Nonequilibrium thermodynamics based on information geometry

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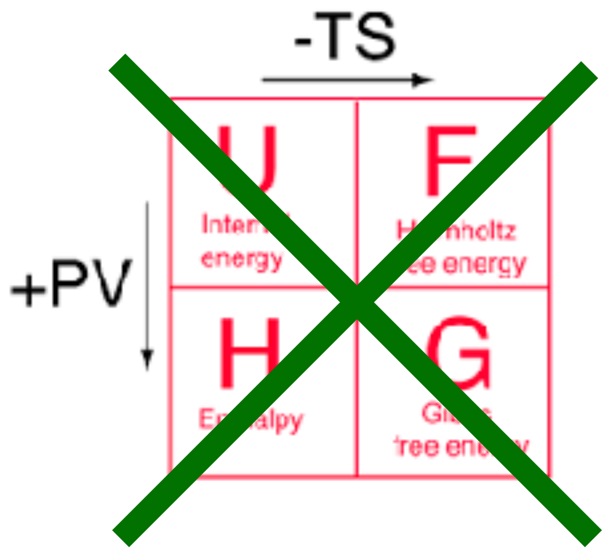
Our interests: Geometry of nonequilibrium thermodynamics

We DO NOT focus on the classical thermodynamics for the equilibrium systems.



Geometry of equilibrium thermodynamics: Weinhold (1975), Ruppeiner (1979) …etc.

Weinhold, F. *The Journal of Chemical Physics*, *63*, 2479 (1975). Ruppeiner, G., *Physical Review A*, *20*, 1608 (1979).

(Thermodynamic potentials are only defined for the equilibrium systems.)

Nonequilibrium thermodynamics:

Textbook: De Groot, S. R., & Mazur, P. *Non-equilibrium thermodynamics*. Courier Corporation (2013).

Non-stationary Dynamics

- The state changes over time.

Violation of the detailed balance condition

- Energy function (thermodynamic potential) is not generally well defined.
- The system is open, and dynamics are irreversible.
- Thermodynamic dissipation (irreversibility) is introduced by the entropy production.

Situations of nonequilibrium thermodynamics

Langevin equation / Fokker-Planck equation (Brownian motion)

$$\dot{\boldsymbol{x}}(t) = \mu \boldsymbol{F}_t(\boldsymbol{x}(t)) + \sqrt{2\mu T}\boldsymbol{\xi}(t)$$

$$\langle \boldsymbol{\xi}(t) \rangle = \boldsymbol{0}, \langle \xi_i(t)\xi_j(t') \rangle = \delta(t-t')\delta_{ij}$$

$$\partial_t P_t(\boldsymbol{x}) = -\nabla \cdot (\mu[\boldsymbol{F}_t(\boldsymbol{x}) - T\nabla \ln P_t(\boldsymbol{x})]P_t(\boldsymbol{x}))$$

Master equation (Markov dynamics)

$$\dot{x}_i = \sum_{\alpha} \sum_{j=1}^{d} [R^\alpha_{ij} x_i - R^\alpha_{ij} x_j]$$

Rate equation (deterministic chemical reaction)

$$\dot{x}_i = \sum_{r=1}^{m} (\kappa_{ri} - \nu_{ri})[k_r^+ \prod_{j=1}^{d} (x_j)^{\nu_{rj}} - k_r^- \prod_{j=1}^{d} (x_j)^{\kappa_{rj}}]$$

$$\sum_{i=1}^{d} \nu_{ri} X_i \underset{k_r^-}{\overset{k_r^+}{\rightleftharpoons}} \sum_{i=1}^{d} \kappa_{ri} X_i$$

Reaction-diffusion equation

Navier-Stokes equation (Fluid dynamics)

Lindblad equation (Quantum Markov dynamics) …etc.

Q: What is a (unified) geometry of nonequilibrium thermodynamics for these systems?

The entropy production is historically defined for these systems.

Two approaches: Information geometry and optimal transport

Information geometry

Based on
- Fisher metric
- Kullback-Leibler divergence
- Bregman divergence
- Duality ⋯etc.

Optimal transport

Based on
- Gradient flow
- Optimization problems
- Cost minimization
- Duality ⋯etc.

Which are useful for nonequilibrium thermodynamics?

Could we consider a unified geometry?

Is it possible to use both theories for the problems of nonequilibrium thermodynamics?

We have done several trials in various forms (2017-).

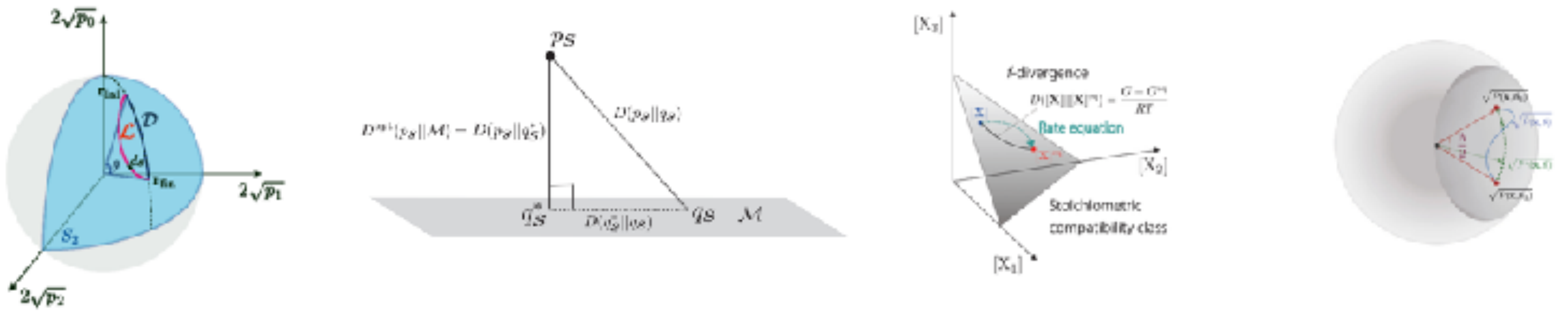
Please check my Google scholar [Sosuke Ito] if you are interested,

Information geometry

Langevin equation/
Fokker-Planck equation (Brownian motion)

Master equation (Markov dynamics)

Rate equation (Chemical reaction)

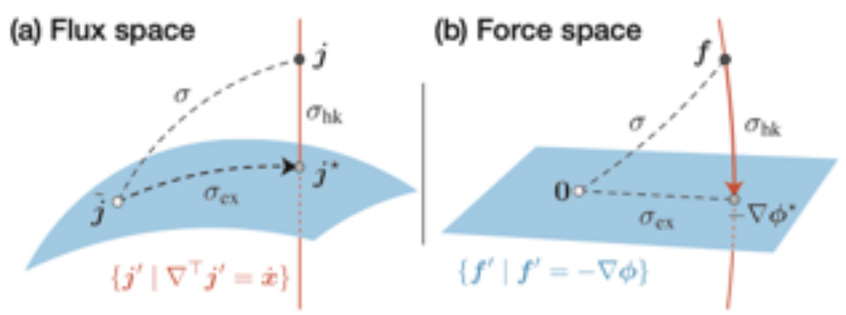


Unified approach

Langevin equations/
Fokker-Planck equations (Brownian motion)

Master equation (Markov dynamics)

Rate equation (Chemical reaction)



Today's talk

Kolchinsky, A., Dechant, A., Yoshimura, K., & SI. *arXiv:2206.14599.*
Kolchinsky, A., Dechant, A., Yoshimura, K., & SI. *arXiv: 2412.08432.*

Optimal transport

Langevin equation/
Fokker-Planck equation (Brownian motion)

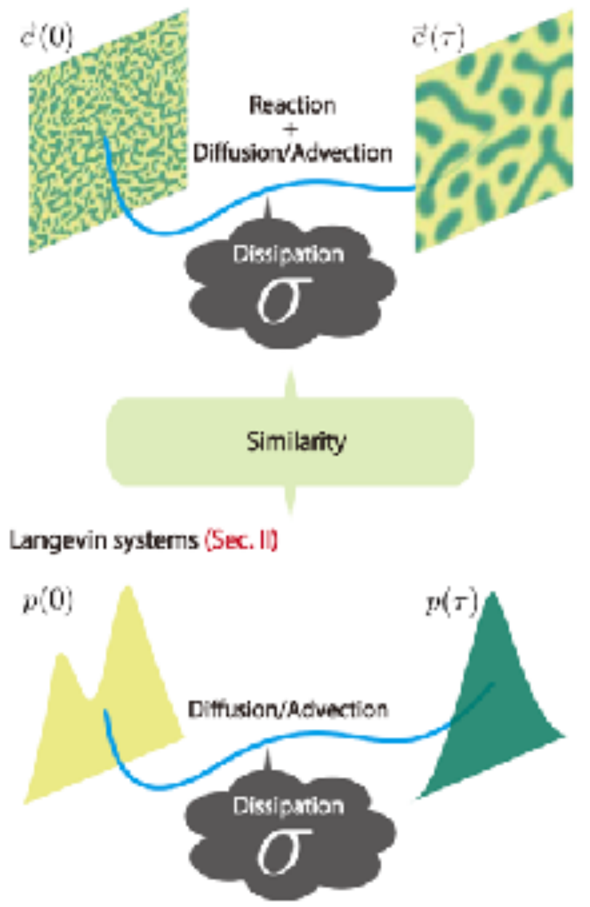
Master equation (Markov dynamics)

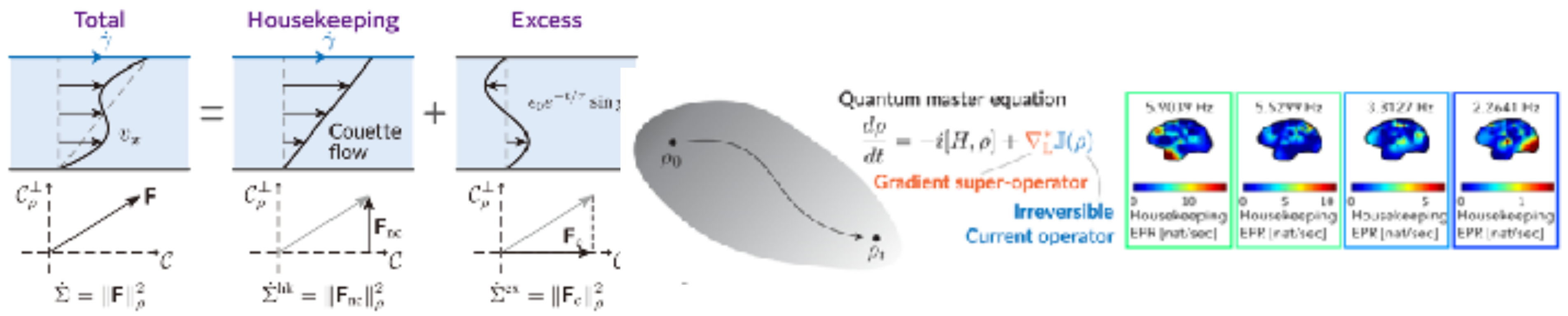
Rate equation (Chemical reaction)

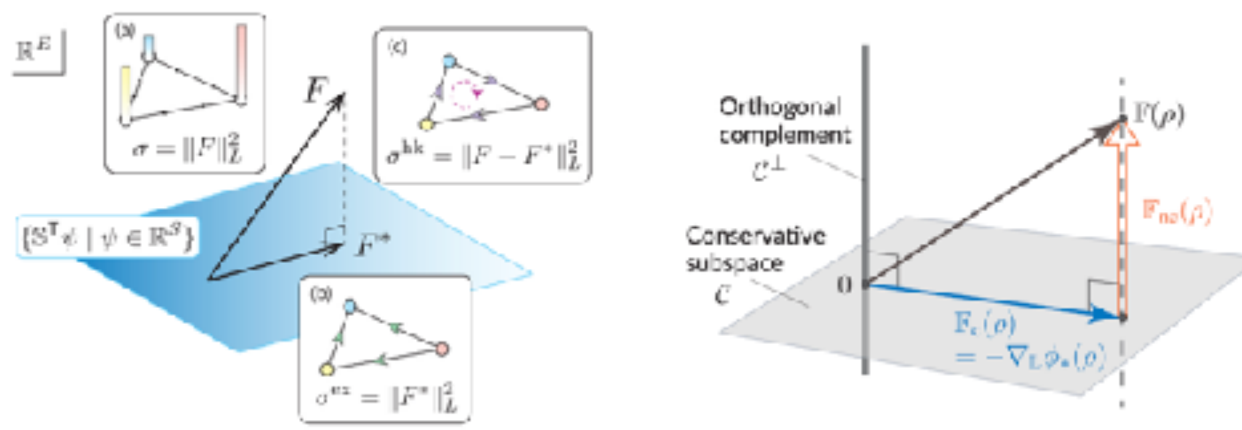
Reaction-diffusion equation

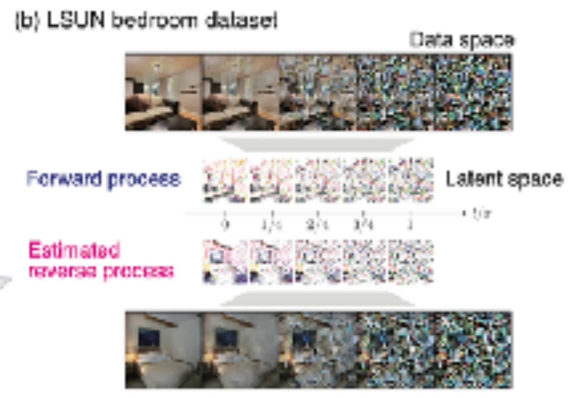
Navier-Stokes equation (Fluid dynamics)

Lindblad equation (Quantum Markov dynamics)



