Towards a Nonequilibrium Thermodynamics of Complex Systems

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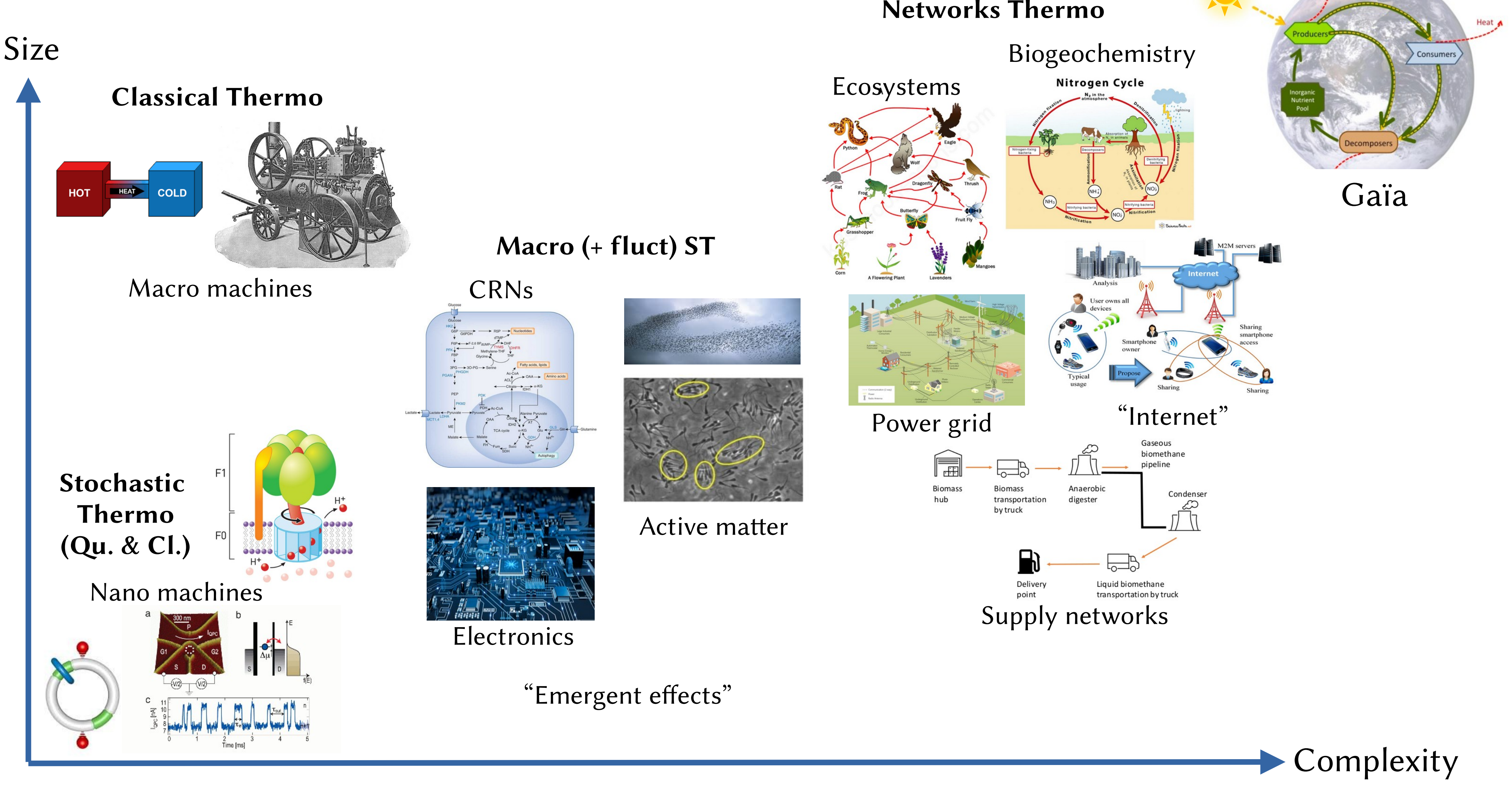
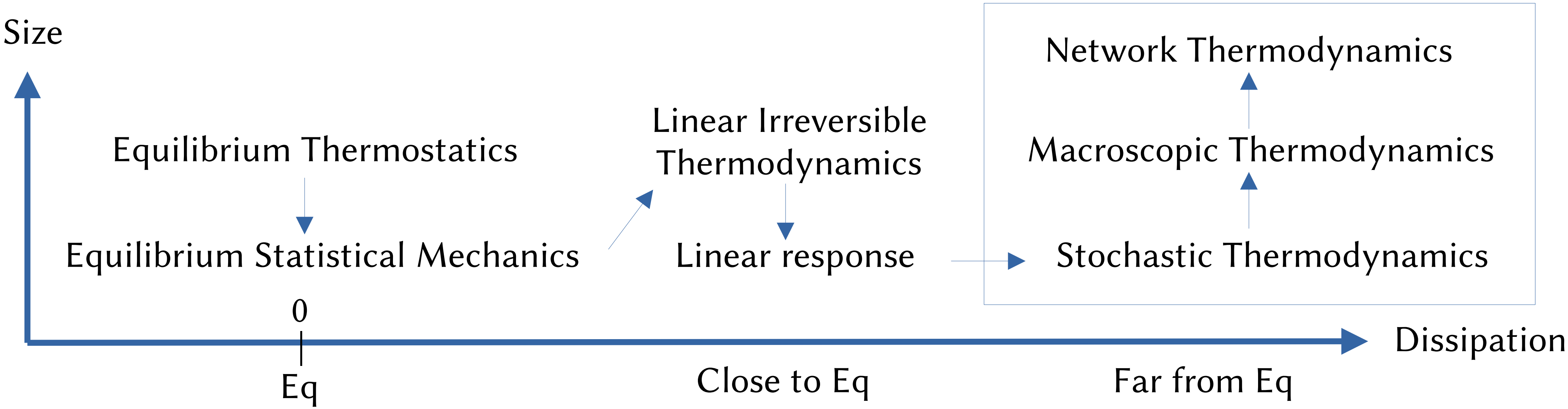
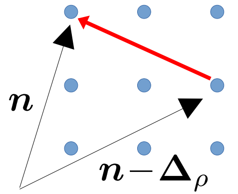
Introduction




