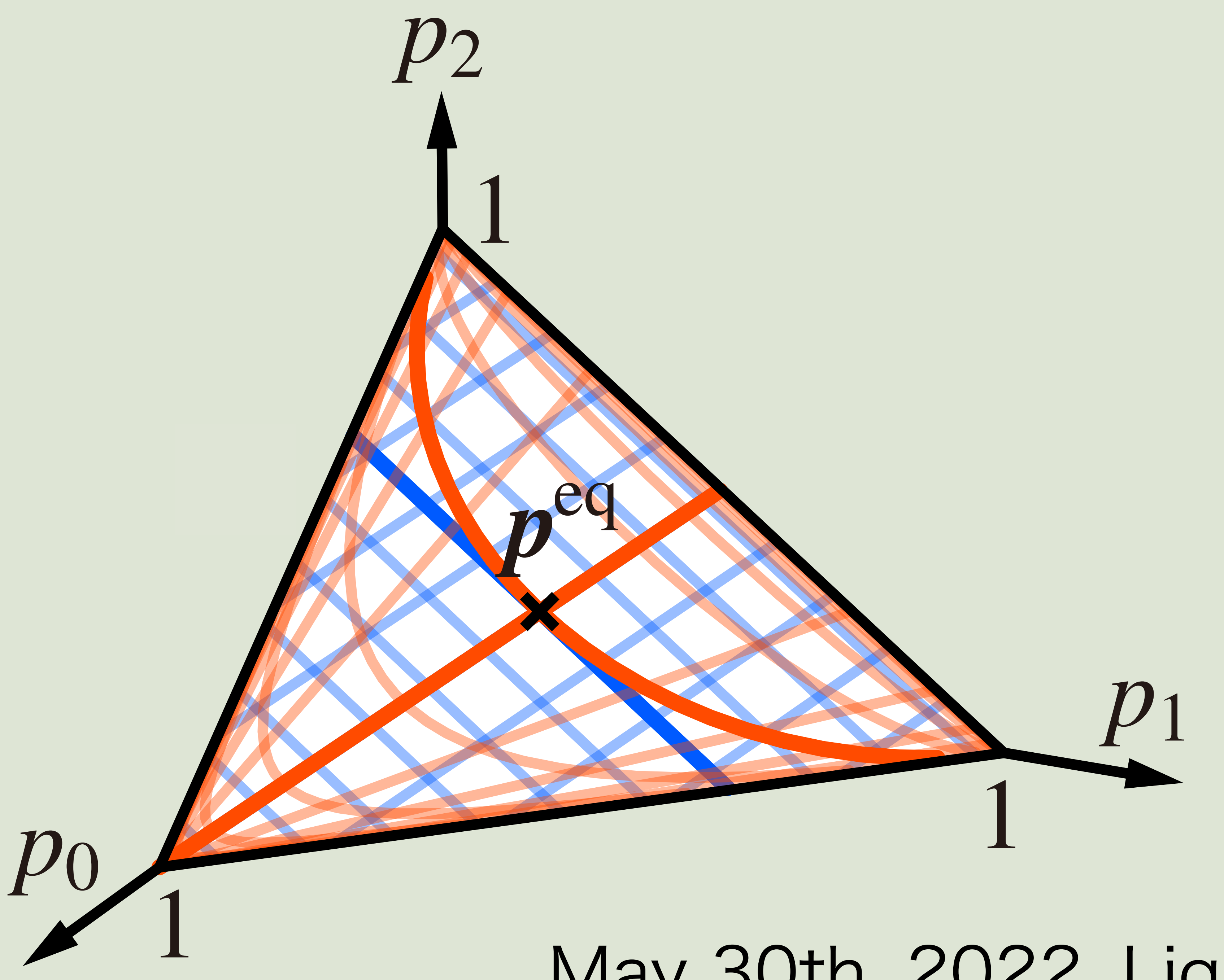
Legendre duality in stochastic thermodynamics: A construction based on information geometry

Preprints:
N. Ohga and S. Ito, arXiv:2112.11008 (Stochastic thermodynamics) ← This talk
N. Ohga and S. Ito, arXiv:2112.13813 (Chemical thermodynamics)



The University of Tokyo
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May 30th, 2022, Lightning Talk at the Workshop on Stochastic Thermodynamics III

Introduction

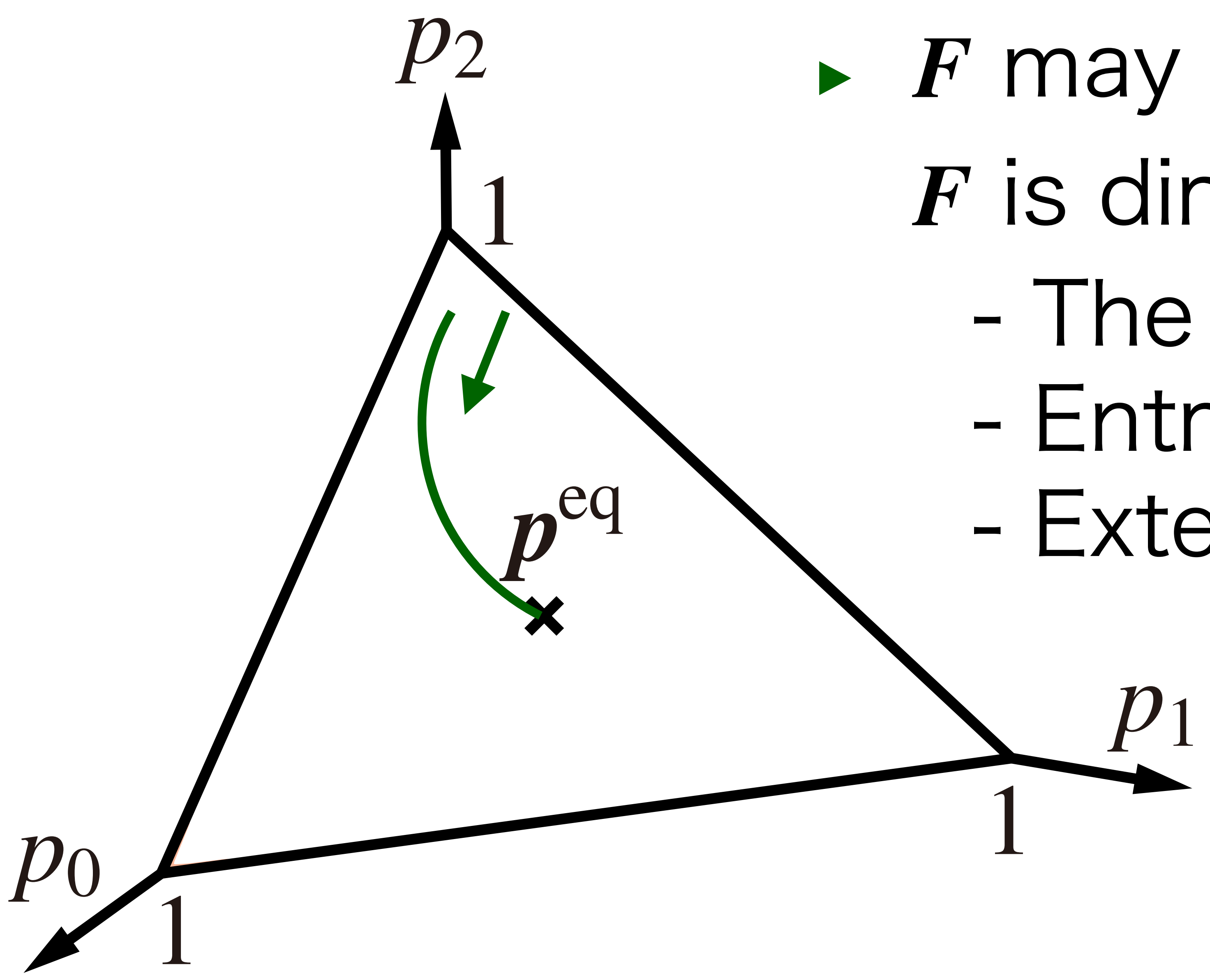
Relaxation processes of an autonomous detailed-balanced system.