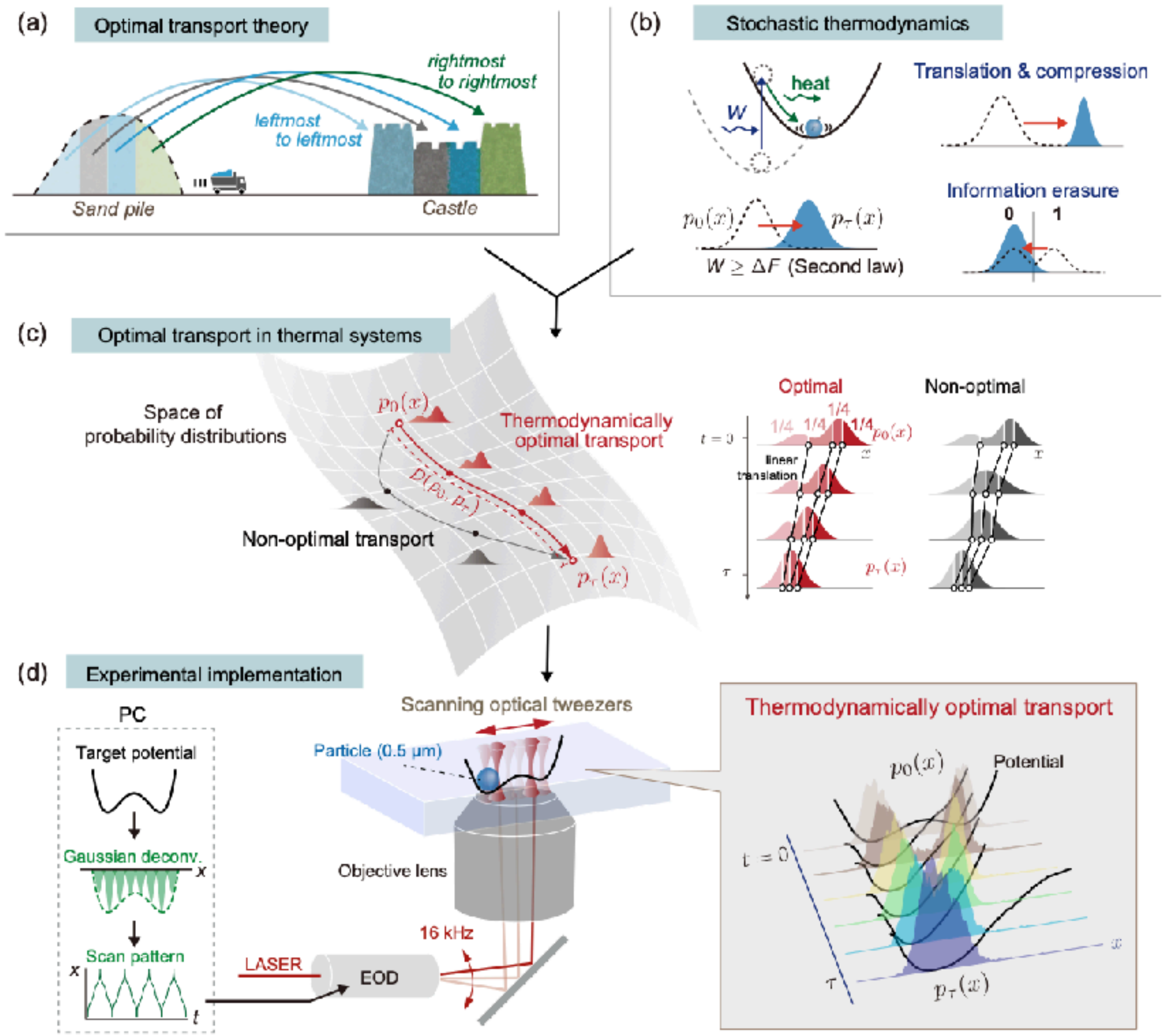


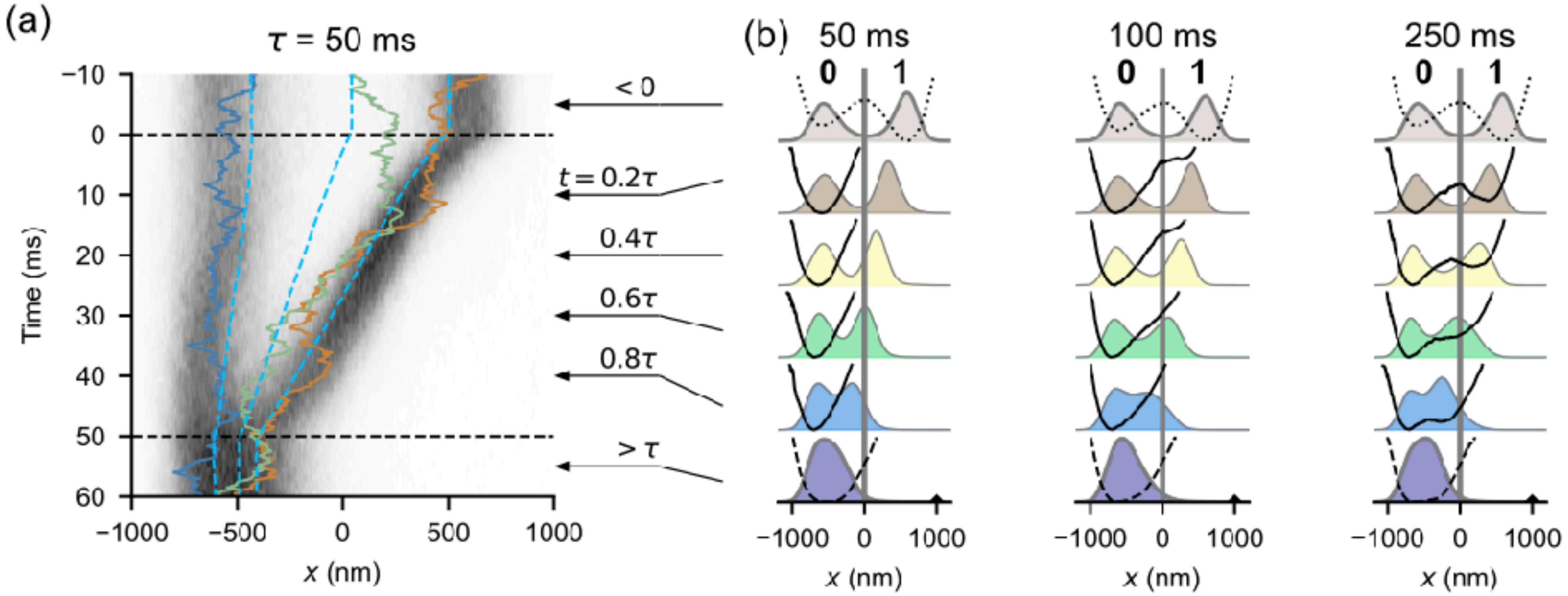




[Example] Recent "experimental" result

Oikawa, S., Nakayama, Y., SI., Sagawa, T., & Toyabe, S. *arXiv preprint arXiv:2503.01200 (2025).*





Optimal transport for Brownian particles with optical tweezers has been experimentally achieved.

We discussed the minimum thermodynamic dissipation for information erasure (e.g., the finite-time Landauer principle) using the 2-Wasserstein distance.

Contributors to today's talk:
Nonequilibrium thermodynamics based on information geometry

Today’s talk

Unified approach for the master/rate equations
A. Kolchinsky, A. Dechant, K. Yoshimura and SI. arXiv:2412.08432 (2024).
(Old ver.) A. Kolchinsky, A. Dechant, K. Yoshimura and SI. arXiv:2206.14599 (2022).

Related topic: Unified approach for the Fokker-Planck equation
SI, Info. Geo. **7**, 441-483 (2024).

Related topic: Optimal transport for the master/rate equations
K. Yoshimura, A. Kolchinsky, A. Dechant and SI, Physical Review Research, **5**, 013017 (2023).

Artemy Kolchinsky (Pompeu-Fabra Univ.)

Andreas Dechant (Kyoto Univ.)

Kohei Yoshimura (Univ. of Tokyo)

Outline

- **Introduction: Nonequilibrium thermodynamics for the Fokker-Planck equation, optimal transport and information geometry**

SI, Info. Geo. **7**, 441-483 (2024). [Special Issue: Half a Century of Information Geometry, Part 1]

- Nonequilibrium thermodynamics for the master/rate equation, optimal transport and information geometry
- Topics of nonequilibrium thermodynamics based on information geometry

SI, Info. Geo. **7**, 441-483 (2024).

Introduction: Fokker-Planck equation and the entropy production rate

Fokker-Planck equation

$$\partial_t P_t(\boldsymbol{x}) = -\nabla \cdot (\mu[\boldsymbol{F}_t(\boldsymbol{x}) - T\nabla \ln P_t(\boldsymbol{x})]P_t(\boldsymbol{x})) = -\nabla \cdot (\boldsymbol{\nu}_t(\boldsymbol{x})P_t(\boldsymbol{x}))$$

[Corresponding Langevin Eq.]

$$\dot{\boldsymbol{x}}(t) = \mu \boldsymbol{F}_t(\boldsymbol{x}(t)) + \sqrt{2\mu T}\boldsymbol{\xi}(t)$$

$$\langle \boldsymbol{\xi}(t) \rangle = \boldsymbol{0}, \langle \xi_i(t)\xi_j(t') \rangle = \delta(t-t')\delta_{ij}$$

Def.) Entropy production rate

Review: Seifert, U. *Reports on progress in physics*, *75*, 126001 (2012).

$$\sigma_t = \frac{1}{\mu T}\int d\boldsymbol{x} \|\boldsymbol{\nu}_t(\boldsymbol{x})\|^2 P_t(\boldsymbol{x}) \; (\geq 0)$$

Non-negativity is physically important.
(The second law of thermodynamics)

A measure of irreversibility (KL divergence between the forward process $\mathbb{P}$ and the backward process $\mathbb{P}_{\mathrm{B}}$)

$$\sigma_t dt = D_{\mathrm{KL}}(\mathbb{P}\|\mathbb{P}_{\mathrm{B}}) + O(dt^2)$$

$$D_{\mathrm{KL}}(\mathbb{P}\|\mathbb{P}_{\mathrm{B}}) := \mathbb{E}_{\mathbb{P}}\left[\ln \frac{\mathbb{P}}{\mathbb{P}_{\mathrm{B}}} + \frac{\mathbb{P}_{\mathrm{B}}}{\mathbb{P}} - 1\right] = \mathbb{E}_{\mathbb{P}}\left[\ln \frac{\mathbb{P}}{\mathbb{P}_{\mathrm{B}}}\right]$$

$$\mathbb{P}(\boldsymbol{x}(t+dt), \boldsymbol{x}(t)) = \mathbb{T}_t(\boldsymbol{x}(t+dt) \,|\, \boldsymbol{x}(t))P_t(\boldsymbol{x}(t))$$

$$\mathbb{P}_{\mathrm{B}}(\boldsymbol{x}(t+dt), \boldsymbol{x}(t)) = \mathbb{T}_t(\boldsymbol{x}(t) \,|\, \boldsymbol{x}(t+dt))P_{t+dt}(\boldsymbol{x}(t+dt))$$

$$\mathbb{T}_t(\boldsymbol{x}(t+dt) \,|\, \boldsymbol{x}(t)) \propto \exp\left[-\frac{\|\boldsymbol{x}(t+dt) - \boldsymbol{x}(t) - \mu \boldsymbol{F}_t(\boldsymbol{x}(t))dt\|^2}{4\mu T dt}\right]$$

SI, Info. Geo. **7**, 441-483 (2024).

Introduction: 2-Wasserstein distance

Def.) 2-Wasserstein distance (Benamou-Brenier, 2000)

Benamou, J. D., & Brenier, Y. *Numerische Mathematik*, *84*, 375 (2000).

$$\mathcal{W}_2(Q_0, Q_\tau) = \sqrt{\inf \left[\tau \int_0^\tau dt \int d\boldsymbol{x} \|\boldsymbol{u}_t(\boldsymbol{x})\|^2 Q_t(\boldsymbol{x}) \right]} \quad \textit{\textbf{s.t.}}$$

Continuity equation

$$\partial_t Q_t(\boldsymbol{x}) = -\nabla \cdot (\boldsymbol{u}_t(\boldsymbol{x}) Q_t(\boldsymbol{x}))$$

$Q_0(\boldsymbol{x}), Q_\tau(\boldsymbol{x})$:fixed

Optimal solution (Benamou-Brenier, 2000):

$$\partial_t Q_t^*(\boldsymbol{x}) = -\nabla \cdot (\nabla \phi_t^*(\boldsymbol{x}) Q_t^*(\boldsymbol{x}))$$

$$\partial_t \phi_t^*(\boldsymbol{x}) = -\frac{1}{2} \|\nabla \phi_t^*(\boldsymbol{x})\|^2 \quad Q_0^*(\boldsymbol{x}) = Q_0(\boldsymbol{x}), Q_\tau^*(\boldsymbol{x}) = Q_\tau(\boldsymbol{x}) \quad \mathcal{W}_2(Q_0, Q_\tau) = \sqrt{\int_0^\tau dt \int d\boldsymbol{x} \|\nabla \phi_t^*(\boldsymbol{x})\|^2 Q_t^*(\boldsymbol{x})}$$

The lower bound on the entropy production rate
[Def.) The excess entropy production rate]

Nakazato, M., & SI. *Physical Review Research*, *3*, 043093 (2021).
Dechant, A., Sasa, S. I., and SI. Physical Review Research, 4, L012034 (2022).

$$\sigma_t = \frac{1}{\mu T} \int d\boldsymbol{x} \|\boldsymbol{\nu}_t(\boldsymbol{x})\|^2 P_t(\boldsymbol{x}) \geq \frac{1}{\mu T} \left(\lim_{\Delta t \to +0} \frac{\mathcal{W}_2(P_t, P_{t+\Delta t})}{\Delta t} \right)^2 = \sigma_t^{\mathrm{ex}}$$

$$\sigma_t^{\mathrm{ex}} := \inf_{\boldsymbol{u}_t} \frac{1}{\mu T} \int d\boldsymbol{x} \|\boldsymbol{u}_t(\boldsymbol{x})\|^2 P_t(\boldsymbol{x}) \quad \textit{\textbf{s.t.}} \quad \partial_t P_t(\boldsymbol{x}) = -\nabla \cdot (\boldsymbol{u}_t(\boldsymbol{x}) P_t(\boldsymbol{x}))$$

SI, Info. Geo. **7**, 441-483 (2024).