Size
Equilibrium Thermostatics
Equilibrium Statistical Mechanics
Linear Irreversible Thermodynamics
Linear response
Network Thermodynamics
Macroscopic Thermodynamics
Stochastic Thermodynamics
0
Eq
Close to Eq
Far from Eq
Dissipation

Stochastic thermodynamics

$$\partial_t P_t(\boldsymbol{n}) = \sum_\rho \left[\lambda_\rho(\boldsymbol{n}-\boldsymbol{\Delta}_\rho) P_t(\boldsymbol{n}-\boldsymbol{\Delta}_\rho) - \lambda_\rho(\boldsymbol{n}) P_t(\boldsymbol{n})\right]$$



Thermodynamic consistency is introduced via the **local detailed balance** condition:

$$\log \frac{\lambda_\rho(\boldsymbol{n})}{\lambda_{-\rho}(\boldsymbol{n}+\boldsymbol{\Delta}_\rho)} = -\beta\left[\Phi(\boldsymbol{n}+\boldsymbol{\Delta}_\rho) - \Phi(\boldsymbol{n}) - W_\rho(\boldsymbol{n})\right]$$

Free energy of the state $\Phi(\boldsymbol{n}) = E(\boldsymbol{n}) - TS(\boldsymbol{n})$

Nonconservative work

Simplifying assumption: Isothermal, autonomous

Rao, Esposito, *NJP* **20**, 023007 (2018)

1st Law: $d_t\langle E\rangle = \langle \dot{W}\rangle + \langle \dot{Q}\rangle$

2nd Law: $\dot{\Sigma} = d_t S - \frac{\langle \dot{Q}\rangle}{T} = \frac{\langle \dot{W}\rangle - d_t\Phi}{T} \geqslant 0$

$j_\rho(\boldsymbol{n}) = \lambda_\rho(\boldsymbol{n}) P_t(\boldsymbol{n})$

$\langle \dot{Q}\rangle = \sum_{\rho,\boldsymbol{n}} Q_\rho(\boldsymbol{n}) j_\rho(\boldsymbol{n})$

$\langle \dot{W}\rangle = \sum_{\rho,\boldsymbol{n}} W_\rho(\boldsymbol{n}) j_\rho(\boldsymbol{n})$

Entropy production $\dot{\Sigma} = \frac{k_b}{2}\sum_{\rho,\boldsymbol{n}} \left(j_\rho(\boldsymbol{n}) - j_{-\rho}(\boldsymbol{n}+\boldsymbol{\Delta}_\rho)\right) \log \frac{j_\rho(\boldsymbol{n})}{j_{-\rho}(\boldsymbol{n}+\boldsymbol{\Delta}_\rho)} \geqslant 0$

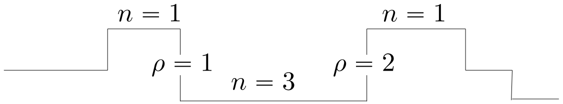
System entropy $S = \sum_{\boldsymbol{n}} P_t(\boldsymbol{n})\big(S(\boldsymbol{n}) - k_b \log P_t(\boldsymbol{n})\big)$ (**Shannon**)

Free energy $\Phi = \langle E\rangle - TS$ $\Phi - \Phi^{eq} = k_b T D(p|p^{eq}) \geqslant 0$

$\left(D(p_i|p_i') \equiv \sum_i p_i \ln \frac{p_i}{p_i'} \geq 0 \right.$ Kullback-Leibler divergence $\left.\right)$

Detailed balance ($W_\rho(\boldsymbol{n}) = 0$) dynamics minimizes free energy

Entropy production along a stochastic trajectory $\Gamma_{\rightarrow}$:



$$\sigma = k_B \ln \frac{\mathcal{P}[\Gamma_{\rightarrow}]}{\mathcal{P}[\Gamma_{\leftarrow}]}$$

