Nonequilibrium phase transitions: Energetics and macroscopic fluctuations

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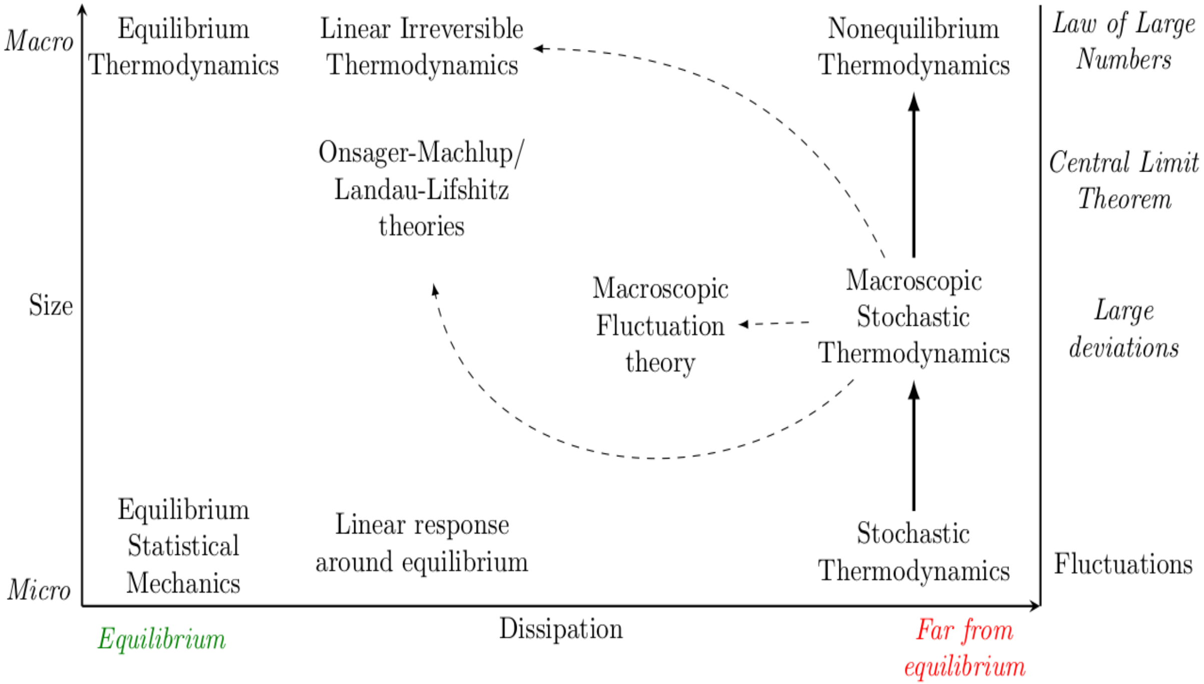
Introduction

Current picture:

Falasco, Esposito,
Macroscopic Stochastic Thermodynamics,
arXiv:2307.12406



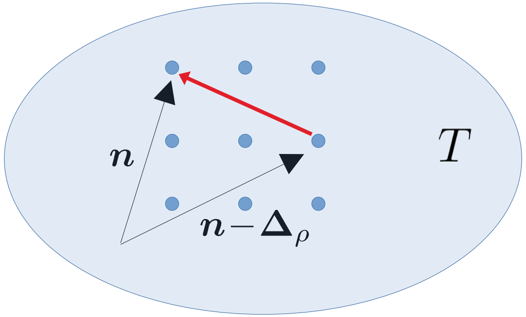
We can use it to study the Thermodynamics of Nonequilibrium Phase Transitions:

- Energetics of synchronization and minimum EP principle in nonequilibrium Potts model
- Energetics of dissipative structures in non-ideal reaction diffusion
- Finite-time dynamical phase transition after quenches in Ising model

Stochastic thermodynamics

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:

$$\log \frac{\lambda_\rho(\boldsymbol{n})}{\lambda_{-\rho}(\boldsymbol{n}+\boldsymbol{\Delta}_\rho)} = -\frac{1}{k_b T}\left[\Phi(\boldsymbol{n}+\boldsymbol{\Delta}_\rho) - \Phi(\boldsymbol{n}) - W_\rho(\boldsymbol{n})\right]$$

For simplicity: isothermal, autonomous

In general see:

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

Free energy of the state

$$\Phi(\boldsymbol{n}) = E(\boldsymbol{n}) - TS(\boldsymbol{n})$$

Nonconservative work

Reservoirs causing the transitions are at equilibrium

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

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

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

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

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

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

Shannon

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

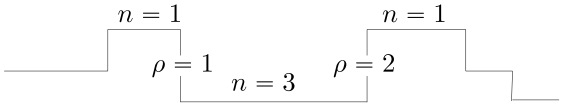
Free energy $\Phi = \langle E\rangle - TS$ $\quad \Phi - \Phi^{eq} = k_b T D(p|p^{eq}) \geqslant 0$

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

Detailed balance dynamics, $W_\rho(\boldsymbol{n}) = 0$, 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

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

Overview: Rao, Esposito, *Entropy* **20**, **635** (2018)

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

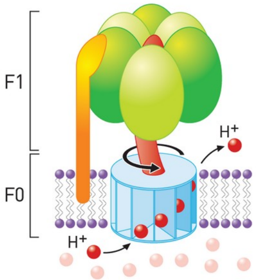
statistical measure
of time-reversal breaking

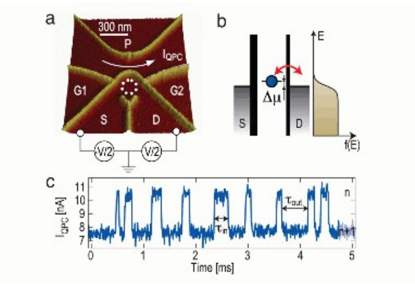
$$\left(D(p_i|p_i') \equiv \sum_i p_i \ln \frac{p_i}{p_i'} \geq 0 \right)$$
(Kullback-Leibler divergence)

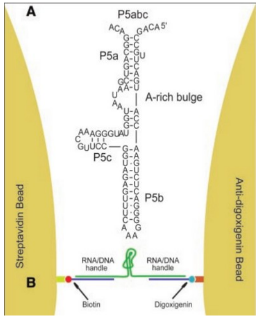
$$\frac{\langle O \rangle^2}{Var(O)} \leqslant \frac{\Sigma}{2k_B}$$

Thermodynamic uncertainty relation

Verified in many setups







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

Macroscopic limit

Macroscopic dynamics

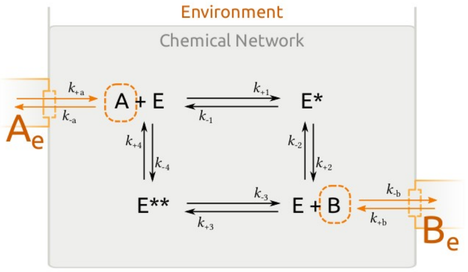
$$\partial_t P(\boldsymbol{n},t) = \sum_\rho [\lambda_\rho(\boldsymbol{n}-\boldsymbol{\Delta}_\rho)P(\boldsymbol{n}-\boldsymbol{\Delta}_\rho,t) - \lambda_\rho(\boldsymbol{n})P(\boldsymbol{n},t)]$$

Scale parameter Ω

$\Omega \to \infty$

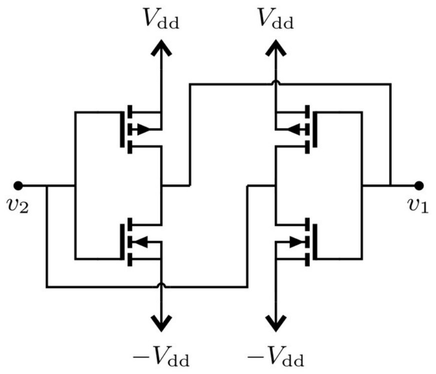
- Density $\boldsymbol{x} = \boldsymbol{n}/\Omega$ remains finite
- Transition rates scale linearly with Ω: $\omega_\rho(\boldsymbol{x}) = \lim_{\Omega\to\infty} \frac{\lambda_\rho(\Omega \boldsymbol{x})}{\Omega}$
- Free energies are extensive: $\phi(\boldsymbol{x}) = \lim_{\Omega\to\infty} \frac{\Phi(\Omega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

Chemical Reaction Networks



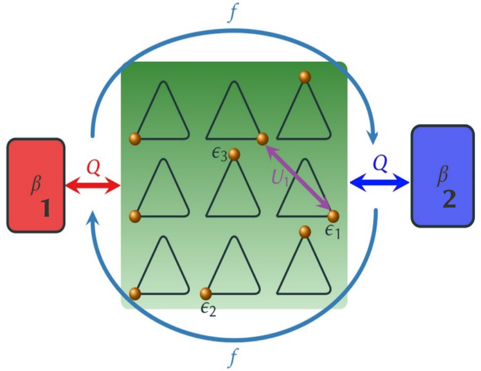
Rao, Esposito,
J. Chem. Phys. **149**, 245101 (2018)

Electronic Circuits



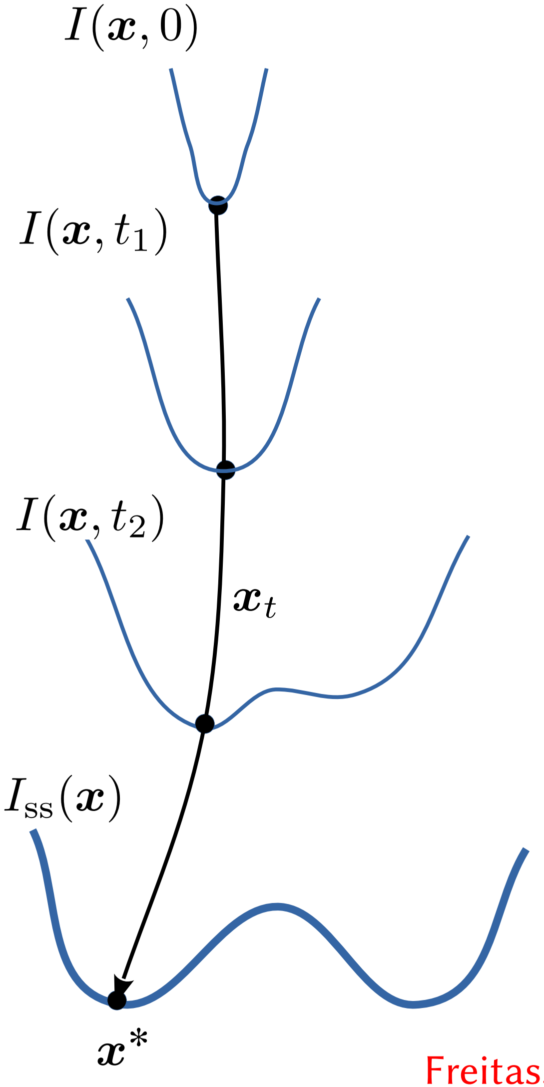
Freitas, Delvenne, Esposito,
Phys. Rev. X **11**, 031064 (2021)

