Geometry and Nonequilibrium Thermodynamic Theories
Far From Steady States

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Nonequilibrium Thermodynamics Beyond Steady States

I. **Counter-intuitive effects where systems evolve beyond stationarity**

-- from Mpemba effect to non-equilibrium shortcuts

II. **Meditation on Geometry: Bird's-Eye View of Thermodynamic Theory**

III. **Geometry & Non-equilibrium Theory Beyond Steady States:**

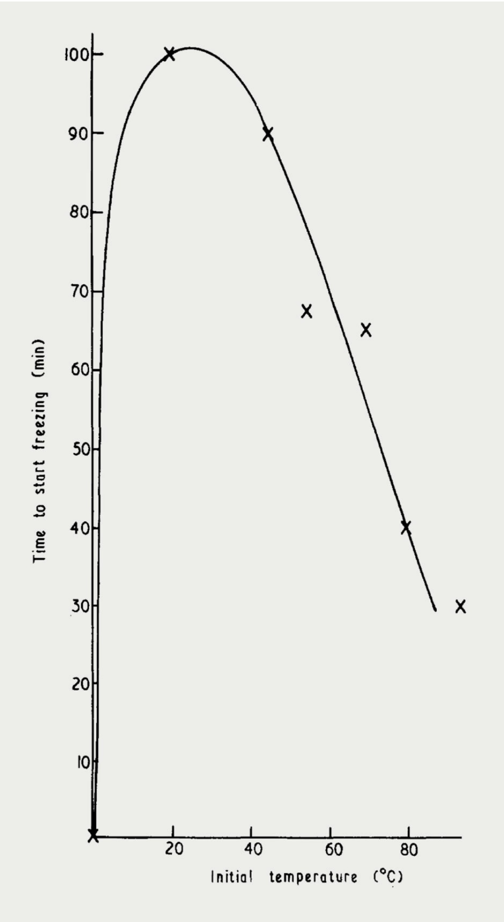
-- general design principle for energy rectifying molecular machines; Mpemba-like response in biological information sensors; a general non-stationary response theory; and many more…

Part II and III are very short and aim to inspire discussions after the session.

Mpemba effect – hot water freezes faster than cold water?! @o@

PA Images / Alamy Stock Photo

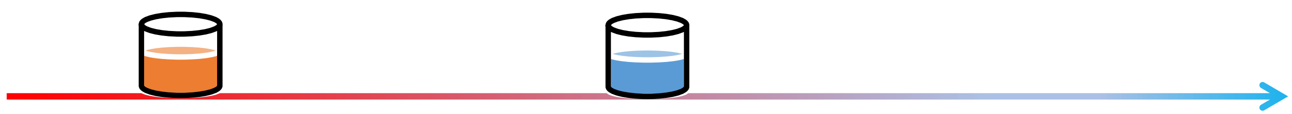
Let us first clean up the definition – . –



Mpemba and Osborne (1969)

Mpemba Effect **Cannot** Happen near Equilibrium (1-Dim space)

$$\frac{\mathrm{d}T}{\mathrm{d}t} = C \cdot (T(t) - T_{\mathrm{cold}})$$



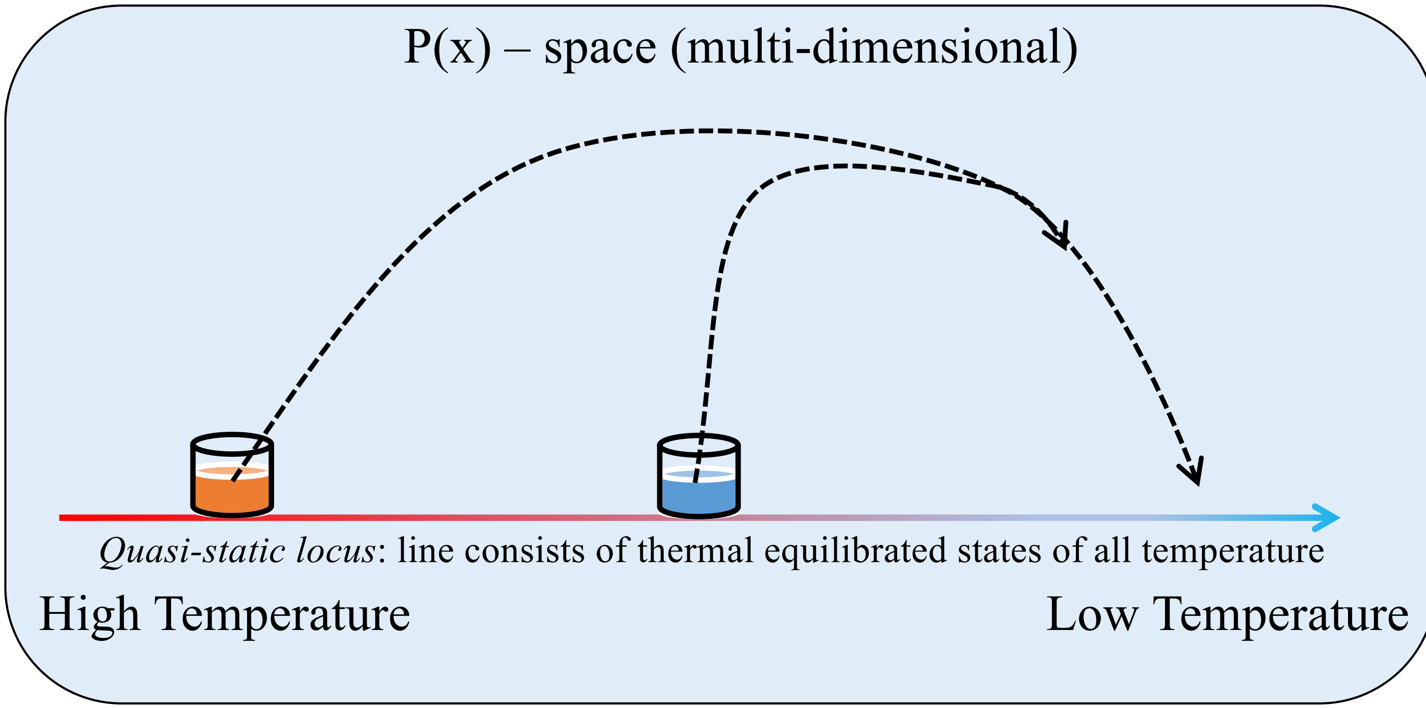
Quasi-static locus: line consists of thermal equilibrated states of all temperature

