Some bounds on entropy production stronger than the second law of thermodynamics

Naoto Shiraishi (Gakushuin University)

N. Shiraishi, K Funo, and K. Saito, PRL 121, 070601 (2018).
N. Shiraishi and K. Saito, PRL 123, 110603 (2019).

Outline

Motivation

Brief review of stochastic thermodynamics

Finite-speed processes

Relaxation processes

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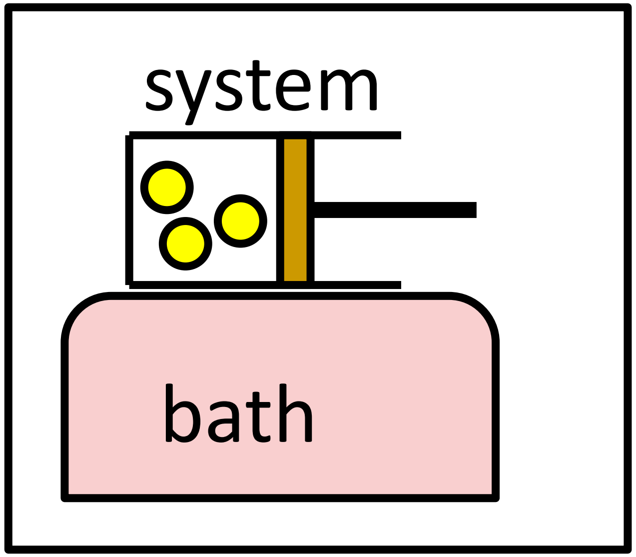
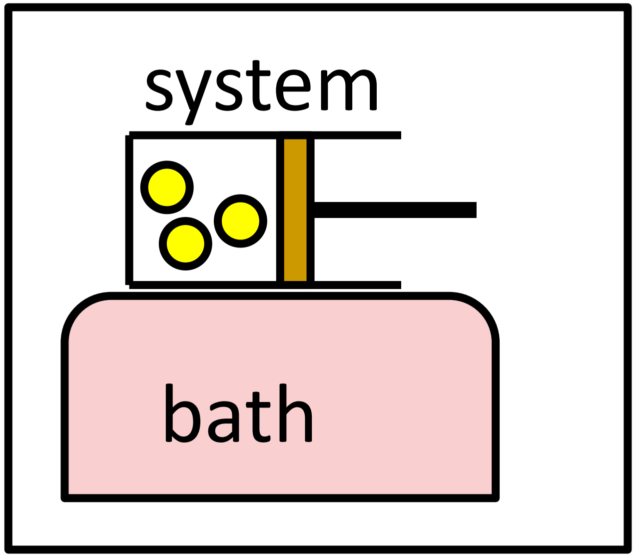
Second law of thermodynamics



Entropy production

$$\sigma := \Delta S_{\mathrm{system}} + \Delta S_{\mathrm{bath}}$$

Second law of thermodynamics



Entropy production

$$\sigma := \Delta S_{\mathrm{system}} + \Delta S_{\mathrm{bath}}$$

Second law of thermodynamics

$$\boldsymbol{\sigma \geq 0}$$

Quasi-static operation achieves equality.

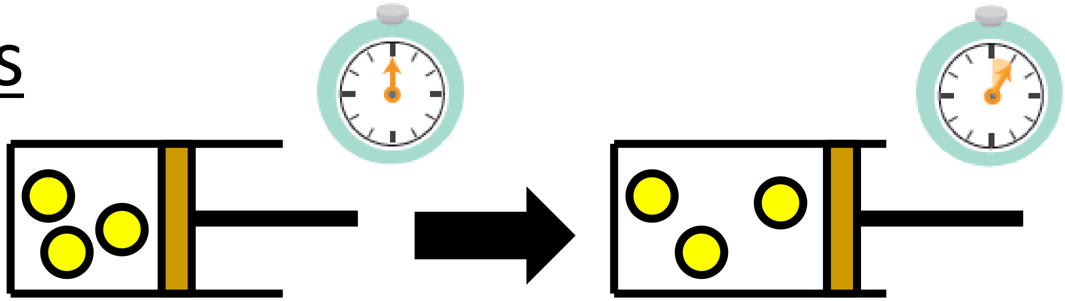
Non quasi-static processes

Various NOT quasi-static processes:

Non quasi-static processes

Various NOT quasi-static processes:

<u>Finite speed process</u>



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Various NOT quasi-static processes:

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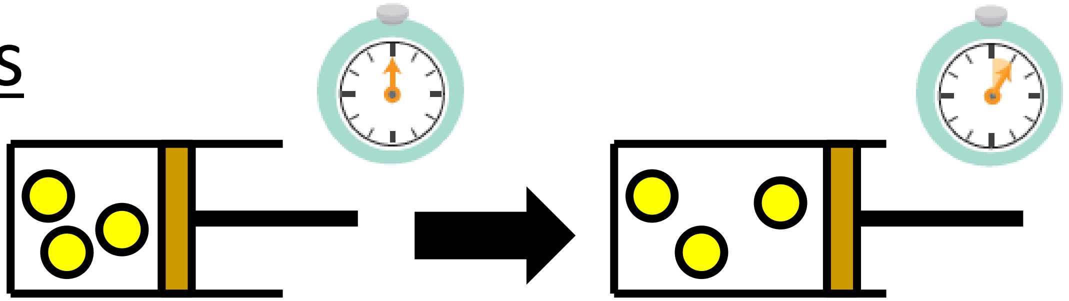
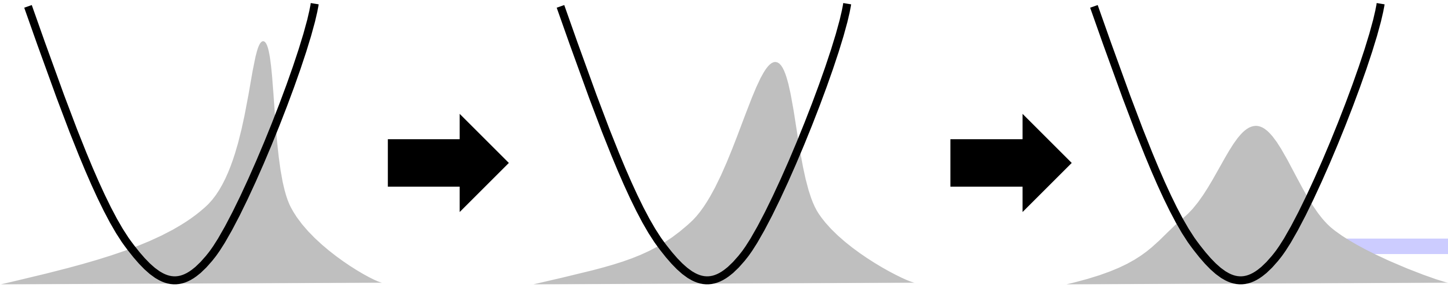
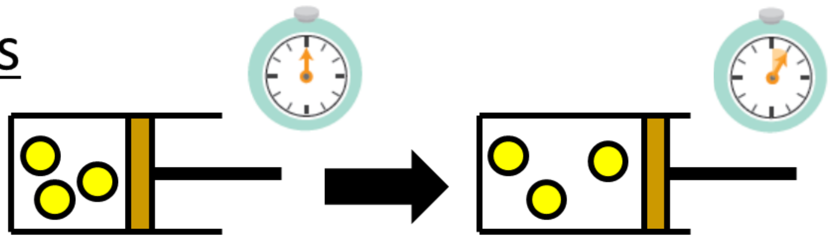


Relaxation process



Stronger bound than the second law?

Finite speed process



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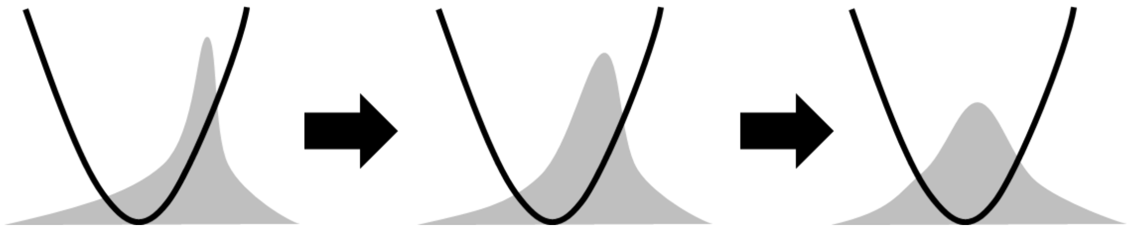

Entropy production must be strictly larger than zero!

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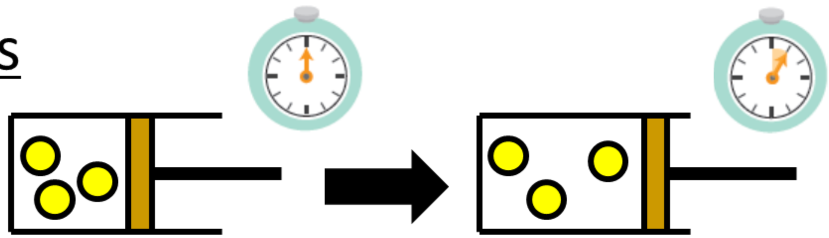

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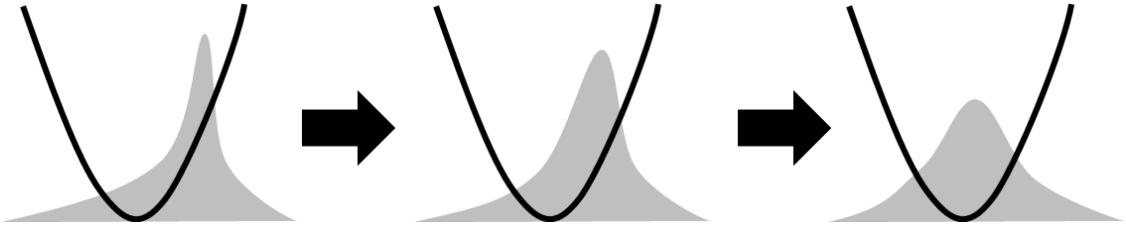

Entropy production must be strictly larger than zero!

But we still do not know a better bound than the second law $\sigma \geq 0$!

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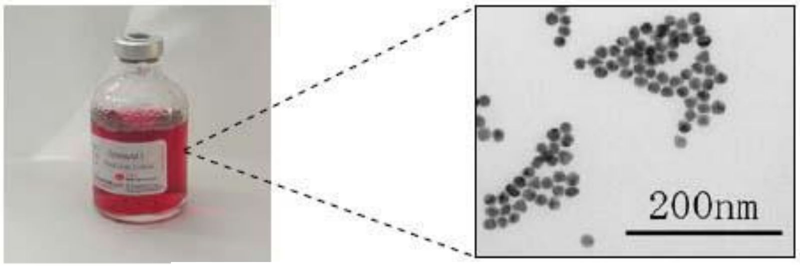
System evolves stochastically due to thermal noise



Colloidal particle

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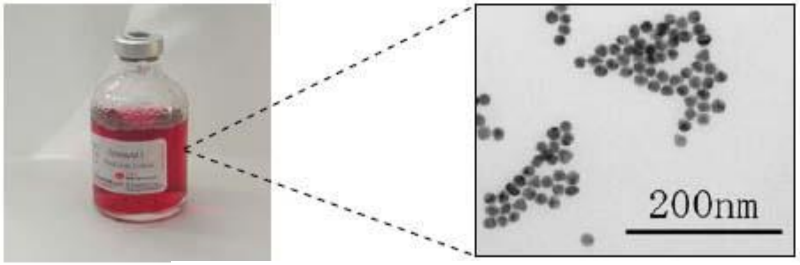
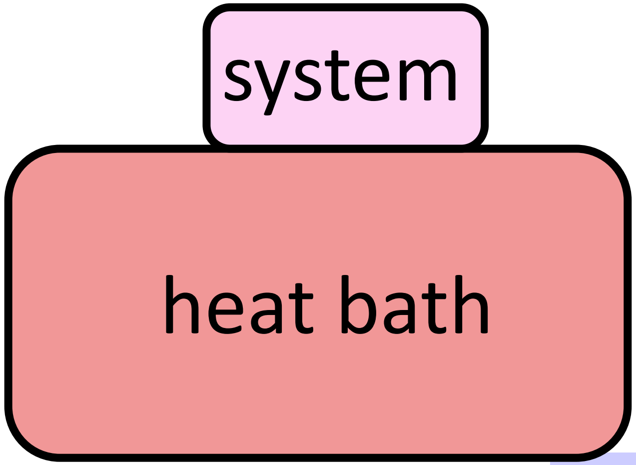


Colloidial particle

<u>Setup throughout this talk</u>

- Heat bath is in equilibrium
  →describe as **Markov process**
- Consider classical system

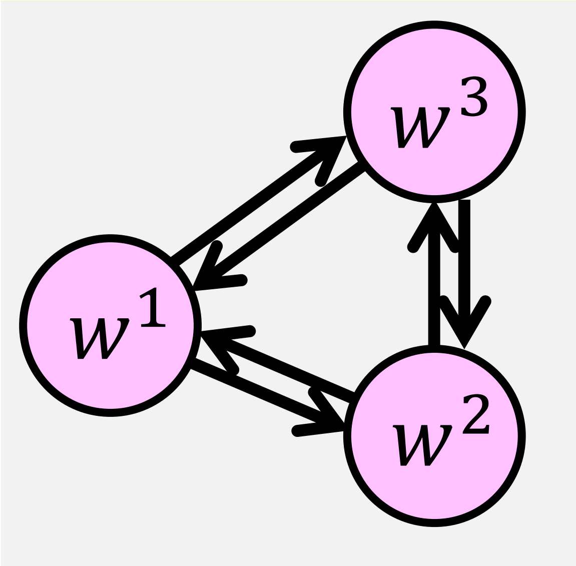


Description of classical stochastic process

State: **probability distribution p**.