Fluctuation theorem

$$\frac{P(\sigma)}{P(-\sigma)} = e^{\sigma/k_B}$$

$$\left(D(p_i|p_i') \equiv \sum_i p_i \ln \frac{p_i}{p_i'} \geq 0 \right)$$

Kullback-Leibler divergence

$$\Sigma = \langle \sigma \rangle = D(\mathcal{P}_{\rightarrow}|\mathcal{P}_{\leftarrow}) \geq 0$$

statistical measure of time-reversal breaking

Coarse graining underestimates entropy production $D(\mathcal{P}_{\rightarrow}|\mathcal{P}_{\leftarrow}) \geq D(\bar{\mathcal{P}}_{\rightarrow}|\bar{\mathcal{P}}_{\leftarrow})$

E.g. in active matter, $\bar{\Gamma}$ is often real space, but Γ should also contain the powering mechanism

Same motion , different dissipation

Macroscopic limit at equilibrium

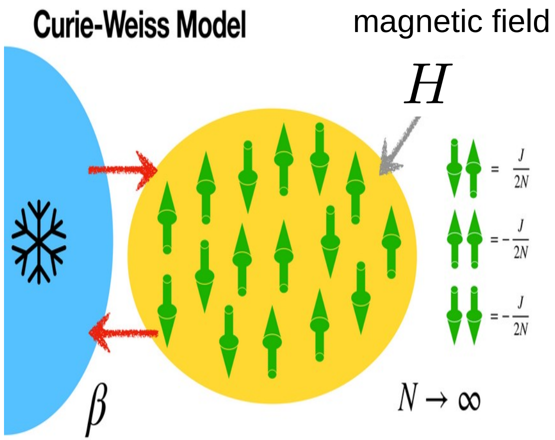
Free energy of state x

$$P_{\mathrm{eq}}(x) = \frac{e^{-\Phi(x)/k_b T}}{Z} \asymp e^{-\Omega(\phi(x)-\phi_{\min})/k_b T}$$

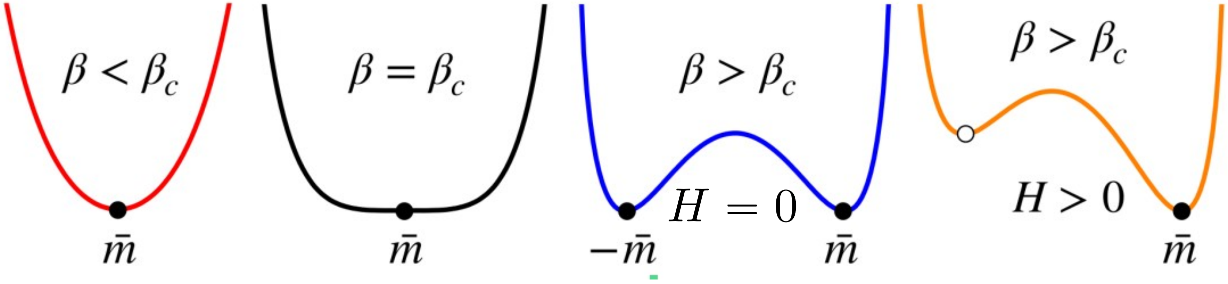
Macro limit

Ω : Scale parameter

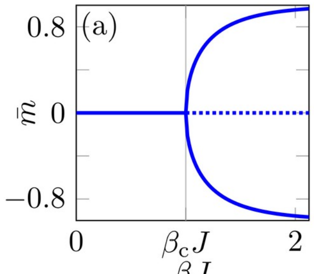
Phase transitions: changes in minima



Magnetization



Bifurcations



$H = 0$

Macroscopic dynamics

$$\partial_t P(\boldsymbol{n},t) = \sum_\rho [\lambda_\rho(\boldsymbol{n}-\boldsymbol{\Delta}_\rho)P(\boldsymbol{n}-\boldsymbol{\Delta}_\rho,t) - \lambda_\rho(\boldsymbol{n})P(\boldsymbol{n},t)]$$

Scale parameter Ω

$\Omega \to \infty$

- Density $\boldsymbol{x} = \boldsymbol{n}/\Omega$ remains finite
- Transition rates scale linearly with Ω: $\omega_\rho(\boldsymbol{x}) = \lim_{\Omega\to\infty} \frac{\lambda_\rho(\Omega \boldsymbol{x})}{\Omega}$
- Free energies are extensive: $\phi(\boldsymbol{x}) = \lim_{\Omega\to\infty} \frac{\Phi(\Omega \boldsymbol{x})}{\Omega}$

Under those conditions a large deviations principle applies:

R. Kubo 1973

Macroscopic Fluctuations

$$P(\boldsymbol{x},t) \asymp e^{-\Omega I(\boldsymbol{x},t)} \qquad \partial_t I(\boldsymbol{x},t) = \sum_\rho \omega_\rho(\boldsymbol{x}) \left[1 - e^{\boldsymbol{\Delta}_\rho \cdot \nabla I(\boldsymbol{x},t)}\right]$$

Peaks around the deterministic trajectory $\boldsymbol{x}_t$: $I(\boldsymbol{x}_t,t) = 0 \quad \nabla I(\boldsymbol{x}_t,t) = 0$

Macroscopic Dynamics

$$d_t \boldsymbol{x}_t = \boldsymbol{u}(\boldsymbol{x}_t) \qquad \boldsymbol{u}(\boldsymbol{x}) = \sum_\rho \omega_\rho(\boldsymbol{x})\boldsymbol{\Delta}_\rho$$