The relaxation is captured by...

- Probability distribution $\boldsymbol{p}$
- Thermodynamic force $\boldsymbol{F}(\boldsymbol{p})$
- Total entropy (sys. + bath) $\bar{S}(\boldsymbol{p})$

↓

$$\begin{cases} \boldsymbol{p} = \boldsymbol{p}^{\mathrm{eq}} \\ \boldsymbol{F}(\boldsymbol{p}^{\mathrm{eq}}) = \boldsymbol{0} \\ \bar{S}(\boldsymbol{p}^{\mathrm{eq}}) = \max . \end{cases}$$



- $\boldsymbol{F}$ may be more informative than $\boldsymbol{p}$:

  $\boldsymbol{F}$ is directly related to ...
  - The degree of nonequilibrium
  - Entropy production rate
  - External force

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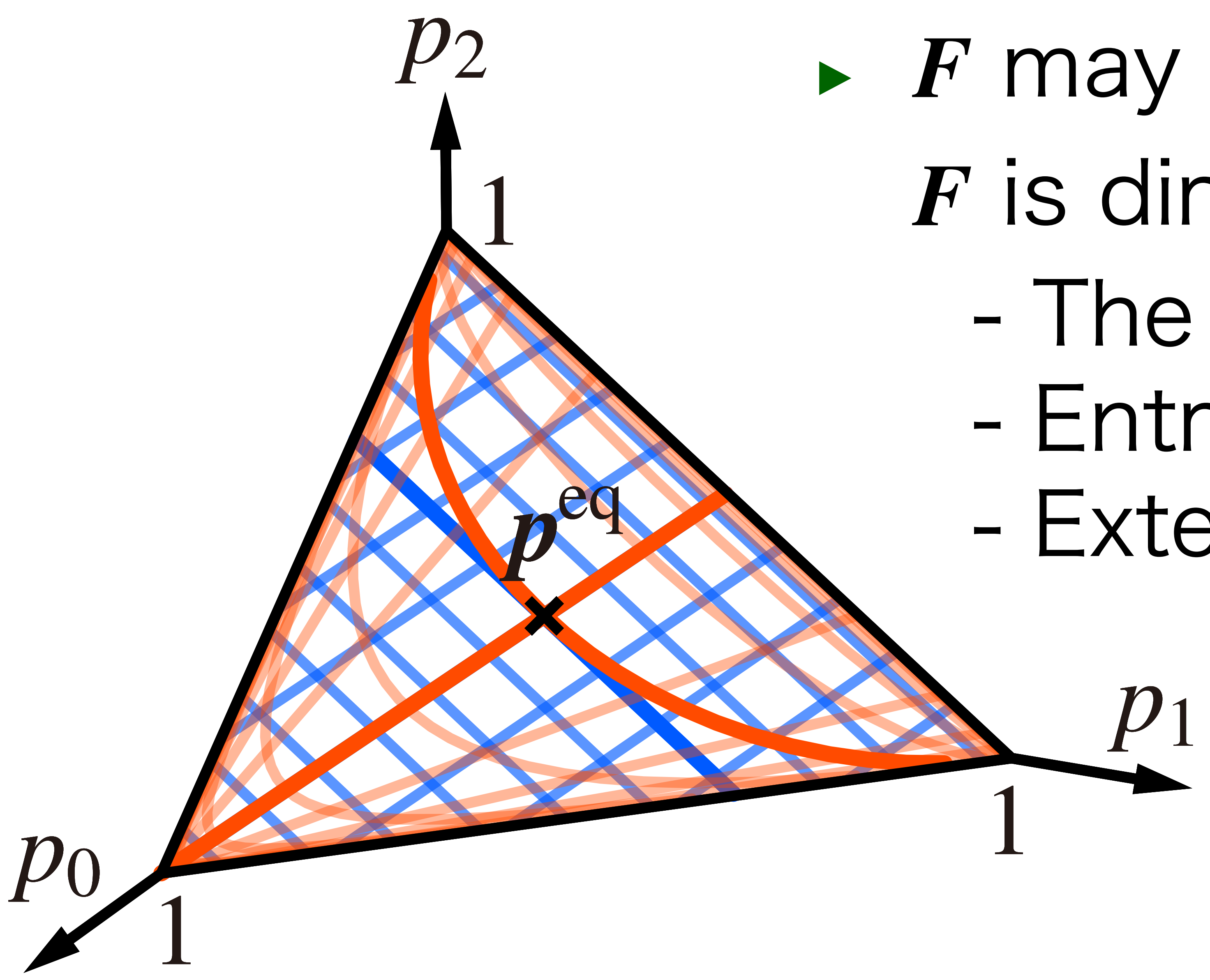

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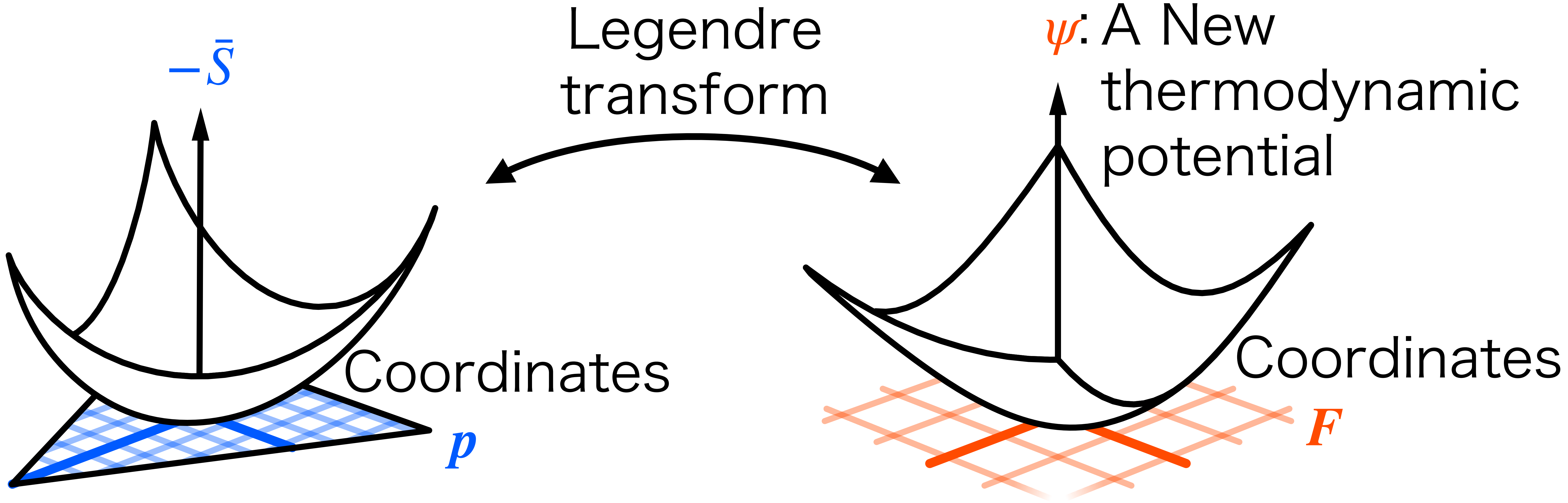