Time evolution of p is given by **master equation.**

$$\frac{d}{dt}p_{w,t} = \sum_{w'} R_{ww'}p_{w',t}$$



Description of classical stochastic process

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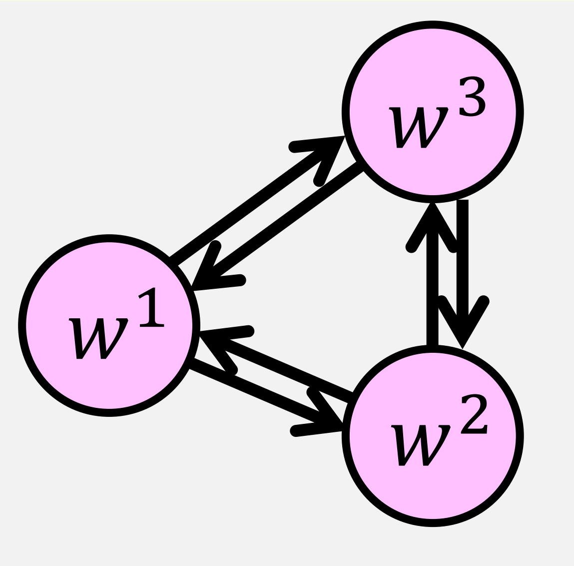
transition matrix



normalization condition: $\sum_w \boldsymbol{R_{ww'}} = \boldsymbol{0}$

(only $R_{w'w'}$ is negative, others are nonnegative)

Definition of entropy production rate

Entropy production rate (single heat bath)

$$\dot{\sigma} = \underbrace{-\sum_w \beta E_w \frac{dp_w}{dt}}_{\text{Entropy increase of bath } (dQ/T)} + \underbrace{\frac{d}{dt}\left(-\sum_w p_w \ln p_w\right)}_{\text{(Shannon) entropy increase of system}}$$

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$$= \sum_{w,w'} R_{w'w} p_w \ln \frac{R_{w'w} p_w}{R_{ww'} p_{w'}}$$

Assuming detailed balance (DB): $\frac{R_{ww'}}{R_{w'w}} = e^{-\beta\left(E_w - E_{w'}\right)}$

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Quick process → much entropy production

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Overdamped Langevin systems
Entropy production increases as speed increases.

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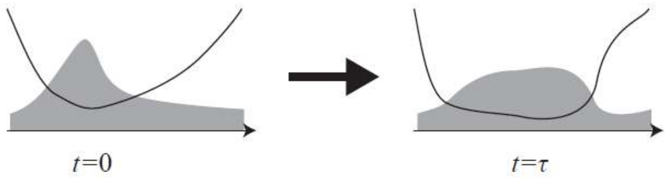

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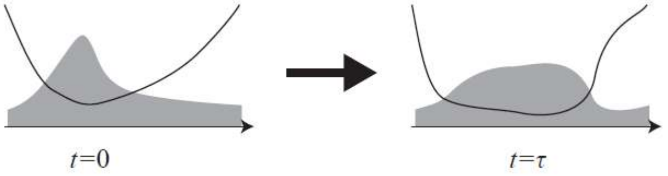

Is it true for general systems?

Result: Classical speed limit

For systems with detailed-balance, we have

$$\boxed{\sigma \geq \frac{\mathcal{L}(p,p')^2}{2\tau\langle A\rangle}}$$

$\mathcal{L}(p,p') := \sum_w |p_w - p'_w|$: total variation distance

τ : length of time of the process

$\langle A\rangle$: averaged dynamical activity $\frac{1}{\tau}\int_0^\tau dt A(t)$

(N. Shiraishi, K. Funo, and K. Saito, Phys. Rev. Lett. 121, 070601 (2018))

What is dynamical activity?

Dynamical activity: How frequently jumps occur.

$$A(t) := \sum_{w,w'} R_{w'w} p_w(t)$$

Activity characterizes **time-scale of dynamics**.

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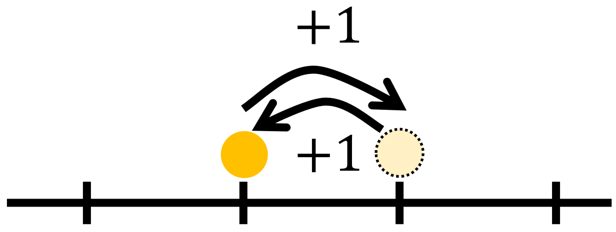
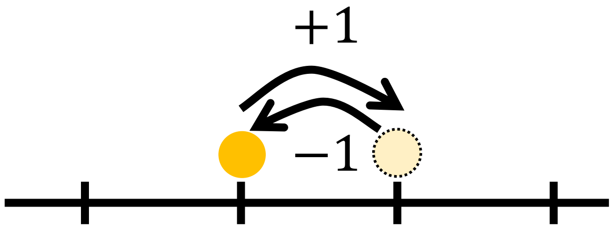


cf) Current



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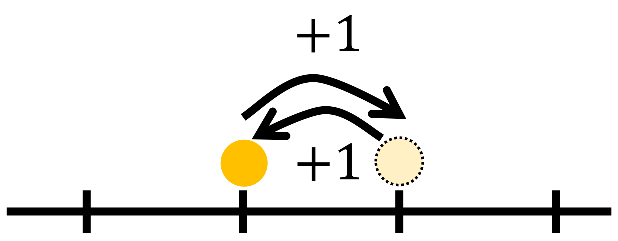

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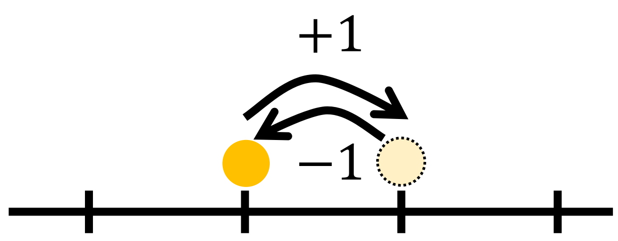

Glassy dynamics: J. P. Garrahan, et al., PRL 98, 195702 (2007).

Nonequilibrium steady state: M. Baiesi, et al., PRL 103, 010602 (2009).

Inequality for entropy production rate

$$(a-b)\ln\frac{a}{b} \geq \frac{2(a-b)^2}{a+b}$$

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Using this, systems with DB satisfy

$$\begin{aligned}\dot{\sigma} &= \sum_{w,w'} R_{w'w}p_w \ln\frac{R_{w'w}p_w}{R_{ww'}p_{w'}} \\ &= \frac{1}{2}\sum_{w,w'} (R_{w'w}p_w - R_{ww'}p_{w'}) \ln\frac{R_{w'w}p_w}{R_{ww'}p_{w'}} \\ &\geq \sum_{w\neq w'} \frac{(R_{w'w}p_w - R_{ww'}p_{w'})^2}{R_{w'w}p_w + R_{ww'}p_{w'}}\end{aligned}$$

Derivation (instantaneous quantities)

$$\sum_{w} \left| \frac{d}{dt} p_w \right|$$

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$$\leq \sum_w \sqrt{\sum_{w'(\neq w)} (R_{w'w} P_w + R_{ww'} P_{w'}) \cdot \sum_{w'(\neq w)} \frac{(R_{w'w} P_w - R_{ww'} P_{w'})^2}{R_{w'w} P_w + R_{ww'} P_{w'}}}$$

Schwarz inequality $\left|\sum_i a_i b_i\right|^2 \leq \left(\sum_i a_i^2\right)\left(\sum_i b_i^2\right)$ is used.

Derivation (instantaneous quantities)

$$\sum_{w}\left|\frac{d}{dt}p_w\right|$$

$$=\sum_{w}\left|\sum_{w'(\neq w)}(R_{w'w}P_w - R_{ww'}P_{w'})\right|$$

$$\leq \sum_{w}\sqrt{\sum_{w'(\neq w)}(R_{w'w}P_w + R_{ww'}P_{w'})\cdot\sum_{w'(\neq w)}\frac{(R_{w'w}P_w - R_{ww'}P_{w'})^2}{R_{w'w}P_w + R_{ww'}P_{w'}}}$$

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$$\leq \sqrt{2A\dot{\sigma}}$$

Derivation (time integration)

$$\mathcal{L}(p_i, p_f) \leq \sum_w \int_0^\tau dt \left| \frac{d}{dt} p_w \right|$$

$$\leq \int_0^\tau dt \sqrt{2\dot{\sigma} A} \leq \sqrt{2\tau\sigma\langle A\rangle}$$

This is the desired result!

$$\boldsymbol{\sigma \geq \frac{\mathcal{L}(p, p')^2}{2\tau\langle A\rangle}}$$

Remark: Systems without detailed-balance condition

Case with detailed-balance condition

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Case without detailed-balance condition ($c_0 = 0.896..$)

$$\sigma_{HS} \geq \frac{c_0\mathcal{L}(p,p')^2}{2\tau\langle A\rangle}$$

σ_{HS}: Hatano-Sasa entropy production

(Heat $\beta Q_{w\to w'}$ is replaced by excess heat $\ln\frac{p_{w'}^{ss}}{p_w^{ss}}$)

(T. Hatano and S.-i. Sasa, Phys. Rev. Lett. **86**, 3463 (2001))

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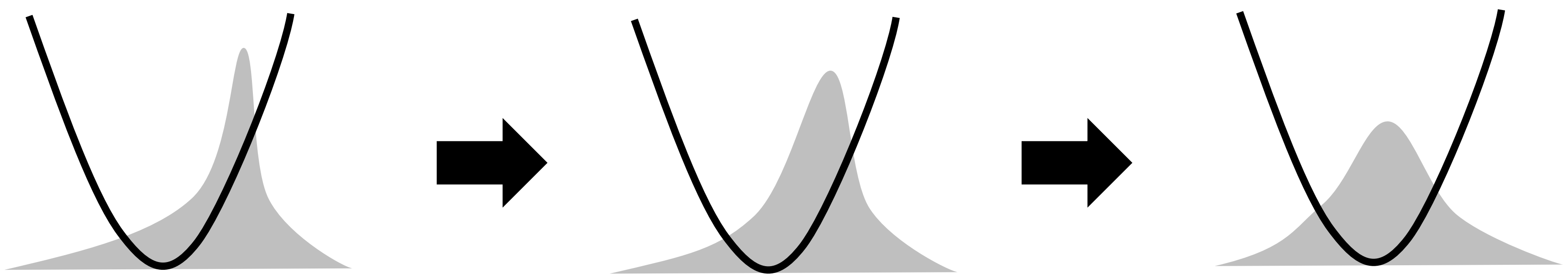
Problem: entropy production in thermal relaxation process

Situation：relaxation process with a single heat bath in continuous time. Suppose detailed balance.