Typically nonlinear

$\neq$ Det Dyn + Gaussian noise

Falasco, Esposito, arXiv:2307.12406

Macroscopic thermodynamics

$$\Omega \to \infty$$

Shannon entropy: $S_{\text{sh}} = -k_b \sum_{\boldsymbol{x}} P_t(\boldsymbol{x}) \log(P_t(\boldsymbol{x})) = k_b \Omega \sum_{\boldsymbol{x}} P_t(\boldsymbol{x}) I(\boldsymbol{x}, t) \simeq k_b \Omega I(\boldsymbol{x}_t, t) = 0$

2nd law $\dot{\Sigma}/\Omega = d_t\langle S\rangle/\Omega - \langle \dot{Q}\rangle/(T\Omega) \simeq \dot{\sigma}(\boldsymbol{x}_t) = d_t s(\boldsymbol{x}_t) - \dot{q}(\boldsymbol{x}_t)/T = (\dot{w}(\boldsymbol{x}_t) - d_t\phi(\boldsymbol{x}_t))/T$

$$= k_b \sum_{\rho>0} (\omega_\rho(\boldsymbol{x}) - \omega_{-\rho}(\boldsymbol{x})) \ln \frac{\omega_\rho(\boldsymbol{x})}{\omega_{-\rho}(\boldsymbol{x})} \geqslant 0$$

1st law $d_t\langle E\rangle/\Omega = \langle \dot{W}\rangle/\Omega + \langle \dot{Q}\rangle/\Omega \simeq d_t e(\boldsymbol{x}_t) = \dot{w}(\boldsymbol{x}_t) + \dot{q}(\boldsymbol{x}_t)$

We have a macroscopic nonequilibrium thermodynamics!

Freitas, Esposito, Nat Com **13**, 5084 (2022)

NESS fluctuations – macroscopic dissipation

Adiabatic non-adiabatic decomposition of entropy production: $\dot\Sigma = \underset{\geqslant 0}{\dot\Sigma_{\rm a}} + \underset{\geqslant 0}{\dot\Sigma_{\rm na}} \geqslant 0$

$$\dot\Sigma_{\rm na} = -k_b\, d_t D \geq 0$$

$$D = \sum_{\boldsymbol{x}} P_t(\boldsymbol{x}) \log(P_t(\boldsymbol{x})/P_{\rm ss}(\boldsymbol{x})) \simeq \Omega \sum_{\boldsymbol{x}} P_t(\boldsymbol{x}) I_{\rm ss}(\boldsymbol{x}) \simeq \Omega I_{\rm ss}(\boldsymbol{x}_t)$$

NESS: $P_{\rm ss}(x) \asymp e^{-\Omega I_{\rm ss}(x)}$

$$\dot\Sigma_{\rm na}/\Omega \simeq -k_b\, d_t I_{\rm ss}(\boldsymbol{x}_t) \geqslant 0$$

Lyapunov fct of the det. dynamics

Emergent 2nd law

$$\dot\Sigma_{\rm a}/\Omega \simeq \dot\sigma(\boldsymbol{x}_t) + k_b\, d_t I_{\rm ss}(\boldsymbol{x}_t) \geq 0$$

Macroscopic entropy production **Steady state fluctuations**

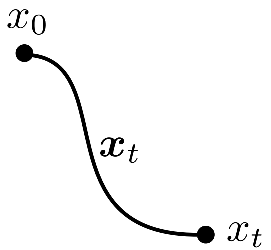
Freitas, Esposito, Nat Com **13**, 5084 (2022)

“Close” to equilibrium:
W_ρ small

Linear response theory for rate functions instead of probabilities !!!

$$\dot\sigma^{(0)}(\boldsymbol{x}_t)/k_b = \beta\big(\dot w^{(0)}(\boldsymbol{x}_t) - d_t\phi(\boldsymbol{x}_t)\big) \simeq -d_t I_{\rm ss}(\boldsymbol{x}_t)$$

solution of the detailed balanced dynamics
$W_\rho = 0$

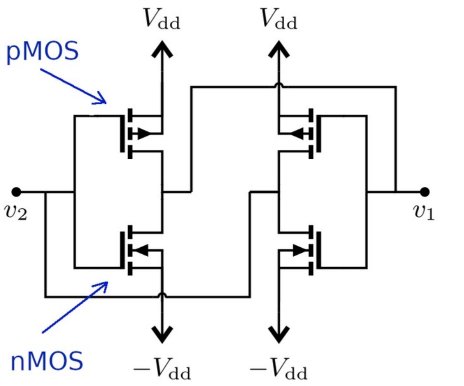


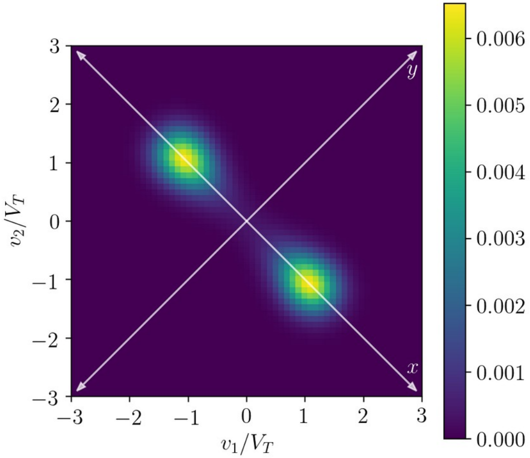
Freitas, Falasco, Esposito, *New J. Phys.* **23**, 093003 (2021)

