_i^{eq} - S_f) = k_B T \ln 2$$

In finite time: accuracy-dissipation trade-offs

[Diana, Bagci, Esposito, *PRE* **85**, 041125 (2012)]

Work Principle





In general (combining 1st and 2nd law): $T\dot{\Sigma} = W - \Delta F \geqslant 0$

nonequilibrium free energy:

$$F := E - TS = F_{eq} + k_B T \mathcal{D}(p \| p^{eq})$$

relative entropy:

$$\mathcal{D}(p \| p^{eq}) := \sum_i p_i \ln \frac{p_i}{p_i^{eq}} \geqslant 0$$

$$W = \Delta F^{eq} + k_B T \underbrace{\mathcal{D}(p_f \| p_f^{eq})}_{\geqslant 0} - k_B T \underbrace{\mathcal{D}(p_i \| p_i^{eq})}_{\leqslant 0} + \underbrace{T \Delta_i S}_{\geqslant 0}$$

[Esposito & Van den Broeck, *EPL* **95**, 40004 (2011)]

Nonequilibrium State as a Resource

Nonequilibrium state in a given energy landscape

$$k_B T\, \mathcal{D}(p_i \| p_i^{eq}) = -(W - \Delta F^{eq}) + T\Delta_i S + k_B T\, \mathcal{D}(p_f \| p_f^{eq})$$

Pure waist:	0	0	x	0
Optimal extraction:	x	0	0	0

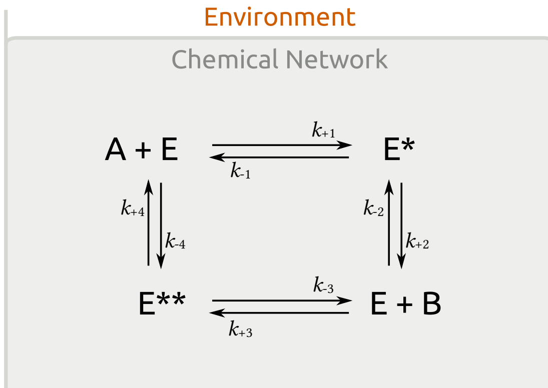
[Esposito & Van den Broeck, *EPL* **95**, 40004 (2011)]

Dynamics of Closed CRNs

$$\boldsymbol{\nu}_+ \cdot \mathbf{Z} \underset{\mathbf{k}_-}{\overset{\mathbf{k}_+}{\rightleftharpoons}} \boldsymbol{\nu}_- \cdot \mathbf{Z}$$

Stoichiometric matrix

$$\boldsymbol{\nu}_- - \boldsymbol{\nu}_+ =: \mathbb{S}$$



$$\mathbb{S} = \begin{array}{cc} \begin{array}{cccc} 1 & 2 & 3 & 4 \end{array} & \\ \begin{pmatrix} -1 & 1 & -1 & 1 \\ 1 & -1 & 0 & 0 \\ 0 & 0 & 1 & -1 \\ -1 & 0 & 0 & 1 \\ 0 & 1 & -1 & 0 \end{pmatrix} & \begin{array}{l} \mathrm{E} \\ \mathrm{E}^* \\ \mathrm{E}^{**} \\ \mathrm{A} \\ \mathrm{B} \end{array} \end{array}$$

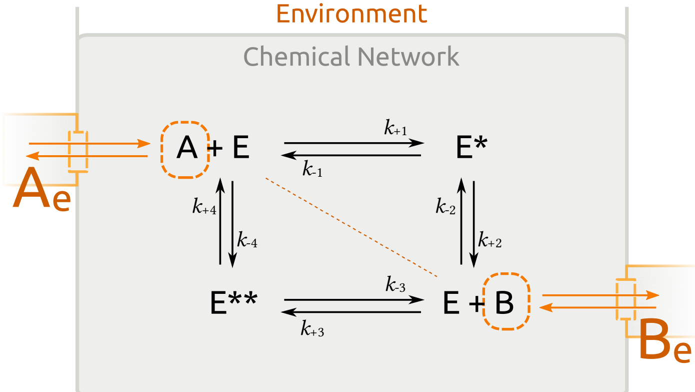
Rate equations $\quad \mathrm{d}_t[\mathbf{Z}] = \boxed{\mathbb{S}\,\mathbf{J}} \quad$ Reactions