Introduction: Thermodynamic force and flux

Entropy production rate (= Sum of flux × force)

$$\sigma_t = \int d\boldsymbol{x} \boldsymbol{f}_t(\boldsymbol{x}) \cdot \boldsymbol{j}_t(\boldsymbol{x})$$

Def.) Fluxes

$$\boldsymbol{j}_t(\boldsymbol{x}) := \boldsymbol{\nu}_t(\boldsymbol{x}) P_t(\boldsymbol{x})$$

Continuity equation

$$\partial_t P_t(\boldsymbol{x}) = -\nabla \cdot \boldsymbol{j}_t(\boldsymbol{x}) = -\nabla \cdot (\mathsf{L}_t(\boldsymbol{x}) \boldsymbol{f}_t(\boldsymbol{x}))$$

Def.) (Thermodynamic) forces

$$\boldsymbol{f}_t(\boldsymbol{x}) := \frac{\boldsymbol{\nu}_t(\boldsymbol{x})}{\mu T} = \frac{\boldsymbol{F}_t(\boldsymbol{x})}{T} - \nabla \ln P_t(\boldsymbol{x})$$

Def.) Onsager coefficient matrix

$$[\mathsf{L}_t(\boldsymbol{x})]_{ij} := \delta_{ij} \frac{[\boldsymbol{j}_t(\boldsymbol{x})]_i}{[\boldsymbol{f}_t(\boldsymbol{x})]_i} = \mu T P_t(\boldsymbol{x}) \delta_{ij}$$

Introduction: Onsager-geometric decomposition

Def.) The housekeeping entropy production rate

Nakazato, M., & SI. *Physical Review Research*, *3*, 043093 (2021).
Dechant, A., Sasa, S. I., and SI. Physical Review Research, 4, L012034 (2022).

$$\sigma_t^{\mathrm{hk}} := \sigma_t - \sigma_t^{\mathrm{ex}}$$

Weighted inner product $\langle \boldsymbol{f}'_t, \boldsymbol{f}_t \rangle_{\mathsf{L}_t} = \int d\boldsymbol{x} [\boldsymbol{f}'_t(\boldsymbol{x})]^{\top} \mathsf{L}_t(\boldsymbol{x}) \boldsymbol{f}_t(\boldsymbol{x})$

$$\sigma_t = \langle \boldsymbol{f}_t, \boldsymbol{f}_t \rangle_{\mathsf{L}_t}$$

$$\sigma_t^{\mathrm{ex}} = \langle \nabla \phi_t^*, \nabla \phi_t^* \rangle_{\mathsf{L}_t}$$ **cf.) Otto metric**

$$\sigma_t^{\mathrm{hk}} = \langle \boldsymbol{f}_t - \nabla \phi_t^*, \boldsymbol{f}_t - \nabla \phi_t^* \rangle_{\mathsf{L}_t}$$

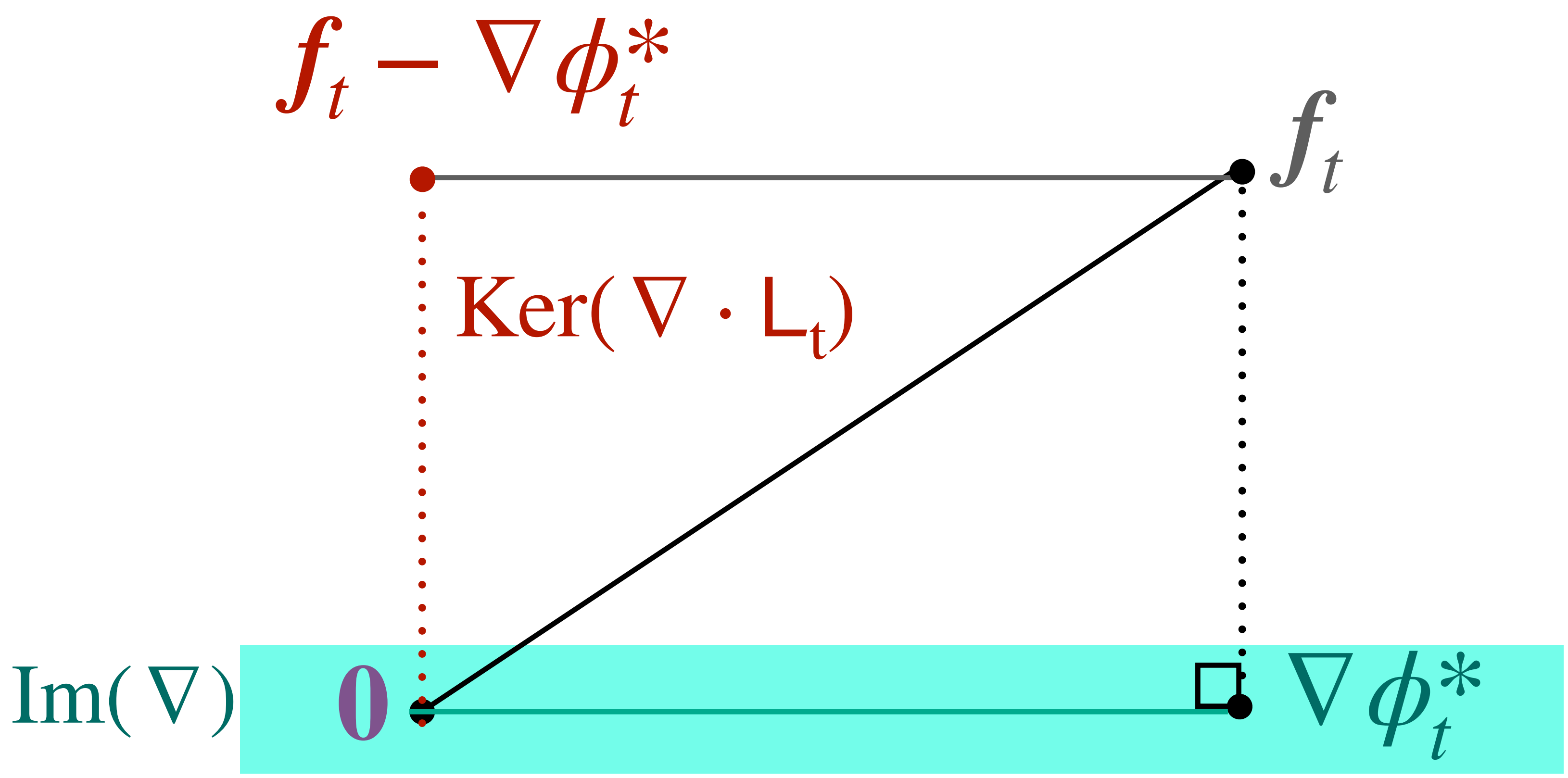
Def.) $\nabla \phi_t^*(\boldsymbol{x})$**: Solution of**

$$\partial_t P_t(\boldsymbol{x}) = -\nabla \cdot (\mathsf{L}_t(\boldsymbol{x}) \boldsymbol{f}_t(\boldsymbol{x})) = -\nabla \cdot (\mathsf{L}_t(\boldsymbol{x}) \nabla \phi_t^*(\boldsymbol{x}))$$

$$\nabla \cdot (\mathsf{L}_t(\boldsymbol{x})[\boldsymbol{f}_t(\boldsymbol{x}) - \nabla \phi_t^*(\boldsymbol{x})]) = 0$$

Pythagorean theorem

$$\sigma_t = \langle \boldsymbol{f}_t, \boldsymbol{f}_t \rangle_{\mathsf{L}_t} = \underbrace{\langle \nabla \phi_t^*, \nabla \phi_t^* \rangle}_{\mathrm{Im}(\nabla)}{}_{\mathsf{L}_t} + \underbrace{\langle \boldsymbol{f}_t - \nabla \phi_t^*, \boldsymbol{f}_t - \nabla \phi_t^* \rangle}_{\mathrm{Ker}(\nabla \cdot \mathsf{L}_t)}{}_{\mathsf{L}_t} = \sigma_t^{\mathrm{ex}} + \sigma_t^{\mathrm{hk}}$$



SI, Info. Geo. **7**, 441-483 (2024).

Introduction: Exponential family for processes

Def.) Probability of interpolated process

$$\bar{\mathbb{P}}^{\theta}_{\boldsymbol{g}_t}(\boldsymbol{x}(t+dt), \boldsymbol{x}(t)) := \mathbb{T}^{\theta}_{t;\boldsymbol{g}_t}(\boldsymbol{x}(t+dt) \,|\, \boldsymbol{x}(t)) P_t(\boldsymbol{x}(t))$$

$$\mathbb{T}^{\theta}_{t;\boldsymbol{g}_t}(\boldsymbol{x}(t+dt) \,|\, \boldsymbol{x}(t)) \propto \exp\left[-\frac{\|\boldsymbol{x}(t+dt) - \boldsymbol{x}(t) - \mu \boldsymbol{F}_t(\boldsymbol{x}(t))dt - \mu T\theta[\boldsymbol{g}_t(\boldsymbol{x}(t)) - \boldsymbol{f}_t(\boldsymbol{x}(t))]\|^2}{4\mu T dt}\right]$$

$\partial_t P_t(\boldsymbol{x}) = -\nabla \cdot (\boldsymbol{f}_t(\boldsymbol{x}) L_t(\boldsymbol{x})) \quad (\theta = 0)$:Fokker-Planck eq.

$\partial_t P_t(\boldsymbol{x}) = -\nabla \cdot (\boldsymbol{g}_t(\boldsymbol{x}) L_t(\boldsymbol{x})) \quad (\theta = 1)$

$$\dot{\boldsymbol{x}}(t) = \mu \boldsymbol{F}_t(\boldsymbol{x}(t)) + \mu T\theta[\boldsymbol{g}_t(\boldsymbol{x}(t)) - \boldsymbol{f}_t(\boldsymbol{x}(t))] + \sqrt{2\mu T}\boldsymbol{\xi}(t)$$

$$\langle \boldsymbol{\xi}(t) \rangle = \boldsymbol{0}, \langle \xi_i(t) \xi_j(t') \rangle = \delta(t-t')\delta_{ij}$$

$[\ln \bar{\mathbb{P}}^{\theta}_{\boldsymbol{g}_t} = (1-\theta) \ln \mathbb{P}^{0}_{\boldsymbol{g}_t} + \theta \ln \mathbb{P}^{1}_{\boldsymbol{g}_t}]$ e-geodesic

Entropy production rate

$$\sigma_t dt = \frac{4 D_{\mathrm{KL}}(\bar{\mathbb{P}}^{0}_{\boldsymbol{0}} \| \bar{\mathbb{P}}^{\theta}_{\boldsymbol{0}})}{\theta^2} + O(dt^2) = 4 D_{\mathrm{KL}}(\bar{\mathbb{P}}^{1}_{\boldsymbol{f}_t} \| \bar{\mathbb{P}}^{1}_{\boldsymbol{0}}) + O(dt^2)$$

$\theta \to 0$: Fisher metric (×2)

SI, Info. Geo. **7**, 441-483 (2024).

Introduction: Information-geometric decomposition

The excess entropy production rate

$$\underline{\sigma_t^{\rm ex}}dt = \underline{\frac{4D_{\rm KL}(\bar{\mathbb{P}}^0_{f_t-\nabla\phi_t^*}\|\bar{\mathbb{P}}^\theta_{f_t-\nabla\phi_t^*})}{\theta^2}} + O(dt^2) = 4D_{\rm KL}(\bar{\mathbb{P}}^1_{f_t}\|\bar{\mathbb{P}}^1_{f_t-\nabla\phi_t^*}) + O(dt^2) = 4D_{\rm KL}(\bar{\mathbb{P}}^1_{\nabla\phi_t^*}\|\bar{\mathbb{P}}^1_{\mathbf{0}}) + O(dt^2)$$

cf.) Otto metric

$\theta \to 0$: Fisher metric (×2)

$$\sigma_t^{\rm ex} = \frac{1}{\mu T}\left(\lim_{\Delta t\to+0}\frac{\mathscr{W}_2(P_t, P_{t+\Delta t})}{\Delta t}\right)^2$$

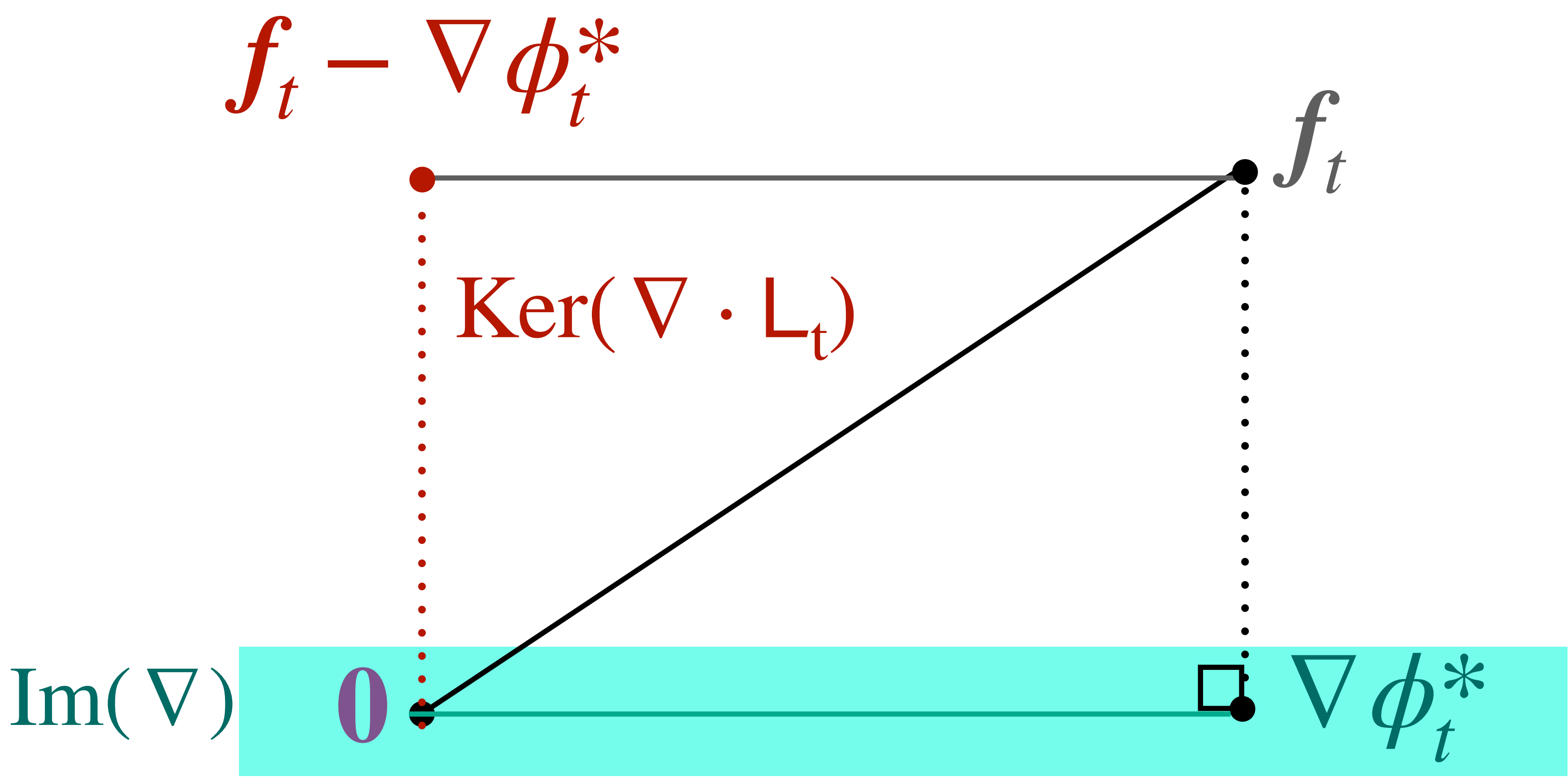
The housekeeping entropy production rate

$$\sigma_t^{\rm hk}dt = \frac{4D_{\rm KL}(\bar{\mathbb{P}}^0_{\nabla\phi_t^*}\|\bar{\mathbb{P}}^\theta_{\nabla\phi_t^*})}{\theta^2} + O(dt^2) = 4D_{\rm KL}(\bar{\mathbb{P}}^1_{f_t-\nabla\phi_t^*}\|\bar{\mathbb{P}}^1_{\mathbf{0}}) + O(dt^2) = 4D_{\rm KL}(\bar{\mathbb{P}}^1_{f_t}\|\bar{\mathbb{P}}^1_{\nabla\phi_t^*}) + O(dt^2)$$