Potts models



Herpich, Cossetto, Falasco, Esposito,
New J. Phys. **22**, 063005 (2020)

Macroscopic dynamics



Macroscopic Fluctuations $P(\boldsymbol{x},t) \asymp e^{-\Omega I(\boldsymbol{x},t)}$

Macroscopic Fluctuations

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

Kubo 1973

Deterministic dynamics (minimum of $I(\boldsymbol{x},t)$)

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

Fixed points $\boldsymbol{u}(\boldsymbol{x}^*) = 0$

Freitas, Esposito, Nat Com **13**, 5084 (2022) Falasco, Esposito, arXiv:2307.12406

Macroscopic nonequilibrium thermodynamics

$$\Omega \to \infty$$

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

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

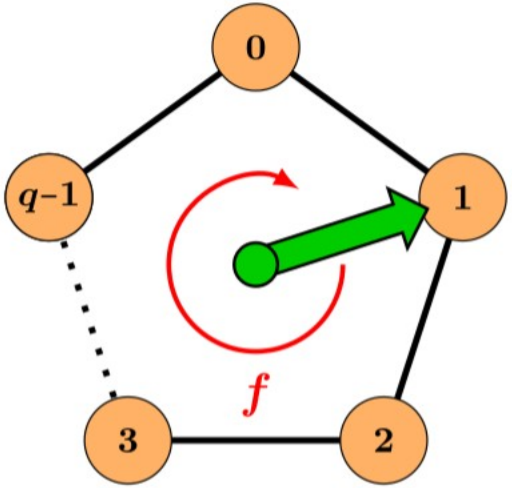
$$= k_b \sum_{\rho > 0} (\omega_\rho(\boldsymbol{x}) - \omega_{-\rho}(\boldsymbol{x})) \ln \frac{\omega_\rho(\boldsymbol{x})}{\omega_{-\rho}(\boldsymbol{x})} \geqslant 0$$

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

Freitas, Esposito, Nat Com **13**, 5084 (2022) Falasco, Esposito, arXiv:2307.12406

Nonequilibrium Potts Model: Synchronization & Minimum dissipation principle

Noninteracting Potts Model



Master equation $\dot{p}_i = j(p_i, p_{i-1})\,|_{\mathcal{J}=0} - j(p_{i+1}, p_i)\,|_{\mathcal{J}=0}$

$$j(p_{i+1}, p_i)\,|_{\mathcal{J}=0} = k^+ p_i - k^- p_{i+1}$$

Local detailed balance $\dfrac{k^\pm}{k^\mp} = e^{\pm\beta f}$

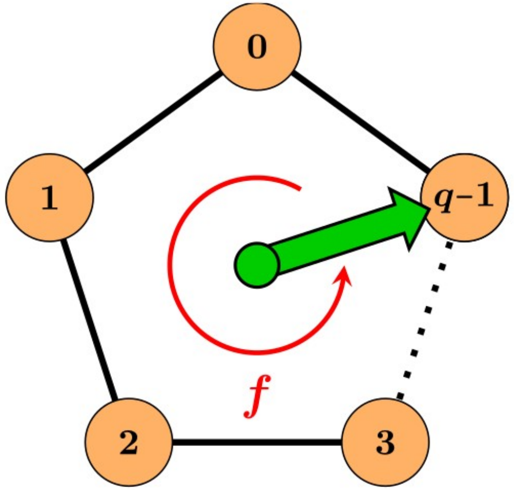
Fourier modes $\hat{p}_k = \sum_{n=0}^{q-1} e^{\frac{i2\pi kn}{q}} p_n$

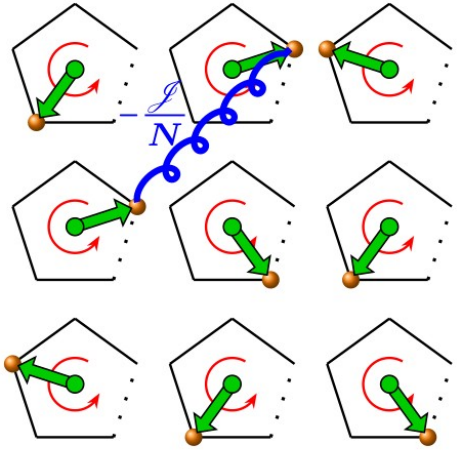
$$\dot{\hat{p}}_k = (\mu_k\,|_{\mathcal{J}=0} + i\omega_k\,|_{\mathcal{J}=0})\hat{p}_k$$

Decoherent fixed point $\boldsymbol{p}^* \equiv \left(\frac{1}{q}, \ldots, \frac{1}{q}\right)^\mathsf{T}$

$$\mu_k\,|_{\mathcal{J}=0} = -2(k^+ + k^-)\sin^2\left(\frac{\pi k}{q}\right) \qquad \omega_k\,|_{\mathcal{J}=0} = (k^+ - k^-)\sin\left(\frac{2\pi k}{q}\right)$$

Interacting Potts Model





$$\boldsymbol{N} = (N_0, N_1, \ldots, N_{q-1})^T$$

$$E(\boldsymbol{N}) = -\frac{\mathcal{J}}{N}(\boldsymbol{N}\cdot\boldsymbol{N} - N)$$

$$S_{int}(\boldsymbol{N}) = \log \Omega(\boldsymbol{N}) \qquad \Omega(\boldsymbol{N}) = \frac{N!}{\prod_{i=0}^{q-1} N_i!}$$

$$F(\boldsymbol{N}) = E(\boldsymbol{N}) - \beta^{-1} S_{int}(\boldsymbol{N})$$

local detailed balance $\quad \dfrac{W_i^{\pm}(\boldsymbol{N})}{W_{i\pm1}^{\mp}(\boldsymbol{N}')} = e^{-\beta(\Delta F \mp f)}$

Macro limit $\quad N \to \infty$

$$\boldsymbol{n} = \boldsymbol{N}/N \qquad \boldsymbol{p}(t) \equiv \langle \boldsymbol{n} \rangle$$

$$P(\boldsymbol{n}, t) \to \delta(\boldsymbol{n} - \boldsymbol{p}(t))$$

$$\dot{p}_i(t) = j(p_i, p_{i-1}) - j(p_{i+1}, p_i)$$

$$j(p_{i+1}, p_i) = k^+(p_{i+1} - p_i)p_i - k^-(p_i - p_{i+1})p_{i+1}$$

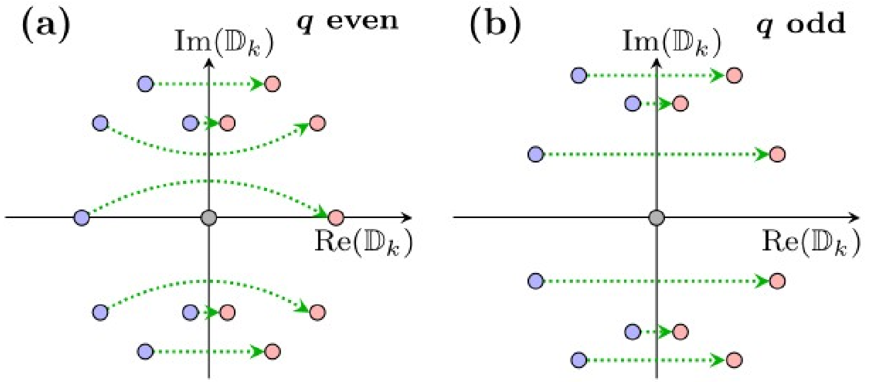
$$\langle \dot{\sigma} \rangle = f \sum_{i=0}^{q-1} j(p_{i+1}, p_i) - \beta \frac{d}{dt}\mathcal{F}[\boldsymbol{p}(t)]$$

Herpich, Esposito, PRX 8, 031056 (2018); PRE 99, 022135 (2019) → Arrhenius rates

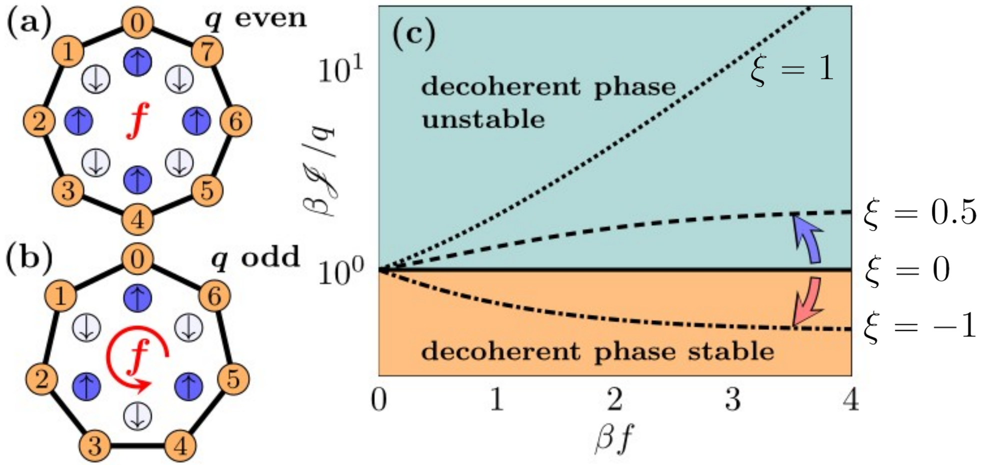
Meibohm, Esposito, arXiv:2401.14980, arXiv:2401.14982

$$\dot{\hat{p}}_k = \hat{h}_k(\hat{\boldsymbol{p}}) \sim (\mu_k + i\omega_k)\hat{p}_k + \hat{h}_k^{(2)}(\hat{\boldsymbol{p}}) + \hat{h}_k^{(3)}(\hat{\boldsymbol{p}})$$