High Temperature Low Temperature

Lu., Z and Raz. O. (2017) PNAS

Mpemba Effect May Occur Beyond Equilibrium (multi-Dim)

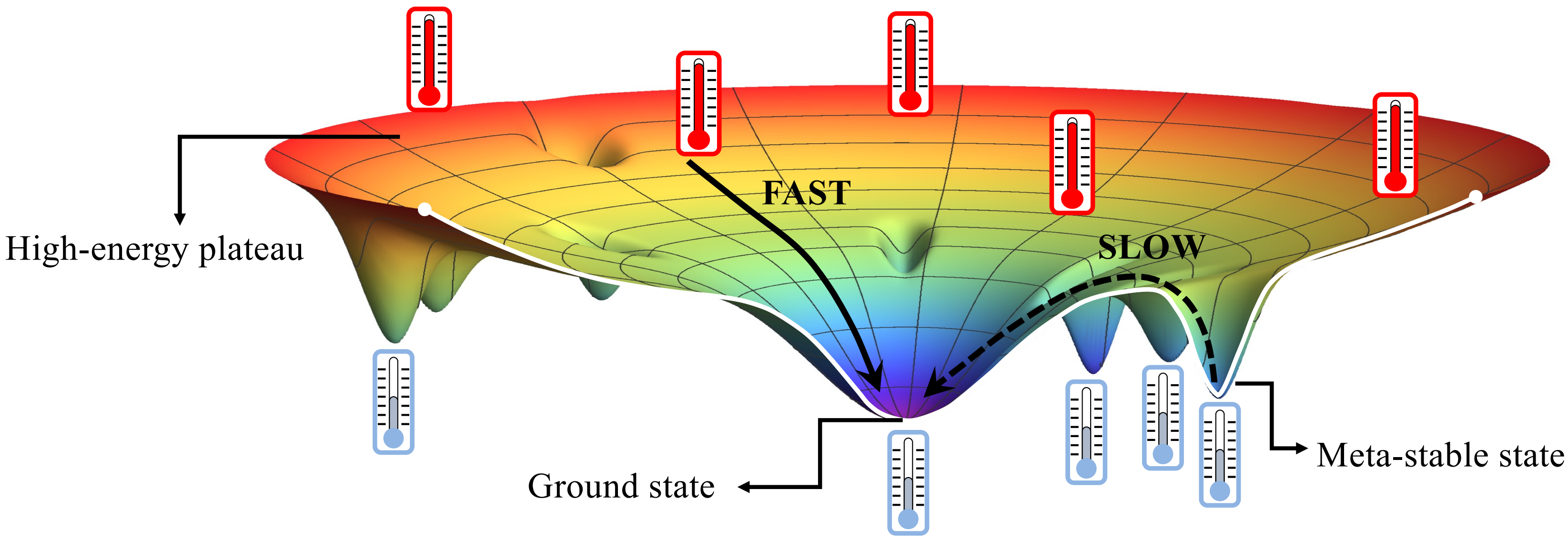
Nonequilibrium evolution of system's probability density: $$\frac{\partial P(x,t)}{\partial t} = \mathcal{L}P(x,t)$$



Lu and Raz (2017)

Intuitive energy landscape to demonstrate the Mpemba effect

Mpemba effect is a shortcut flow for probability distribution into the desired shape.