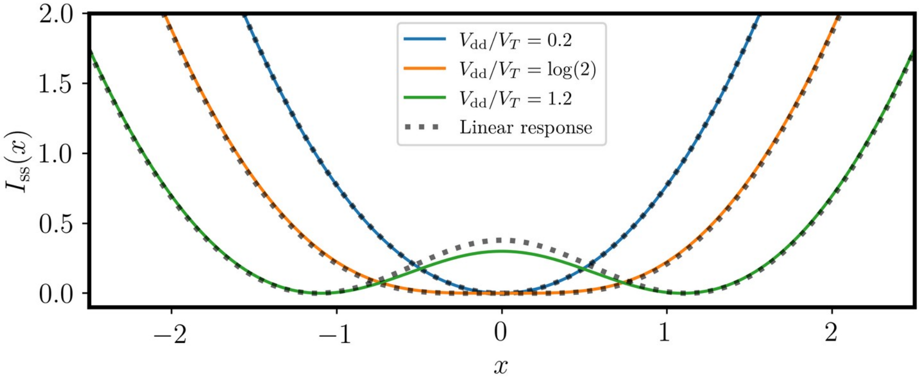
Example of a CMOS bit

$$P_{\mathrm{ss}}(x) \asymp e^{-\Omega I_{\mathrm{ss}}(x)}$$

Freitas, Delvenne, Esposito, Phys. Rev. X **11**, 031064 (2021)



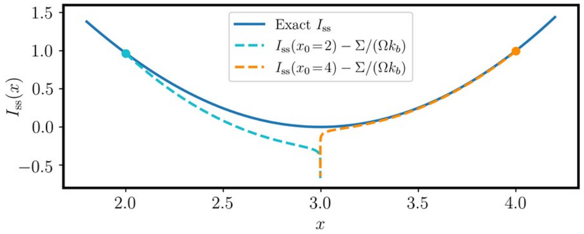


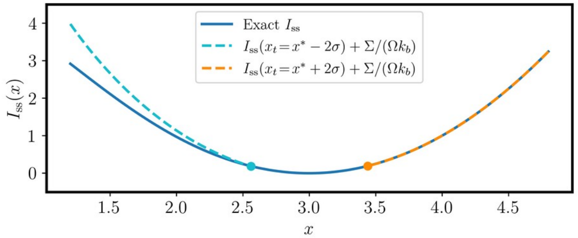


$v_e = q_e/C \qquad V_T = k_b T/q_e$

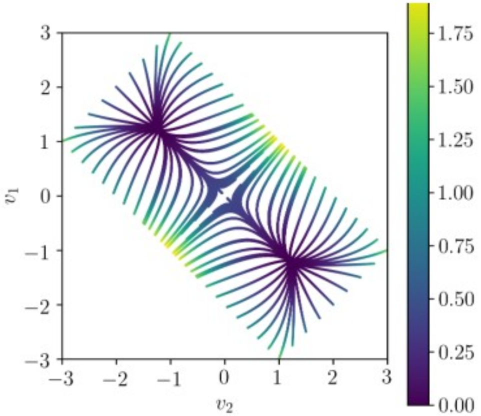
- **Bistability as a nonequilibrium phase transition**
- **Macro can be small !** $\Omega = V_T/v_e = 10$

- Testing the bound





- Reconstructing the NESS:

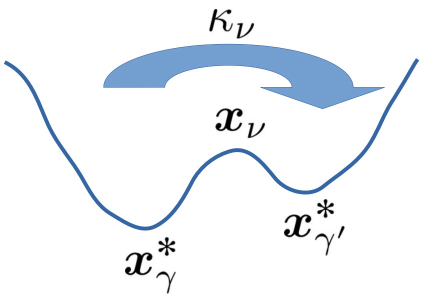


Freitas, [T2a-07B-05] Monday 7, 6:30 PM

Freitas, Esposito, Nat Com **13**, 5084 (2022)

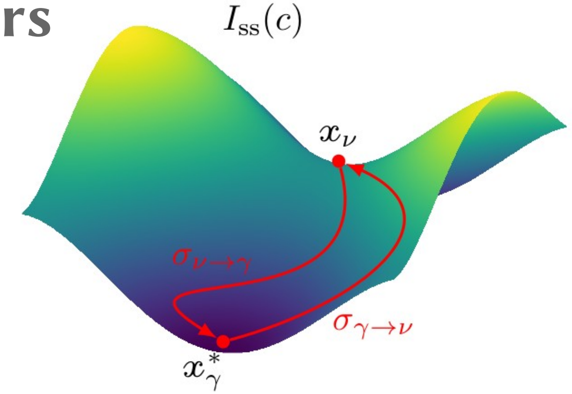
$k_b = 1$

Transition rates between attractors



$$\kappa_\nu \asymp e^{-V[I_{\rm ss}^{(\gamma)}(\boldsymbol{x}_\nu) - I_{\rm ss}^{(\gamma)}(\boldsymbol{x}^*_\gamma)]}$$