High dimensional Hopf bifurcation



When the decoherent phase becomes unstable:
- Alternating stationary pattern
- Oscillations



$$k^{\pm}_{\mathrm{Arr}}(x) = \frac{1}{\tau} e^{\frac{\beta}{2}[(1\mp\xi)\mathscr{J}x \pm f]}$$

and

$$k^{\pm}_{\mathrm{Gla}}(x) = \frac{2}{\tau} \frac{e^{\pm\frac{\beta f}{2}}}{e^{-\beta \mathscr{J} x} + 1}$$

Meibohm, Esposito, arXiv:2401.14980, arXiv:2401.14982

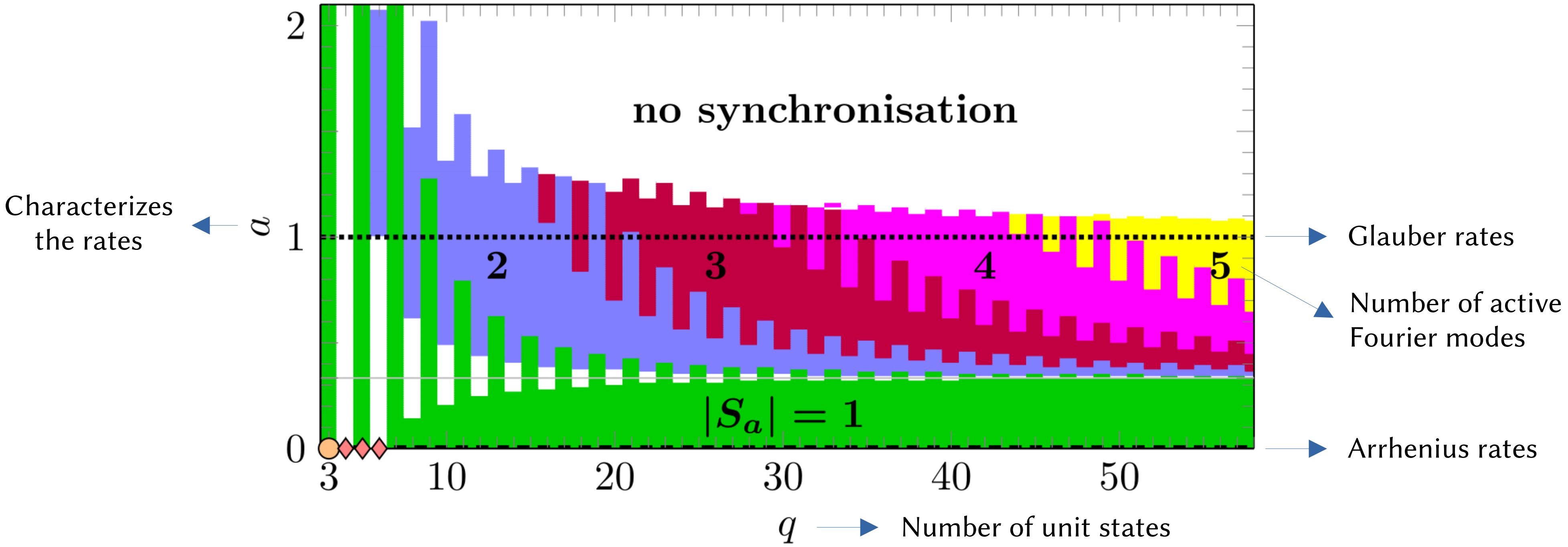
$$\dot{\hat{p}}_k = \hat{h}_k(\hat{\boldsymbol{p}}) \sim (\mu_k + i\omega_k)\hat{p}_k + \hat{h}^{(2)}_k(\hat{\boldsymbol{p}}) + \hat{h}^{(3)}_k(\hat{\boldsymbol{p}})$$

Nonlinear transformation

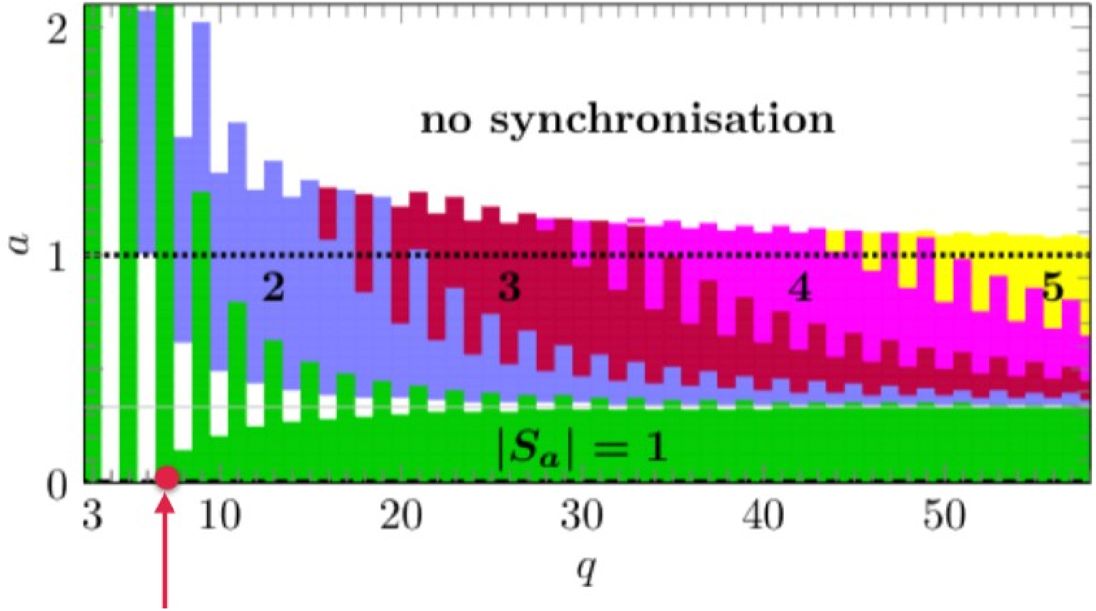
$$\hat{p}'_k = \hat{p}_k + \hat{f}^{(2)}_k(\hat{\boldsymbol{p}}) + \hat{f}^{(3)}_k(\hat{\boldsymbol{p}})$$

Normal form

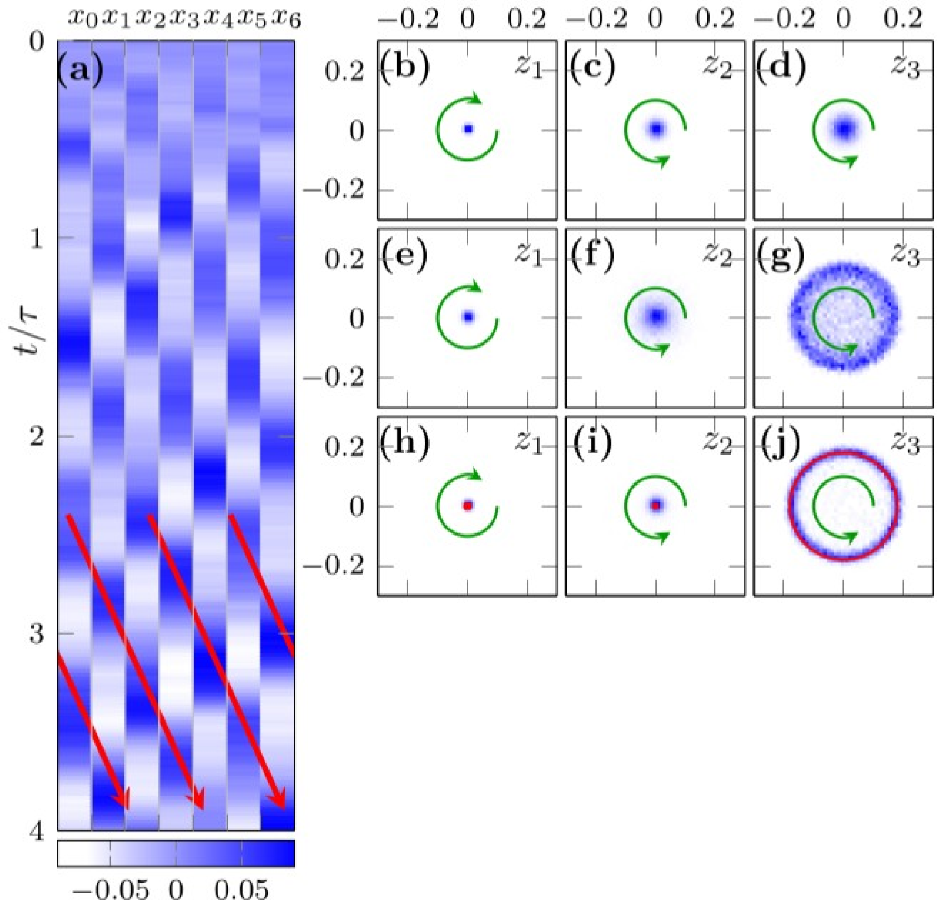
$$\dot{z}'_k = \left(\mathbb{D}_k - \sum_{k=1}^{\lfloor q/2 \rfloor} \mathbb{C}_{kk'} |z'_{k'}|^2 \right) z'_k$$



Meibohm, Esposito, arXiv:2401.14980, arXiv:2401.14982



Arrhenius rates
$q = 7$



Meibohm, Esposito, arXiv:2401.14980, arXiv:2401.14982

Stability-dissipation relation

$$L(\boldsymbol{N}) = W_{\text{in}}(\boldsymbol{N}) - W_{\text{out}}(\boldsymbol{N})$$

$$W_{\text{out}}(\boldsymbol{N}) = \sum_{n=0}^{q-1}\left[W_n^+(\boldsymbol{N}) + W_n^-(\boldsymbol{N})\right]$$

$$W_{\text{in}}(\boldsymbol{N}) = \sum_{n=0}^{q-1}\left[W_n^+(\boldsymbol{N}-\boldsymbol{\Delta}_n^+) + W_n^-(\boldsymbol{N}-\boldsymbol{\Delta}_n^-)\right]$$

$$\mathcal{L} \equiv \lim_{N\to\infty} \langle L(\boldsymbol{N})\rangle = -\nabla_{\boldsymbol{p}} \cdot \dot{\boldsymbol{p}}$$