Legendre transform

ψ: A New thermodynamic potential

Description with $\boldsymbol{p}$

Description with $\boldsymbol{F}$

- Inspired by information geometry

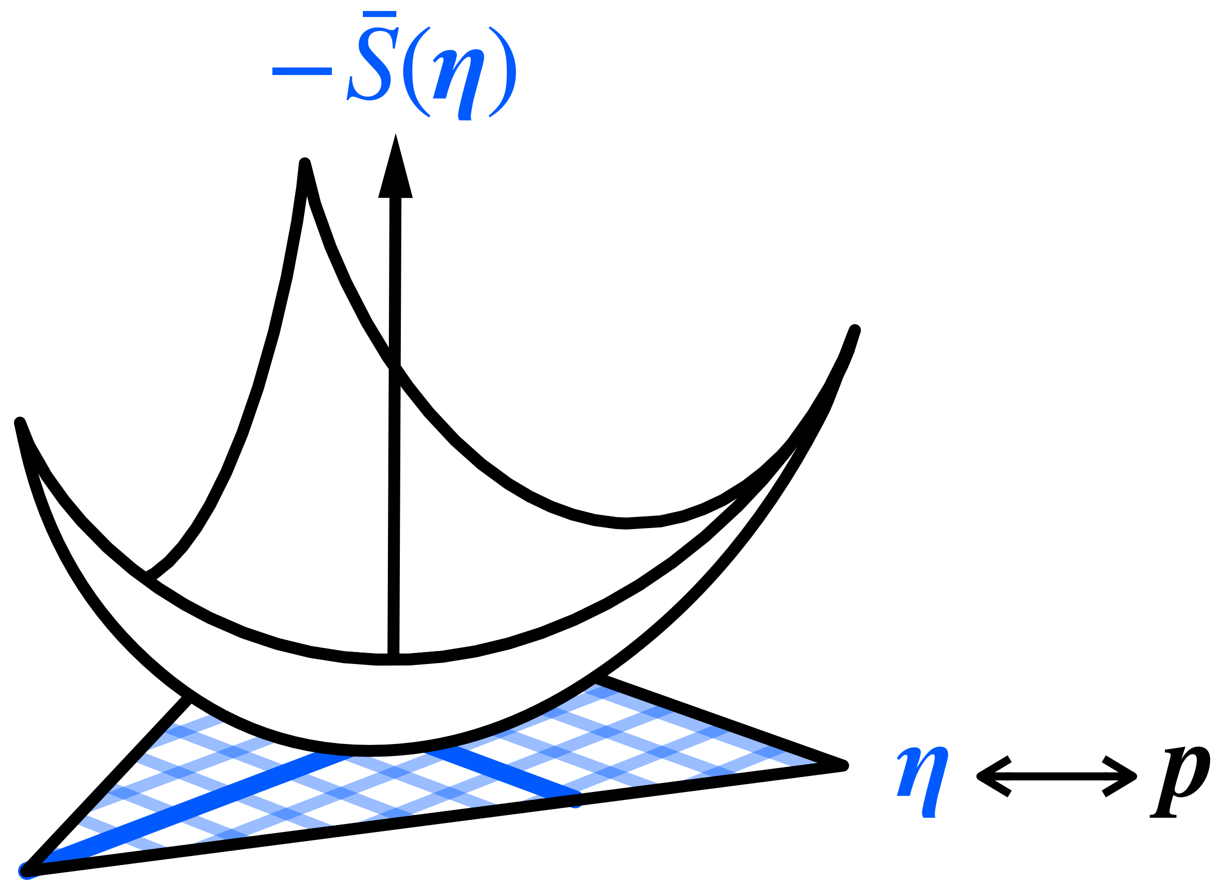
Main concepts & results

Original dynamics

- Free relaxation
- Total entropy: $\bar{S}(\boldsymbol{p})$

Quasi-static dynamics

- The same trajectory, quasi-statically slow
- Realized by a quasi-static driving with external field $\boldsymbol{\nu}$.
- Equilibrium free energy under $\boldsymbol{\nu}$: $-T\psi(\boldsymbol{\nu})$