$t = 0$ $\qquad$ $t = \tau$ $\qquad$ $t = \infty$

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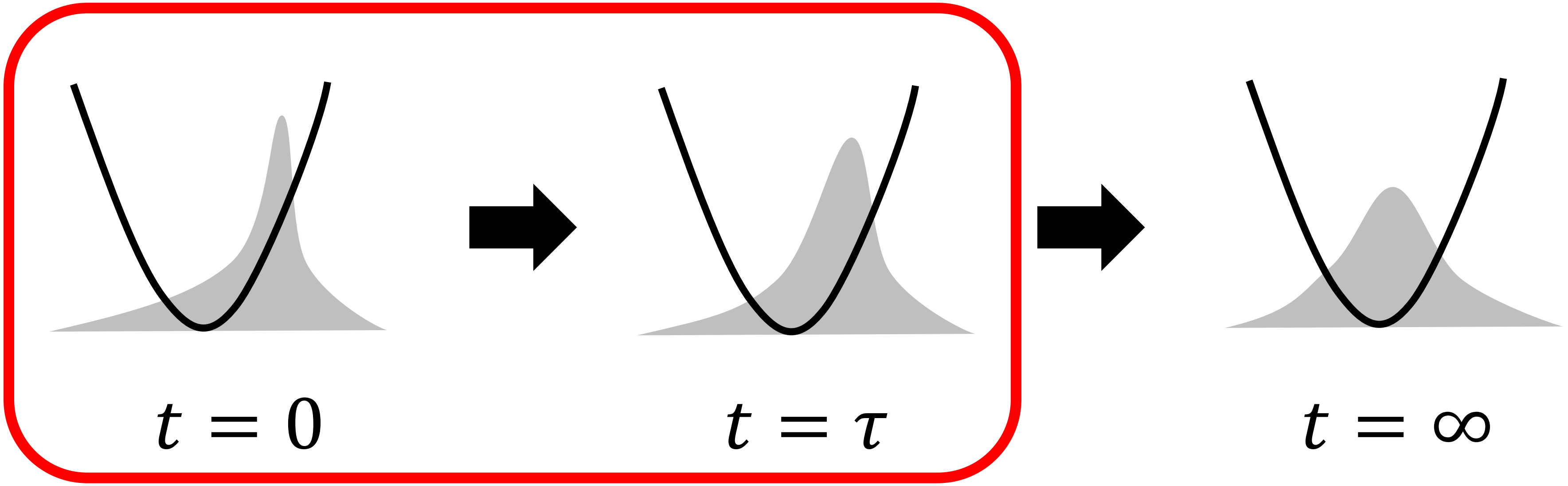


<u>Goal</u>: Deriving lower bound of entropy production within $0 \le t \le \tau$ (denoted by $\sigma_{[0,\tau]}$)

Kullback-Leibler divergence

Kullback-Leibler (KL) divergence

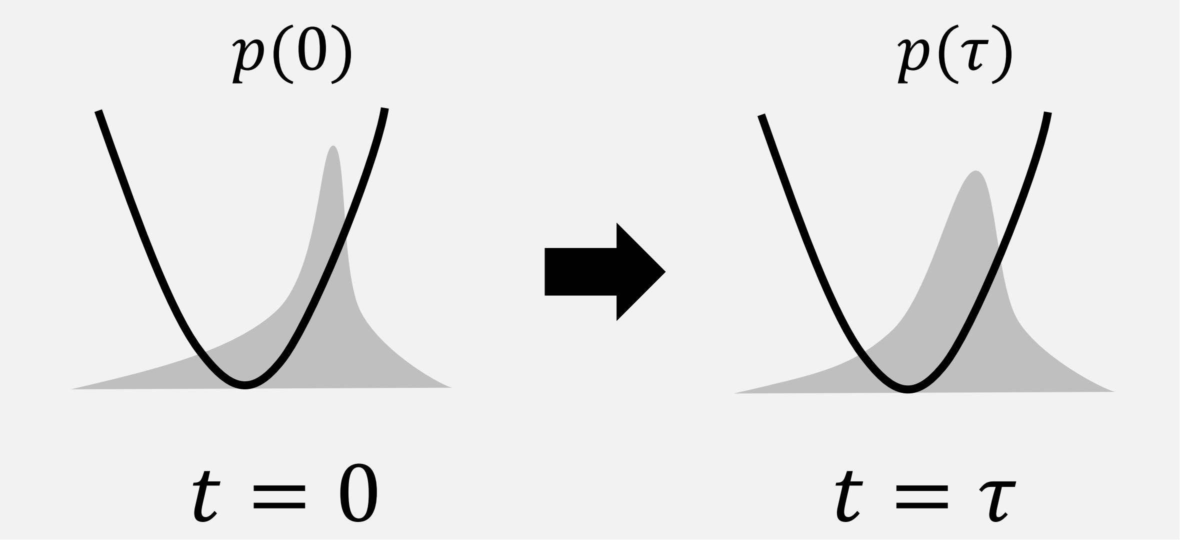
$$D(p||p') := \sum_i p_w \ln \frac{p_w}{p'_w}$$

(Psuedo-)distance between p and p'.

p and p' are close $\rightarrow D(p||p')$ is small.
p and p' are far $\rightarrow D(p||p')$ is large.

Main result

$$\boldsymbol{\sigma_{[0,\tau]} \geq D(p(0)||p(\tau))}$$



Entropy production is bounded by the distance between the initial and final distributions!

Significance

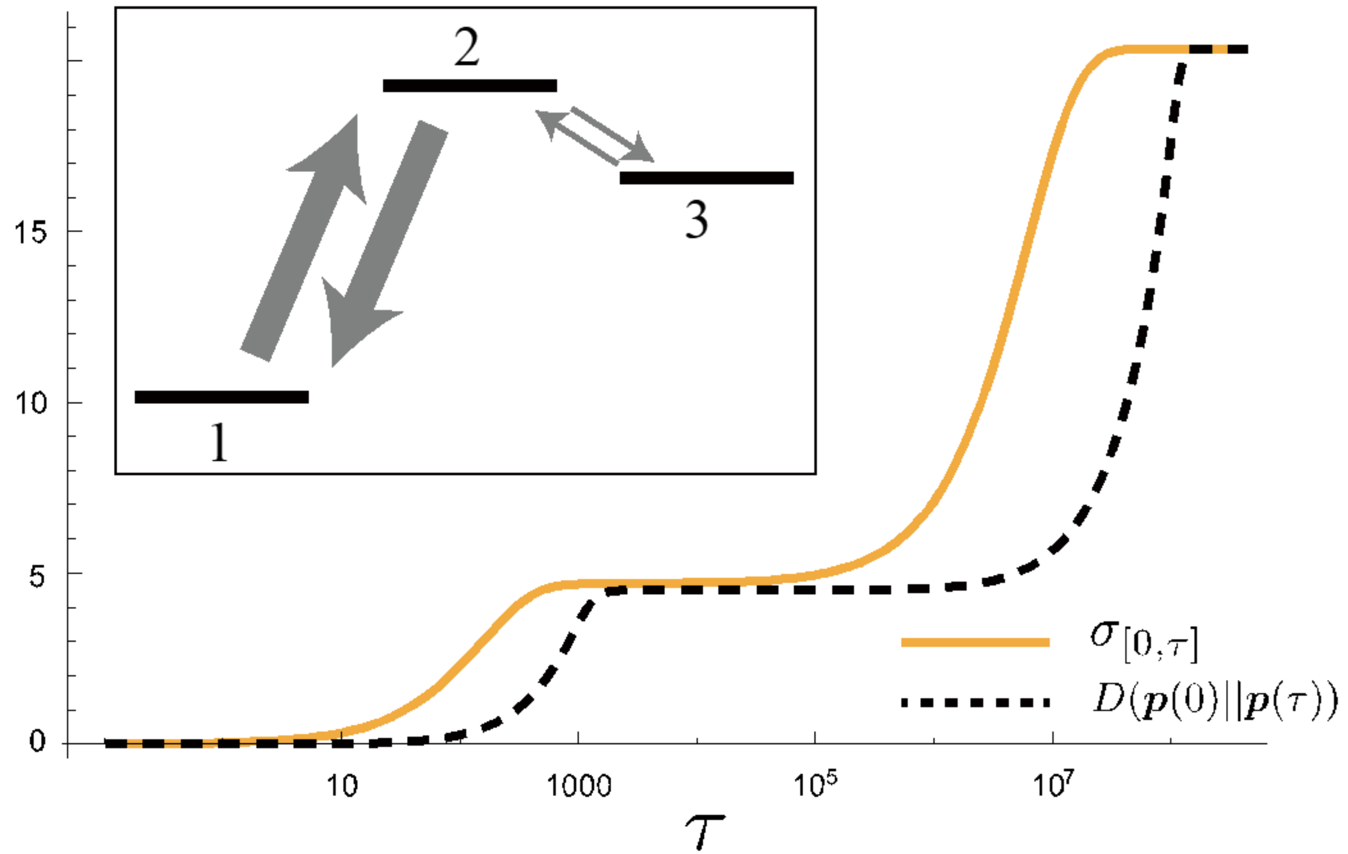
$$\boxed{\boldsymbol{\sigma}_{[\mathbf{0},\boldsymbol{\tau}]} \geq \boldsymbol{D}(\boldsymbol{p}(\mathbf{0})||\boldsymbol{p}(\boldsymbol{\tau}))}$$

- Only for relaxation processes (It does not hold in general process).
- Equality holds for both $\tau = 0$ and $\boldsymbol{\tau} = \infty$
- It does not hold in discrete time Markov chain.

Numerical demonstration

Setup：three-state model

Take a system with anomalous (two-step) relaxation.



Geometric visualization

Relation $\boldsymbol{\sigma}_{[\mathbf{0},\boldsymbol{\tau}]} = \boldsymbol{D}(\boldsymbol{p}(\mathbf{0})||\boldsymbol{p}^{\boldsymbol{eq}}) - \boldsymbol{D}(\boldsymbol{p}(\boldsymbol{\tau})||\boldsymbol{p}^{\boldsymbol{eq}})$ implies

$$\boldsymbol{D}(\boldsymbol{p}(\mathbf{0})||\boldsymbol{p}^{\boldsymbol{eq}}) \geq \boldsymbol{D}\big(\boldsymbol{p}(\mathbf{0})\big|\big|\boldsymbol{p}(\boldsymbol{\tau})\big) + \boldsymbol{D}(\boldsymbol{p}(\boldsymbol{\tau})||\boldsymbol{p}^{\boldsymbol{eq}})$$

Remark:

KL-divergence $\leftrightarrow$ square of distance (in Euclid space)

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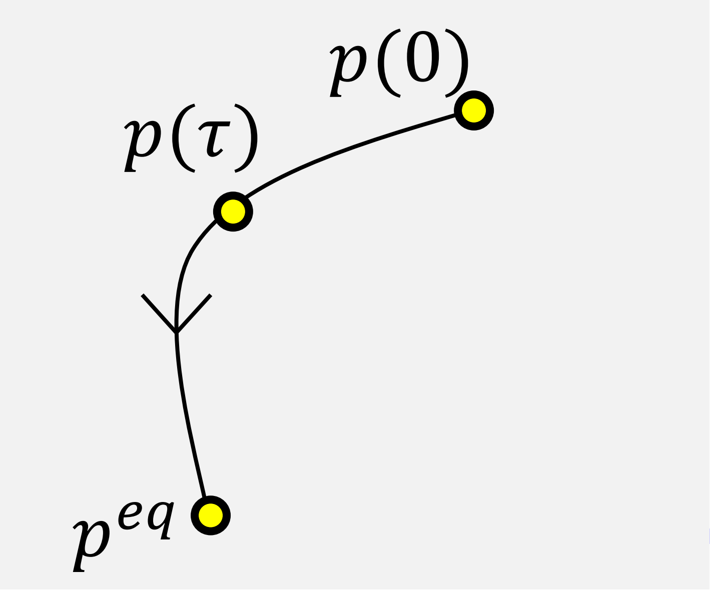