Ideal Dilute Solution + Elementary Reactions
= Mass action kinetics

$$\mathbf{J} = \mathbf{J}_+ - \mathbf{J}_-$$

$$\mathbf{J}_\pm = \mathbf{k}_\pm [\mathbf{Z}]^{\cdot \boldsymbol{\nu}_\pm}$$

Dynamics of Open CRNs



$$\boldsymbol{\nu}_+ \cdot \mathbf{Z} \underset{\mathbf{k}_-}{\overset{\mathbf{k}_+}{\rightleftharpoons}} \boldsymbol{\nu}_- \cdot \mathbf{Z}$$

Stoichiometric matrix

$$\boldsymbol{\nu}_- - \boldsymbol{\nu}_+ =: \mathbb{S} = \begin{pmatrix} \mathbb{S}^{\mathrm{X}} \\ \mathbb{S}^{\mathrm{Y}} \end{pmatrix}$$

$$[\mathbf{Z}] = \begin{pmatrix} [\mathbf{X}] \\ [\mathbf{Y}] \end{pmatrix} \begin{matrix} \text{Internal} \\ \text{Chemostatted} \end{matrix}$$

$$\mathbb{S} = \begin{array}{c} \left(\begin{array}{cccc} -1 & 1 & -1 & 1 \\ 1 & -1 & 0 & 0 \\ 0 & 0 & 1 & -1 \\ \hdashline -1 & 0 & 0 & 1 \\ 0 & 1 & -1 & 0 \end{array}\right) \end{array} \begin{array}{l} \mathbb{S}^{\mathrm{X}} \\ \\ \\ \mathbb{S}^{\mathrm{Y}} \\ \end{array}$$

Rate equations

$$\mathrm{d}_t[\mathbf{X}] = \mathbb{S}^{\mathrm{X}}\mathbf{J}$$

$$\mathrm{d}_t[\mathbf{Y}] = \underbrace{\mathbb{S}^{\mathrm{Y}}\mathbf{J}}_{\text{Reactions}} + \underbrace{\mathbf{I}}_{\text{Exchange}}$$

In open *nondriven* CN $\quad \mathrm{d}_t[\mathbf{Y}] = 0$

Thermodynamics of CRNs

Enthalpy of formation

Entropy of formation

Ideal Dilute Solutions

Local equilibrium

$$\boldsymbol{\mu} = \underbrace{\boldsymbol{h}^\circ \overbrace{- \mathrm{T}\boldsymbol{s}^\circ}^{-\mathrm{T}\boldsymbol{s}}}_{\boldsymbol{\mu}^\circ} + \mathrm{RT}\ln[\mathbf{Z}]$$

Standard-state chemical potential

Local Detailed Balance

$$\ln\frac{\mathbf{k}_+}{\mathbf{k}_-} = -\frac{\boldsymbol{\mu}^\circ\cdot\mathbb{S}}{\mathrm{RT}}$$

0^{th} law of Thermodynamics: Closed CRN relax to equilibrium

$$\mathbf{J}^{\mathrm{eq}} = \mathbf{J}_+^{\mathrm{eq}} - \mathbf{J}_-^{\mathrm{eq}} = 0$$

detailed-balance

First and Second Law

CRN Enthalpy:

$$\mathrm{H} = \boldsymbol{h}^\circ \cdot [\mathbf{Z}]$$

CRN Entropy:

$$\mathrm{S} = \left(\boldsymbol{s}^\circ - \mathrm{T}\ln[\mathbf{Z}]\right) \cdot [\mathbf{Z}] + \mathrm{R}\underbrace{[\mathrm{Z}]}^{\text{total concentration}}$$