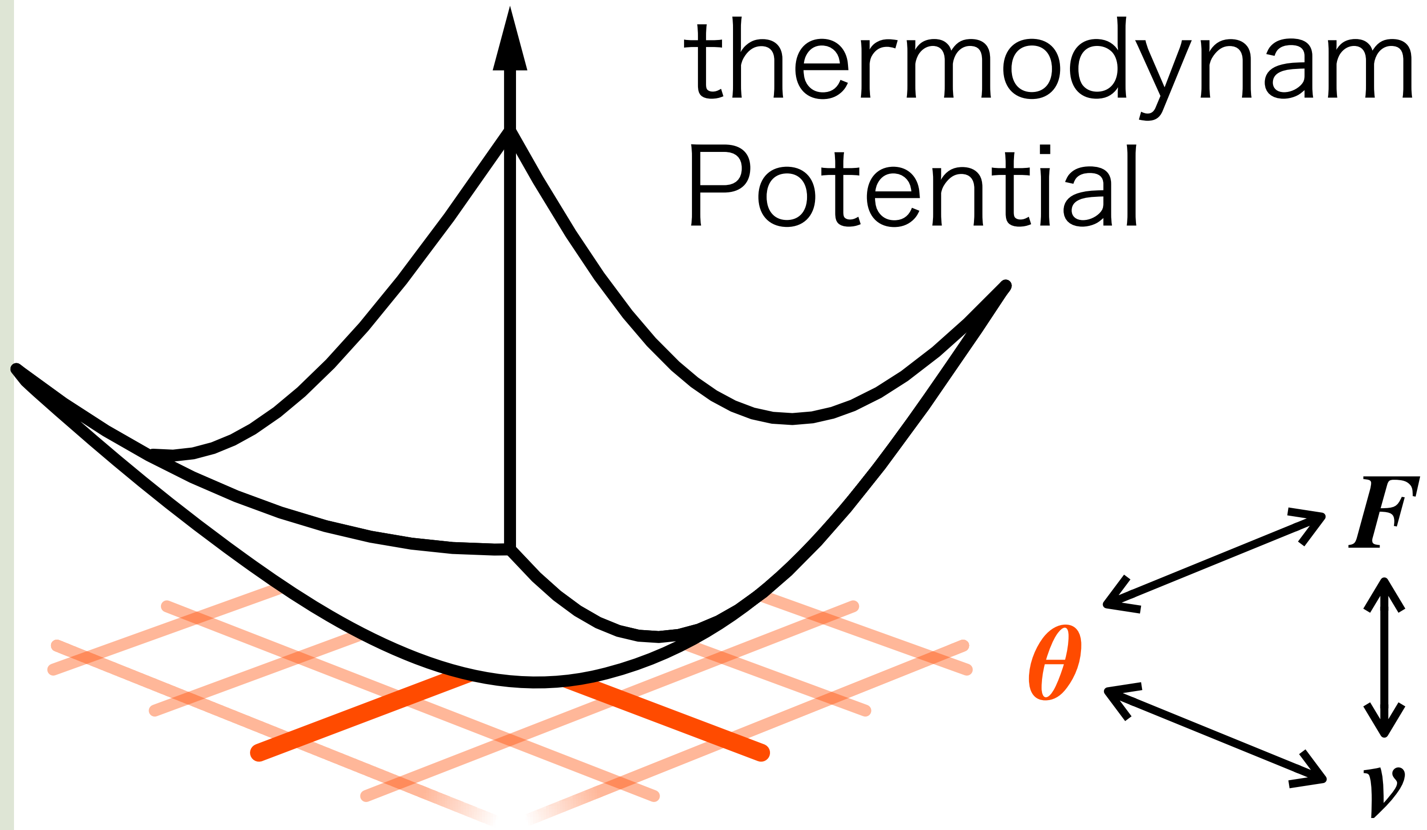
Legendre transform

$$\theta^{\alpha} = \frac{\partial(-\bar{S})}{\partial\eta_{\alpha}}, \quad \eta_{\alpha} = \frac{\partial\psi}{\partial\theta^{\alpha}}$$

$$\psi = \sum_{\alpha}\theta^{\alpha}\eta_{\alpha} - (-\bar{S})$$

Result 1

$\psi(\boldsymbol{\theta})$: A New thermodynamic Potential



$\longleftrightarrow$: linear, one-to-one correspondence

$$\frac{d\bar{S}}{dt} \geq 0$$

The second law of thermodynamics

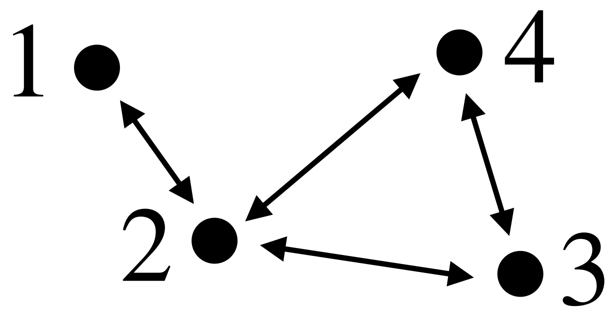
Result 2

$$-T\frac{d\psi}{dt} \geq 0$$

A new constraint on relaxation processes

Setup: Markov jump system

e.g.)



- $N+1$ states: $i = 0, 1, \ldots, N$ Energy ϵ^i
- Single heat bath T
- $\boldsymbol{p}(t) \equiv (p_0(t), p_1(t), \ldots, p_N(t))$ $p_i^{\mathrm{eq}} \propto \exp(-\epsilon^i / k_{\mathrm{B}} T)$

- $\dfrac{dp_i}{dt} = \sum_j \left[W_{ij} p_j(t) - W_{ji} p_i(t)\right]$ Irreducible, detailed-balanced $\Longrightarrow \boldsymbol{p}(t) \to \boldsymbol{p}^{\mathrm{eq}} \quad (t \to \infty)$

- Total entropy (system + bath) $\bar{S}(\boldsymbol{p}) = -k_{\mathrm{B}} \sum_i p_i \ln p_i - \dfrac{1}{T} \sum_i \epsilon^i p_i$
- Thermodynamic force conjugate to the transition $j \to i$

$$F^{ij}(\boldsymbol{p}) := \frac{\epsilon^j - \epsilon^i}{T} + k_{\mathrm{B}} \left(\ln p_j - \ln p_i\right) \qquad \left(\leftarrow \frac{d}{dt} \bar{S}(\boldsymbol{p}) = \sum_{ij} \left[W_{ij} p_j - W_{ji} p_i\right] F^{ij}(\boldsymbol{p}) \right)$$

- $F^{ji} = -F^{ij}$, $\boldsymbol{F}(\boldsymbol{p}^{\mathrm{eq}}) = 0$

Construction

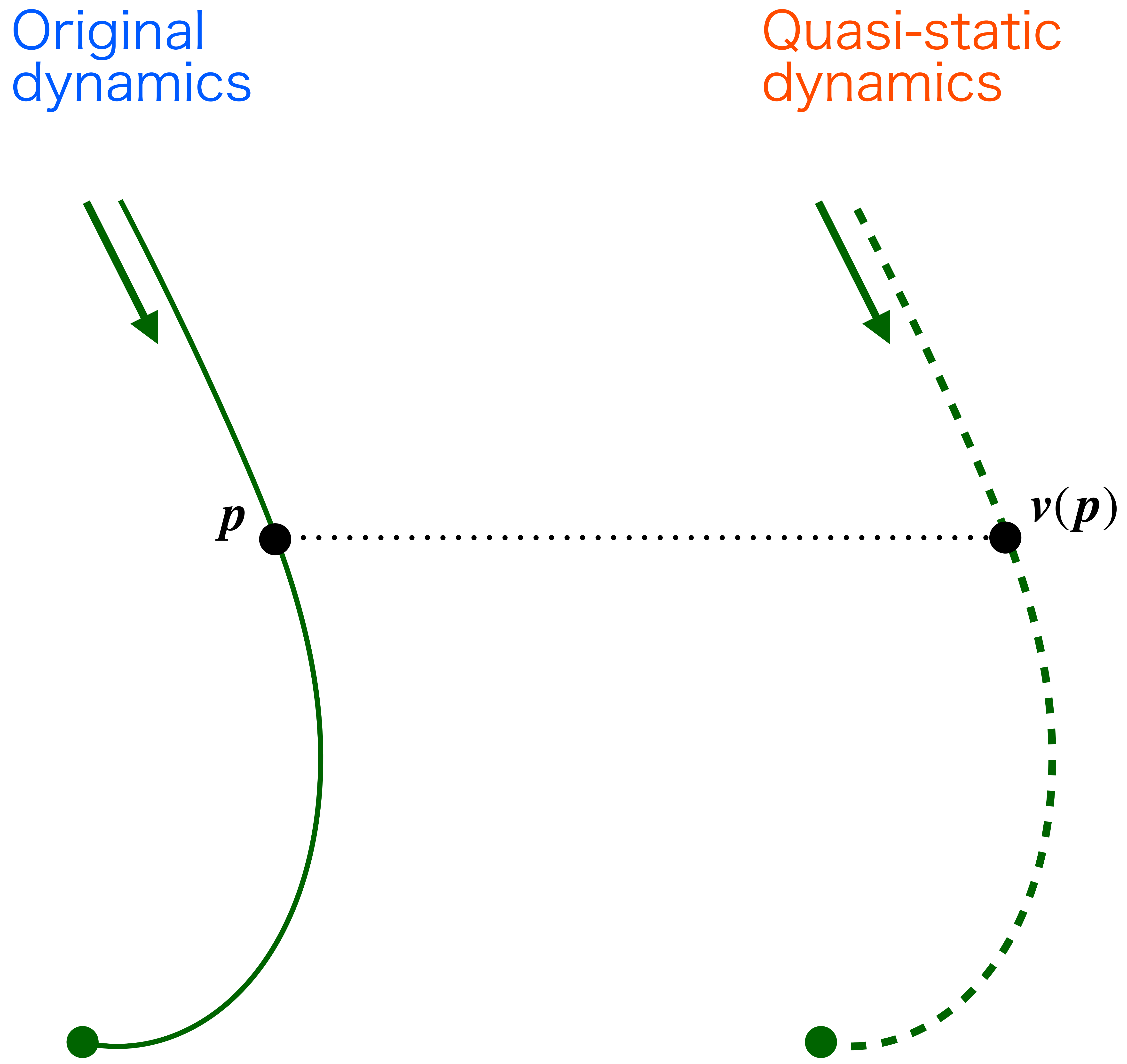
External field $\boldsymbol{v} \equiv (v^i)_{i=0}^N$: $\epsilon^i \;\to\; \epsilon^i - v^i$