$\boldsymbol{u}(\boldsymbol{x}^*) = 0$ Fixed points of the det. dynamics



- W_ρ small ➡ Local detailed balance Falasco, Esposito, PRE **103**, 042114 (2021)

$$\lim_{V\to\infty} \frac{1}{V} \ln \frac{\kappa_\nu}{\kappa_{-\nu}} = \beta(\phi(\boldsymbol{x}_\gamma^{\rm eq}) - \phi(\boldsymbol{x}_{\gamma'}^{\rm eq})) + \sigma_\nu^{(0)}$$

$$\sigma_\nu^{(0)} := -\sigma_{\rm nc}^{(0)}(\boldsymbol{x}_\nu, \boldsymbol{x}_\gamma^{\rm eq}) + \sigma_{\rm nc}^{(0)}(\boldsymbol{x}_\nu, \boldsymbol{x}_{\gamma'}^{\rm eq})$$

$$\sigma_{\rm nc}^{\nu\to\gamma}(\boldsymbol{x}, \boldsymbol{x}') := \beta \int_{\boldsymbol{x}}^{\boldsymbol{x}'} dt \sum_\rho W_\rho \, \omega_\rho(\boldsymbol{x}(t))$$

- General bound

relaxation ← → instanton

$$-\sigma_{\nu\to\gamma} \leqslant \lim_{V\to\infty} \frac{1}{V} \ln \kappa_\nu \leqslant \sigma_{\gamma\to\nu}$$

Falasco, Esposito, arXiv:2307.12406

W_ρ small ➡ $-\sigma_{\nu\to\gamma} = \lim_{V\to\infty} \frac{1}{V} \ln \kappa_\nu = \sigma_{\gamma\to\nu} < 0$

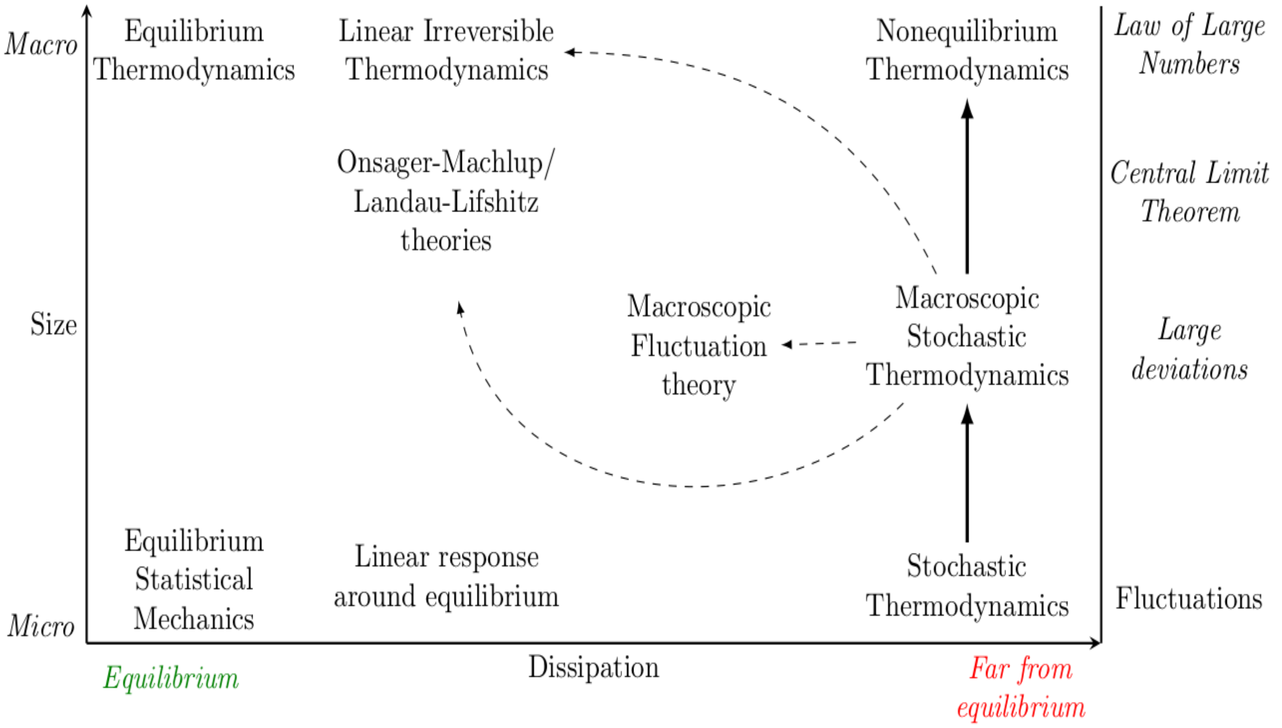
(smallest κ_ν) (largest $\sigma_{\nu\to\gamma}$)

Attractor with largest lifetime has the largest relaxation entropy production !