Phase space contraction rate

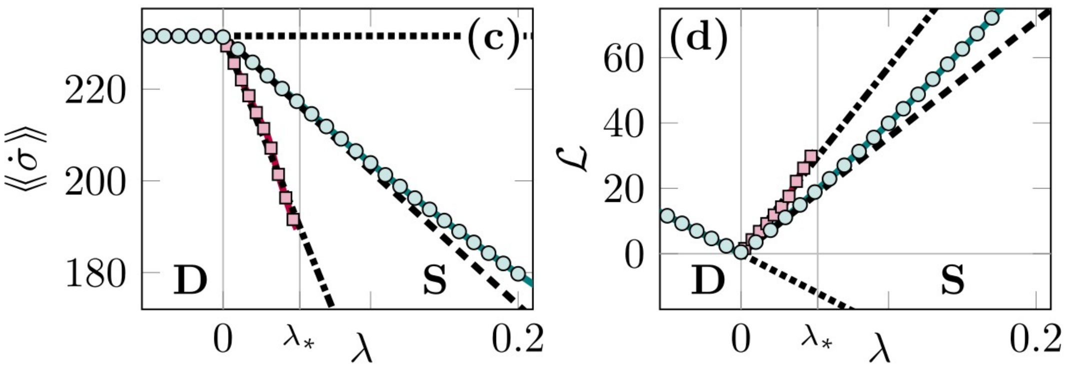
Close to the bifurcation:

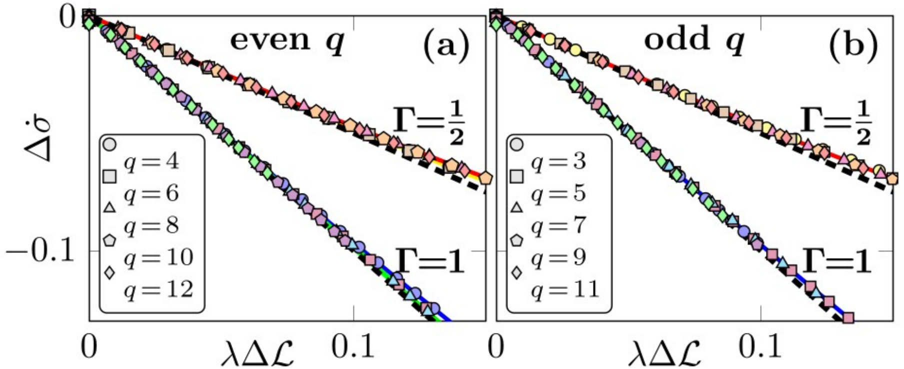
$$\Delta\dot{\sigma} \sim -\overbrace{\Gamma\lambda}^{>0}\,\overbrace{\Delta\mathcal{L}}^{>0}$$

$$\Delta\dot{\mathcal{O}} \equiv \frac{\langle\dot{\mathcal{O}}\rangle - \langle\dot{\mathcal{O}}\rangle_0}{|\langle\dot{\mathcal{O}}\rangle_0|}$$

→ Free unit

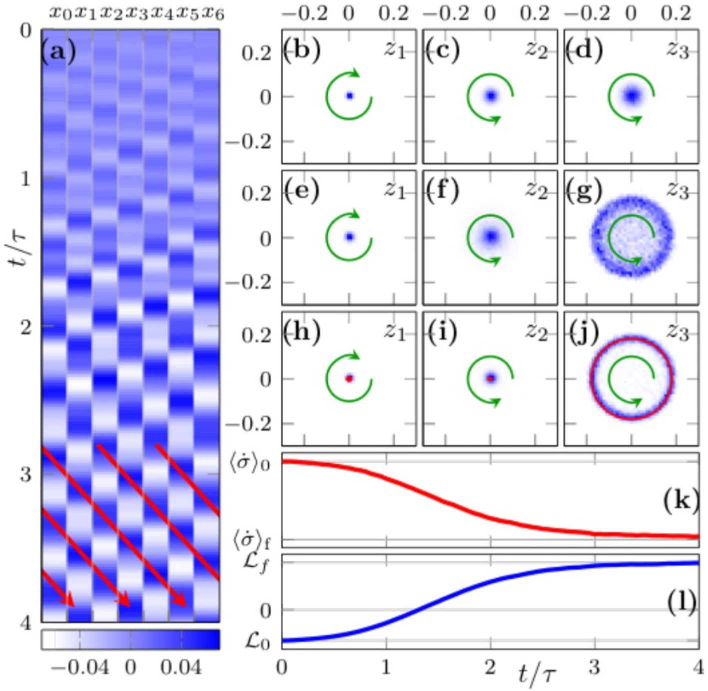
Synchronization decreases dissipation and increases phase space contraction rate

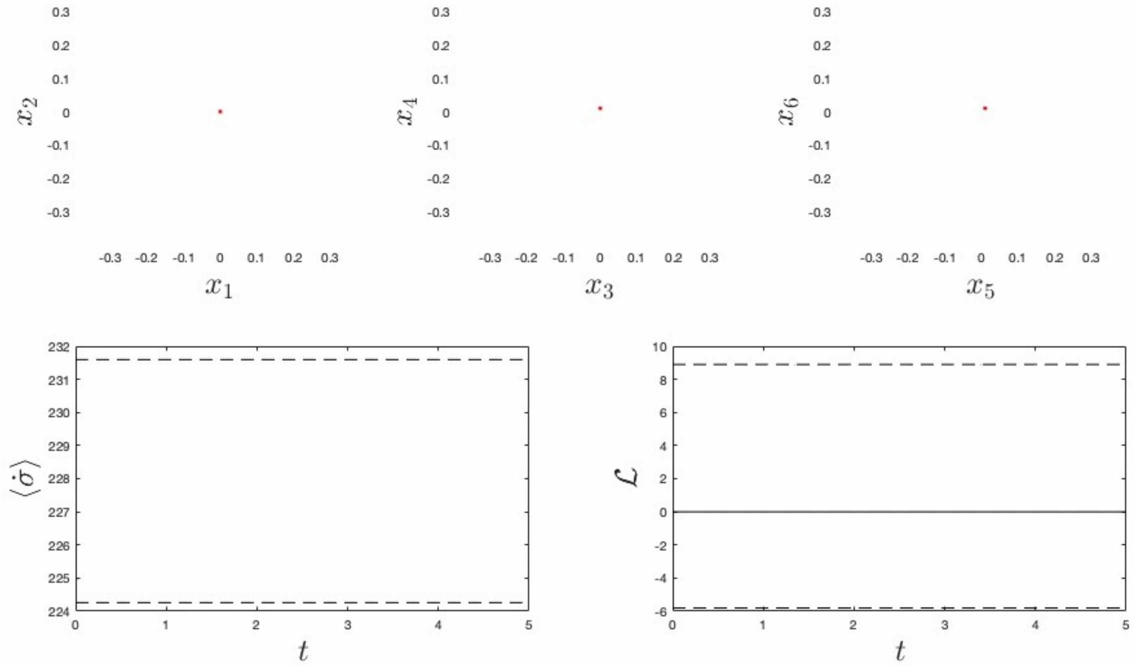




Meibohm, Esposito, arXiv:2401.14980, arXiv:2401.14982

N=10^5
q=7
1 stable
states



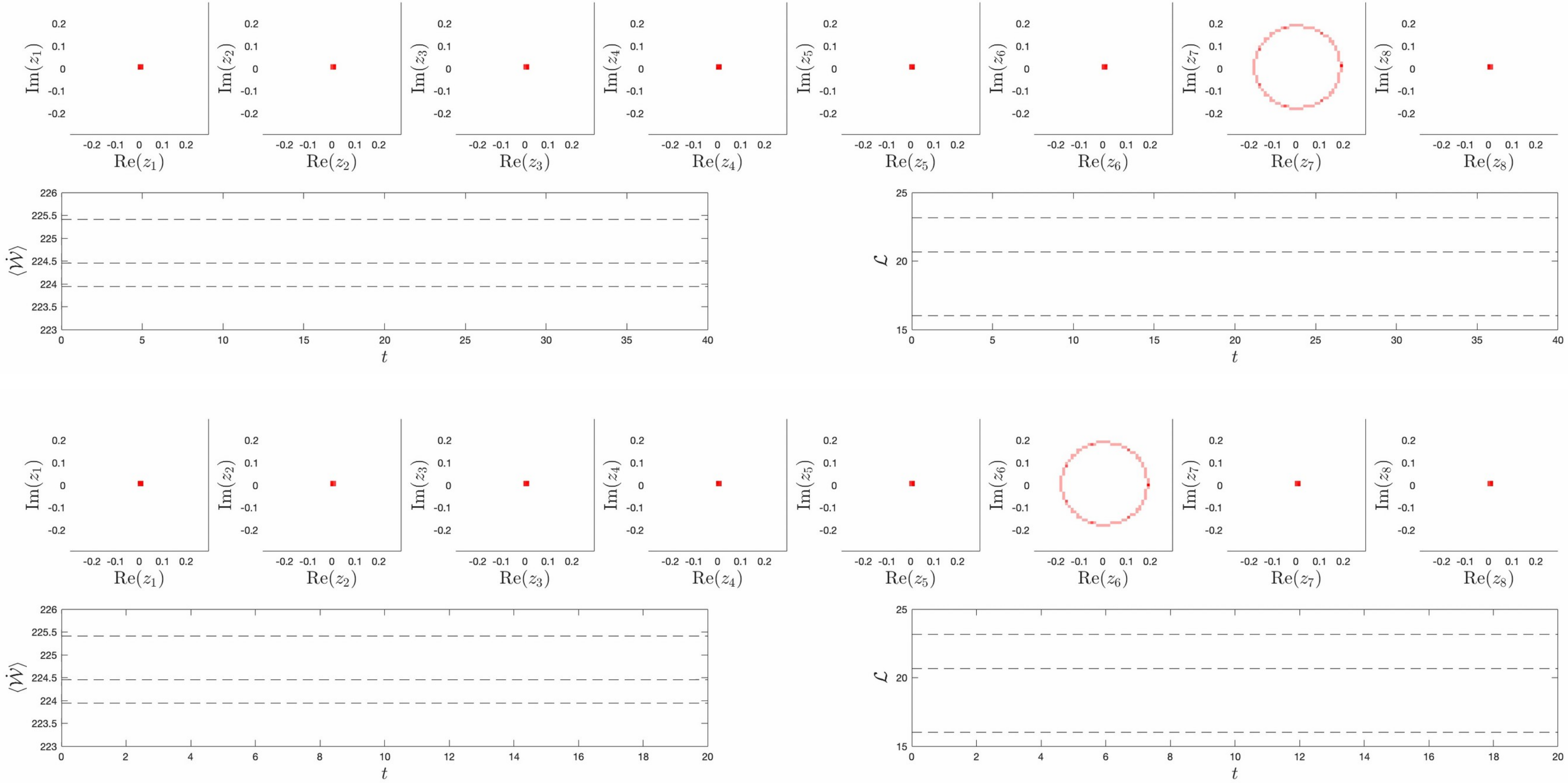


Meibohm, Esposito, arXiv:2401.14980, arXiv:2401.14982

Minimum entropy production principle

For large, but not infinite systems, the state selected in the long time limit is the one with minimum dissipation (maximum phase space contraction) is selected