Define $\boldsymbol{v}(\boldsymbol{p})$ by

- $$p_i \propto \exp\left(-\frac{\epsilon^i - v^i(\boldsymbol{p})}{k_{\mathrm{B}}T}\right)$$
  ↑ ambiguity $(v^i \;\to\; v^i + \mathrm{const}\,.)$
- $\sum_i p_i^{\mathrm{eq}} v^i(\boldsymbol{p}) = 0$

Relation to $\boldsymbol{F}(\boldsymbol{p})$

- $\boldsymbol{v}(\boldsymbol{p})$ cancels out the thermodynamic force $F^{ij}(\boldsymbol{p})$
  $\Longrightarrow v^j(\boldsymbol{p}) - v^i(\boldsymbol{p}) = TF^{ij}(\boldsymbol{p})$



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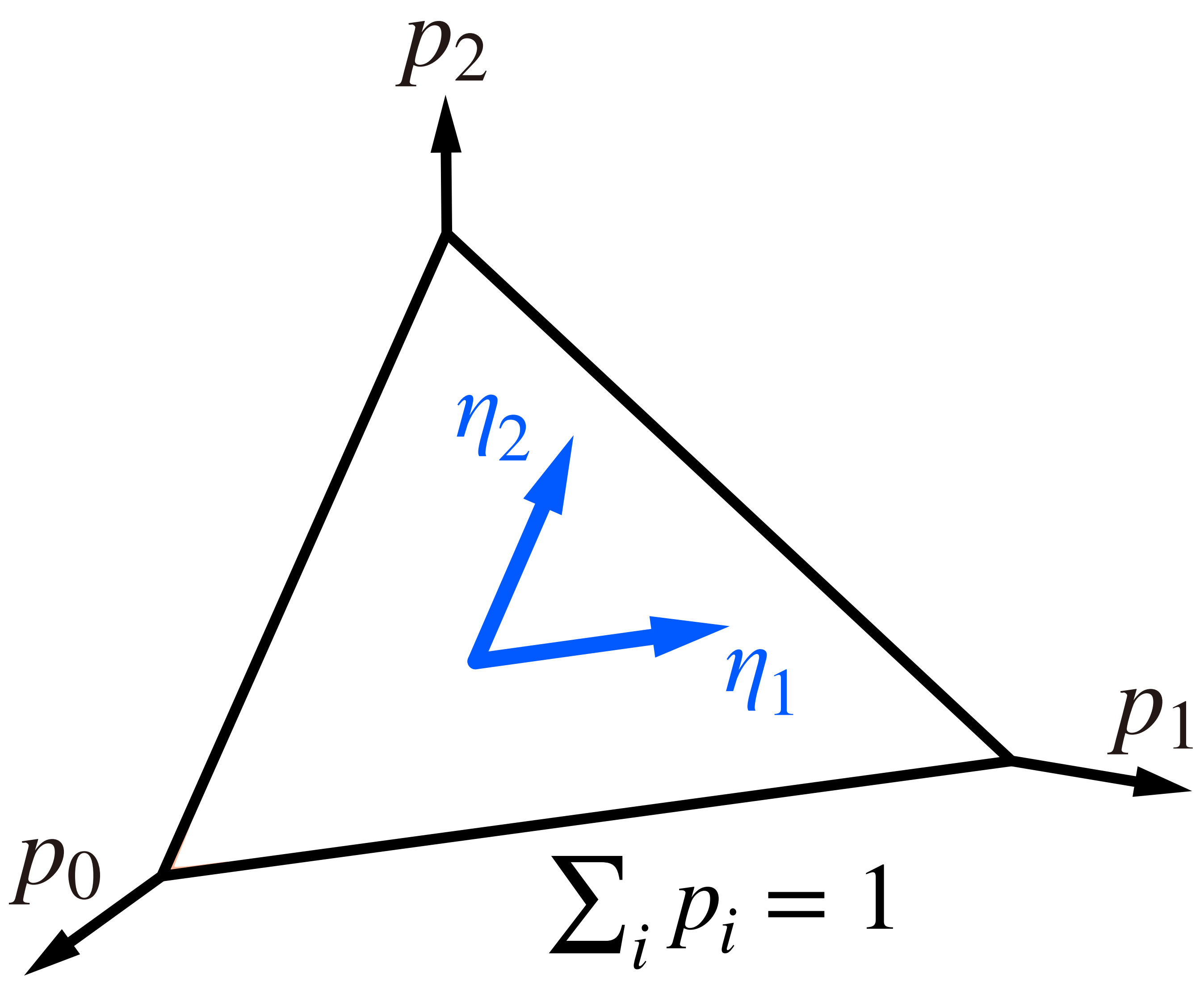