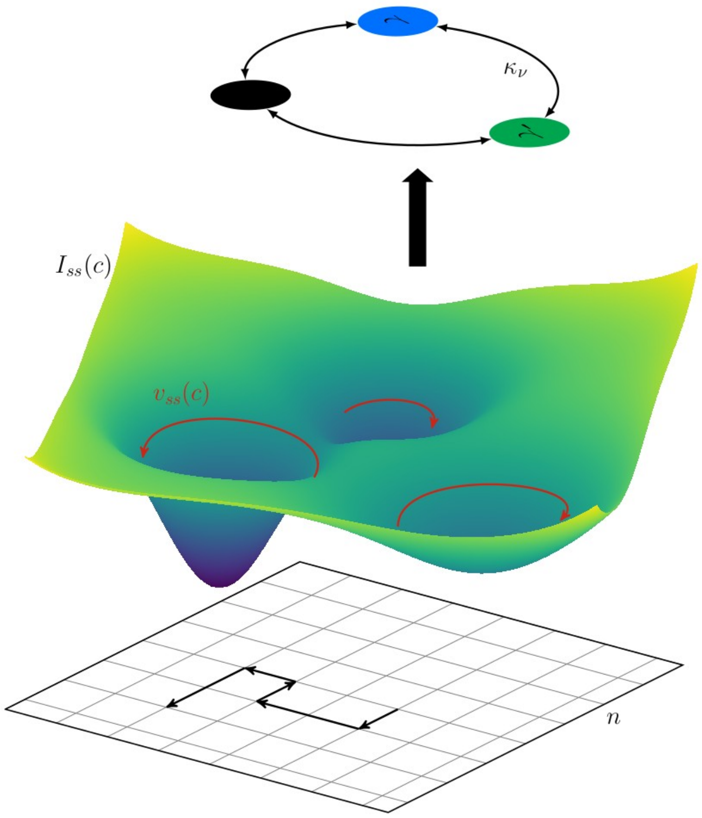
Maximum entropy production principle **if** most $\sigma_{\nu\to\gamma}$ occurs close to $\boldsymbol{x}^*_\gamma$

There is much more…

Falasco, Esposito, *Macroscopic Stochastic Thermodynamics*, arXiv:2307.12406



Stochastic Thermo on NonEq attractors



Field theory: x=(r,c)

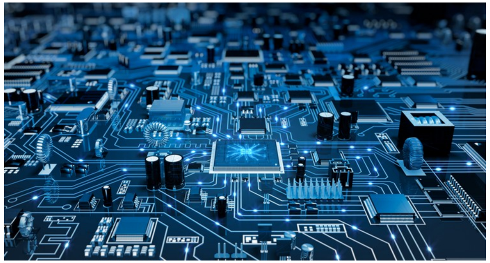
- Real space (diffusive scaling)
- Internal dof e.g. chemistry (not diffusive)

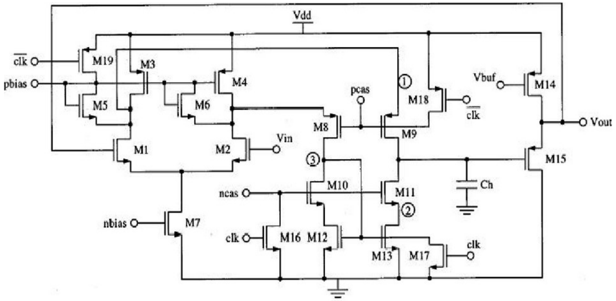
TDDFT (Dean Equation): If no internal dof x=r

A few words about Network Thermodynamics

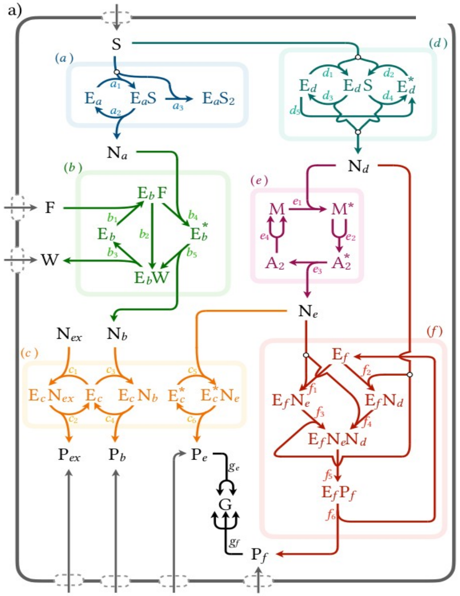
Circuit theory: Description based on modules characterized by an I-V curve + Kirchhoff laws