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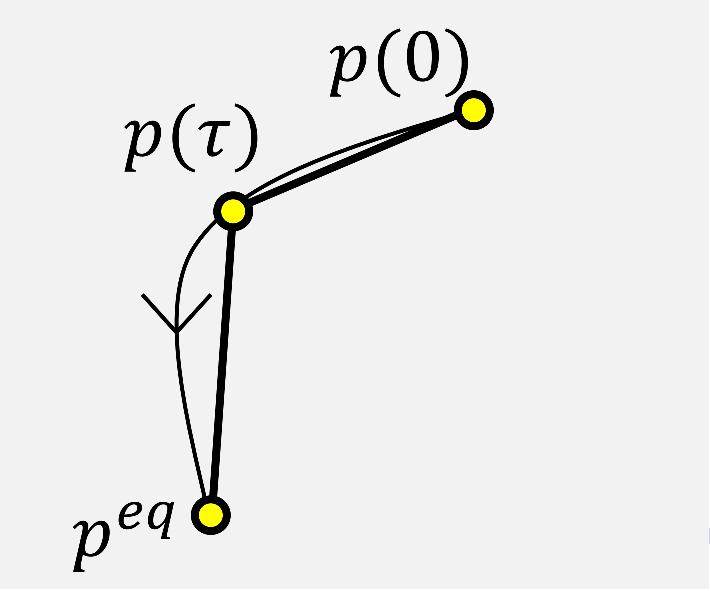

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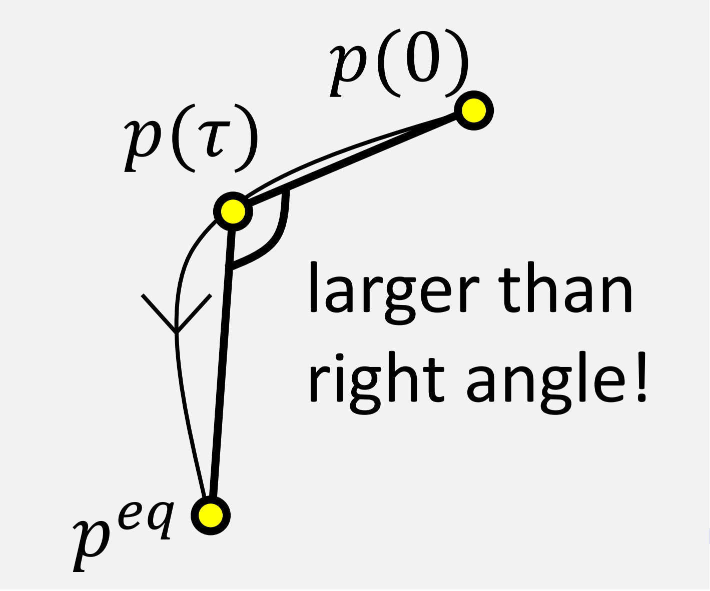
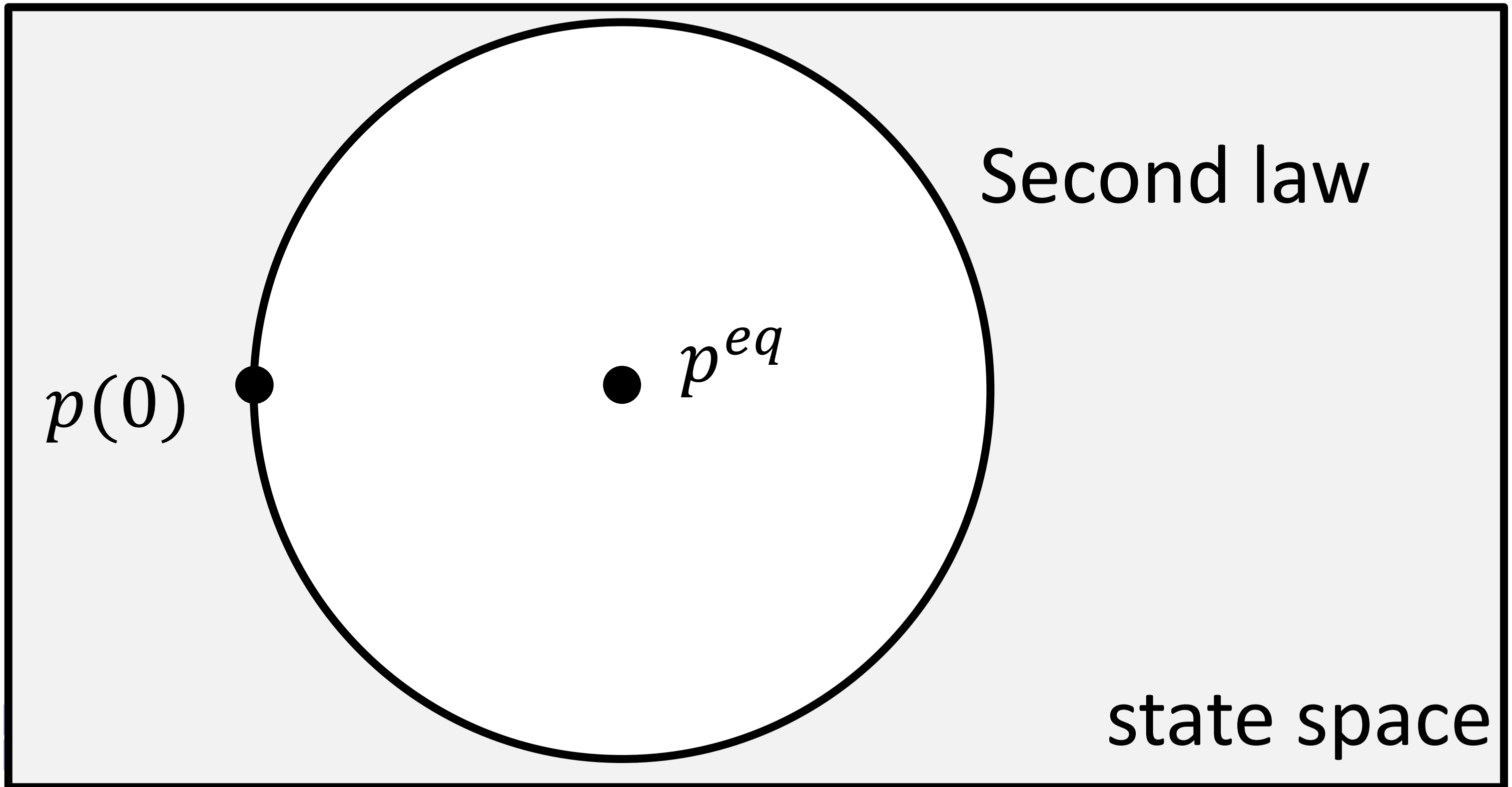


Restriction on possible trajectory

Given both initial and equilibrium distribution.
What is possible pass of relaxation processes?



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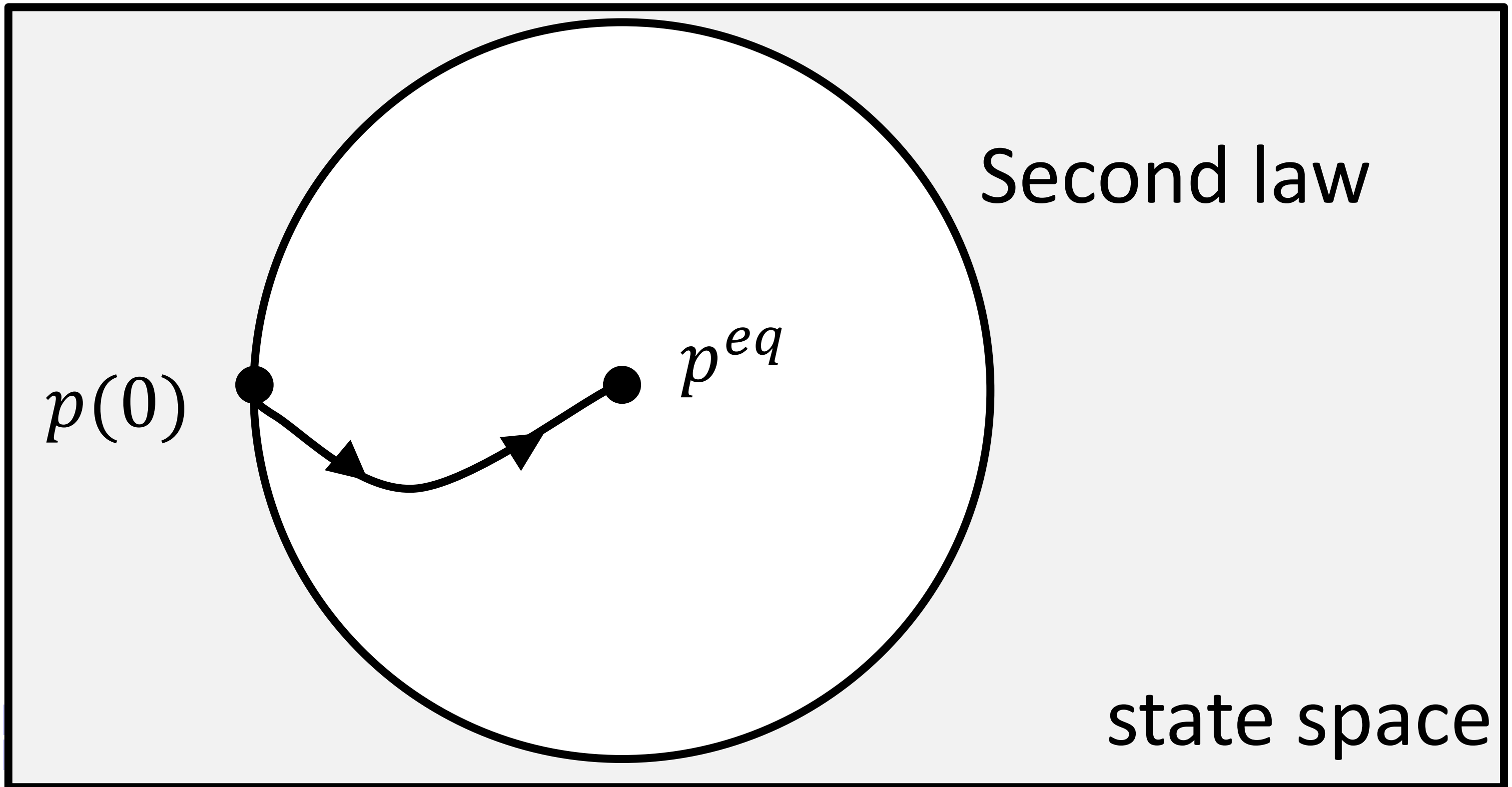