N=10^5
q=17
3 stable states



Meibohm, Esposito, arXiv:2401.14980, arXiv:2401.14982

Energetics of Dissipative Structures in Nonideal Reaction-Diffusion

Motivation

Active Phase Separation is important in biology.
We need tools to study dynamics and thermodynamics of APS

Many studies are not thermodynamically consistent or focus on linear reactions

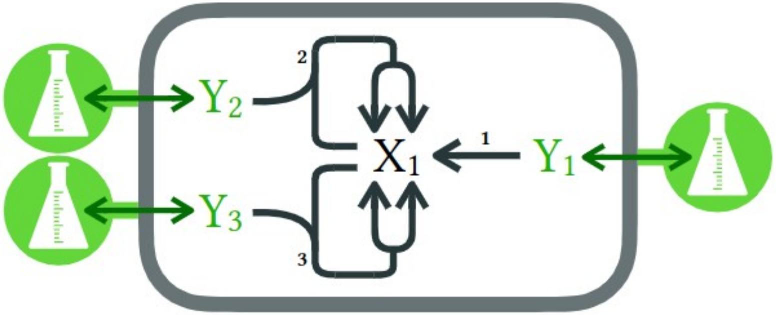
We need to bring together:

- Dynamics of phase separation (Cahn-Hilliard and Flory-Huggins theories)
  Intermolecular interaction but no reactions: dynamics goes to equilibrium

- Dynamics of Turing patterns
  Reactions but no interactions: dynamics remains out-of-equilibrium

- Thermodynamics of
  - Ideal reaction-diffusion (Turing Patterns Falasco, Rao, Esposito, PRL **121**, 108301 (2018);
    & Chemical Waves Avanzini, Falasco, Esposito, J. Chem. Phys. **151**, 234103 (2019))
  - Non-ideal reactions Avanzini, Penocchio, Falasco, Esposito, JCP **154**, 094114 (2021)

Nonideal Reaction-Diffusion



$$\sum_x \nu_{x,\rho} Z_x + \sum_y \nu_{y,\rho} Z_y \underset{-\rho}{\overset{\rho}{\rightleftharpoons}} \sum_x \nu_{x,-\rho} Z_x + \sum_y \nu_{y,-\rho} Z_y$$

X: internal species Y: chemostatted species

Dynamics: $$\partial_t c_i(\boldsymbol{r}) = \underbrace{-\nabla \cdot \boldsymbol{J}_i(\boldsymbol{c}(\boldsymbol{r}))}_{\textbf{diffusion}} + \underbrace{\sum_{\rho>0} S_{i,\rho}\, j_\rho(\boldsymbol{c}(\boldsymbol{r}))}_{\textbf{reactions}} + \underbrace{I_i(\boldsymbol{r})}_{\textbf{chemostats}}$$

$$S_{i,\rho} = \nu_{i,-\rho} - \nu_{i,\rho}$$

Free energy: $$F[\boldsymbol{c}] = F^{\mathrm{id}}[\boldsymbol{c}] + F^{\mathrm{ni}}[\boldsymbol{c}]$$

$$\mu_i(\boldsymbol{c}(\boldsymbol{r})) = \frac{\delta F[\boldsymbol{c}]}{\delta c_i(\boldsymbol{r})} = \underbrace{\mu_i^{\mathrm{id}}(c_i(\boldsymbol{r}))}_{\mu_i^\circ + RT \ln c_i(\boldsymbol{r})} + RT \ln \gamma_i(\boldsymbol{c}(\boldsymbol{r}))$$

Diffusion: $$\boldsymbol{J}_i(\boldsymbol{c}(\boldsymbol{r})) = -\sum_j O_{i,j}(\boldsymbol{c}(\boldsymbol{r})) \nabla \mu_j(\boldsymbol{c}(\boldsymbol{r}))$$

Reactions: $$\begin{cases} j_\rho(\boldsymbol{c}(\boldsymbol{r})) = \omega_\rho(\boldsymbol{c}(\boldsymbol{r})) - \omega_{-\rho}(\boldsymbol{c}(\boldsymbol{r})) \\ RT \ln \dfrac{\omega_\rho(\boldsymbol{c}(\boldsymbol{r}))}{\omega_{-\rho}(\boldsymbol{c}(\boldsymbol{r}))} = -\left(\sum_x \mu_x(\boldsymbol{c}(\boldsymbol{r})) S_{x,\rho} + \sum_y \mu_y(\boldsymbol{c}(\boldsymbol{r})) S_{y,\rho} \right) \end{cases}$$

Avanzini, Aslyamov, Fodor, Esposito, arXiv:2407.09128

Entropy Production

Dissipation due to diffusion:

$$T\dot{\Sigma}_{\mathrm{dff}}[\boldsymbol{c}] = -\sum_i \int_V \mathrm{d}\boldsymbol{r}\, \boldsymbol{\nabla}\mu_i(\boldsymbol{c}(\boldsymbol{r})) \cdot \boldsymbol{J}_i(\boldsymbol{c}(\boldsymbol{r}))$$

Dissipation due to reactions:

$$T\dot{\Sigma}_{\mathrm{rct}}[\boldsymbol{c}] = -\sum_i \sum_{\rho>0} \int_V \mathrm{d}\boldsymbol{r}\, \mu_i(\boldsymbol{c}(\boldsymbol{r})) S_{i,\rho} j_\rho(\boldsymbol{c}(\boldsymbol{r}))$$

$$T\dot{\Sigma}_{\mathrm{dff}}[\boldsymbol{c}] = \int_V \mathrm{d}\boldsymbol{r} \underbrace{\sum_{i,j} \boldsymbol{\nabla}\mu_i(\boldsymbol{c}(\boldsymbol{r})) \cdot O_{i,j}(\boldsymbol{c}(\boldsymbol{r}))\boldsymbol{\nabla}\mu_j(\boldsymbol{c}(\boldsymbol{r}))}_{\equiv T\dot{\sigma}_{\mathrm{dff}}(\boldsymbol{r})\geq 0} \geq 0$$

$$T\dot{\Sigma}_{\mathrm{rct}}[\boldsymbol{c}] = \int_V \mathrm{d}\boldsymbol{r} \underbrace{RT \sum_{\rho>0} j_\rho(\boldsymbol{c}(\boldsymbol{r})) \ln \frac{\omega_\rho(\boldsymbol{c}(\boldsymbol{r}))}{\omega_{-\rho}(\boldsymbol{c}(\boldsymbol{r}))}}_{\equiv T\dot{\sigma}_{\mathrm{rct}}(\boldsymbol{r})\geq 0} \geq 0$$

Avanzini, Aslyamov, Fodor, Esposito, arXiv:2407.09128

Model

X: internal species diffuse, interact and react
Y: chemostatted species react but are homogeneous & ideal

Cahn-Hilliard-like $$F^{\mathrm{ni}}[\boldsymbol{c}] = \frac{RT}{2} \sum_{x,x'} \int_V \mathrm{d}\boldsymbol{r} \left[c_x(\boldsymbol{r}) M_{x,x'} c_{x'}(\boldsymbol{r}) + \boldsymbol{\nabla} c_x(\boldsymbol{r}) \cdot K_{x,x'} \boldsymbol{\nabla} c_{x'}(\boldsymbol{r}) \right]$$

interface cost

No cross-diffusion $$O_{i,j}(\boldsymbol{c}(\boldsymbol{r})) = D_i c_i(\boldsymbol{r}) \mathbb{1}_{i,j}$$

Arrhenius-like $$\omega_\rho(\boldsymbol{c}(\boldsymbol{r})) = A_\rho\, e^{\frac{\sum_X \mu_X(\boldsymbol{c}(\boldsymbol{r}))\, \nu_{X,\rho}}{RT}}\, e^{\frac{\sum_Y \mu_Y \nu_{Y,\rho}}{RT}}$$

Stability of the Homogeneous Solution

Evolution of a small perturbation around the NESS in Fourier space

$$\partial_t \delta\tilde{\boldsymbol{c}}(q) = \boxed{\mathbb{B}(q)\cdot\mathbb{M}(q)}\cdot\delta\tilde{\boldsymbol{c}}(q)$$

Unstable if an eigenvalue becomes positive

$$\mathbb{B}(q) = -q^2 \underset{\geqslant 0}{\mathbb{A}} + \mathbb{C}$$

reactions

$$C_x^{x'} = S_x^\rho s_\rho \left[\nu_{+\rho}^{x'} \mu_{x''}^* \nu_{+\rho}^{x''} + \mu_y \nu_{+\rho}^y - \nu_{-\rho}^{x'} \mu_{x''}^* \nu_{-\rho}^{x''} + \mu_y \nu_{-\rho}^y \right]$$

interactions

$$M_{xx'}(q) = \frac{\partial^2 f_0(\boldsymbol{c}^*)}{\partial c_x \partial c_{x'}} + q^2 K_{x,x'}(\boldsymbol{c}^*)$$