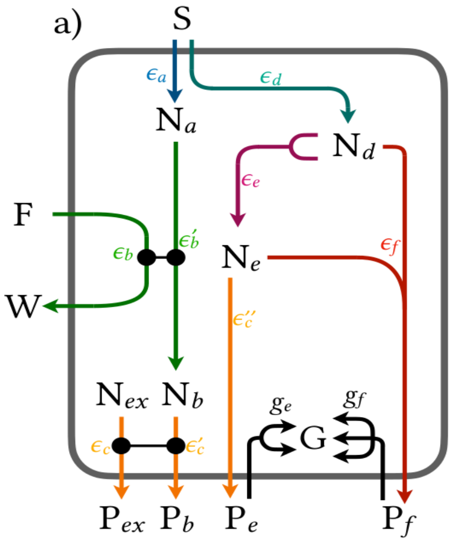
Electrical circuits

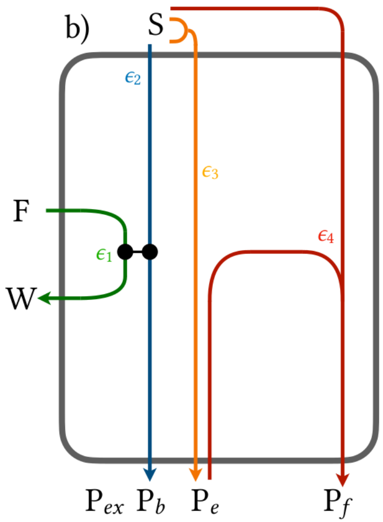




Chemical reaction networks





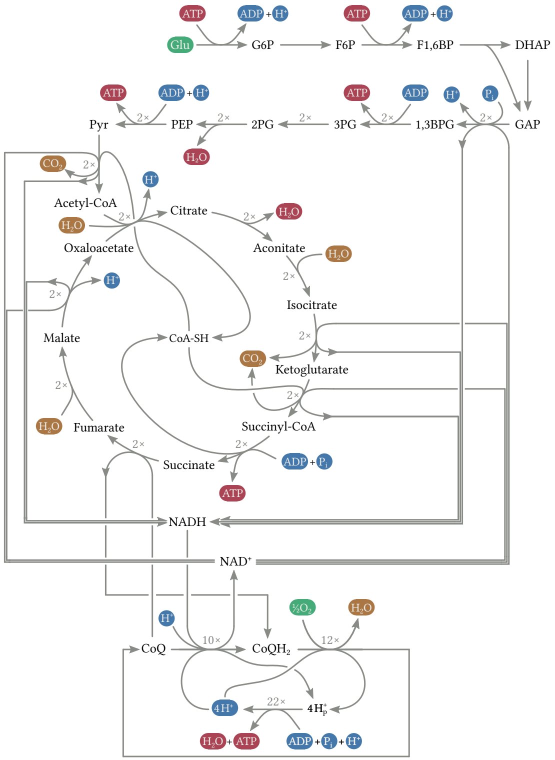


Avanzini, Freitas, Esposito,
Phys. Rev. X **13**, 021041 (2023)

Avanzini [T2-07A-06]
Monday 7, 4:30 PM

Applications

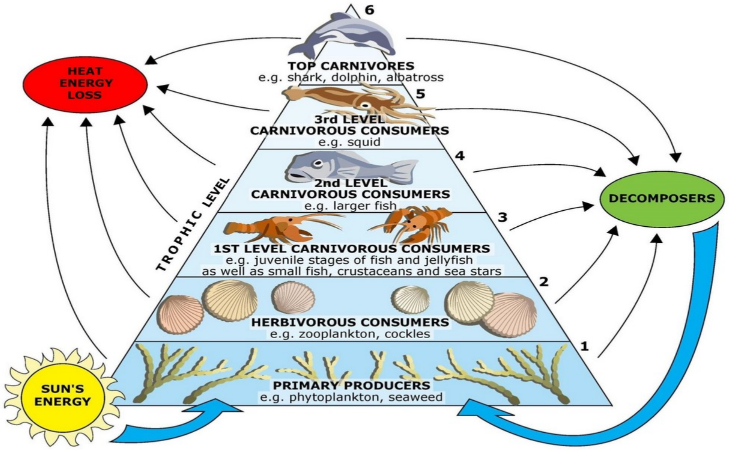
Metabolism



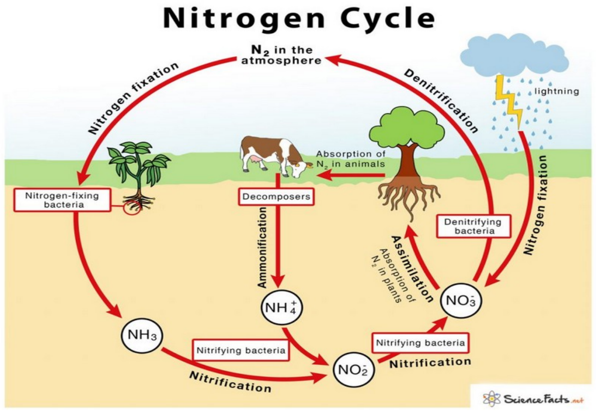
$$\mathrm{Glu} + 6\mathrm{O}_2 + 26\mathrm{ADP} + 26\mathrm{P_i} + 26\mathrm{H}^+ \rightleftharpoons 6\mathrm{CO}_2 + 32\mathrm{H_2O} + 26\mathrm{ATP}$$

Wachtel, Rao, Esposito,
J. Chem. Phys. **157**, 024109 (2022)

Trophic pyramid



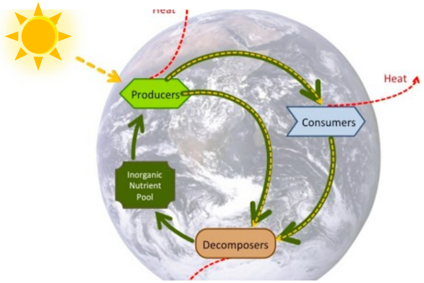
Biogeochemistry



Conclusions

Towards a Thermodynamics of Complex Systems:

Nonlinear dynamics,
Fluctuations,
Out-of-Eq,
Networks



Gaïa