Pythagorean theorem

$$\frac{dt}{4}\sigma_t = D_{\rm KL}(\bar{\mathbb{P}}^1_{f_t}\|\bar{\mathbb{P}}^1_{\mathbf{0}}) = D_{\rm KL}(\bar{\mathbb{P}}^1_{f_t}\|\bar{\mathbb{P}}^1_{\nabla\boldsymbol{\phi}_t^*}) + D_{\rm KL}(\bar{\mathbb{P}}^1_{\nabla\phi_t^*}\|\bar{\mathbb{P}}^1_{\mathbf{0}}) = \frac{dt}{4}[\sigma_t^{\rm hk} + \sigma_t^{\rm ex}]$$

$$\frac{dt}{4}\sigma_t = D_{\rm KL}(\bar{\mathbb{P}}^1_{f_t}\|\bar{\mathbb{P}}^1_{\mathbf{0}}) = D_{\rm KL}(\bar{\mathbb{P}}^1_{f_t}\|\bar{\mathbb{P}}^1_{f_t-\nabla\phi_t^*}) + D_{\rm KL}(\bar{\mathbb{P}}^1_{f_t-\nabla\phi_t^*}\|\bar{\mathbb{P}}^1_{\mathbf{0}}) = \frac{dt}{4}[\sigma_t^{\rm ex} + \sigma_t^{\rm hk}]$$



Outline

- Introduction: Nonequilibrium thermodynamics for the Fokker-Planck equation, optimal transport and information geometry
- **Nonequilibrium thermodynamics for the master/rate equation, optimal transport and information geometry**
- Topics of nonequilibrium thermodynamics based on information geometry

Two approaches for the master/rate equations

Onsager-geometric approach

$$\langle f_t, f_t \rangle_{\mathsf{L}_t} = \langle \nabla \phi_t^*, \nabla \phi_t^* \rangle_{\mathsf{L}_t} + \langle f_t - \nabla \phi_t^*, f_t - \nabla \phi_t^* \rangle_{\mathsf{L}_t}$$

Information-geometric approach

$$D_{\mathrm{KL}}(\bar{\mathbb{P}}^1_{f_t} \| \bar{\mathbb{P}}^1_{\mathbf{0}}) = D_{\mathrm{KL}}(\bar{\mathbb{P}}^1_{f_t} \| \bar{\mathbb{P}}^1_{\nabla \phi_t^*}) + D_{\mathrm{KL}}(\bar{\mathbb{P}}^1_{\nabla \phi_t^*} \| \bar{\mathbb{P}}^1_{\mathbf{0}})$$

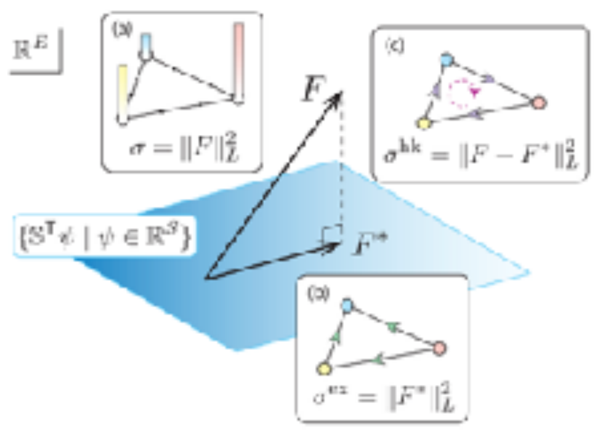
Unlike the situation with the Fokker-Planck equation, the two approaches provide different decompositions.

2-Wasserstein distance and gradient flow

J. Maas, *Journal of Functional Analysis* **261**, 2250 (2011).

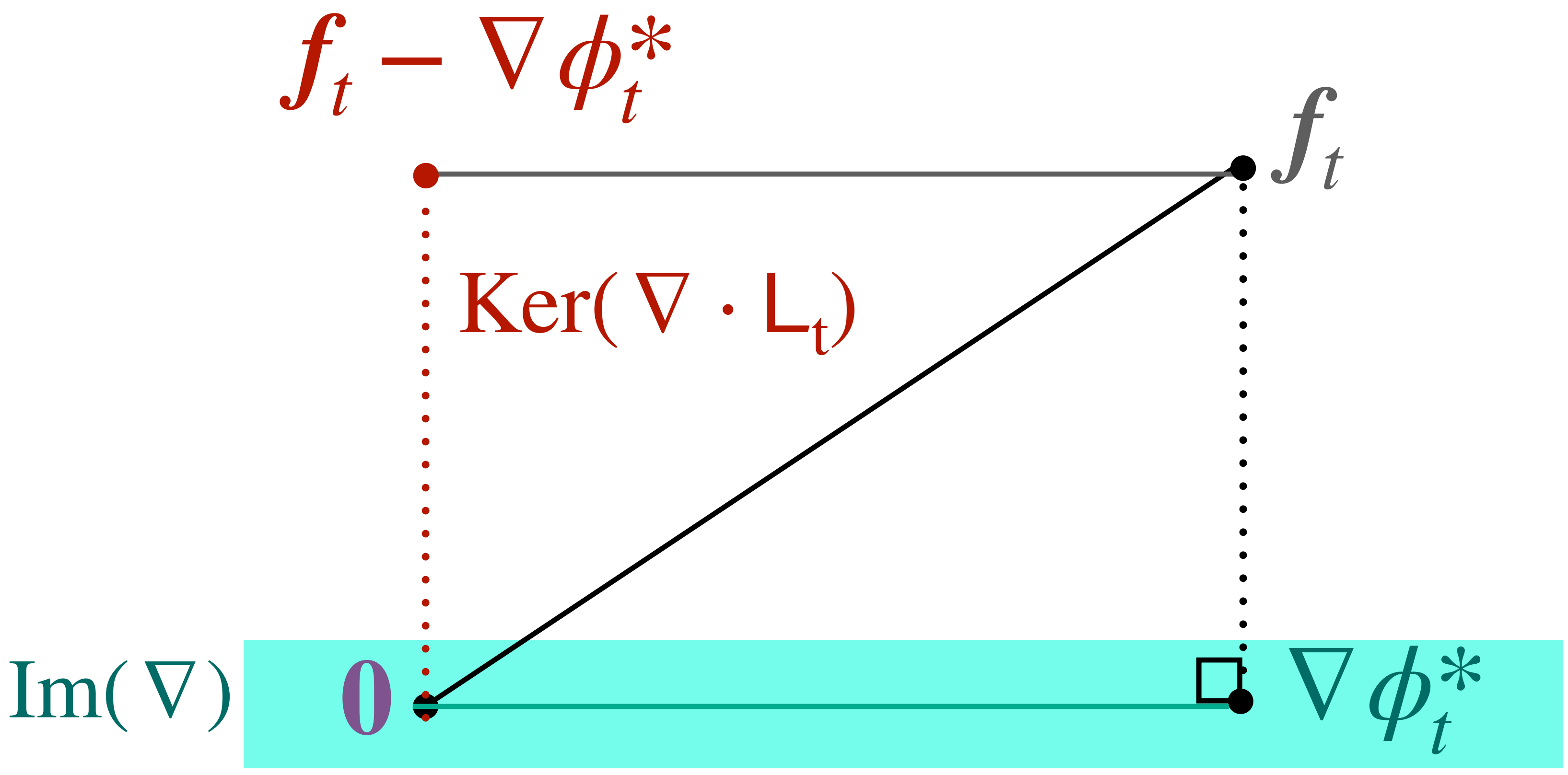
Nonequilibrium thermodynamics

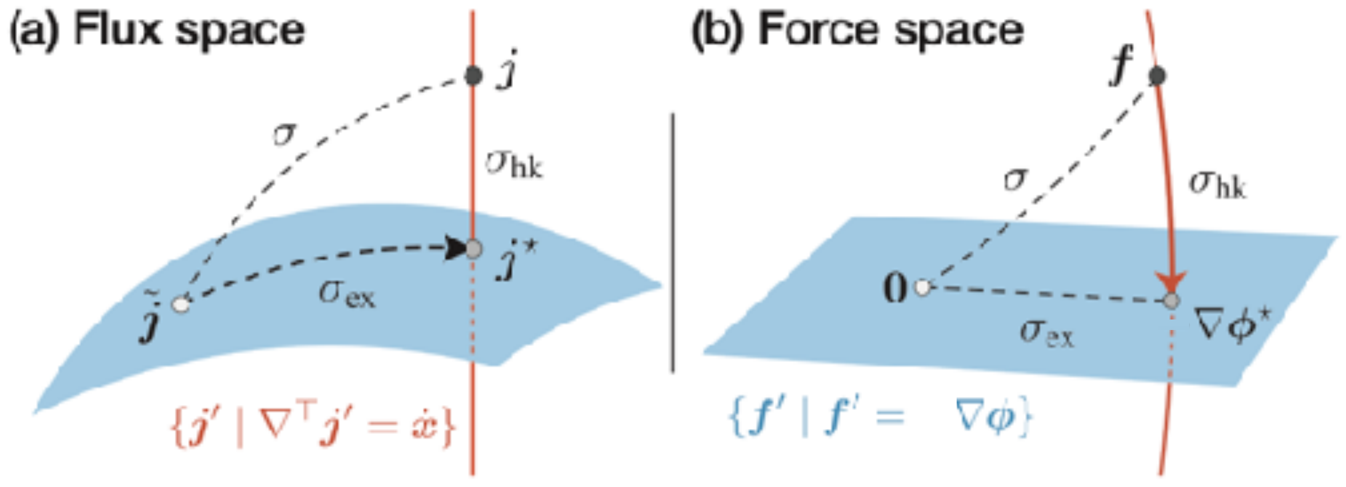
K. Yoshimura, A. Kolchinsky, A. Dechant and SI, Physical Review Research, **5**, 013017 (2023).



Today's talk

Kolchinsky, A., Dechant, A., Yoshimura, K., & SI. *arXiv:2206.14599* (2022).
Kolchinsky, A., Dechant, A., Yoshimura, K., & SI. *arXiv: 2412.08432* (2024).





Kolchinsky, A., Dechant, A., Yoshimura, K., & SI. *arXiv:2206.14599* (2022). *arXiv: 2412.08432* (2024).

Setup: Master/rate equations

Unified expression of master/rate equations (cf. the continuity equation)

$$\dot{\boldsymbol{x}} = \nabla^\top \boldsymbol{j}$$

State (probability/concentrations): $\boldsymbol{x} \in \mathbb{R}_+^d$

(Transpose of) Incidence/Stoichiometric matrix: $\nabla \in \mathbb{Z}^{2m \times d}$

One-way fluxes: $\boldsymbol{j} = (j_1(\boldsymbol{x}, t), \ldots, j_{2m}(\boldsymbol{x}, t))^\top \in \mathbb{R}_+^{2m}$

e.g.,) Master equation

$$\dot{x}_i = \sum_\alpha \sum_{j=1}^d [R_{ij}^\alpha x_i - R_{ij}^\alpha x_j] \qquad \sum_{i=1}^d x_i = 1$$

$\nabla_{\rho k} := \delta_{kj} - \delta_{ki}$ for a transition $\rho : (i \to j, \alpha)$

$j_\rho := R_{ji}^\alpha x_i$ for a transition $\rho : (i \to j, \alpha)$

e.g.,) Rate equation

$$\sum_{i=1}^d \nu_{ri} X_i \underset{k_r^-}{\overset{k_r^+}{\rightleftharpoons}} \sum_{i=1}^d \kappa_{ri} X_i$$

$$\dot{x}_i = \sum_{r=1}^m (\kappa_{ri} - \nu_{ri})[k_r^+ \prod_{j=1}^d (x_j)^{\nu_{rj}} - k_r^- \prod_{j=1}^d (x_j)^{\kappa_{rj}}]$$

$\nabla_{\rho i} := \kappa_{\rho i} - \nu_{\rho i}$

$j_\rho := k_r^+ \prod_{j=1}^d (x_j)^{\nu_{rj}}$ for a reaction $\rho : (r, +)$

$j_\rho := k_r^- \prod_{j=1}^d (x_j)^{\kappa_{rj}}$ for a reaction $\rho : (r, -)$

Kolchinsky, A., Dechant, A., Yoshimura, K., & SI. *arXiv:2206.14599* (2022). *arXiv: 2412.08432* (2024).

Reverse flux and thermodynamic force

Reverse fluxes $\tilde{\boldsymbol{j}} \in \mathbb{R}_+^{2m}$

e.g.,) Master equation

$$j_\rho = R_{ji}^{\alpha} x_i \longrightarrow \tilde{j}_\rho := R_{ij}^{\alpha} x_j$$

e.g.,) Rate equation

$$j_\rho = k_\rho^+ \prod_j (x_j)^{\nu_{\rho j}} \longrightarrow \tilde{j}_\rho := k_\rho^- \prod_j (x_j)^{\kappa_{\rho j}}$$

$$j_\rho = k_\rho^- \prod_j (x_j)^{\kappa_{\rho j}} \longrightarrow \tilde{j}_\rho := k_\rho^+ \prod_j (x_j)^{\nu_{\rho j}}$$

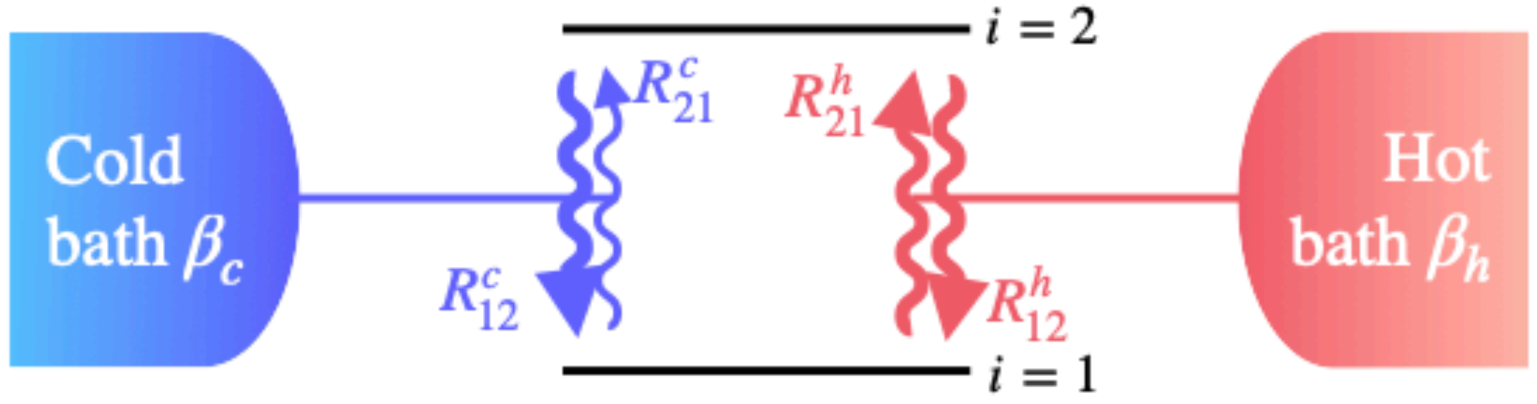
Def.) Thermodynamic forces $\boldsymbol{f} \in \mathbb{R}^{2m}$

$$f_\rho := \ln \frac{j_\rho}{\tilde{j}_\rho}$$

Kolchinsky, A., Dechant, A., Yoshimura, K., & SI. *arXiv:2206.14599* (2022). *arXiv: 2412.08432* (2024).

e.g.,) Master/rate equations

Example: 2-level Markov jump process (MJP)