Independent of reactions

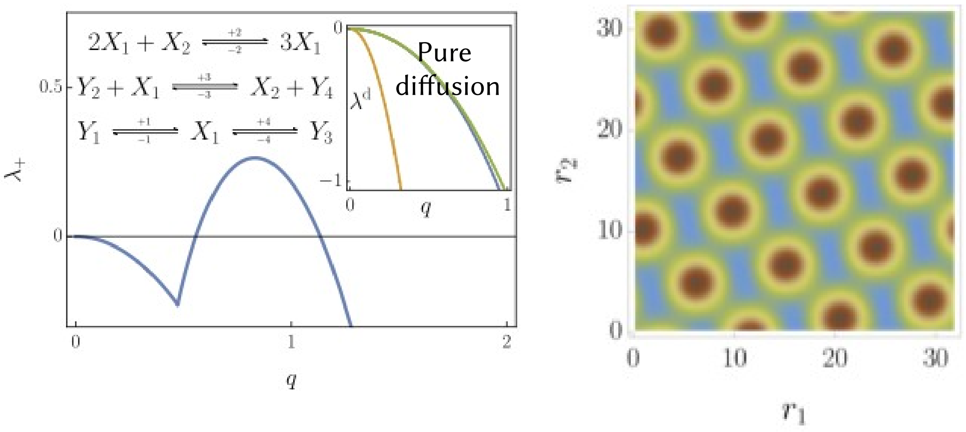
We look for $\det(\mathbb{B}(q_0)\cdot\mathbb{M}(q_0)) = (\det\mathbb{B}(q_0))(\det\mathbb{M}(q_0)) = 0$

R-type instability (from $\det\mathbb{B}(q_0)$)

E-type instability (from $\det\mathbb{M}(q_0)$)

Aslyamov, Avanzini, Fodor, Esposito, PRL **131**, 138301 (2023)

R-type instability

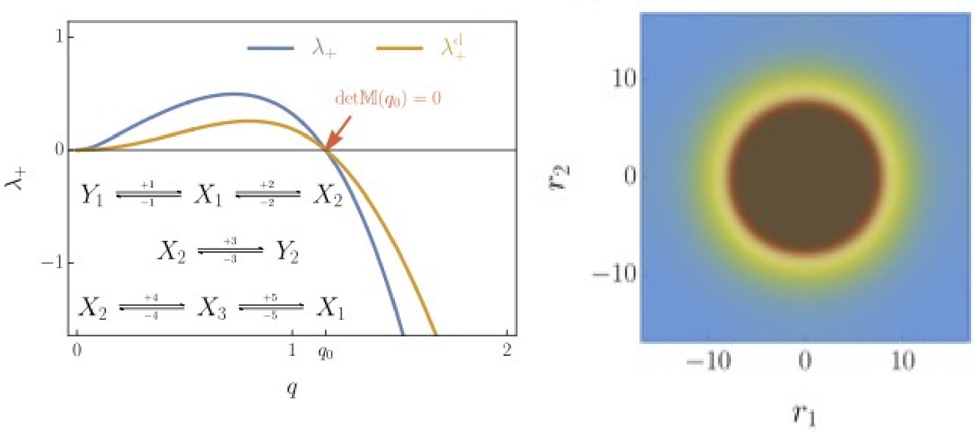


- Impossible in pseudo-unimolecular and certain multimolecular CRNs

$$\nu^y_{+\rho} Z_y + m_\rho \varepsilon_{x,+\rho} Z_x \underset{-\rho}{\overset{+\rho}{\rightleftharpoons}} \nu^y_{-\rho} Z_y + m_\rho \varepsilon_{x',-\rho} Z_{x'}$$

- Caused by multimolecular reactions but controlled by intermolecular interactions

E-type instability



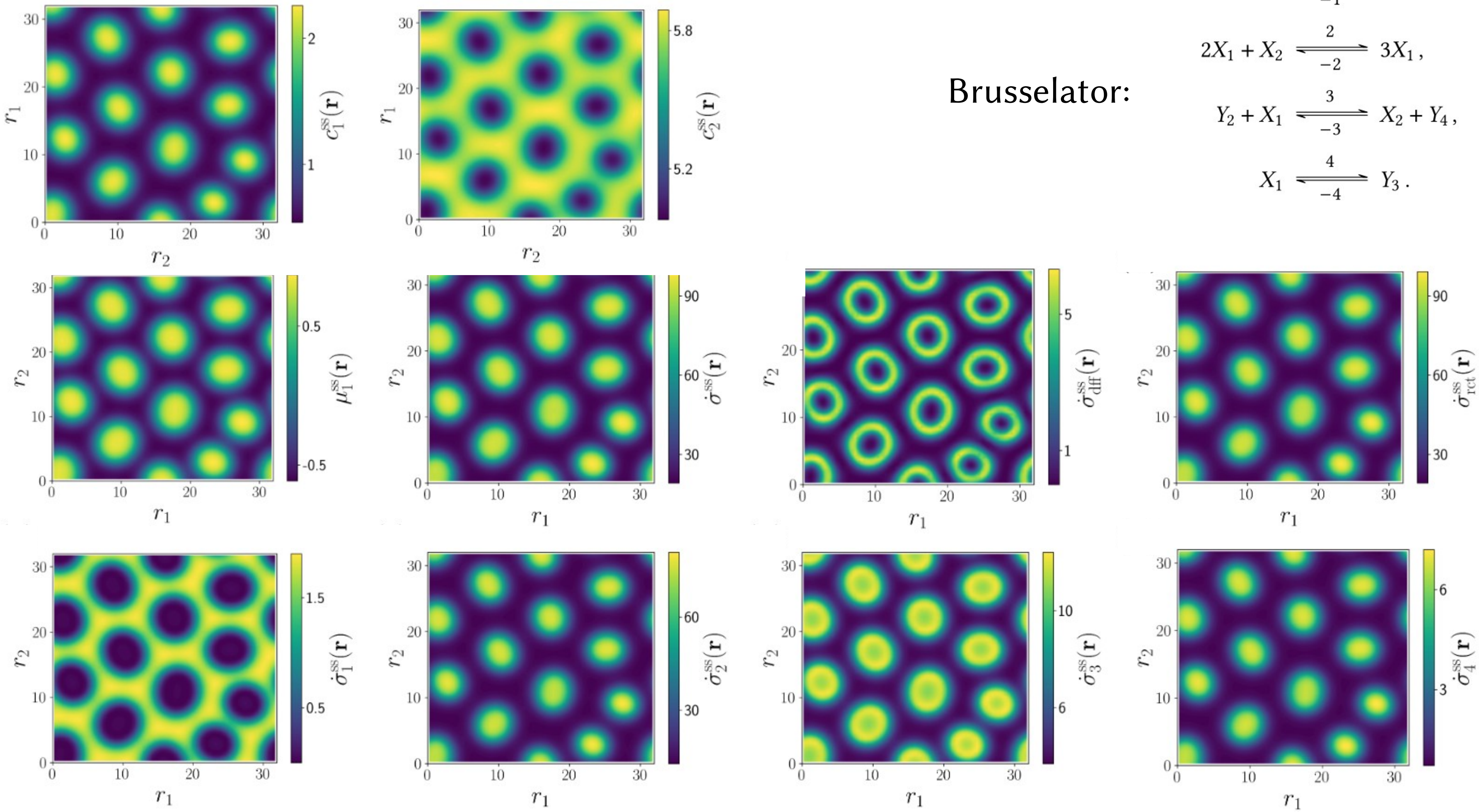
- Caused by intermolecular interactions

Aslyamov, Avanzini, Fodor, Esposito, PRL **131**, 138301 (2023)

Space-Resolved Entropy Production

Brusselator:

$$
\begin{aligned}
Y_1 &\underset{-1}{\overset{1}{\rightleftharpoons}} X_1\,,\\
2X_1 + X_2 &\underset{-2}{\overset{2}{\rightleftharpoons}} 3X_1\,,\\
Y_2 + X_1 &\underset{-3}{\overset{3}{\rightleftharpoons}} X_2 + Y_4\,,\\
X_1 &\underset{-4}{\overset{4}{\rightleftharpoons}} Y_3\,.
\end{aligned}
$$



Avanzini, Aslyamov, Fodor, Esposito, arXiv:2407.09128

Pseudo Detailed Balanced & Complex Balanced CRNs

Any flux

Reactions dissipate but diffusion equilibrates

$$\dot{\sigma}^{ss}_{rct}(\boldsymbol{r}) > 0 \qquad \dot{\sigma}^{ss}_{dff}(\boldsymbol{r}) = 0$$

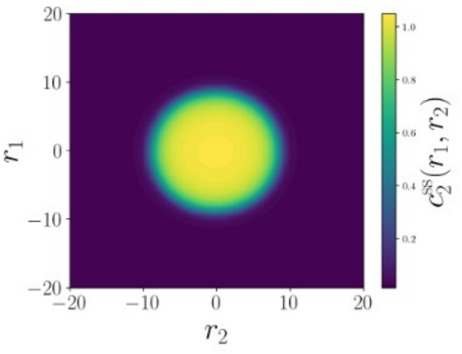
Arrhenius fluxes

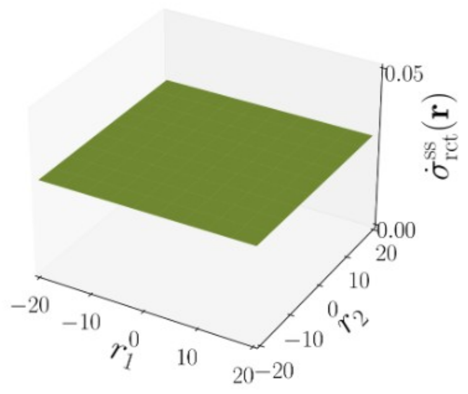
$\{X_1, X_2, X_{nr}\}$

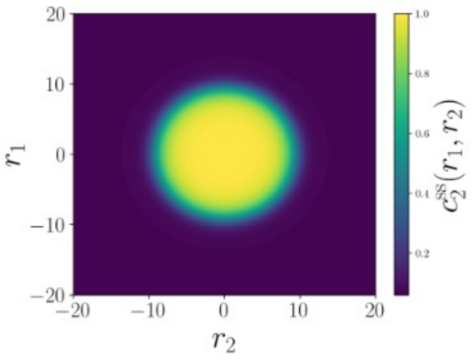
$$X_1 + Y_1 \underset{-1}{\overset{1}{\rightleftharpoons}} X_2 + Y_2\,,$$
$$X_1 \underset{-2}{\overset{2}{\rightleftharpoons}} X_2\,.$$