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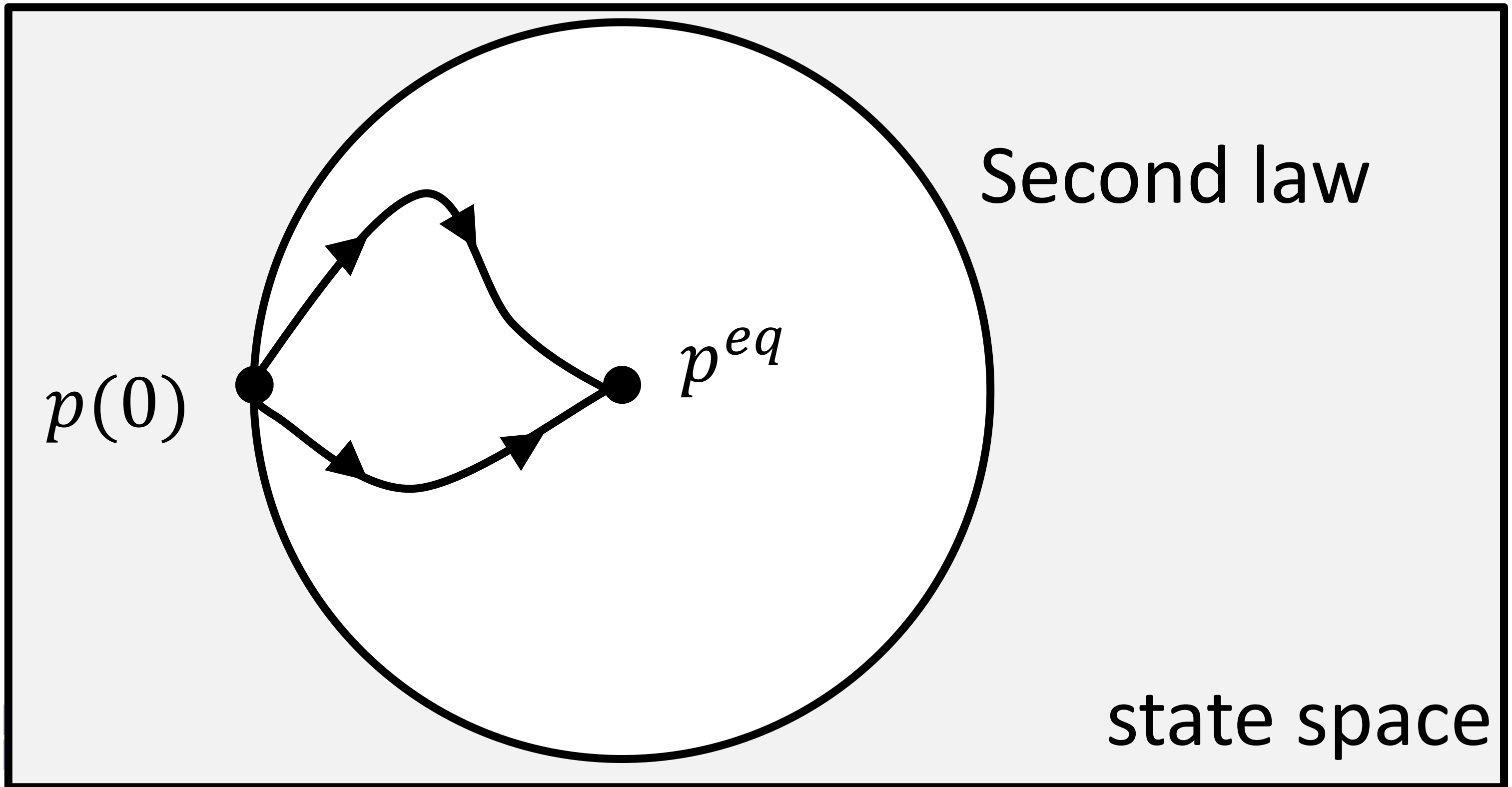

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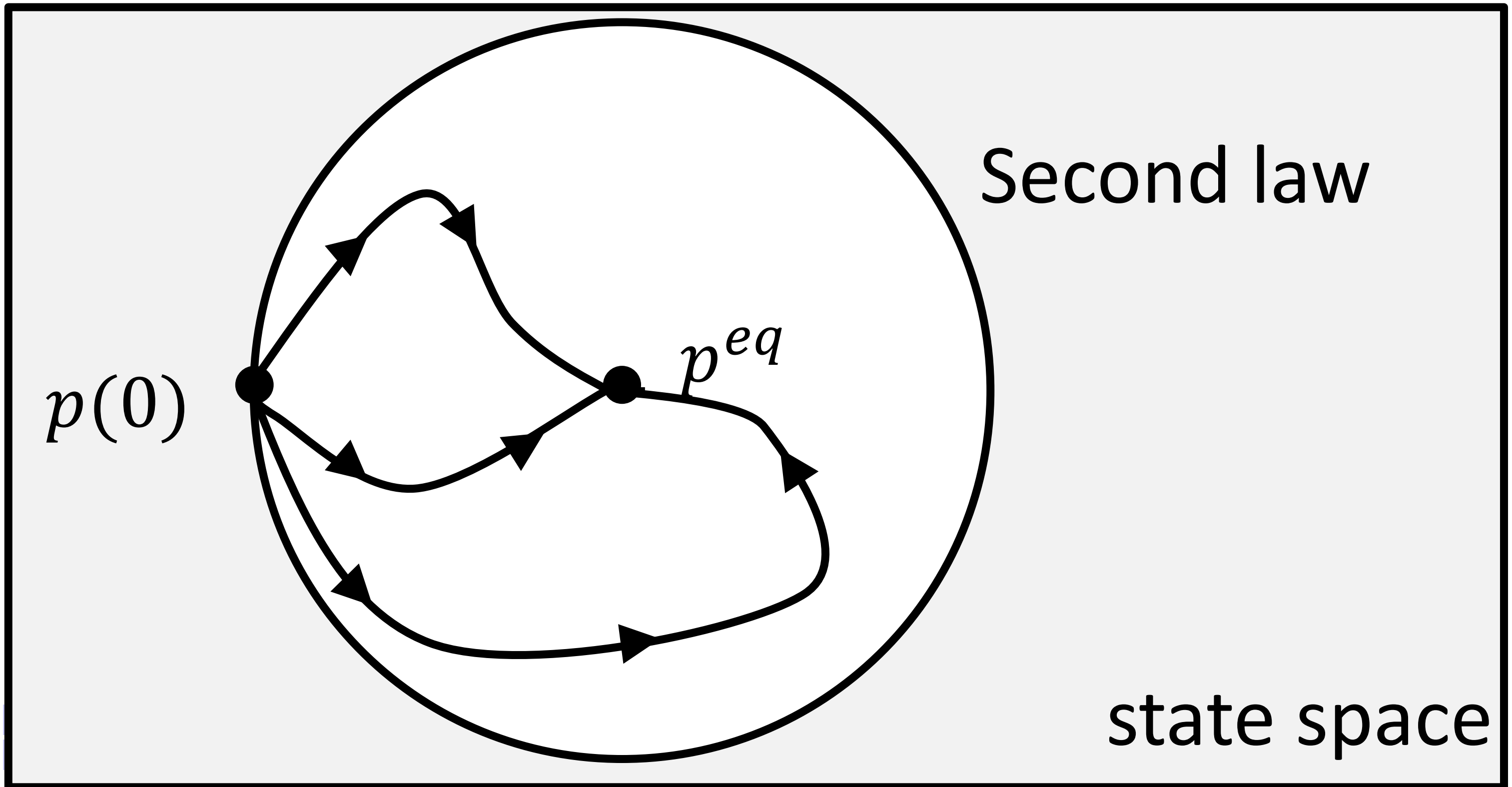

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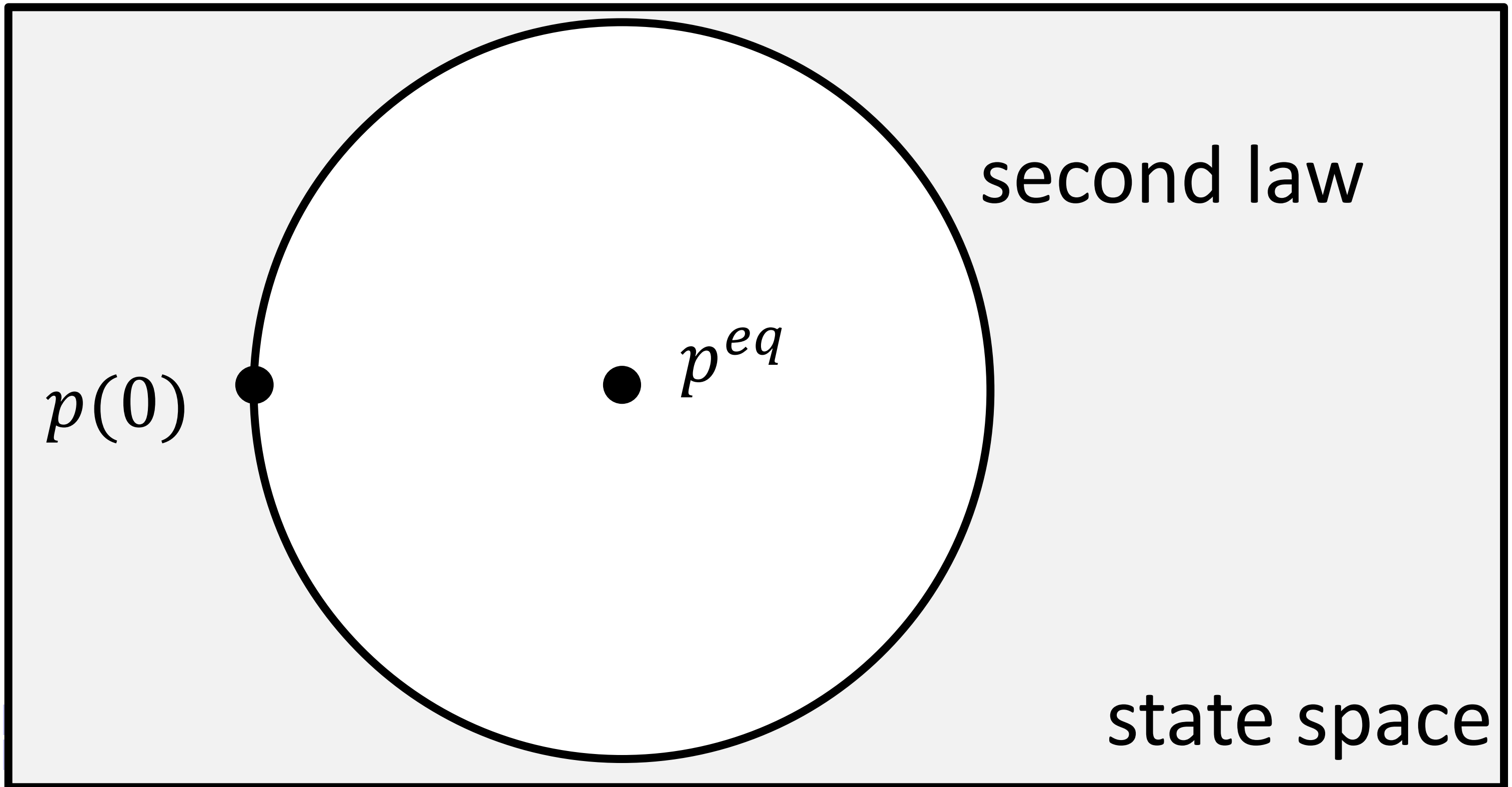
Obtained relation

$$\boldsymbol{D}(\boldsymbol{p}(\boldsymbol{0})||\boldsymbol{p}^{\boldsymbol{eq}}) \geq \boldsymbol{D}(\boldsymbol{p}(\boldsymbol{0})\big|\big|\boldsymbol{p}(\boldsymbol{\tau})\big) + \boldsymbol{D}(\boldsymbol{p}(\boldsymbol{\tau})||\boldsymbol{p}^{\boldsymbol{eq}})$$