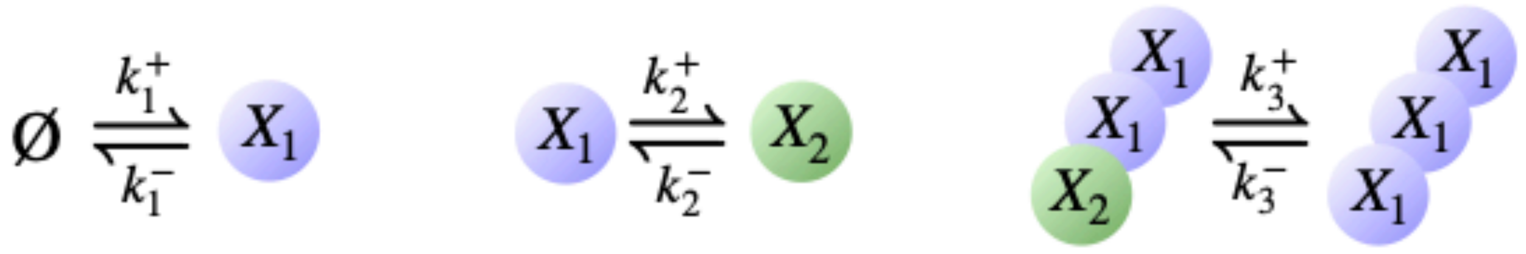
(Transpose of) Incidence matrix | **Fluxes** | **Reverse fluxes** | **Forces**

$$\begin{array}{c} 1\xrightarrow{c}2 \\ 2\xrightarrow{c}1 \\ 1\xrightarrow{h}2 \\ 2\xrightarrow{h}1 \end{array} \quad \nabla = \begin{bmatrix} -1 & 1 \\ 1 & -1 \\ -1 & 1 \\ 1 & -1 \end{bmatrix} \quad \boldsymbol{j} = \begin{bmatrix} x_1 R^c_{21} \\ x_2 R^c_{12} \\ x_1 R^h_{21} \\ x_2 R^h_{12} \end{bmatrix} \quad \tilde{\boldsymbol{j}} = \begin{bmatrix} x_2 R^c_{12} \\ x_1 R^c_{21} \\ x_2 R^h_{12} \\ x_1 R^h_{21} \end{bmatrix} \quad \boldsymbol{f} = \begin{bmatrix} \ln \frac{x_1 R^c_{21}}{x_2 R^c_{12}} \\ \ln \frac{x_2 R^c_{12}}{x_1 R^c_{21}} \\ \ln \frac{x_1 R^h_{21}}{x_2 R^h_{12}} \\ \ln \frac{x_2 R^h_{12}}{x_1 R^h_{21}} \end{bmatrix}$$

Continuity equation

$$\dot{\boldsymbol{x}} = \nabla^\top \boldsymbol{j} = \begin{bmatrix} j_1 - j_2 + j_3 - j_4 \\ j_2 - j_1 + j_4 - j_3 \end{bmatrix}$$

Example: Chemical Reaction Network (CRN)



Stoichiometric matrix | **Fluxes** | **Reverse fluxes** | **Forces**

$$\begin{array}{c} \varnothing \to X_1 \\ X_1 \to \varnothing \\ X_1 \to X_2 \\ X_2 \to X_1 \\ 2X_1 + X_2 \to 3X_1 \\ 3X_1 \to 2X_1 + X_2 \end{array} \quad \nabla = \begin{bmatrix} 1 & 0 \\ -1 & 0 \\ -1 & 1 \\ 1 & -1 \\ 1 & -1 \\ -1 & 1 \end{bmatrix} \quad \boldsymbol{j} = \begin{bmatrix} k_1^+ \\ x_1 k_1^- \\ x_1 k_2^+ \\ x_2 k_2^- \\ x_1^2 x_2 k_3^+ \\ x_1^3 k_3^- \end{bmatrix} \quad \tilde{\boldsymbol{j}} = \begin{bmatrix} x_1 k_1^- \\ k_1^+ \\ x_2 k_2^- \\ x_1 k_2^+ \\ x_1^3 k_3^- \\ x_1^2 x_2 k_3^+ \end{bmatrix} \quad \boldsymbol{f} = \begin{bmatrix} \ln \frac{k_1^+}{x_1 k_1^-} \\ \ln \frac{x_1 k_1^-}{k_1^+} \\ \ln \frac{x_1 k_2^+}{x_2 k_2^-} \\ \ln \frac{x_2 k_2^-}{x_1 k_2^+} \\ \ln \frac{x_2 k_3^+}{x_1 k_3^-} \\ \ln \frac{x_1 k_3^-}{x_2 k_3^+} \end{bmatrix}$$

Continuity equation

$$\dot{\boldsymbol{x}} = \nabla^\top \boldsymbol{j} = \begin{bmatrix} j_1 - j_2 + j_4 - j_3 + j_5 - j_6 \\ j_2 - j_1 + j_3 - j_4 + j_6 - j_5 \end{bmatrix}$$

Kolchinsky, A., Dechant, A., Yoshimura, K., & SI. *arXiv:2206.14599* (2022). *arXiv: 2412.08432* (2024).

Entropy production rate

Def.) Entropy production rate (= Sum of flux × force)

$$\sigma := \boldsymbol{j}^{\top}\boldsymbol{f} = \frac{1}{2}\sum_{\rho=1}^{2m}(j_\rho - \tilde{j}_\rho)\ln\frac{j_\rho}{\tilde{j}_\rho} = \sum_{\rho=1}^{2m}\left[j_\rho \ln\frac{j_\rho}{\tilde{j}_\rho} - \tilde{j}_\rho + j_\rho\right]$$

$$\sum_\rho \tilde{j}_\rho = \sum_\rho j_\rho$$

The Onsager coefficient matrix L

$$\mathsf{L}_{\rho\rho'} := \delta_{\rho\rho'}\frac{j_\rho - \tilde{j}_\rho}{f_\rho} = \frac{j_\rho - \tilde{j}_\rho}{\ln j_\rho - \ln \tilde{j}_\rho}$$

(logarithmic mean)

Onsager-geometric approach

K. Yoshimura, A. Kolchinsky, A. Dechant and SI,
Physical Review Research, **5**, 013017 (2023).

$$\sigma = \frac{1}{2}\sum_{\rho=1}^{2m}\boldsymbol{f}^{\top}\mathsf{L}\boldsymbol{f} := \langle \boldsymbol{f}, \boldsymbol{f}\rangle_{\mathsf{L}}$$

The Kullback-Leibler divergence

$$D_{\mathrm{KL}}(\boldsymbol{j}\|\boldsymbol{j}') := \sum_{\rho=1}^{2m}\left[j_\rho \ln\frac{j_\rho}{j'_\rho} - j'_\rho + j_\rho\right]$$

Information-geometric approach

Yoshimura, K., & SI. *Physical Review Research*, *3*(1), 013175 (2021).

$$\sigma = D_{\mathrm{KL}}(\boldsymbol{j}\|\tilde{\boldsymbol{j}})$$

Kolchinsky, A., Dechant, A., Yoshimura, K., & SI. *arXiv:2206.14599* (2022). *arXiv: 2412.08432* (2024).

Onsager-geometric approach

Onsager-geometric decomposition

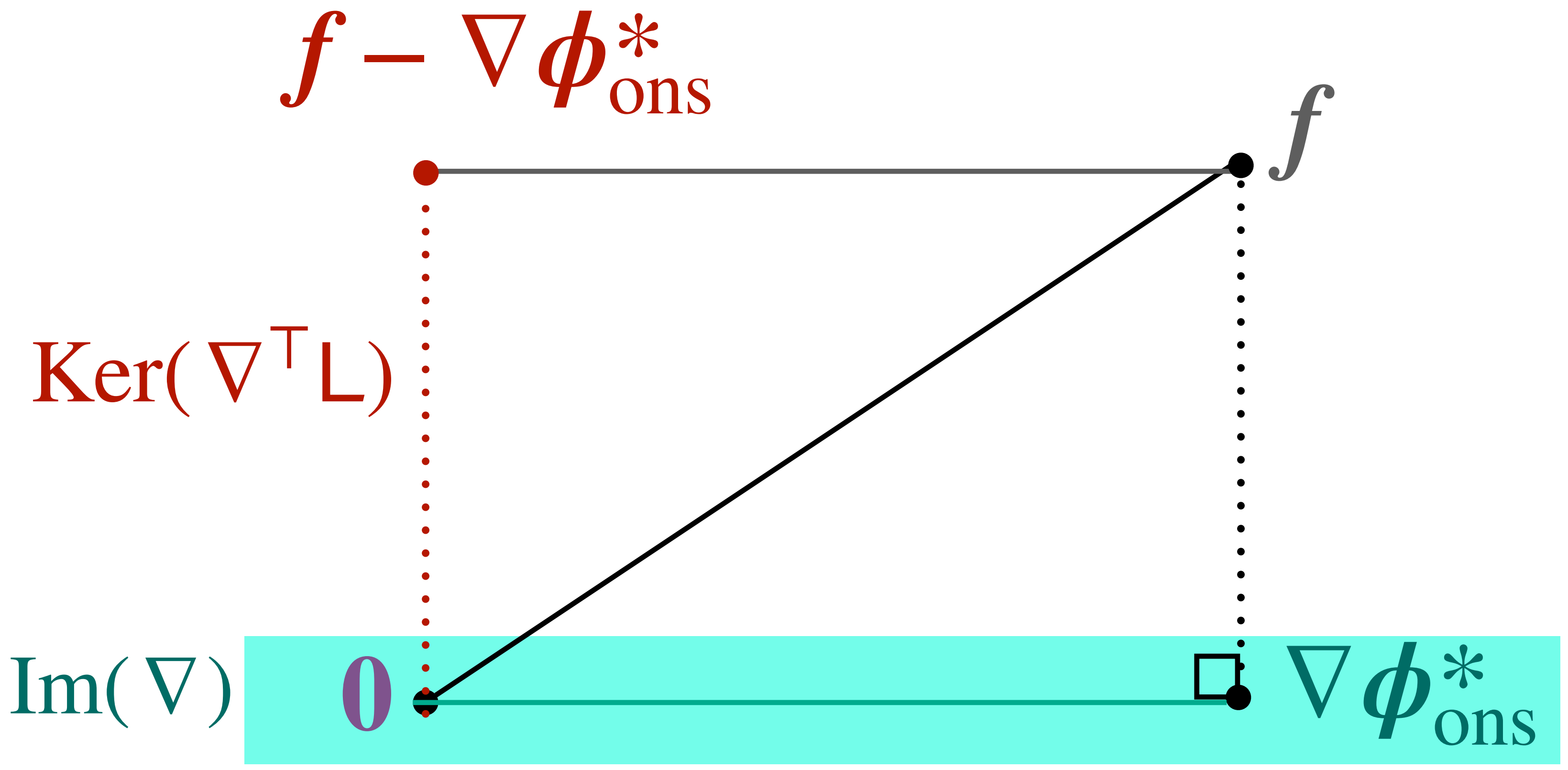
K. Yoshimura, A. Kolchinsky, A. Dechant and SI, Physical Review Research, **5**, 013017 (2023).

$$\sigma_{\rm ons}^{\rm ex} := \inf_{f' \in \mathbb{R}_+^{2m}} \langle f', f' \rangle_{\mathsf{L}} \quad \textit{\textbf{s.t.}} \quad \dot{x} = \nabla^\top \mathsf{L} f'$$

$$\sigma_{\rm ons}^{\rm hk} := \sigma - \sigma_{\rm ons}^{\rm ex}$$

Def.) $\nabla \phi_{\rm ons}^*$ **: Solution of** $\dot{x} = \nabla^\top \mathsf{L} f = \nabla^\top \mathsf{L} \nabla \phi_{\rm ons}^*$

$$\nabla^\top \mathsf{L}[f - \nabla \phi_{\rm ons}^*] = 0$$



$$\sigma = \langle f, f \rangle_{\mathsf{L}} = \underbrace{\langle \nabla \phi_{\rm ons}^*, \nabla \phi_{\rm ons}^* \rangle_{\mathsf{L}}}_{= \sigma_{\rm ons}^{\rm ex}} + \underbrace{\langle f - \nabla \phi_{\rm ons}^*, f - \nabla \phi_{\rm ons}^* \rangle_{\mathsf{L}}}_{= \sigma_{\rm ons}^{\rm hk}}$$

cf.) 2-Wasserstein distance defined by J. Maas
(Master equation with the detailed balance condition)

J. Maas, *Journal of Functional Analysis* **261**, 2250 (2011).

$$\tilde{\mathscr{W}}(x(0), x(1)) = \sqrt{\inf \int_0^1 dt \langle \nabla \psi, \nabla \psi \rangle_{\mathsf{L}(x(t))}} \quad \textit{\textbf{s.t.}} \quad \begin{array}{l} \dot{x}(t) = \nabla^\top \mathsf{L}(x(t)) \nabla \psi(t) \\ x(0), x(1) \text{ :fixed} \end{array}$$

Kolchinsky, A., Dechant, A., Yoshimura, K., & SI. *arXiv:2206.14599* (2022). *arXiv: 2412.08432* (2024).

Information-geometric approach: Exponential family

Def.) g-parameterized fluxes $\bar{\boldsymbol{j}}^{\boldsymbol{g}} \in \mathbb{R}^{2m}_{+}$

$$\boldsymbol{g} \in \mathbb{R}^{2m}$$

$$\bar{j}^{\boldsymbol{g}}_{\rho} = \exp(g_{\rho})\tilde{j}_{\rho}$$

$$[\ln \bar{j}^{\theta f}_{\rho} = (1-\theta)\ln \tilde{j}_{\rho} + \theta \ln j_{\rho}]$$ e-geodesic

Entropy production rate

$$\sigma = \underline{D_{\mathrm{KL}}(\boldsymbol{j}\|\tilde{\boldsymbol{j}})} = D_{\mathrm{KL}}(\boldsymbol{j}^{\boldsymbol{f}}\|\boldsymbol{j}^{\boldsymbol{0}}) =: \underline{\mathscr{D}_{\mathrm{KL}}(\boldsymbol{f}\|\boldsymbol{0})}$$

Fluxes space

Forces space

Kolchinsky, A., Dechant, A., Yoshimura, K., & SI. *arXiv:2206.14599* (2022). *arXiv: 2412.08432* (2024).

Information-geometric approach: Excess entropy production rate

Def.) Excess entropy production rate

$$\sigma^{\rm ex}_{\rm IG} := \inf_{\boldsymbol{j}'\in\mathbb{R}^{2m}_+} D_{\rm KL}(\boldsymbol{j}'\|\tilde{\boldsymbol{j}}) \qquad \textbf{\textit{s.t.}} \qquad \dot{\boldsymbol{x}} = \nabla^\top \boldsymbol{j}'$$

cf.) Excess entropy production based on the 2-Wasserstein distance [Benamou-Brenier forumla], the 2-Wasserstein distance defined by J. Maas

For the Fokker-Planck Eq.

$$\sigma^{\rm ex}_t := \inf_{\boldsymbol{u}_t} \frac{1}{\mu T}\int d\boldsymbol{x}\|\boldsymbol{u}_t(\boldsymbol{x})\|^2 P_t(\boldsymbol{x}) \qquad \textbf{\textit{s.t.}} \qquad \partial_t P_t(\boldsymbol{x}) = -\nabla\cdot(\boldsymbol{u}_t(\boldsymbol{x})P_t(\boldsymbol{x}))$$

Benamou, J. D., & Brenier, Y. *Numerische Mathematik*, *84*, 375 (2000).