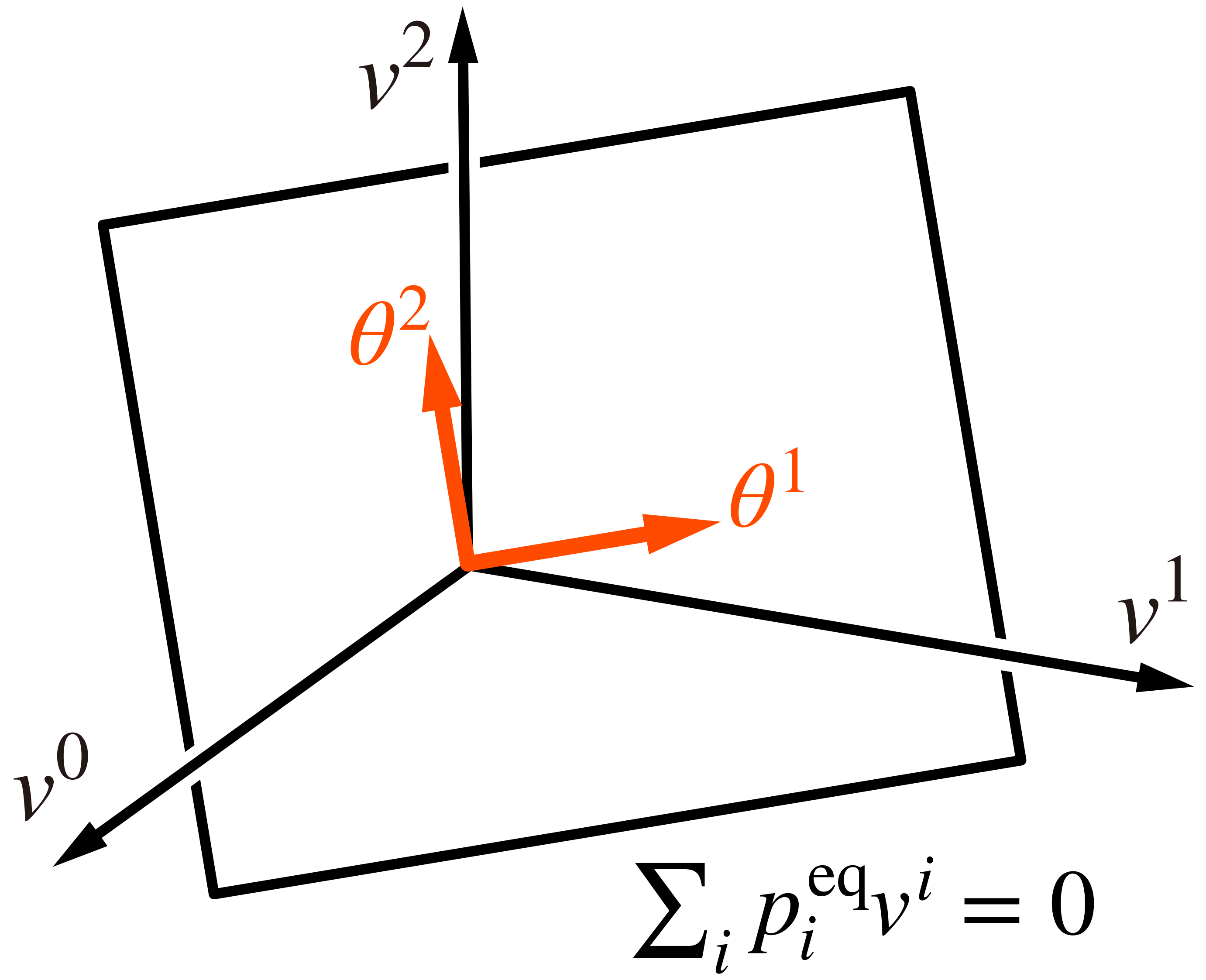

$\boldsymbol{p}$: $(N+1)$-component

$\longrightarrow$ $\boldsymbol{\eta}$: N-component

$p_i = p_i^{\mathrm{eq}} + \sum_\alpha A_i^{\ \alpha} \eta_\alpha$

$\boldsymbol{v}$: $(N+1)$-component

$\longrightarrow$ $\boldsymbol{\theta}$: N-component

$\theta^\alpha = T^{-1} \sum_i v^i A_i^{\ \alpha}$

(A: an arbitrary $(N+1) \times N$ matrix with $\sum_i A_i^{\ \alpha} = 0$)

- Total entropy (cumulative dissipation)

$$\bar{S}(\boldsymbol{\eta}) = -k_{\mathrm{B}} \sum_i p_i(\boldsymbol{\eta}) \ln p_i(\boldsymbol{\eta}) - \frac{1}{T} \sum_i \epsilon^i p_i(\boldsymbol{\eta})$$

- Equilibrium free energy under $\boldsymbol{v}$ (cumulative work)

$$-T\psi(\boldsymbol{\theta}) = -k_{\mathrm{B}}T \ln\left[\sum_i \exp\left(-\frac{\epsilon^i - v^i(\boldsymbol{\theta})}{k_{\mathrm{B}}T}\right)\right]$$

Construction / Result 1: Legendre duality

External field $\boldsymbol{v} \equiv (v^i)_{i=0}^N$: $\epsilon^i \rightarrow \epsilon^i - v^i$

Define $\boldsymbol{v}(\boldsymbol{p})$ by

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- $\boldsymbol{v}(\boldsymbol{p})$ cancels out the thermodynamic force $F^{ij}(\boldsymbol{p})$

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Result 1

Legendre transform $\theta^\alpha = \frac{\partial(-\bar{S})}{\partial \eta_\alpha}$, $\psi = \sum_\alpha \theta^\alpha \eta_\alpha - (-\bar{S})$

The inverse transform $\eta_\alpha = \frac{\partial \psi}{\partial \theta^\alpha}$, $(-\bar{S}) = \sum_\alpha \theta^\alpha \eta_\alpha - \psi$

$\boldsymbol{p}$: $(N+1)$-component

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Result 2: Information geometry

Result 2

The set ($\boldsymbol{\eta}$, $\boldsymbol{\varphi}$, $\boldsymbol{\theta}$, ψ) serves as **dual affine coordinates** in information geometry.

As one of its consequences,

$$-\bar{S}(\boldsymbol{p}) = k_{\mathrm{B}}\, D_{\mathrm{KL}}(\boldsymbol{p}\|\boldsymbol{p}^{\mathrm{eq}}) + \mathrm{const}\,.$$

$$\psi(\boldsymbol{\theta}(\boldsymbol{p})) = k_{\mathrm{B}}\, D_{\mathrm{KL}}(\boldsymbol{p}^{\mathrm{eq}}\|\boldsymbol{p}) + \mathrm{const}\,.$$

Kullback–Leibler divergence

$$D_{\mathrm{KL}}(\boldsymbol{p}\|\boldsymbol{q}) \equiv \sum_i p_i \ln \frac{p_i}{q_i}$$

Consequences of Result 2

- $D_{\mathrm{KL}}(\boldsymbol{p}\|\boldsymbol{q})$ is minimum at $\boldsymbol{p} = \boldsymbol{q}$ $\Longrightarrow$ $\bar{S}$ and $-T\psi$ are maximum at $\boldsymbol{p}^{\mathrm{eq}}$
- $\frac{d}{dt} D_{\mathrm{KL}}(\boldsymbol{p}(t)\|\boldsymbol{q}(t)) \leq 0$ $\Longrightarrow$ $\frac{d\bar{S}}{dt} \geq 0\,,$ $\quad -T\frac{d\psi}{dt} \geq 0$