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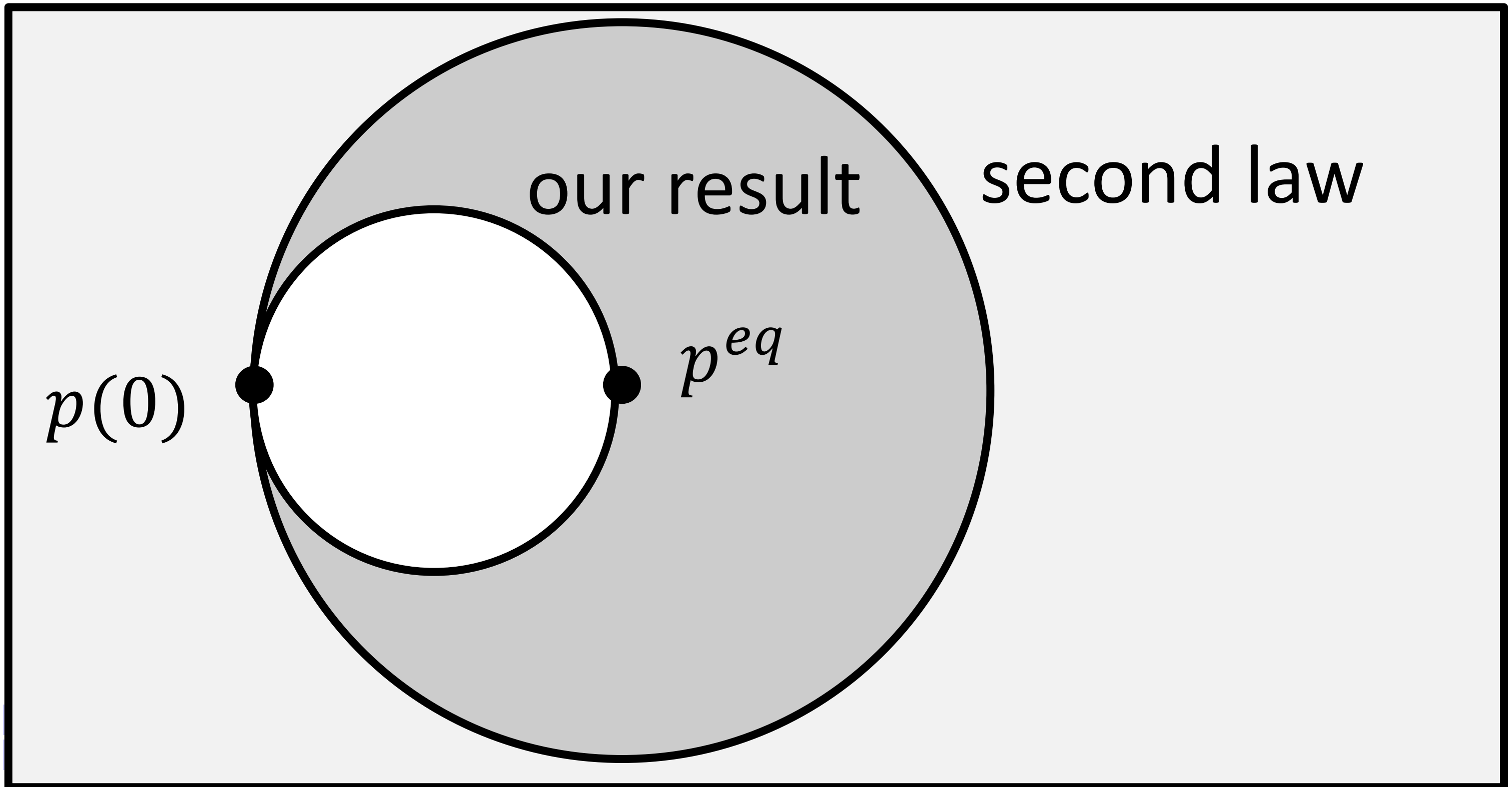

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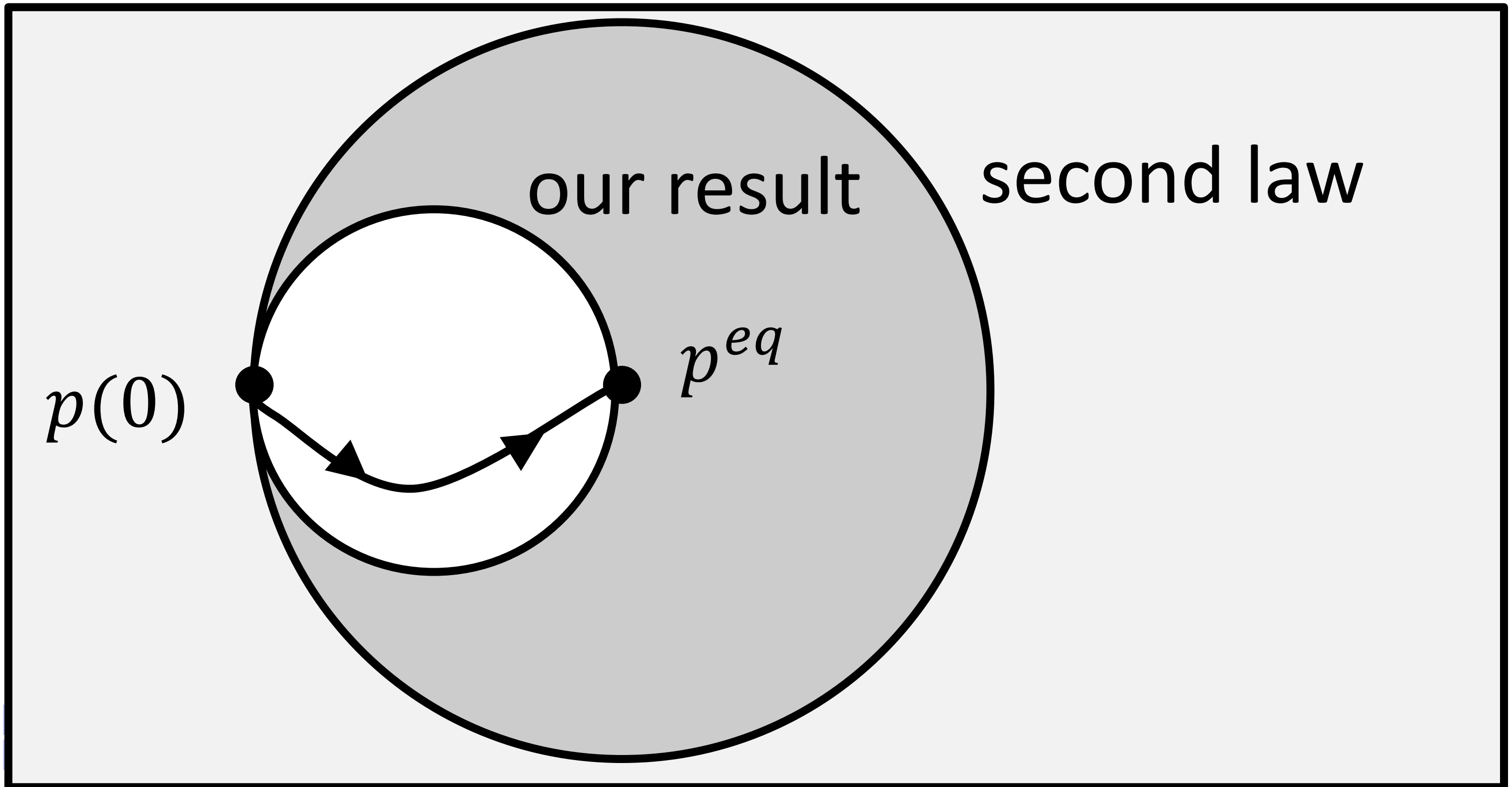

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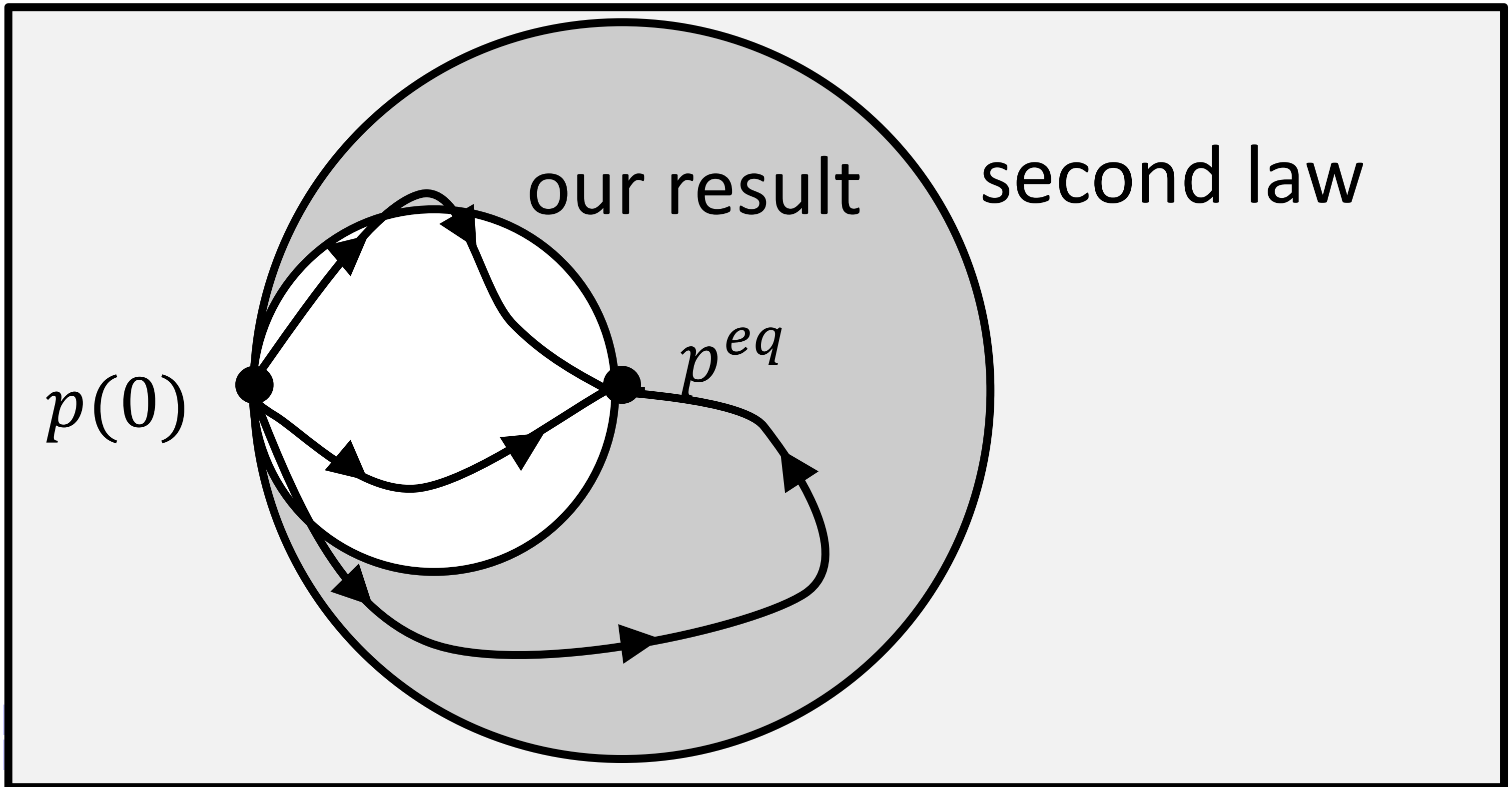
Obtained relation

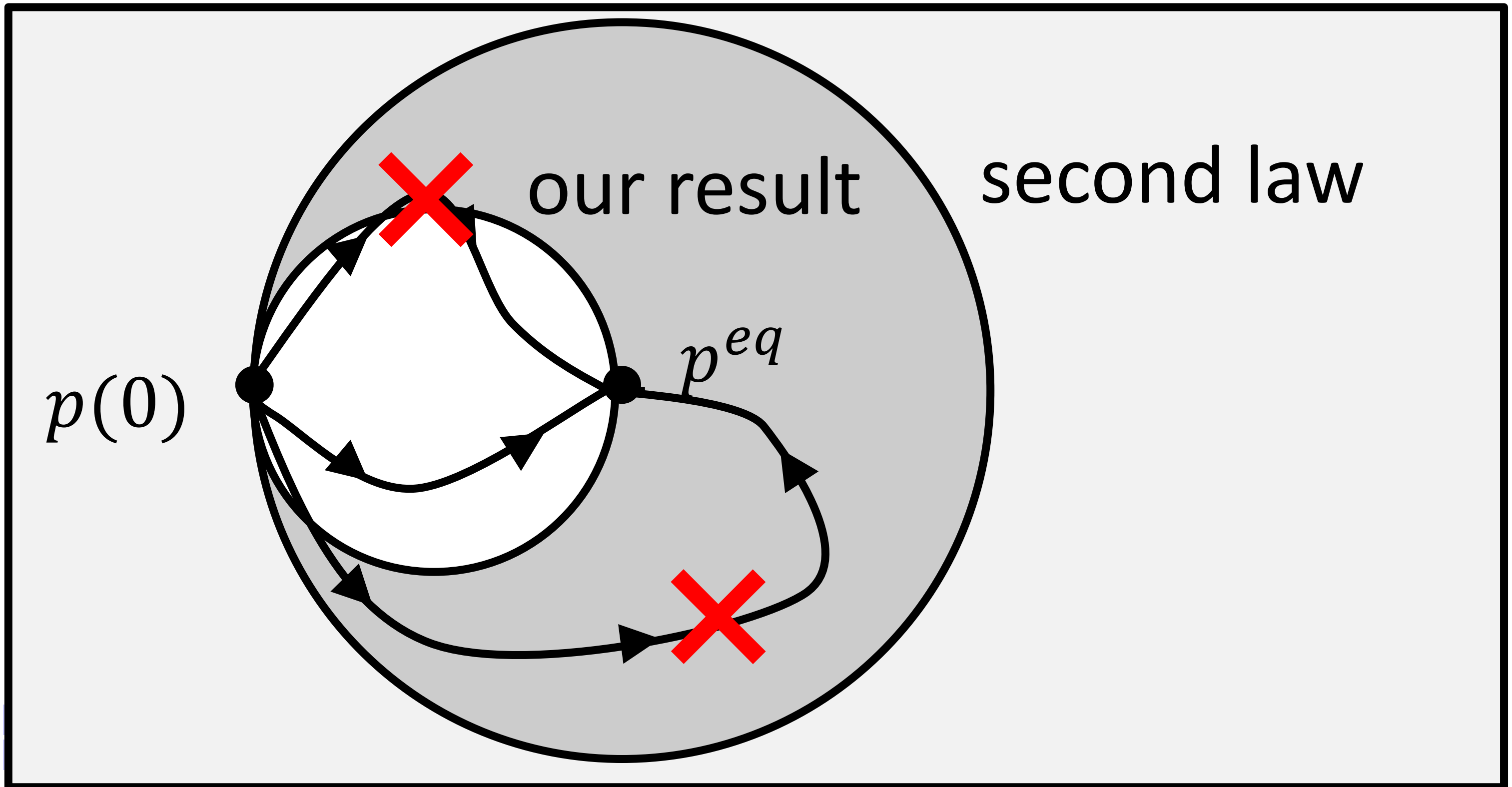
$$D(p(0)||p^{eq}) \geq D\big(p(0)||p(\tau)\big) + D(p(\tau)||p^{eq})$$