Nakazato, M., & SI. *Physical Review Research*, *3*, 043093 (2021).
Dechant, A., Sasa, S. I., and SI. Physical Review Research, 4, L012034 (2022).

For the master Eq.

$$\sigma^{\rm ex}_{\rm ons} := \inf_{\boldsymbol{f}'\in\mathbb{R}^{2m}} \langle \boldsymbol{f}', \boldsymbol{f}'\rangle_{\mathsf{L}} \qquad \textbf{\textit{s.t.}} \qquad \dot{\boldsymbol{x}}(t) = \nabla^\top \mathsf{L}\boldsymbol{f}'$$

J. Maas, *Journal of Functional Analysis* **261**, 2250 (2011).
K. Yoshimura, A. Kolchinsky, A. Dechant and SI, Physical Review Research, **5**, 013017 (2023).

Kolchinsky, A., Dechant, A., Yoshimura, K., & SI. *arXiv:2206.14599* (2022). *arXiv: 2412.08432* (2024).

Information-geometric approach: Information-geometric decomposition

Def.) Housekeeping entropy production rate

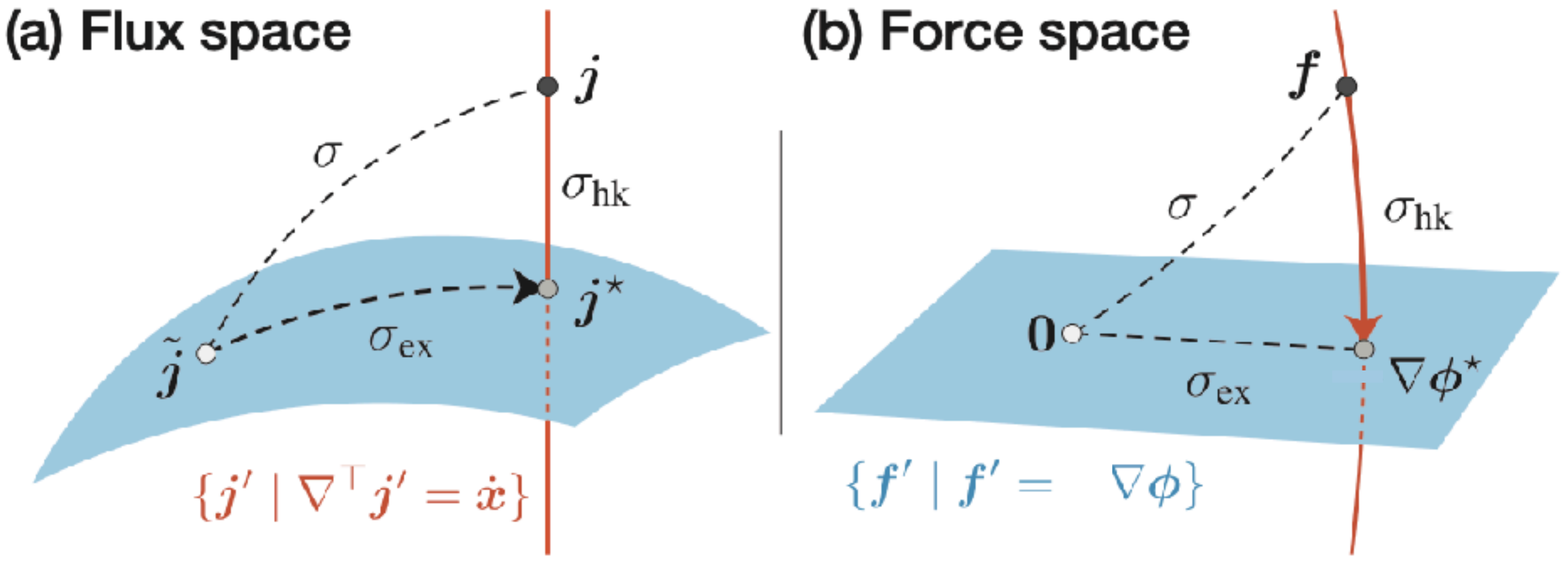
$$\sigma_{\mathrm{IG}}^{\mathrm{hk}} := \sigma - \sigma_{\mathrm{IG}}^{\mathrm{ex}}$$

$$\boldsymbol{j}^{\nabla\boldsymbol{\phi}^*} := \boldsymbol{j}^* := \mathrm{argmin}_{\boldsymbol{j}' \in \mathbb{R}_+^{2m}} D_{\mathrm{KL}}(\boldsymbol{j}' \| \tilde{\boldsymbol{j}})$$

$$\textbf{\textit{s.t.}} \quad \dot{\boldsymbol{x}} = \nabla^\top \boldsymbol{j}'$$

$$\sigma_{\mathrm{IG}}^{\mathrm{ex}} = \mathscr{D}_{\mathrm{KL}}(\nabla\boldsymbol{\phi}^* \| \mathbf{0})$$

$$\sigma_{\mathrm{IG}}^{\mathrm{hk}} = \mathscr{D}_{\mathrm{KL}}(\boldsymbol{f} \| \nabla\boldsymbol{\phi}^*)$$



Information-geometric decomposition

$$\sigma = \mathscr{D}_{\mathrm{KL}}(\boldsymbol{f} \| \mathbf{0}) = \mathscr{D}_{\mathrm{KL}}(\boldsymbol{f} \| \nabla\boldsymbol{\phi}^*) + \mathscr{D}_{\mathrm{KL}}(\nabla\boldsymbol{\phi}^* \| \mathbf{0}) = \sigma_{\mathrm{IG}}^{\mathrm{hk}} + \sigma_{\mathrm{IG}}^{\mathrm{ex}}$$

Kolchinsky, A., Dechant, A., Yoshimura, K., & SI. *arXiv:2206.14599* (2022). *arXiv: 2412.08432* (2024).

Dual optimization problem

Excess entropy production rate

$$\sigma_{\mathrm{IG}}^{\mathrm{ex}} = \sup_{\boldsymbol{\phi}\in\mathbb{R}^d} \left[\dot{\boldsymbol{x}}^\top \boldsymbol{\phi} - \boldsymbol{j}^\top (\boldsymbol{e}^{-\nabla\boldsymbol{\phi}} - \boldsymbol{1})\right] \qquad \boldsymbol{e}^{\boldsymbol{f}} = (e^{f_1}, e^{f_2}, \cdots, e^{f_{2m}})^\top$$

$$= \sup_{\boldsymbol{\phi}\in\mathbb{R}^d} \left[2\dot{\boldsymbol{x}}^\top \boldsymbol{\phi} - \boldsymbol{j}^\top (\boldsymbol{e}^{-\nabla\boldsymbol{\phi}} + \nabla\boldsymbol{\phi} - \boldsymbol{1})\right]$$

Optimal solution $\boldsymbol{\phi}^*$: $\dot{\boldsymbol{x}} = -\nabla^\top \bar{\boldsymbol{j}}^{-\nabla\boldsymbol{\phi}^*}$

$$\sigma_{\mathrm{IG}}^{\mathrm{ex}} \geq 0 \qquad -\boldsymbol{j}^\top (\boldsymbol{e}^{-\nabla\boldsymbol{\phi}^*} + \nabla\boldsymbol{\phi}^* - \boldsymbol{1}) \leq 0 \qquad ➡ \qquad \dot{\boldsymbol{x}}^\top \boldsymbol{\phi}^* \geq 0$$

$-\boldsymbol{\phi}^*$: Generalized Free energy potential

Kolchinsky, A., Dechant, A., Yoshimura, K., & SI. *arXiv:2206.14599* (2022). *arXiv: 2412.08432* (2024).

Relation to the Onsager-geometric decomposition

$$\mathscr{D}_{\mathrm{KL}}(\boldsymbol{f}\|\boldsymbol{f}') \geq \langle \boldsymbol{f}-\boldsymbol{f}', \boldsymbol{f}-\boldsymbol{f}' \rangle_{\mathsf{L}}$$

∵) $$\mathscr{D}_{\mathrm{KL}}(\boldsymbol{f}\|\boldsymbol{f}') - \langle \boldsymbol{f}-\boldsymbol{f}', \boldsymbol{f}-\boldsymbol{f}' \rangle_{\mathsf{L}} = \frac{1}{2}\sum_{\rho} \tilde{j}_{\rho} h(f_{\rho}-f'_{\rho}, f_{\rho})$$

$$h(a,b) := \left[\frac{(e^{a}-a-1)+e^{b}(e^{-a}+a-1)}{a^{2}} - \frac{e^{b}-1}{b}\right] a^{2} \geq 0$$

➡ **Inequality**

$$\sigma_{\mathrm{IG}}^{\mathrm{hk}} = \inf_{\boldsymbol{\phi}\in\mathbb{R}^{d}} \mathscr{D}_{\mathrm{KL}}(\boldsymbol{f}\|\nabla\boldsymbol{\phi}) \geq \inf_{\boldsymbol{\phi}\in\mathbb{R}^{d}} \langle \boldsymbol{f}-\nabla\boldsymbol{\phi}, \boldsymbol{f}-\nabla\boldsymbol{\phi} \rangle_{\mathsf{L}} = \sigma_{\mathrm{ons}}^{\mathrm{hk}}$$

$$\sigma_{\mathrm{IG}}^{\mathrm{ex}} = \sigma - \sigma_{\mathrm{IG}}^{\mathrm{hk}} \leq \sigma - \sigma_{\mathrm{ons}}^{\mathrm{hk}} = \sigma_{\mathrm{ons}}^{\mathrm{ex}}$$

Kolchinsky, A., Dechant, A., Yoshimura, K., & SI. *arXiv:2206.14599* (2022). *arXiv: 2412.08432* (2024).

Invariance under the coarse graining

Coarse-graining of dynamcis

$$\dot{\boldsymbol{x}} = \nabla^{\top}\boldsymbol{j} = (\nabla^{\mathrm{cg}})^{\top}\boldsymbol{j}^{\mathrm{cg}}$$

Def.) Coarse-grained incidence/stoichiometric matrix ∇^{cg}

Any duplicate raws of ∇ are merged.

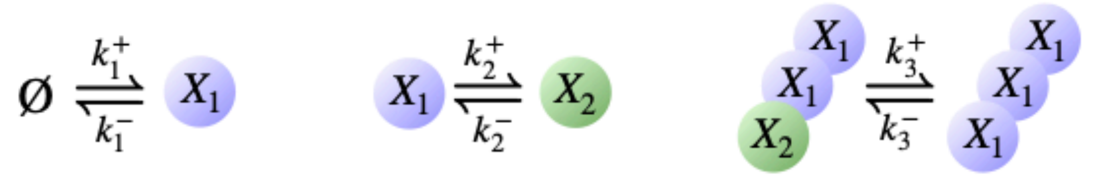
Def.) Coarse-grained fluxes $\boldsymbol{j}^{\mathrm{cg}}$

Corresponding duplicate raws of ∇ are merged.

$$\sigma^{\mathrm{ex}}_{\mathrm{IG}} = \sup_{\boldsymbol{\phi}\in\mathbb{R}^d}\left[\dot{\boldsymbol{x}}^{\top}\boldsymbol{\phi} - \boldsymbol{j}^{\top}(\boldsymbol{e}^{-\nabla\boldsymbol{\phi}} - \boldsymbol{1})\right]$$

$$= \sup_{\boldsymbol{\phi}\in\mathbb{R}^d}\left[\dot{\boldsymbol{x}}^{\top}\boldsymbol{\phi} - (\boldsymbol{j}^{\mathrm{cg}})^{\top}(\boldsymbol{e}^{-\nabla^{\mathrm{cg}}\boldsymbol{\phi}} - \boldsymbol{1})\right]$$

Example: Chemical Reaction Network (CRN)



$$\begin{array}{ccccccccc}
 & & \text{Stoichiometric matrix} & & \text{Fluxes} & & \text{Reverse fluxes} & & \text{Forces}\\
\begin{array}{c}\varnothing \to X_1\\ X_1 \to \varnothing\\ X_1 \to X_2\\ X_2 \to X_1\\ 2X_1+X_2 \to 3X_1\\ 3X_1 \to 2X_1+X_2\end{array} & \nabla = & \begin{bmatrix}1 & 0\\ -1 & 0\\ \multicolumn{2}{c}{\boxed{-1\;\;1}}\\ \multicolumn{2}{c}{\boxed{\begin{matrix}1 & -1\\ 1 & -1\end{matrix}}}\\ \multicolumn{2}{c}{\boxed{-1\;\;1}}\end{bmatrix} & \boldsymbol{j} = & \begin{bmatrix}k_1^+\\ x_1k_1^-\\ x_1k_2^+\\ x_2k_2^-\\ x_1^2x_2k_3^+\\ x_1^3k_3^-\end{bmatrix} & \tilde{\boldsymbol{j}} = & \begin{bmatrix}x_1k_1^-\\ k_1^+\\ x_2k_2^-\\ x_1k_2^+\\ x_1^3k_3^-\\ x_1^2x_2k_3^+\end{bmatrix} & \boldsymbol{f} = & \begin{bmatrix}\ln\frac{k_1^+}{x_1k_1^-}\\ \ln\frac{x_1k_1^-}{k_1^+}\\ \ln\frac{x_1k_2^+}{x_2k_2^-}\\ \ln\frac{x_2k_2^-}{x_1k_2^+}\\ \ln\frac{x_2k_3^+}{x_1k_3^-}\\ \ln\frac{x_1k_3^-}{x_2k_3^+}\end{bmatrix}
\end{array}$$

Continuity equation

$$\dot{\boldsymbol{x}} = \nabla^{\top}\boldsymbol{j} = \begin{bmatrix} j_1 - j_2 + j_4 - j_3 + j_5 - j_6\\ j_2 - j_1 + j_3 - j_4 + j_6 - j_5\end{bmatrix} = (\nabla^{\mathrm{cg}})^{\top}\boldsymbol{j}^{\mathrm{cg}}$$

$$\nabla^{\mathrm{cg}} = \begin{bmatrix}1 & 0\\ -1 & 0\\ \multicolumn{2}{c}{\boxed{-1\quad 1}}\\ \multicolumn{2}{c}{\boxed{1\quad -1}}\end{bmatrix} \qquad \boldsymbol{j}^{\mathrm{cg}} = \begin{bmatrix}j_1\\ j_2\\ j_3 + j_6\\ j_4 + j_5\end{bmatrix}$$

Outline

- Introduction: Nonequilibrium thermodynamics for the Fokker-Planck equation, optimal transport and information geometry
- Nonequilibrium thermodynamics for the master/rate equation, optimal transport and information geometry
- **Topics of nonequilibrium thermodynamics based on information geometry**

Kolchinsky, A., Dechant, A., Yoshimura, K., & SI. *arXiv:2206.14599* (2022). *arXiv: 2412.08432* (2024).