1st law
Enthalpy Balance

$$\boxed{\mathrm{d_t H} = \boldsymbol{h}^\circ \cdot \mathbb{S}\mathbf{J} + \boldsymbol{h}_{\mathrm{Y}} \cdot \mathbf{I} = \boldsymbol{h}^\circ \cdot \underbrace{\mathbb{S}\mathbf{J} + \mathrm{T}\boldsymbol{s}_{\mathrm{Y}} \cdot \mathbf{I}}_{\text{Heat Flow } \dot{\mathrm{Q}}} + \overbrace{\boldsymbol{\mu}_{\mathrm{Y}} \cdot \mathbf{I}}^{\text{Chemical Work } \dot{W}_{\mathrm{chem}}}}$$

2nd law
Entropy Balance

$$\boxed{\dot{\Sigma} = \mathrm{d_t S} \underbrace{- \dot{\mathrm{Q}}/\mathrm{T}}_{\text{Entropy change in (thermal \& chemical) reservoirs}}}$$

Entropy production: $\mathrm{T}\dot{\Sigma} = -\boldsymbol{\mu} \cdot \mathbb{S}\,\mathbf{J} = (\mathbf{J}_+ - \mathbf{J}_-) \cdot \mathrm{RT}\ln\frac{\mathbf{J}_+}{\mathbf{J}_-} \geqslant 0$

[Rao & Esposito, *Phys. Rev. X* **6**, 041064 (2016)]

Cost for manipulating Nonequilibrium States

Closed CRN

Non-Eq. Gibbs free energy $\quad G := H - TS = G_{\mathrm{eq}} + RT\,\underbrace{\mathcal{L}\left([\mathbf{Z}] \,\middle|\, [\mathbf{Z}]_{\mathrm{eq}}\right)}_{\text{“Relative entropy”}}$

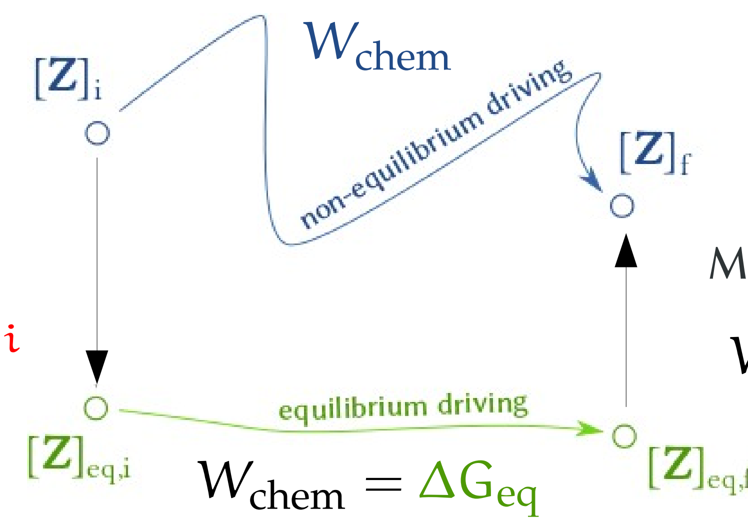
$$= [\mathbf{Z}] \cdot \ln \frac{[\mathbf{Z}]}{[\mathbf{Z}]_{\mathrm{eq}}} - \left([\mathrm{Z}] - [\mathrm{Z}]_{\mathrm{eq}}\right) \geqslant 0$$

$$W_{\mathrm{chem}} = \Delta G + T\Sigma = \Delta G_{\mathrm{eq}} + RT\,\underbrace{\Delta\mathcal{L}}_{\mathcal{L}_f - \mathcal{L}_i} + \underbrace{T\Sigma}_{\geqslant 0}$$

Relaxation to Eq: $\Sigma = RT\mathcal{L}_i$

or

Max work extracted: $W^{\max}_{\mathrm{chem}} = -RT\,\mathcal{L}_i$



Min work produced:

$W^{\min}_{\mathrm{chem}} = RT\,\mathcal{L}_f$

[Rao & Esposito, *Phys. Rev. X* **6**, 041064 (2016)]