Restriction on possible trajectory

Obtained relation

$$D(p(0)||p^{eq}) \geq D(p(0)\big|\big|p(\tau)\big) + D(p(\tau)||p^{eq})$$



Key relation: variational expression of entropy production rate

$$\dot{\sigma} = -\frac{d}{dt} D(p(t)||p^{eq})$$

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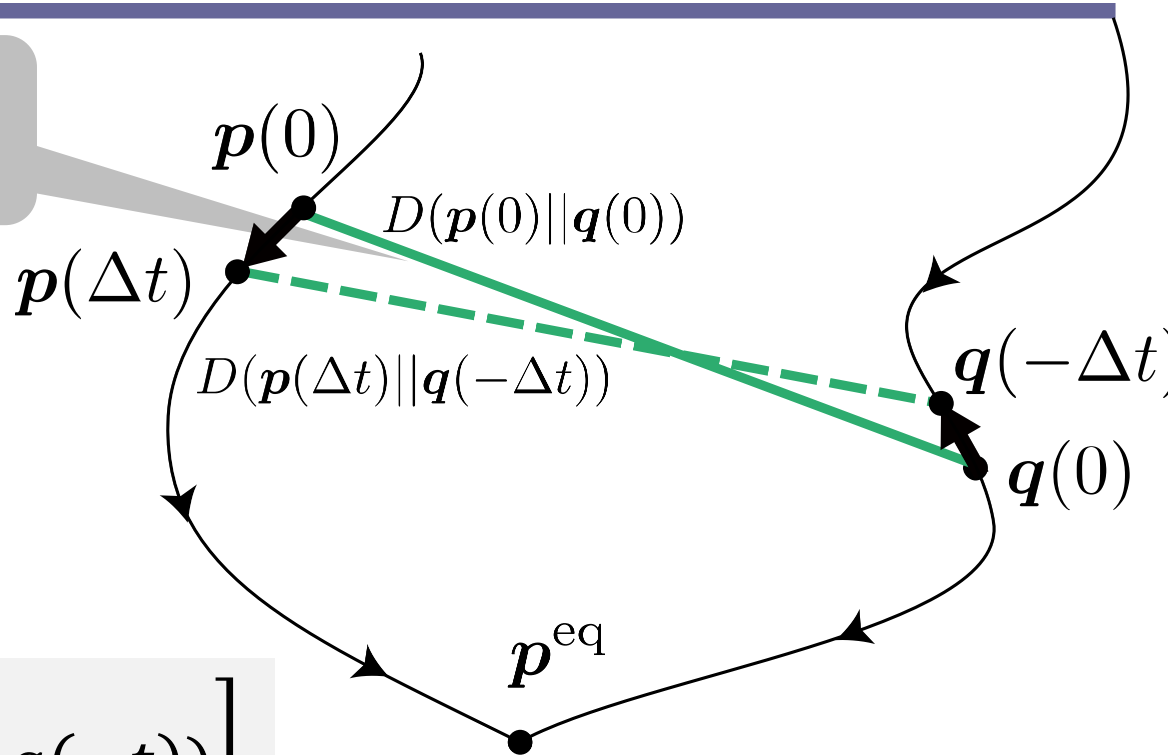
$$\dot{\sigma} = -\frac{d}{dt} D(p(t)||p^{eq})$$

$$= \max_{\boldsymbol{q}} \left[-\frac{\boldsymbol{d}}{\boldsymbol{dt}} \boldsymbol{D}(\boldsymbol{p}(\boldsymbol{t})||\boldsymbol{q}(-\boldsymbol{t})) \right]$$

$q(-t)$: distribution evolves backward in time under the same transition matrix with $p(t)$.

Schematic of variational expression

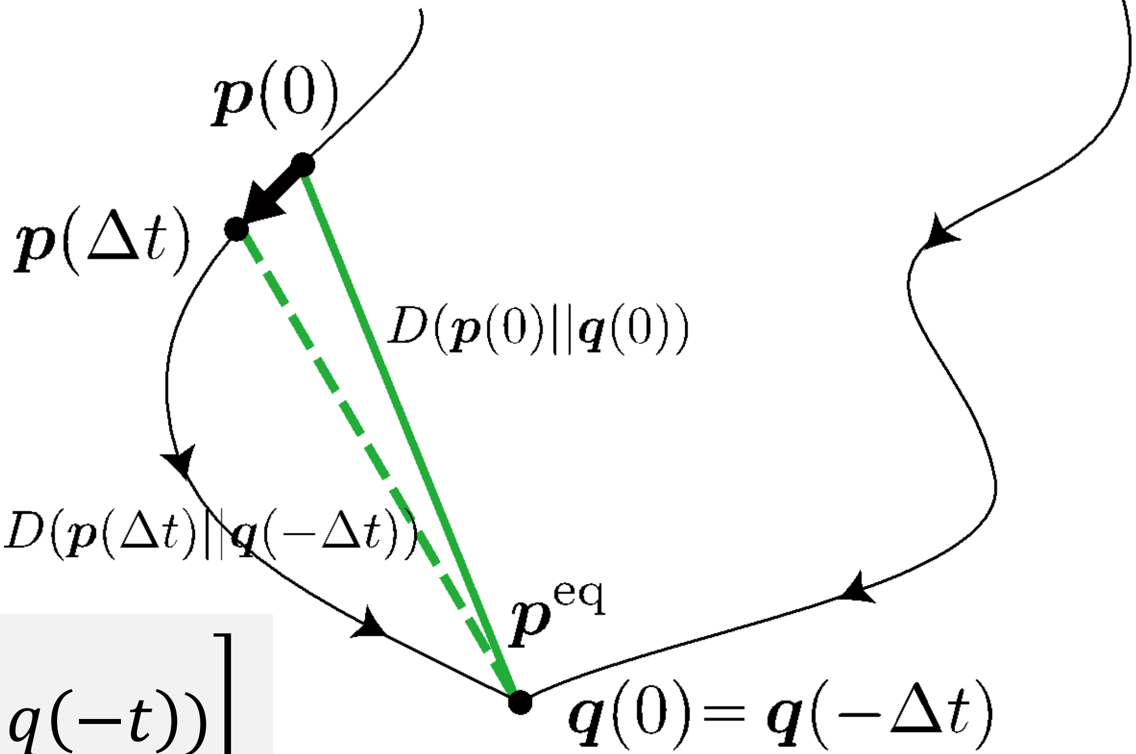
KL divergence $D(p||q)$



$$\dot{\sigma} = \max_q \left[-\frac{d}{dt} D(p(t)||q(-t)) \right]$$

Difference of solid line from dashed line takes maximum when $q = p^{eq}$.

Schematic of variational expression



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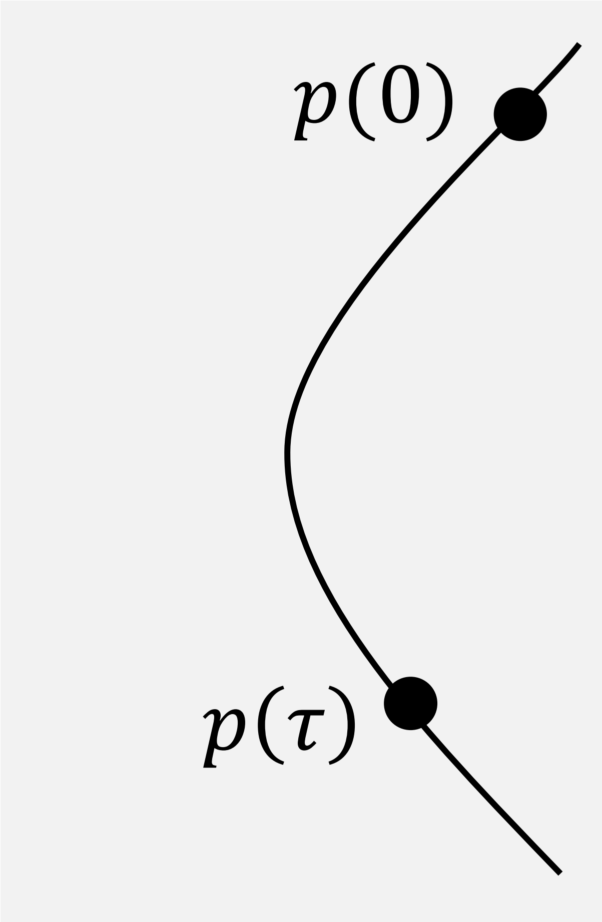
Variational expression leads to bound on relaxation processes



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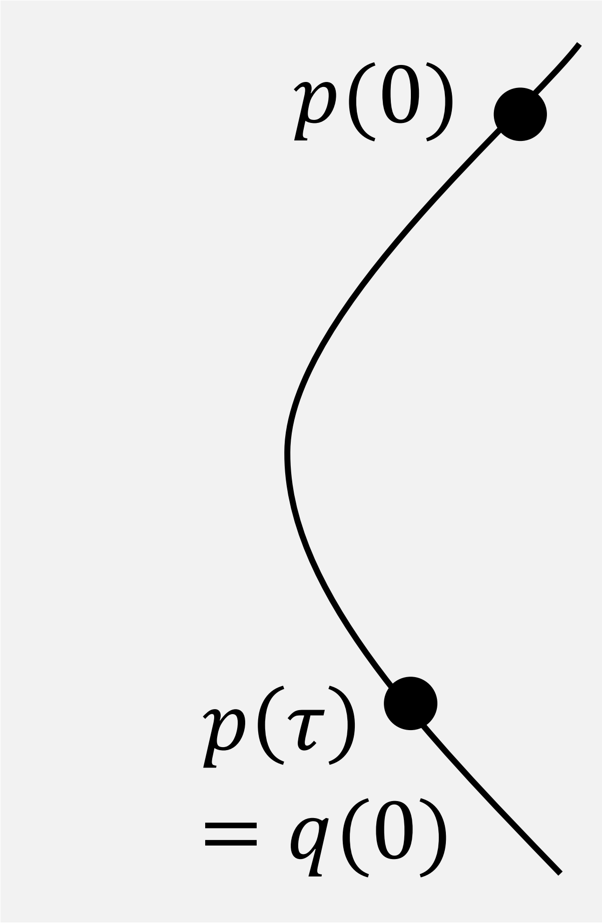
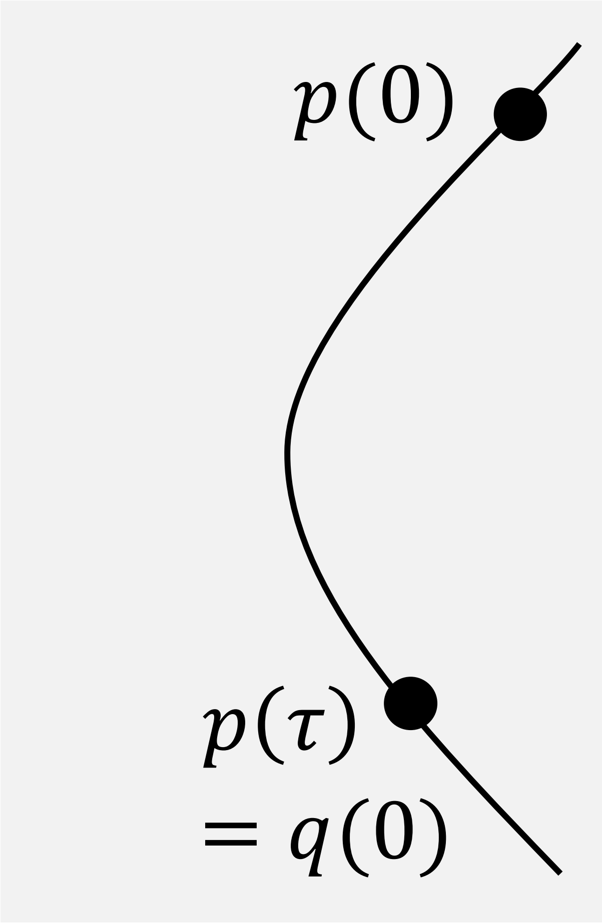