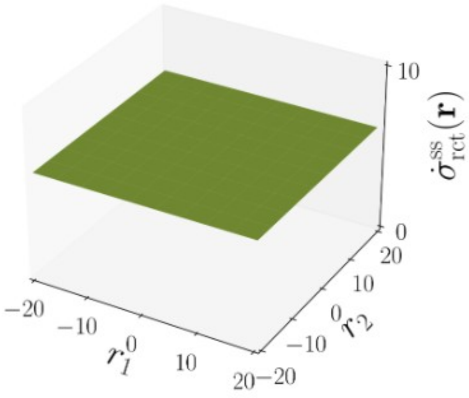
$\{X_1, X_2, X_3, X_{nr}\}$

$$X_1 + Y_1 \underset{-1}{\overset{1}{\rightleftharpoons}} X_2 + Y_2\,,$$
$$X_2 \underset{-2}{\overset{2}{\rightleftharpoons}} X_3\,,$$
$$X_3 \underset{-3}{\overset{3}{\rightleftharpoons}} X_1\,.$$







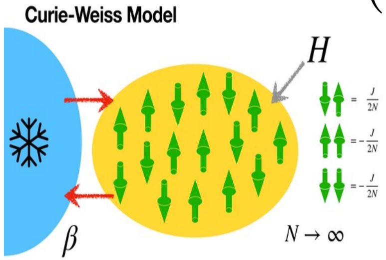


Avanzini, Aslyamov, Fodor, Esposito, arXiv:2407.09128

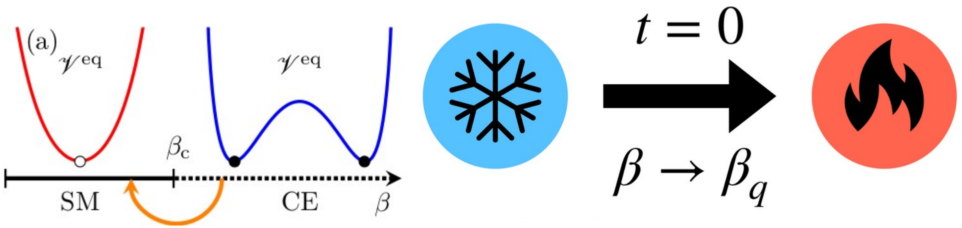
Finite-time dynamical phase transitions

Finite time dynamical phase transitions

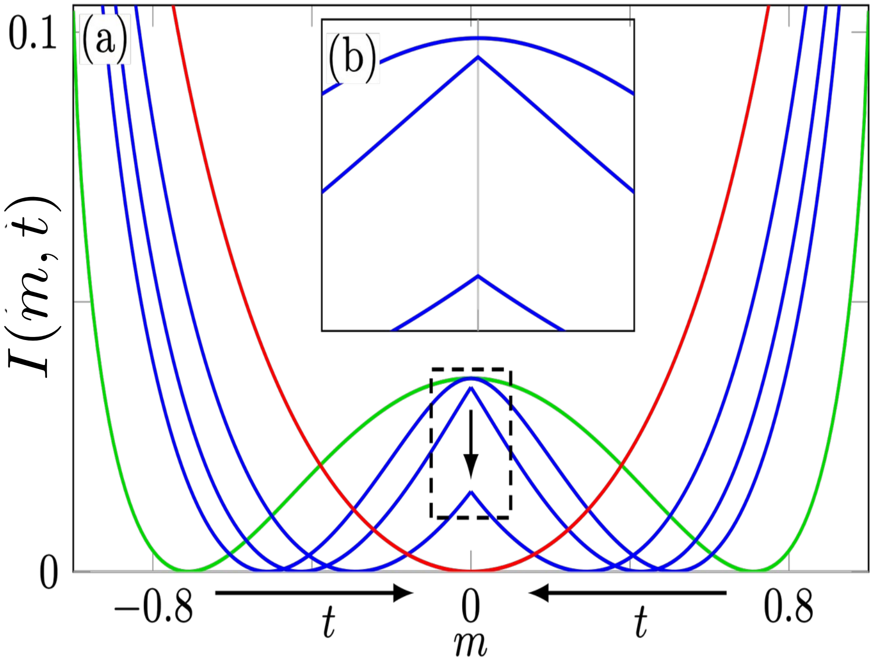
$P(x,t) \asymp e^{-\Omega I(x,t)}$ → appearance of a kink at a critical time



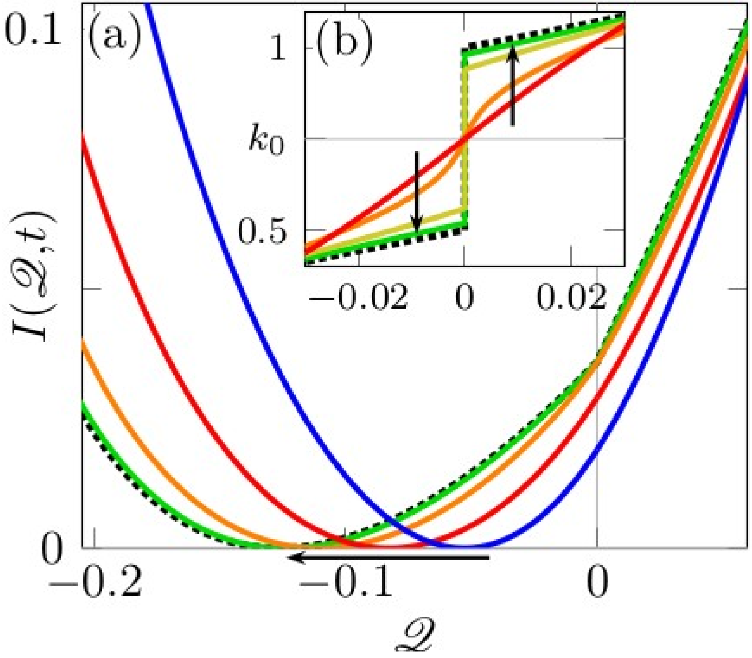
Temperature **quench**



Magnetization



Heat



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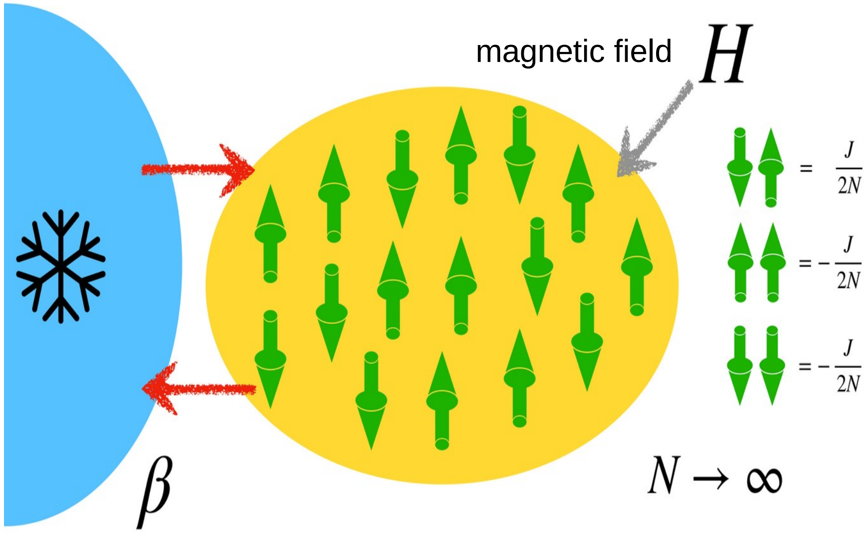
Dynamics of Curie-Weiss Model



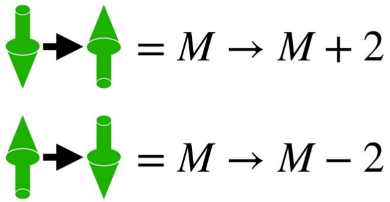
Express in terms of **total magnetisation** $M = N_\uparrow - N_\downarrow$.

$$F(M) = -\frac{J}{2N}\left(M^2 - N\right) - MH - \beta^{-1}S(M)$$

Internal entropy

Stochastic dynamics

$$\dot{P}(M,t) = \sum_{\pm}\left[W_\pm(M \mp 2)P(M \mp 2, t) - W_\pm(M)P(M,t)\right]$$



Rates with properties

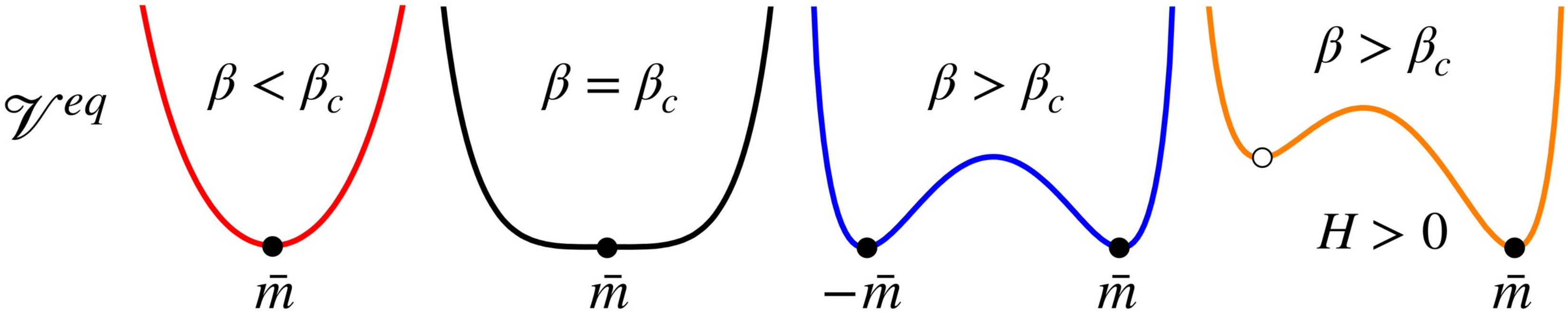
$$W_\pm(M)\,|_{H=0} = W_\mp(-M)\,|_{H=0} \text{ and } W_\pm(M)P^{eq}(M) = W_\mp(M \pm 2)P^{eq}(M \pm 2)$$