Reaction—Diffusion

Reaction—Diffusion Equations

$$d_t[\mathbf{X}]_\mathbf{r} = \boxed{-\nabla\cdot\mathbf{J}^{X}_\mathbf{r}} + \boxed{\mathbb{S}^{X}\mathbf{j}_\mathbf{r}}$$

$$d_t[\mathbf{Y}]_\mathbf{r} = \boxed{-\nabla\cdot\mathbf{J}^{Y}_\mathbf{r}} + \boxed{\mathbb{S}^{Y}\mathbf{j}_\mathbf{r}} + \boxed{\mathbf{I}_\mathbf{r}}$$

Diffusion Reactions Exchange

Mass-action kinetics

$$\mathbf{j}^{\pm}_\mathbf{r} = \mathbf{k}_{\pm}[\mathbf{Z}]_\mathbf{r}^{\circ\boldsymbol{\nu}_{\pm}}$$

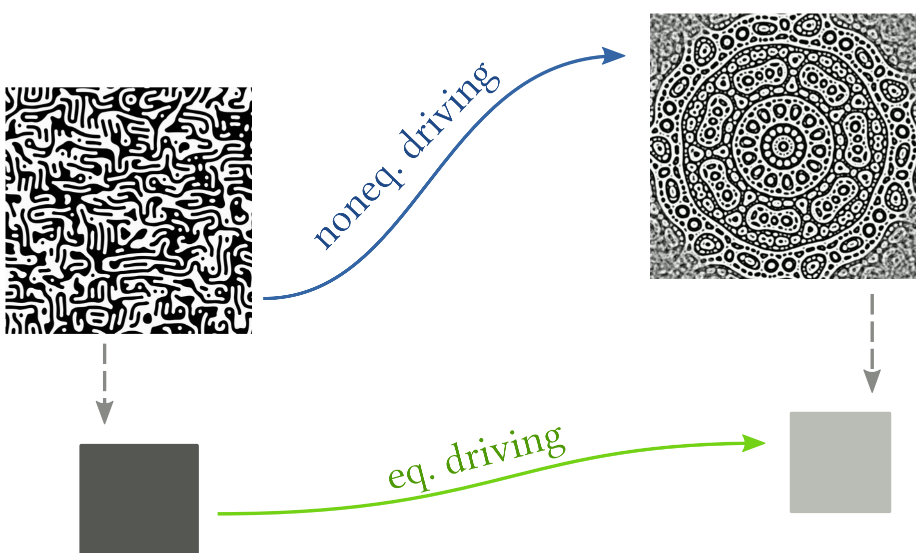
Diffusion: Fick's Law

$$\mathbf{J}_\mathbf{r} = -\mathbb{D}\nabla[\mathbf{Z}]_\mathbf{r}$$

Diffusion coefficients

$$\boxed{W = \Delta G_{eq} + RT\,\Delta\mathcal{L} + \underbrace{T\Sigma}_{\geqslant 0}}$$

$$= \int_{\mathcal{V}} d\mathbf{r}\left[[\mathbf{Z}]_\mathbf{r}\circ\ln\frac{[\mathbf{Z}]_\mathbf{r}}{[\mathbf{Z}]_{eq}} - ([Z]_\mathbf{r} - [Z]_{eq})\right] \geqslant 0$$



Spacial structuring takes work:

$$\mathcal{L}\left([\mathbf{Z}]_{patt}\middle|[\mathbf{Z}]_{eq}\right) \geqslant \mathcal{L}\left([\bar{\mathbf{Z}}]\middle|[\mathbf{Z}]_{eq}\right)$$

[Falasco, Rao & Esposito, *Phys. Rev. Lett.* **121**, 108301 (2018)]

Conclusions

- Stochastic dynamics: multiple reservoirs & conservation laws

  [Rao & Esposito. *New J. Phys.* **20**, 023007 (2018)]

- Stochastic CRNs

  [Rao & Esposito, *JCP* **149** , 245101 (2018)]