Topic 1: Linear response regime (Slow time evolution)

$\dot{\boldsymbol{x}} \simeq \mathbf{0}$ $\quad\quad$ $\boldsymbol{\phi}^* \simeq \mathbf{0}$

$$\sigma^{\mathrm{ex}}_{\mathrm{IG}} = \sup_{\boldsymbol{\phi}\in\mathbb{R}^d} \left[2\dot{\boldsymbol{x}}^\top\boldsymbol{\phi} - \boldsymbol{j}^\top(\boldsymbol{e}^{-\nabla\boldsymbol{\phi}} + \nabla\boldsymbol{\phi} - \mathbf{1})\right] \simeq \sup_{\boldsymbol{\phi}\in\mathbb{R}^d} \left[2\dot{\boldsymbol{x}}^\top\boldsymbol{\phi} - \boldsymbol{\phi}^\top \mathsf{H} \boldsymbol{\phi}\right]$$

$$\mathsf{H} := \frac{1}{2}\nabla^\top \mathrm{diag}(\boldsymbol{j})\,\nabla$$

$\boldsymbol{\phi}^* = \mathsf{H}^+\dot{\boldsymbol{x}}$ $\quad\quad$ $(\dot{\boldsymbol{x}} = \mathbf{0} \Rightarrow \boldsymbol{\phi}^* = \mathbf{0})$

H^+: **pseudo-inverse**

$\sigma^{\mathrm{ex}}_{\mathrm{IG}} \simeq \dot{\boldsymbol{x}}^\top \mathsf{H}^+ \dot{\boldsymbol{x}}$

cf.) Least dissipation principle
(Onsager variational principle)

Kolchinsky, A., Dechant, A., Yoshimura, K., & SI. *arXiv:2206.14599* (2022). *arXiv: 2412.08432* (2024).

Topic 2-1: Cumulant generating function

Markovian stochastic systems (corresponding Markov jump process) observed during $[t, t+dt]$

N_ρ: Number of times that reaction ρ occurs during $[t, t+dt]$

φ_i: State observable during $[t, t+dt]$

$\Delta\varphi := \boldsymbol{N}^\top \nabla \boldsymbol{\varphi}$: The displacement of observable

Cumulant generative function: $\Lambda_\varphi(\lambda) = \ln \mathbb{E}[\exp[\lambda \Delta\varphi]]$

k-th cumulant: $K_\varphi^{(k)} := (\partial_\lambda)^k \Lambda_\varphi(\lambda)\Big|_{\lambda=0} = \sum_\rho j_\rho (\sum_i \nabla_{\rho i}\varphi_i)^k dt + O(dt^2)$

$$K_\varphi^{(1)} \simeq \dot{\boldsymbol{x}}^\top \boldsymbol{\varphi} dt \qquad K_\varphi^{(2)} \simeq 2\boldsymbol{\varphi}^\top \mathsf{H} \boldsymbol{\varphi} dt$$

Kolchinsky, A., Dechant, A., Yoshimura, K., & SI. *arXiv:2206.14599* (2022). *arXiv: 2412.08432* (2024).

Topic 2-2: Large deviation

Empirical mean for the system copy

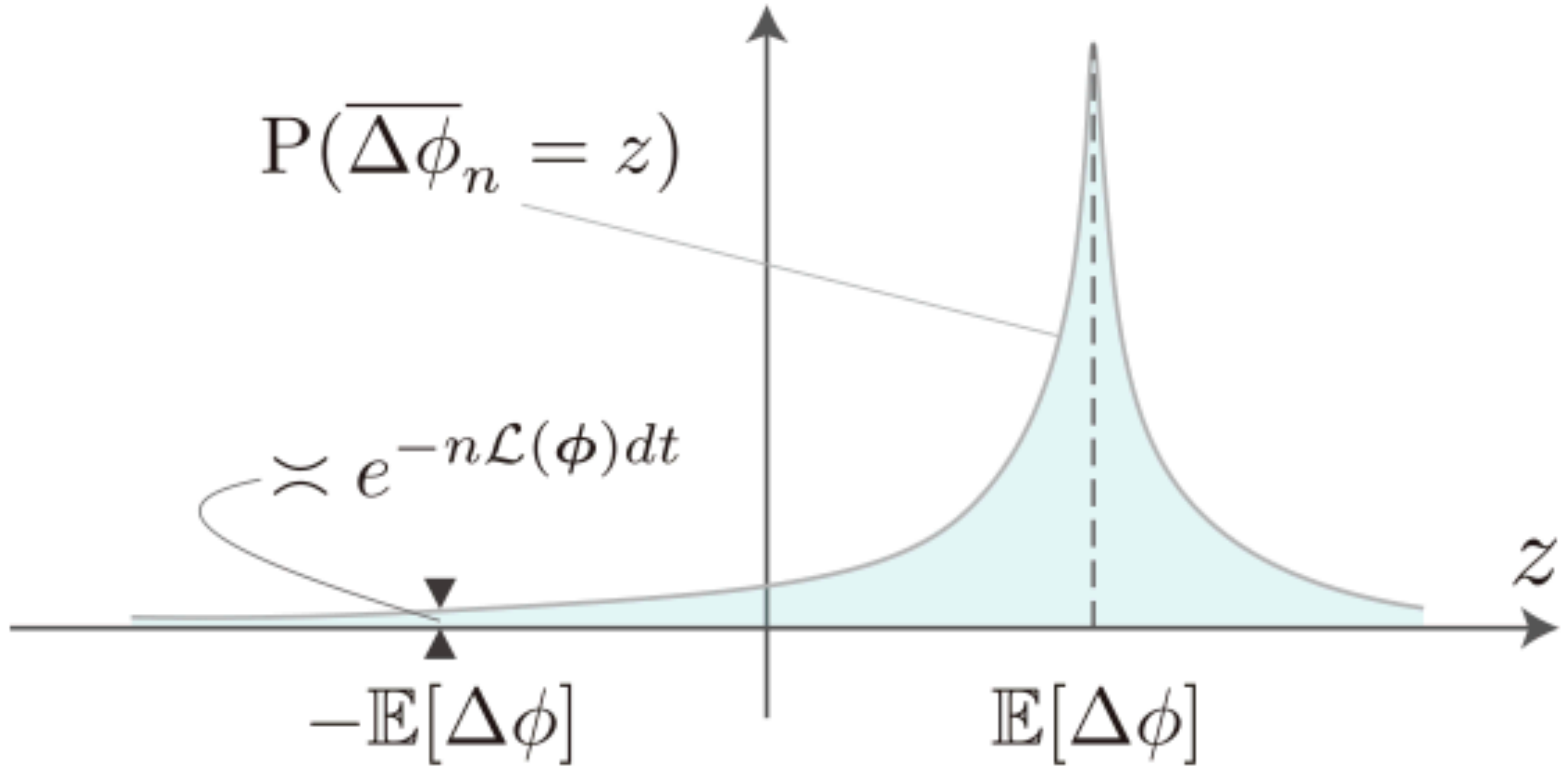
$$\overline{\Delta\varphi} := \frac{1}{n}\sum_{k=1}^{n}[\boldsymbol{N}^{(k)}]^{\top}\nabla\boldsymbol{\varphi}$$

$\boldsymbol{N}^{(k)}$: The reaction count for copy k

Large deviation

$$\mathrm{P}(\overline{\Delta\varphi} \approx -\mathbb{E}[\Delta\varphi]) \asymp \exp(-n\mathscr{L}(\boldsymbol{\varphi})dt)$$

$$\mathscr{L}(\boldsymbol{\varphi}) := \sup_{\lambda\in\mathbb{R}}[\lambda(\dot{x}^{\top}\boldsymbol{\varphi}) - \boldsymbol{j}^{\top}(\boldsymbol{e}^{-\lambda\nabla\boldsymbol{\varphi}} - \boldsymbol{1})]$$



cf.) Large deviation for chemical reactions

Mielke, A., Patterson, R. I., Peletier, M. A., & Michiel Renger, D. *SIAM Journal on Applied Mathematics*, *77*, 1562 (2017).

Excess entropy production rate

$$\sigma_{\mathrm{IG}}^{\mathrm{ex}} = \sup_{\varphi\in\mathbb{R}^d}\mathscr{L}(\boldsymbol{\varphi}) = \mathscr{L}(\boldsymbol{\phi}^*)$$

Kolchinsky, A., Dechant, A., Yoshimura, K., & SI. *arXiv:2206.14599* (2022). *arXiv: 2412.08432* (2024).

Topic 3: Relation to the Kullback-Leibler divergence of probabilities for relaxing Markov jump processes

Markov jump process

$$\frac{d}{dt}x_i(t) = \sum_{j,\alpha} [R_{ij}^{\alpha} x_j(t) - R_{ji}^{\alpha} x_i(t)] \qquad \sum_i x_i(t) = 1$$

Markov jump process evolving “backwards in time”

$$-\frac{d}{dt}y_i(-t) = \sum_{j,\alpha} [R_{ij}^{\alpha} y_j(-t) - R_{ji}^{\alpha} y_i(-t)] \qquad \sum_i y_i(-t) = 1$$

Excess entropy production rate

$$\sigma_{\mathrm{IG}}^{\mathrm{ex}} = \sup_{\boldsymbol{\phi}\in\mathbb{R}^d} \left[\sum_i \dot{x}_i \phi_i - \sum_{i\neq j,\alpha} x_j R_{ij}^{\alpha} (e^{\phi_j - \phi_i} - 1) \right] \underset{\uparrow}{=} \sup_{\boldsymbol{y}} \left[-\frac{d}{dt}[D_{\mathrm{KL}}(\boldsymbol{x}(t) \| \boldsymbol{y}(-t))] \right]$$

$$\ln y_i = \ln x_i - \phi_i + \mathrm{const}\,.$$

Kolchinsky, A., Dechant, A., Yoshimura, K., & SI. *arXiv:2206.14599* (2022). *arXiv: 2412.08432* (2024).

Topic 4-1: Relation to the bound on the speed of observable

Time-independent observable φ

$$d_t\langle\varphi\rangle := \dot{\boldsymbol{x}}^\top \boldsymbol{\varphi}$$

Def.) Activity of observable $a(\boldsymbol{\varphi}) := \sum_\rho j_\rho \left| \sum_i \nabla_{\rho i}\varphi_i \right|$

Lower bound on the excess entropy production rate

$$\sigma_{\mathrm{IG}}^{\mathrm{ex}} \geq 2 d_t\langle\varphi\rangle \tanh^{-1}\left(\frac{d_t\langle\varphi\rangle}{a(\boldsymbol{\varphi})}\right) \geq \frac{2(d_t\langle\varphi\rangle)^2}{a(\boldsymbol{\varphi})} \geq \frac{2(d_t\langle\varphi\rangle)^2}{\|\boldsymbol{j}\|_1 \|\nabla\boldsymbol{\varphi}\|_\infty}$$

cf.) Thermodynamic uncertainty relation (a.k.a. Wasserstein-Cramer-Rao bound)

Bound on the entropy production rate
  Dechant, A., and Sasa, S. I. *Journal of Statistical Mechanics 2018*, 063209 (2018).
  SI and Dechant, A. *Physical Review X*, *10*, 021056 (2020).
Bound on the "excess" entropy production rate (i.e., the 2-Wasserstein distance)
  Dechant, A., Sasa, S. I., and SI. Physical Review Research, 4, L012034 (2022).
  Dechant, A., Sasa, S. I., and SI. *Physical Review E*, *106*, 024125 (2022).
  K. Yoshimura, A. Kolchinsky, A. Dechant and SI, Physical Review Research, **5**, 013017 (2023).
  SI, Info. Geo. **7**, 441-483 (2024).

Wasserstein-Cramér-Rao bound
 Li, W., & Zhao, J. *Information Geometry*, *6*(1), 203-255 (2023).

$$\sigma_t^{\mathrm{ex}} = \frac{1}{\mu T}\left(\lim_{\Delta t \to +0} \frac{\mathscr{W}_2(P_t, P_{t+\Delta t})}{\Delta t}\right)^2 \geq \frac{(\partial_t \mathbb{E}_{P_t}[\varphi]])^2}{\mu T \int d\boldsymbol{x} \|\nabla\varphi(\boldsymbol{x})\|^2}$$

Kolchinsky, A., Dechant, A., Yoshimura, K., & SI. *arXiv:2206.14599* (2022). *arXiv: 2412.08432* (2024).

Topic 4-2: Relation to the 1-Wasserstein distance

Def.) 1-Wasserstein distance

$$\mathscr{W}_1(\boldsymbol{x}(t),\boldsymbol{x}(t')) := \inf_{\boldsymbol{u}\in\mathbb{R}_+^{2m}} \|\boldsymbol{u}\|_1 \qquad \textbf{\textit{s.t.}} \qquad \boldsymbol{x}(t)-\boldsymbol{x}(t') = \nabla^\top \boldsymbol{u}$$

Def.) Speed of 1-Wasserstein distance

$$\dot{\mathscr{W}}_1(t) := \lim_{\Delta t\to+0} \frac{\mathscr{W}_1(\boldsymbol{x}(t),\boldsymbol{x}(t+\Delta t))}{\Delta t}$$

$$\dot{\mathscr{W}}_1(t) = \sup_{\boldsymbol{\phi}\in\mathbb{R}^d} (\dot{\boldsymbol{x}}(t))^\top \boldsymbol{\varphi} \qquad \textbf{\textit{s.t.}} \qquad \|\nabla\boldsymbol{\varphi}\|_\infty \le 1$$

Bound by the 1-Wasserstein distance

$$\sigma_{\rm IG}^{\rm ex} \ge 2\dot{\mathscr{W}}_1 \tanh^{-1}\frac{\dot{\mathscr{W}}_1}{\|\boldsymbol{j}\|_1} \ge \frac{(\dot{\mathscr{W}}_1)^2}{\|\boldsymbol{j}\|_1/2}$$

cf.) Hölder-type inequality (continuous state)

$$[\mathscr{W}_2(P_t,P_{t+\Delta t})]^2 \ge [\mathscr{W}_1(P_t,P_{t+\Delta t})]^2$$

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Application of topic 4: Oscillating chemical reaction