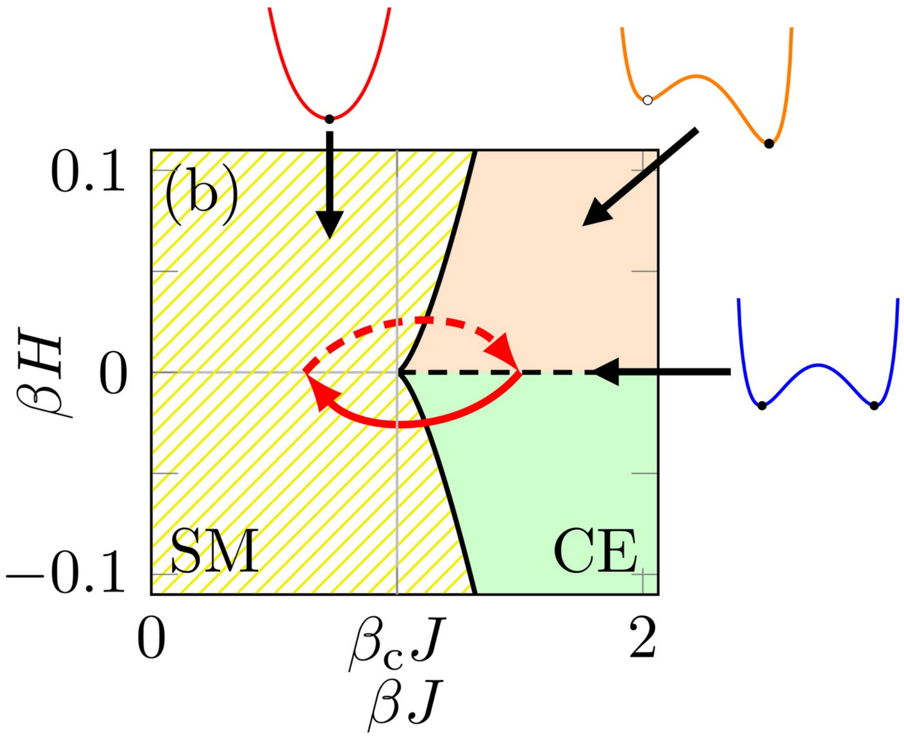
Review of the equilibrium phase transition

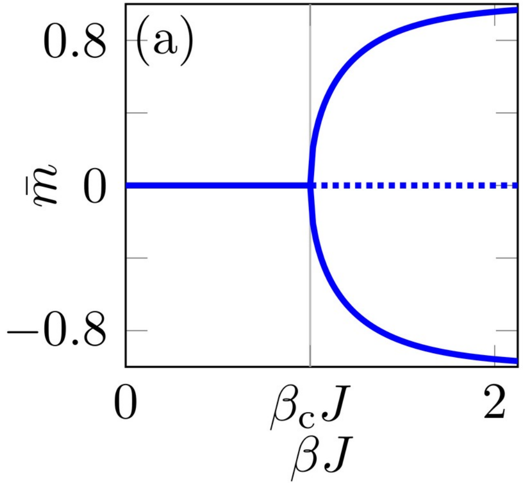
Define intensive quantities $m = M/N$ and $\mathcal{F}(m) = F(M)/N$.

Equilibrium distribution takes **large-deviation form** $P^{eq}(m) \approx \exp[-N\mathcal{V}^{eq}(m)]$, with equilibrium **rate function** $\mathcal{V}^{eq}(m) = \beta\left[\mathcal{F}(m) - \mathcal{F}_{min}\right]$.

Equilibrium phase transition at $\beta_c = 1/J$:







Continuous phase transition $\bar{m} \sim |\beta - \beta_c|^{1/2}$

Equation of state $\beta H \sim -J\left(\beta - \beta_c\right)\bar{m} + \frac{\bar{m}^3}{3}$

We will quench: $\xrightarrow[\beta \to \beta_q]{t=0}$

Dynamics in the macroscopic limit

In thermodynamic limit $P(m,t) \approx \exp[-NV(m,t)]$, and master equation becomes **Hamilton-Jacobi equation** for $V(m,t)$.

$0 = \partial_t V(m,t) + \mathcal{H}[m, \partial_m V(m,t)]$, with $V(m,0) = \mathcal{V}^{eq}(m)$ and $V(m,\infty) = \mathcal{V}^{eq}_q(m)$.

Solved by **characteristics** that obey Hamilton equations $\dot{q}(s) = \partial_p \mathcal{H}(q,p)$, $\dot{p}(s) = -\partial_q \mathcal{H}(q,p)$, and boundary conditions $p(0) = \frac{d}{dm}\mathcal{V}^{eq}[q(0)]$, $q(t) = m$.

Rate function obtained by $V(m,t) = \int_0^t ds \left[p\dot{q} - \mathcal{H}(q,p)\right] + \mathcal{V}^{eq}[q(0)]$, and obeys **variational principle** $\delta V(m,t) = 0$.

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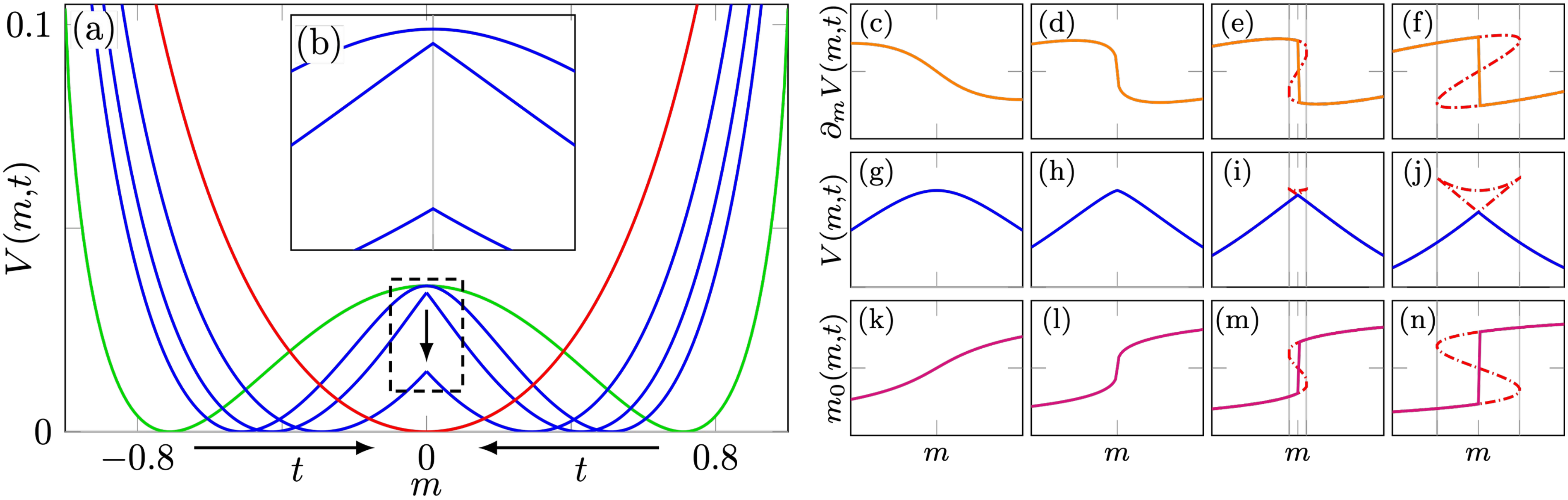
Dynamical phase transition

Hamilton equations solved by numerical **shooting method**.

Method generates **three fields**, $V(m,t)$, $\partial_m V(m,t)$, and $m_0(m,t)$.



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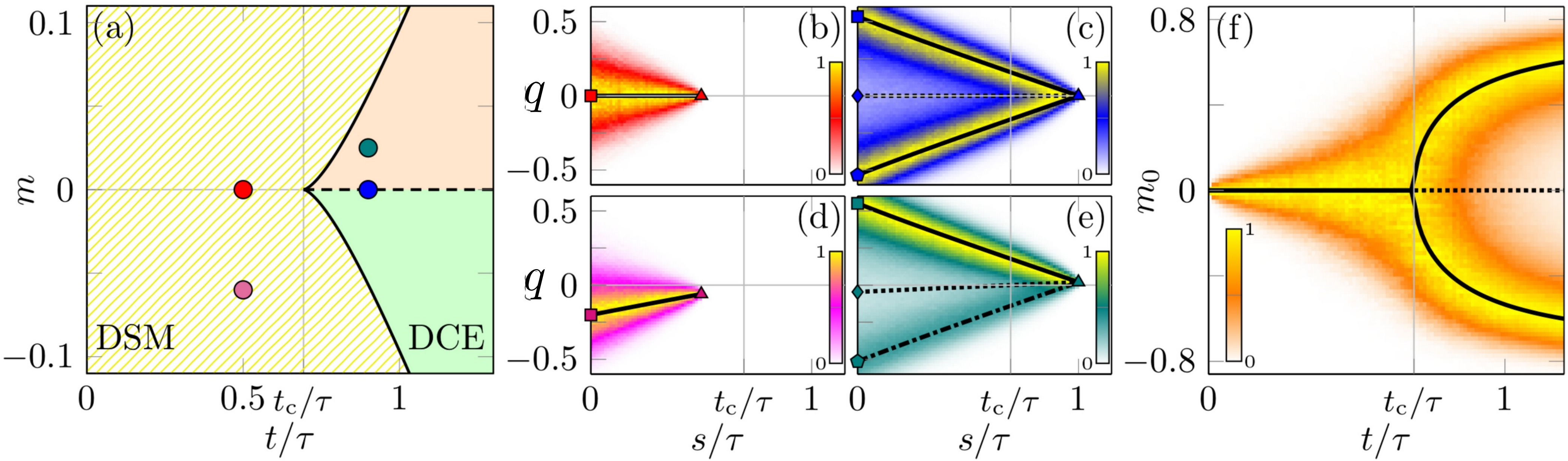
Dynamical phase diagram

Critical time: $t_c/\tau = \ln\left[(\beta-\beta_q)/(\beta-\beta_c)\right]/[4(\beta_c-\beta_q)J]$



Equilibrium → dynamical phase transition mapping: $\beta \to t\ ,\ \bar{m} \to m_0\ ,\ H \to m$

Continuous phase transition: $m_0 \propto |t - t_c|^{1/2}$

Dynamical equation of state: $m \sim -a_1\tau^{-1}(t-t_c)m_0 + b_0 m_0^3$

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Conclusions

We now have tools to study the **nonequilibrium thermodynamics of macroscopic nonlinear phenomena** (provided we know the underlying stochastic thermodynamics description of it)