Variational expression leads to bound on relaxation processes

$$\sigma_{[0,\tau/2]} \geq -\int_0^{\tau/2} dt \frac{d}{dt} D(p(t)||q(-t))$$



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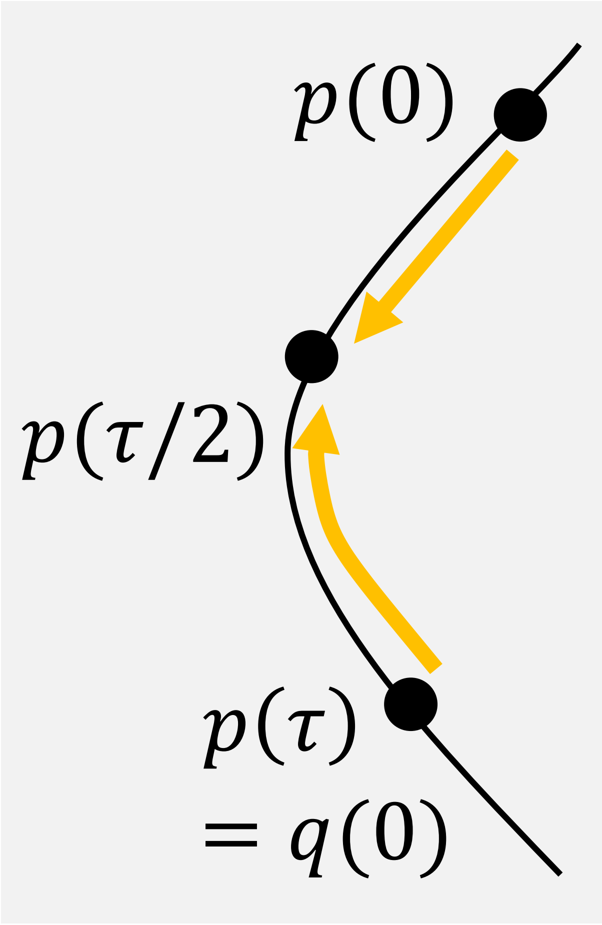

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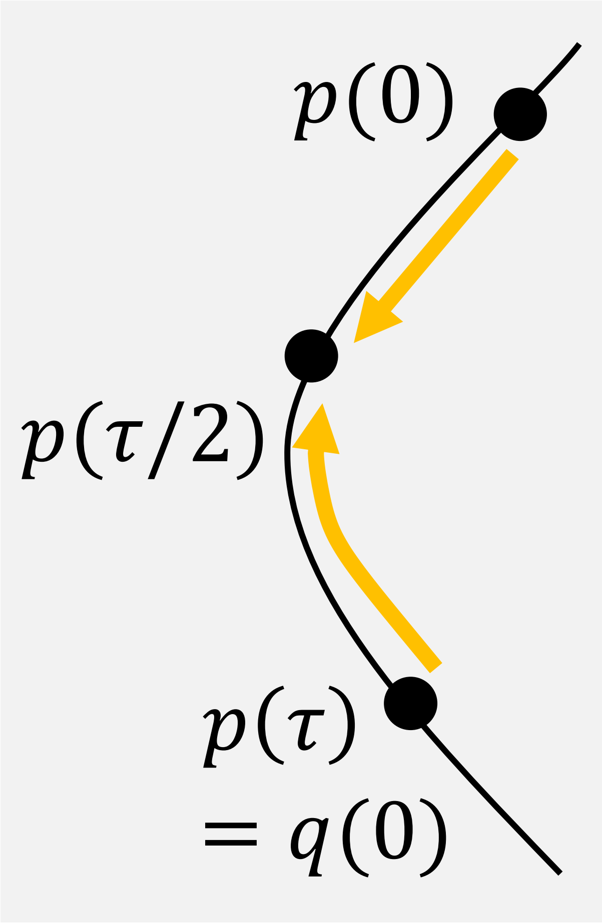
$$= D(p(0)||p(\tau))$$



Variational expression leads to bound on relaxation processes

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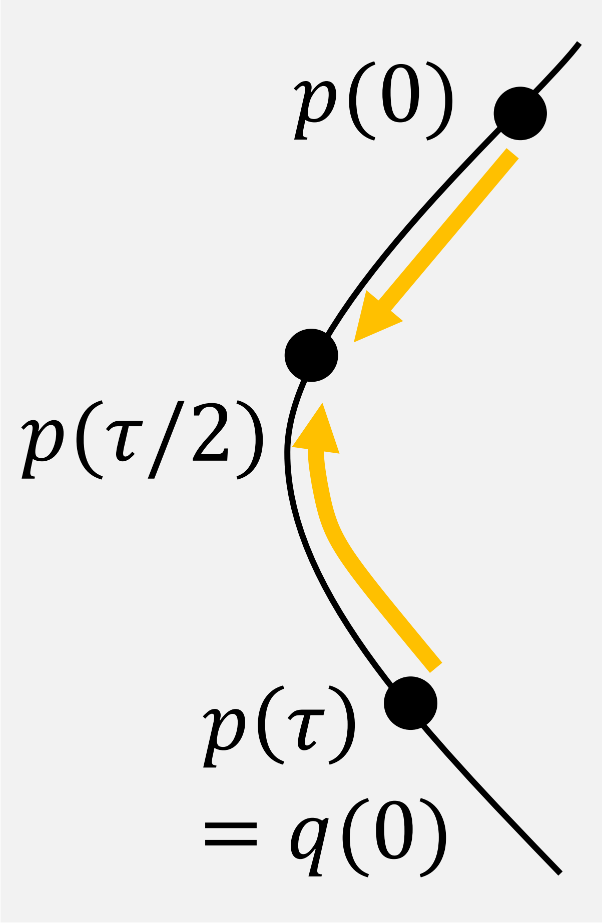

From $\sigma_{[0,\tau]} \geq \sigma_{[0,\tau/2]}$, we have

$$\boldsymbol{\sigma_{[0,\tau]} \geq D(p(0)||p(\tau))}$$

Proof of variational expression

It suffices to prove

$$\frac{d}{dt}\left[D(p(t)||q(-t)) - D(p(t)||p^{eq})\right] \geq 0$$

for any q.

Proof of variational expression

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$$\frac{d}{dt}\left[D\left(p(t)\middle\|q(-t)\right) - D(p(t)||p^{eq})\right] \geq 0$$

for any q.

The left-hand side is equal to

$$\frac{d}{dt}\left[\sum_i p_i(t) \ln \frac{p_i^{eq}}{q_i(-t)}\right]$$

Proof of variational expression

$$\frac{d}{dt}\left[\sum_i p_i(t)\ln\left(\frac{p_i^{\mathrm{eq}}}{q_i(-t)}\right)\right]$$

$$=\sum_i\sum_j R_{ij}p_j\ln\left(\frac{p_i^{\mathrm{eq}}}{q_i}\right)+\sum_i p_i\sum_j\frac{R_{ij}q_j}{q_i}$$

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We used $\sum_{i(\neq j)}R_{ij}p_j\ln\left(\frac{q_j}{p_j^{\rm eq}}\right)=-R_{jj}p_j\ln\left(\frac{q_j}{p_j^{\rm eq}}\right)$

Proof of variational expression

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$$= \sum_{i \neq j} R_{ij} p_j \ln\left(\frac{p_i^{\mathrm{eq}} q_j}{p_j^{\mathrm{eq}} q_i}\right) + \sum_{i \neq j} p_i \frac{R_{ij} q_j}{q_i} + \sum_i R_{ii} p_i$$

Proof of variational expression

$$\frac{d}{dt}\left[\sum_i p_i(t)\ln\left(\frac{p_i^{\mathrm{eq}}}{q_i(-t)}\right)\right]$$

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$$=\sum_{i\neq j}R_{ij}p_j\ln\left(\frac{R_{ij}q_j}{R_{ji}q_i}\right)+\sum_{i\neq j}R_{ij}p_j\frac{R_{ji}q_i}{R_{ij}q_j}-\sum_{i\neq j}R_{ij}p_j$$

Proof of variational expression

$$
\begin{aligned}
&\frac{d}{dt}\left[\sum_i p_i(t)\ln\left(\frac{p_i^{\mathrm{eq}}}{q_i(-t)}\right)\right] \\
&=\sum_i\sum_j R_{ij}p_j\ln\left(\frac{p_i^{\mathrm{eq}}}{q_i}\right)+\sum_i p_i\sum_j\frac{R_{ij}q_j}{q_i} \\
&=\sum_{i\neq j}R_{ij}p_j\ln\left(\frac{p_i^{\mathrm{eq}}q_j}{p_j^{\mathrm{eq}}q_i}\right)+\sum_{i\neq j}p_i\frac{R_{ij}q_j}{q_i}+\sum_i R_{ii}p_i \\
&=\sum_{i\neq j}R_{ij}p_j\ln\left(\frac{R_{ij}q_j}{R_{ji}q_i}\right)+\sum_{i\neq j}R_{ij}p_j\frac{R_{ji}q_i}{R_{ij}q_j}-\sum_{i\neq j}R_{ij}p_j \\
&=\sum_{i\neq j}R_{ij}p_j\left[\frac{R_{ji}q_i}{R_{ij}q_j}-1-\ln\left(\frac{R_{ji}q_i}{R_{ij}q_j}\right)\right]
\end{aligned}
$$

Proof of variational expression

$$\frac{d}{dt}\left[\sum_i p_i(t)\ln\left(\frac{p_i^{\mathrm{eq}}}{q_i(-t)}\right)\right]$$

$$=\sum_i\sum_j R_{ij}p_j\ln\left(\frac{p_i^{\mathrm{eq}}}{q_i}\right)+\sum_i p_i\sum_j\frac{R_{ij}q_j}{q_i}$$

$$=\sum_{i\neq j}R_{ij}p_j\ln\left(\frac{p_i^{\mathrm{eq}}q_j}{p_j^{\mathrm{eq}}q_i}\right)+\sum_{i\neq j}p_i\frac{R_{ij}q_j}{q_i}+\sum_i R_{ii}p_i$$

$$=\sum_{i\neq j}R_{ij}p_j\ln\left(\frac{R_{ij}q_j}{R_{ji}q_i}\right)+\sum_{i\neq j}R_{ij}p_j\frac{R_{ji}q_i}{R_{ij}q_j}-\sum_{i\neq j}R_{ij}p_j$$

$$=\sum_{i\neq j}R_{ij}p_j\left[\frac{R_{ji}q_i}{R_{ij}q_j}-1-\ln\left(\frac{R_{ji}q_i}{R_{ij}q_j}\right)\right]$$

$$\geq 0.$$

（We used $x-1-\ln x\geq 0$）

Summary

- Bound on entropy production in finite-speed processes:

$$\boldsymbol{\sigma \geq \frac{\mathcal{L}(p, p')^2}{2\tau\langle A\rangle}}$$

- Bound on entropy production in relaxation process:

$$\boldsymbol{\sigma \geq D(p(0)||p(\tau))}$$

END