Brusselator

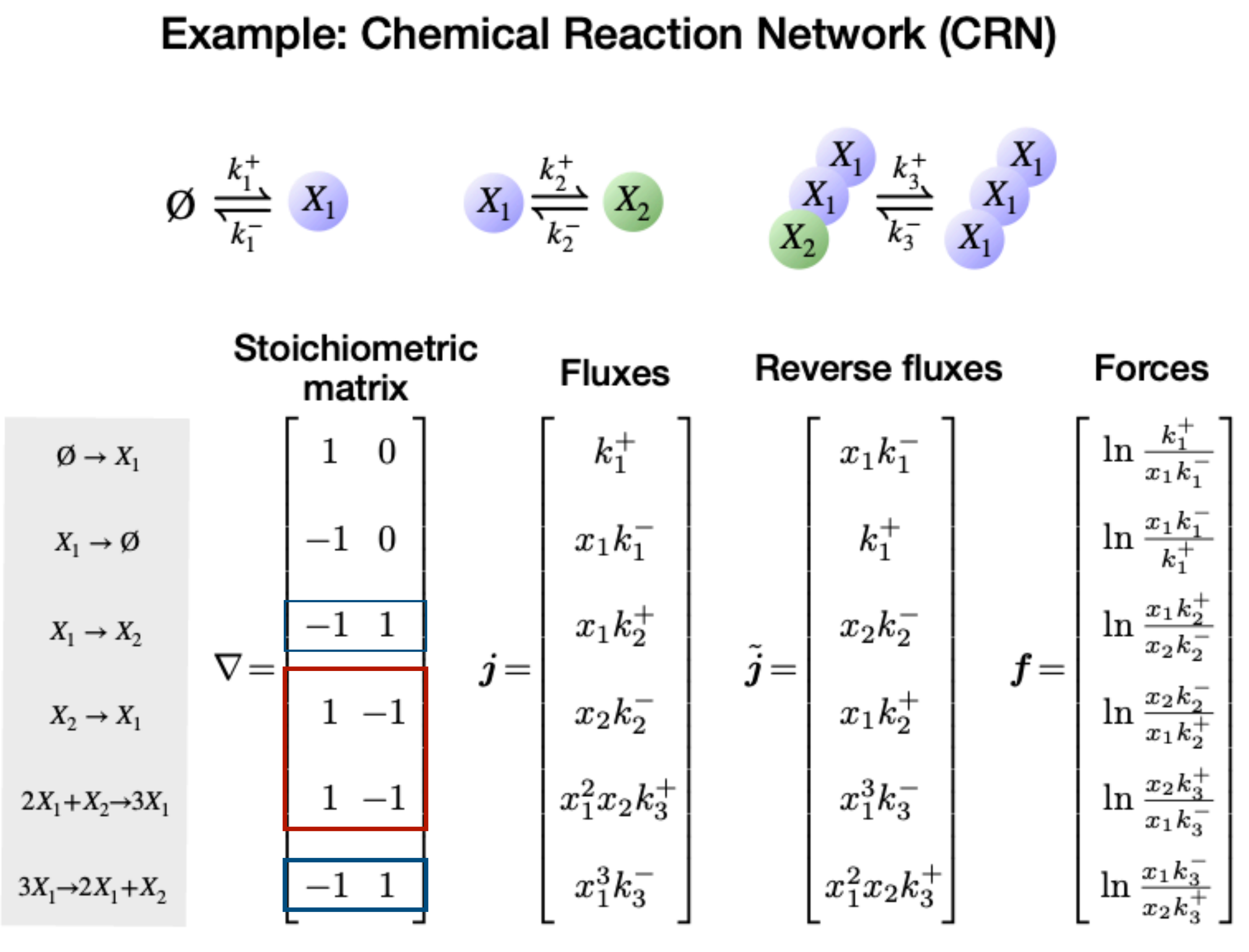
$$\varnothing \underset{k_1^-}{\overset{k_1^+}{\rightleftharpoons}} X_1 \qquad X_1 \underset{k_2^-}{\overset{k_2^+}{\rightleftharpoons}} X_2 \qquad X_2 + 2X_1 \underset{k_3^-}{\overset{k_3^+}{\rightleftharpoons}} 3X_1$$

Optimal potential

$$\boldsymbol{\phi}^* = \left(-\ln \frac{x_1 k_1^-}{k_1^+}, -\ln \frac{x_1 k_1^-}{k_1^+} - \ln \frac{x_2(k_2^- + x_1^2 k_3^+)}{x_1(k_2^+ + x_1^2 k_3 -)} \right)^\top$$

Excess entropy production rate

$$\sigma_{\rm IG}^{\rm ex} = \dot{\boldsymbol{x}}^\top \boldsymbol{\phi}^* (\geq 0)$$



Example: Chemical Reaction Network (CRN)

$$\varnothing \underset{k_1^-}{\overset{k_1^+}{\rightleftharpoons}} X_1 \qquad X_1 \underset{k_2^-}{\overset{k_2^+}{\rightleftharpoons}} X_2 \qquad X_2\, X_1\, X_1 \underset{k_3^-}{\overset{k_3^+}{\rightleftharpoons}} X_1\, X_1\, X_1$$

Stoichiometric matrix, Fluxes, Reverse fluxes, Forces

$$\begin{array}{c} \varnothing \to X_1 \\ X_1 \to \varnothing \\ X_1 \to X_2 \\ X_2 \to X_1 \\ 2X_1+X_2\to 3X_1 \\ 3X_1 \to 2X_1+X_2 \end{array} \quad \nabla = \begin{bmatrix} 1 & 0 \\ -1 & 0 \\ \boxed{-1 \;\; 1} \\ 1 & -1 \\ 1 & -1 \\ \boxed{-1 \;\; 1} \end{bmatrix} \quad \boldsymbol{j} = \begin{bmatrix} k_1^+ \\ x_1 k_1^- \\ x_1 k_2^+ \\ x_2 k_2^- \\ x_1^2 x_2 k_3^+ \\ x_1^3 k_3^- \end{bmatrix} \quad \tilde{\boldsymbol{j}} = \begin{bmatrix} x_1 k_1^- \\ k_1^+ \\ x_2 k_2^- \\ x_1 k_2^+ \\ x_1^3 k_3^- \\ x_1^2 x_2 k_3^+ \end{bmatrix} \quad \boldsymbol{f} = \begin{bmatrix} \ln \frac{k_1^+}{x_1 k_1^-} \\ \ln \frac{x_1 k_1^-}{k_1^+} \\ \ln \frac{x_1 k_2^+}{x_2 k_2^-} \\ \ln \frac{x_2 k_2^-}{x_1 k_2^+} \\ \ln \frac{x_2 k_3^+}{x_1 k_3^-} \\ \ln \frac{x_1 k_3^-}{x_2 k_3^+} \end{bmatrix}$$

Continuity equation

$$\dot{\boldsymbol{x}} = \nabla^\top \boldsymbol{j} = \begin{bmatrix} j_1 - j_2 + j_4 - j_3 + j_5 - j_6 \\ j_2 - j_1 + j_3 - j_4 + j_6 - j_5 \end{bmatrix} = (\nabla^{\rm cg})^\top \boldsymbol{j}^{\rm cg}$$

$$\nabla^{\rm cg} = \begin{bmatrix} 1 & 0 \\ -1 & 0 \\ -1 & 1 \\ 1 & -1 \end{bmatrix} \qquad \boldsymbol{j}^{\rm cg} = \begin{bmatrix} j_1 \\ j_2 \\ j_3 + j_6 \\ j_4 + j_5 \end{bmatrix}$$

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Application of topic 4: Bound on dissipation for oscillating reaction

Def.) (Excess) entropy production incurred during one cycle

$$\Sigma_{\mathrm{IG}}^{\mathrm{ex}} = \int_0^{T_{\mathrm{cyc}}} dt \sigma_{\mathrm{IG}}^{\mathrm{ex}} \qquad \Sigma = \int_0^{T_{\mathrm{cyc}}} dt \sigma$$

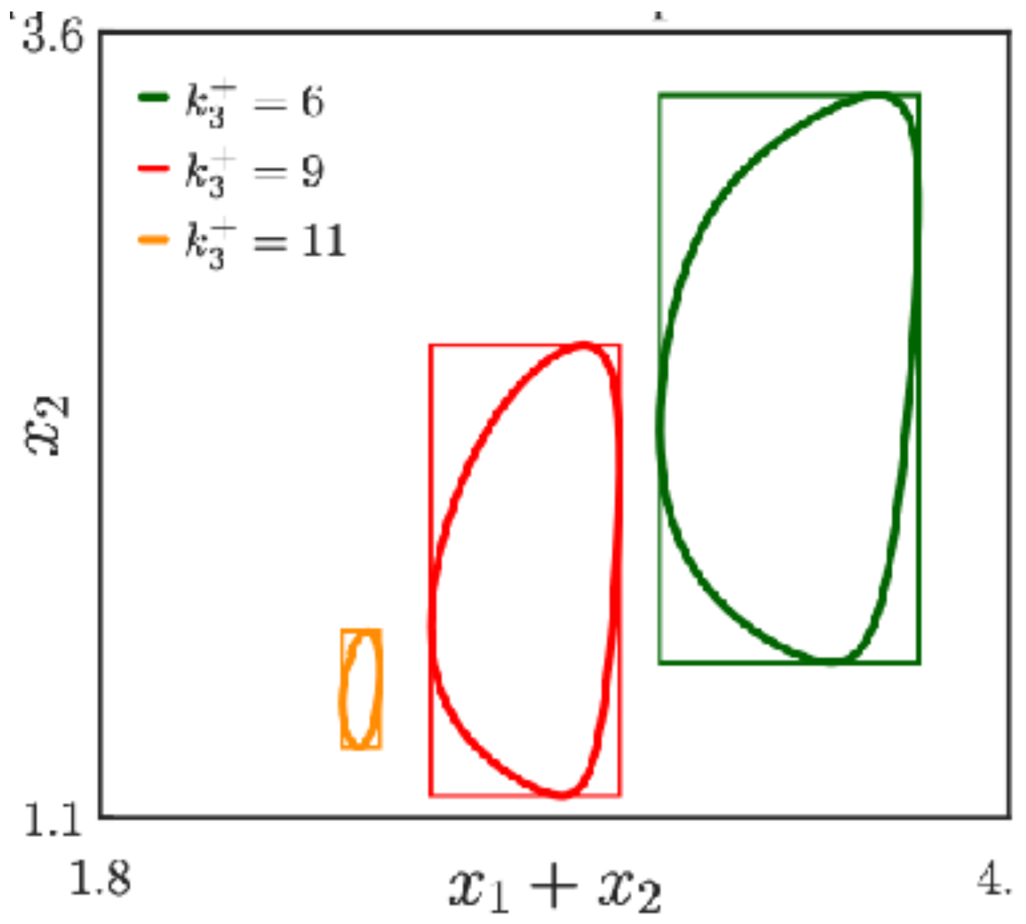
T_{cyc}: The period of a limit cycle

Bound on the (excess) entropy production (Thermodynamic speed limit, TSL)

$$\Sigma \geq \Sigma_{\mathrm{IG}}^{\mathrm{ex}} \geq 2 D_{\mathrm{T}} \tanh^{-1} \frac{D_{\mathrm{T}}}{\int_0^{\mathrm{T_{cyc}}} dt \|\boldsymbol{j}\|_1} \qquad D_{\mathrm{T}} := \int_0^{T_{\mathrm{cyc}}} dt \dot{\mathscr{W}}_1 \qquad \dot{\mathscr{W}}_1 = |\dot{x}_1 + \dot{x}_2| + |\dot{x}_2|$$

D_{T}: Taxicab (Manhattan) distance

for the coordinate $(x_1 + x_2, x_2)$



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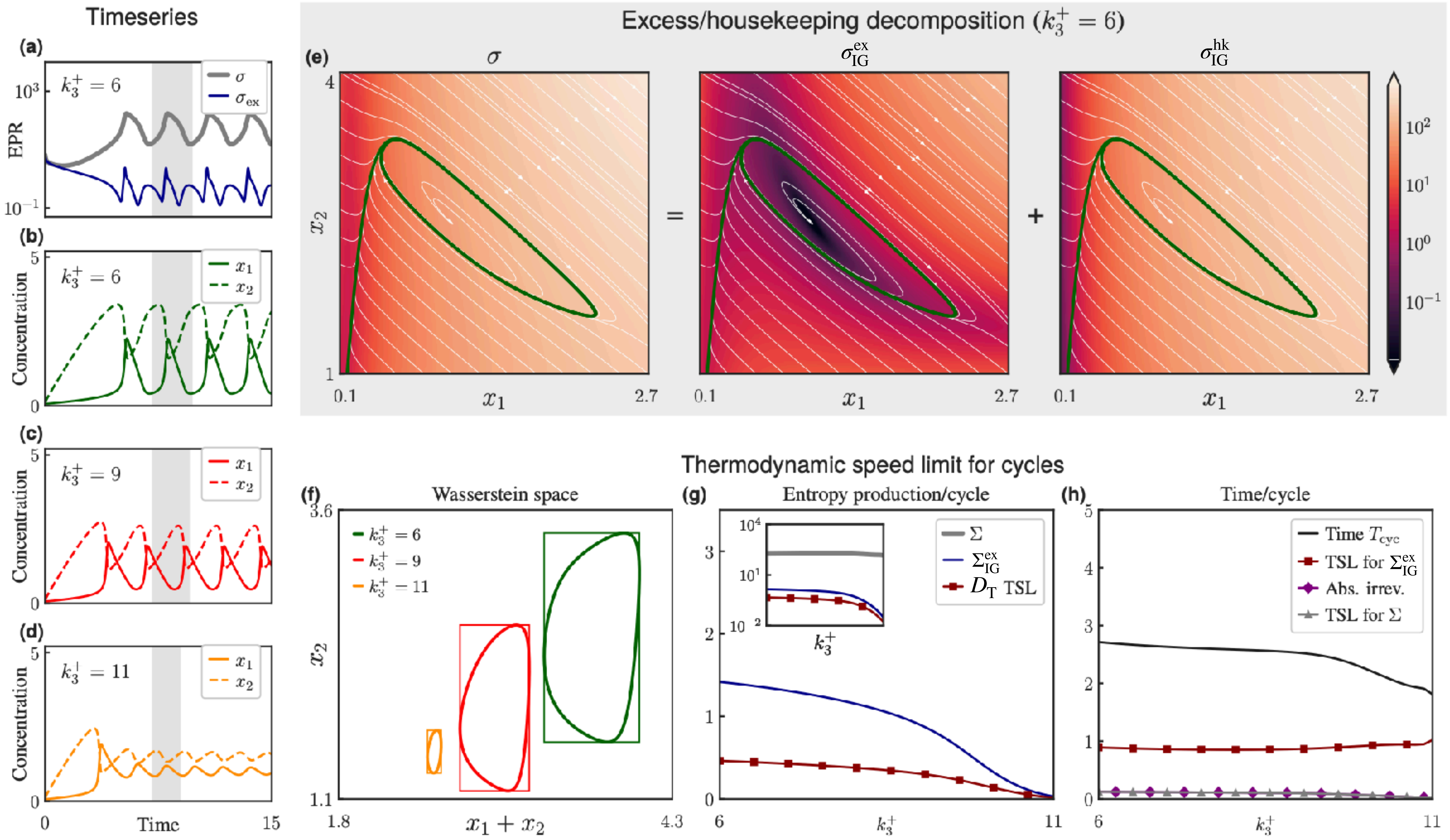
Application of topic 4: Numerics



Summary

For the master/rate equations, we introduce the excess entropy production rate as a minimization problem of the KL divergence of the fluxes in parallel with the definition of the 2-Wasserstein distance introduced by Benamou-Brenier and Jan Maas.

This excess entropy production rate has rich mathematical properties, such as the lower bound on Jan Maas's definition of the 2-Wasserstein distance, invariance under coarse-graining for dynamics, the least variation principle, the large deviation theory, the Kullback-Leibler divergence between two probabilities, the Cramér-Rao-Wasserstein type bound, and the 1-Wasserstein distance.

Our theory is applicable to important problems in nonequilibrium physics, i.e., the inevitable dissipation in an oscillating chemical reaction. For example, our result implies that the taxicab geometry for the limit cycle on concentrations explains the amount of inevitable dissipation.

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Thank you for your attention!