Second law of thermodynamics

New constraint on relaxation processes

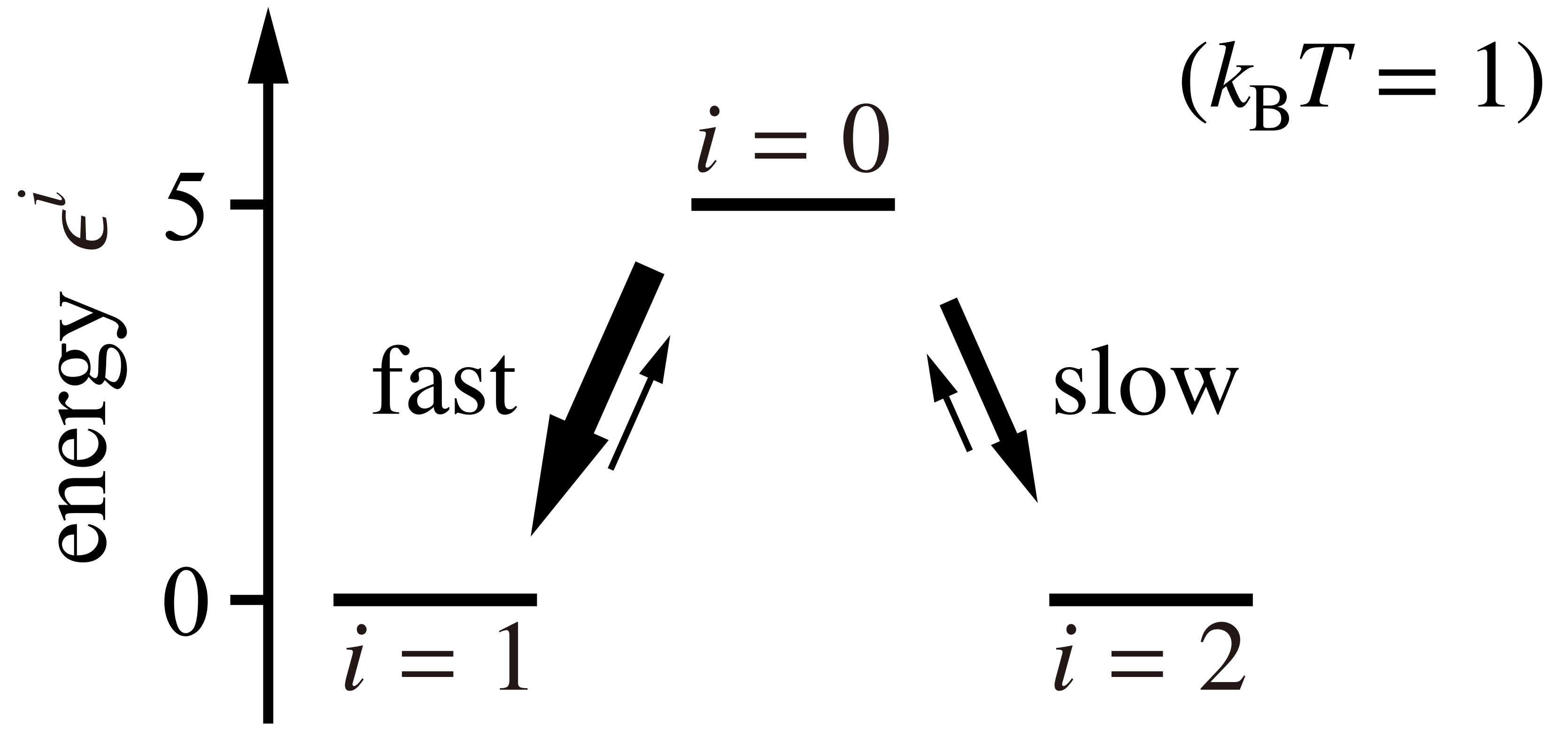
Example: A three-state system

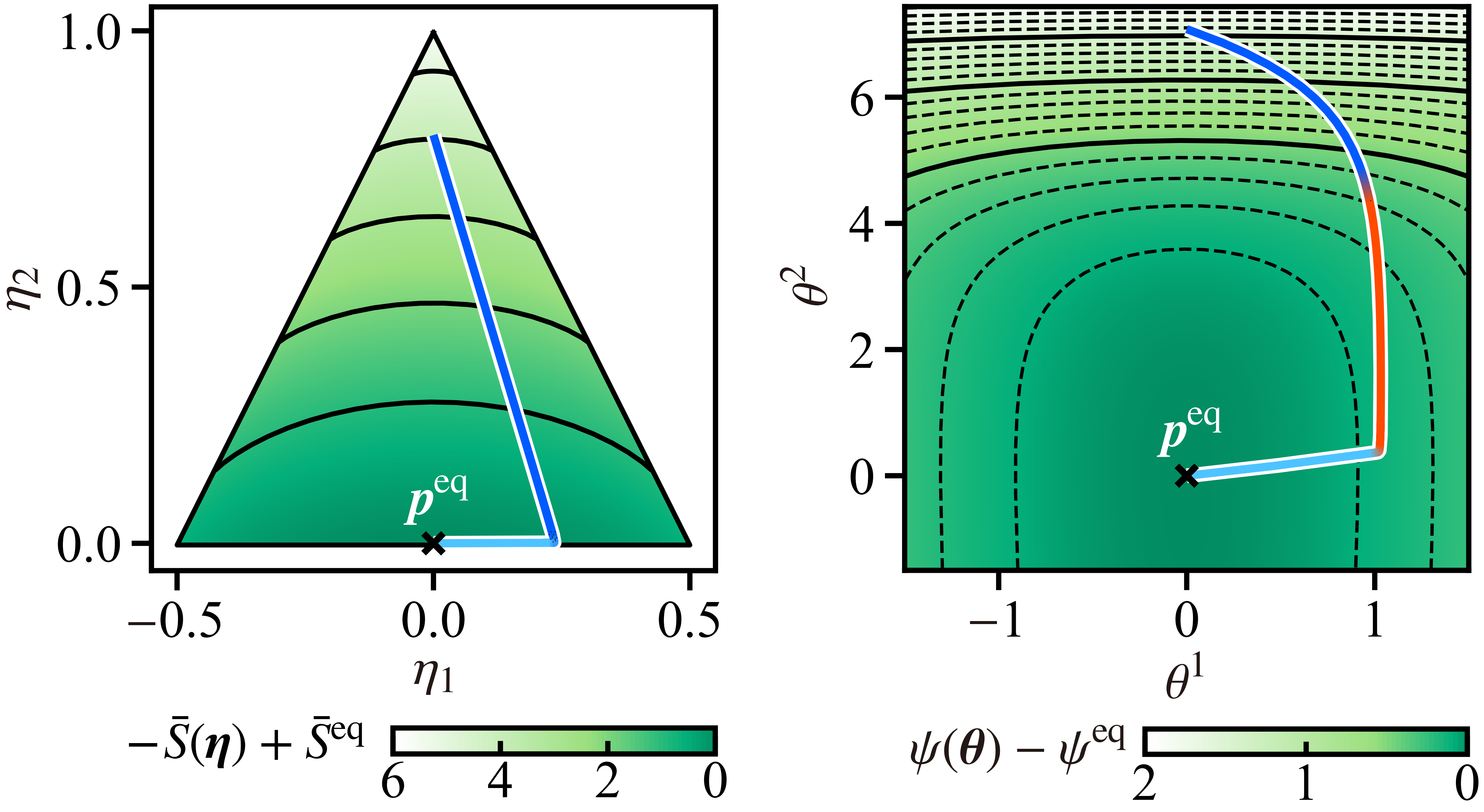
Coordinates $\eta_\alpha = \sum_i (A^-)_\alpha{}^i (p_i - p_i^{\mathrm{eq}})$: Probability

Potential $\bar{S}(\boldsymbol{p})$: Cumulative dissipation

Coordinates $\theta^\alpha = T^{-1} \sum_i v^i A_i^\alpha$: Thermodynamic forces

Potential $-T\psi(\boldsymbol{\theta})$: Cumulative work





- Init. dist.: $(p_0, p_1, p_2) = (0.8, 0.1, 0.1)$

- Choice of the coordinates:

$\eta_1 = (p_1 - p_2)/2$ $\theta^1 = F^{21}$: Imbalance in probability between 1 and 2

$\eta_2 = p_0 - p_0^{\mathrm{eq}}$ $\theta^2 = (F^{10} + F^{20})/2$: Excess probability of 0

$\boldsymbol{\theta}$ can capture a new stage in the trajectory. The new stage can be explained by $-d\psi/dt \geq 0$.

Summary

See our preprints

- N. Ohga and S. Ito, arXiv:2112.11008 (This talk)
- N. Ohga and S. Ito, arXiv:2112.13813 (Chemical thermodynamics)

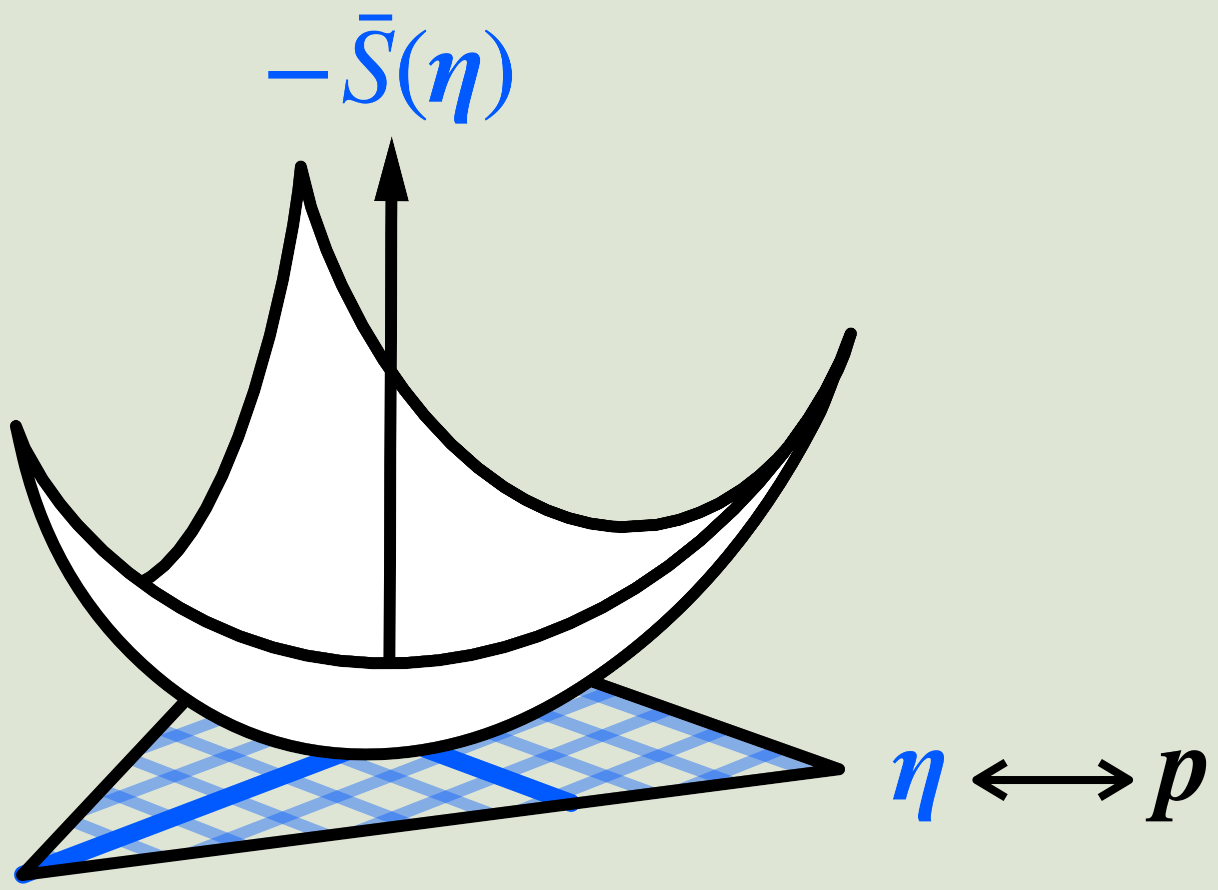
Two descriptions of a relaxation trajectory:

Original dynamics

- Free relaxation
- Total entropy: $\bar{S}(\boldsymbol{p})$ (Cumulative dissipation)

Quasi-static dynamics

- Quasi-static driving by $\boldsymbol{v}$
- Equilibrium free energy under $\boldsymbol{v}$: $-T\psi(\boldsymbol{v})$ (Cumulative work)



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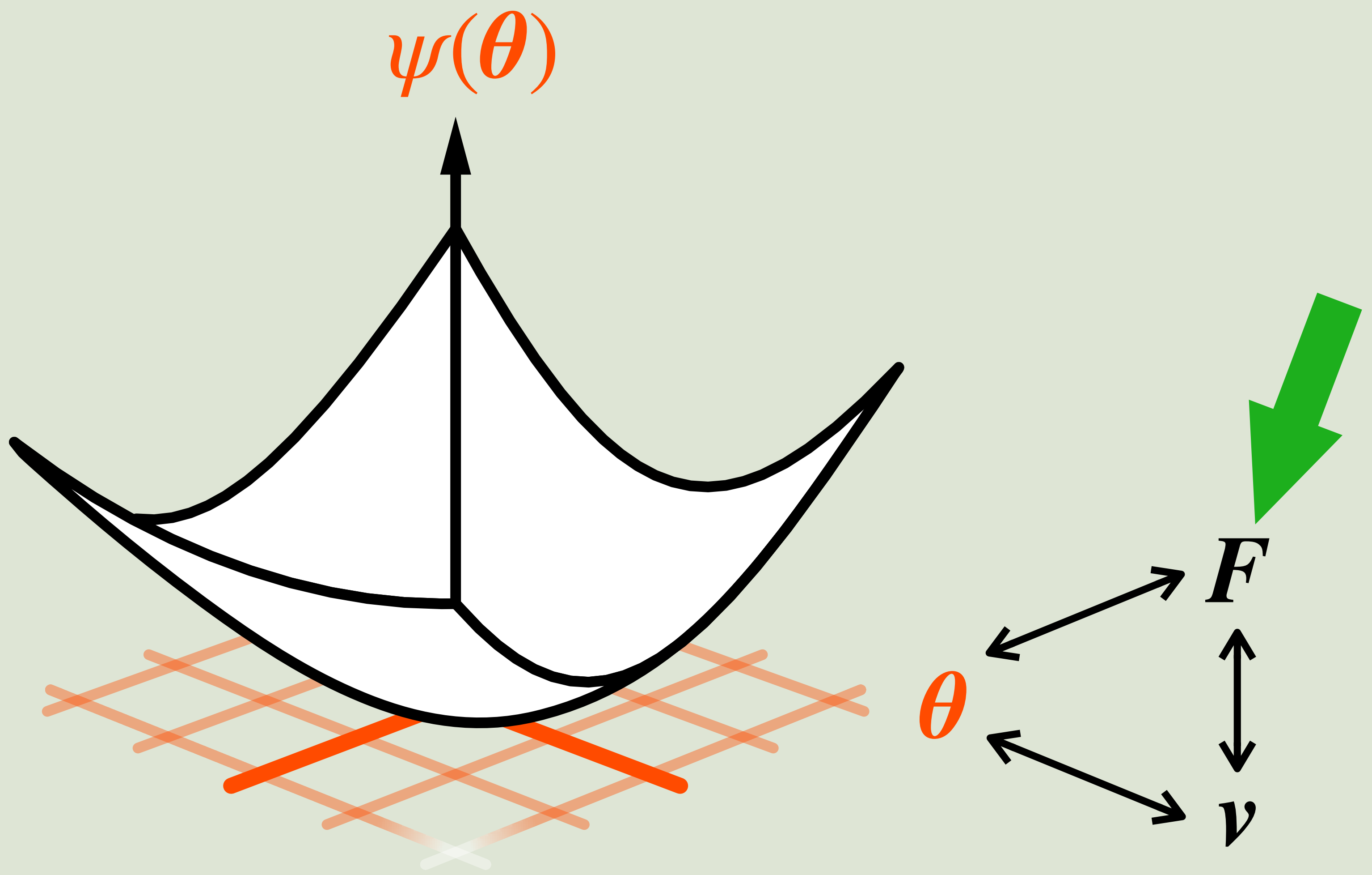

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$\dfrac{d\bar{S}}{dt} \geq 0$ The second law of thermodynamics

$-T\dfrac{d\psi}{dt} \geq 0$ A new constraint on relaxation processes Result 2