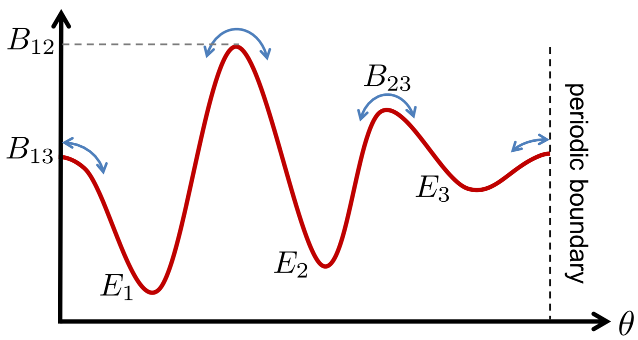
-- at high temperature: system occupies high-energy plateau.

-- at low temperature: system trapped in meta-stable states.

Lu., Z and Raz. O. (2017) PNAS

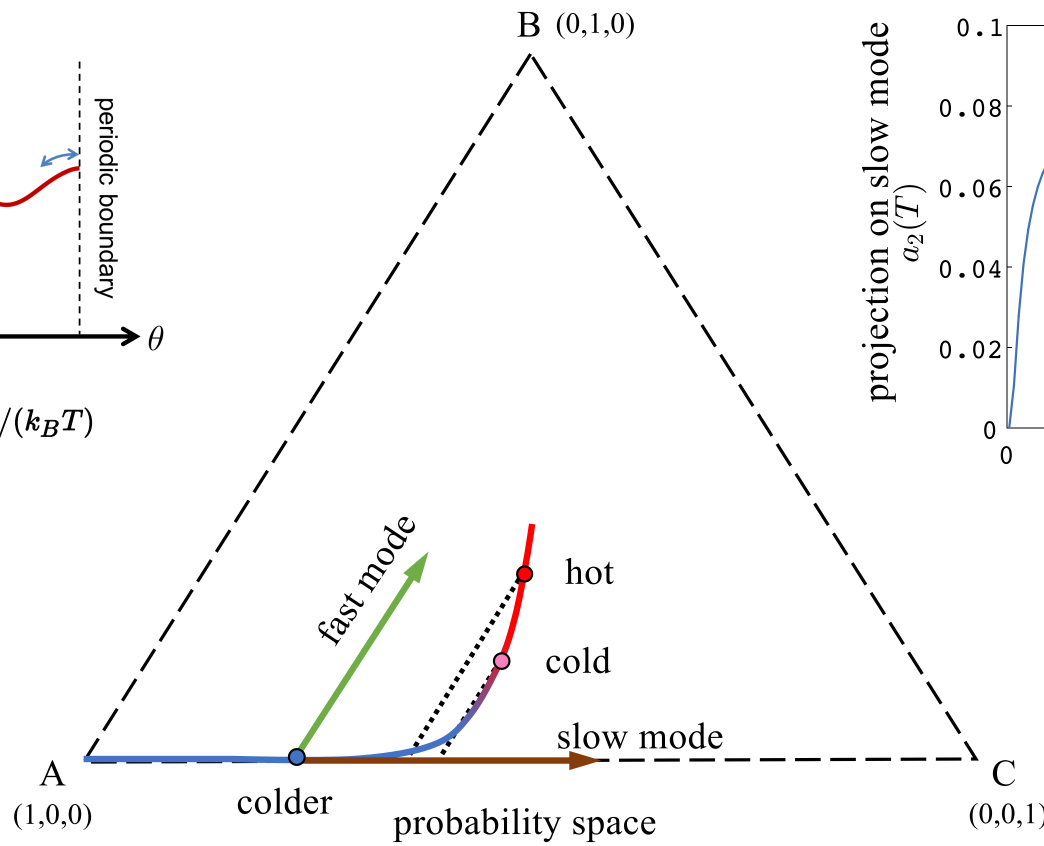
Necessary Condition of the Mpemba effect

$\vec{p} = (A\%, B\%, C\%)$

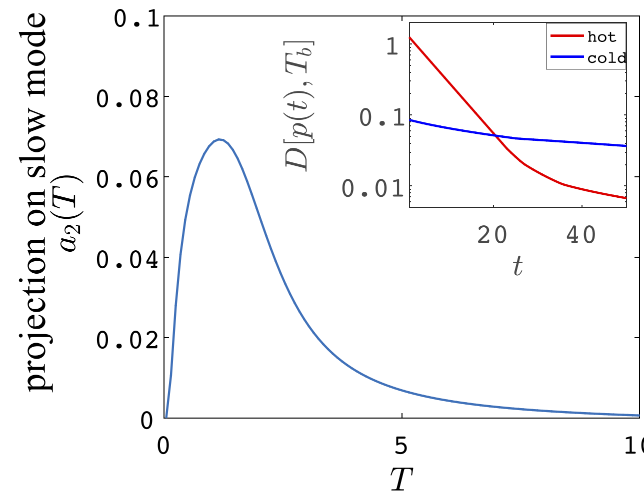


Arrhenius Law: $\boldsymbol{k = Ae^{-E_a/(k_B T)}}$

$$\mathrm{d}\vec{p}/\mathrm{d}t = R\ \vec{p}$$



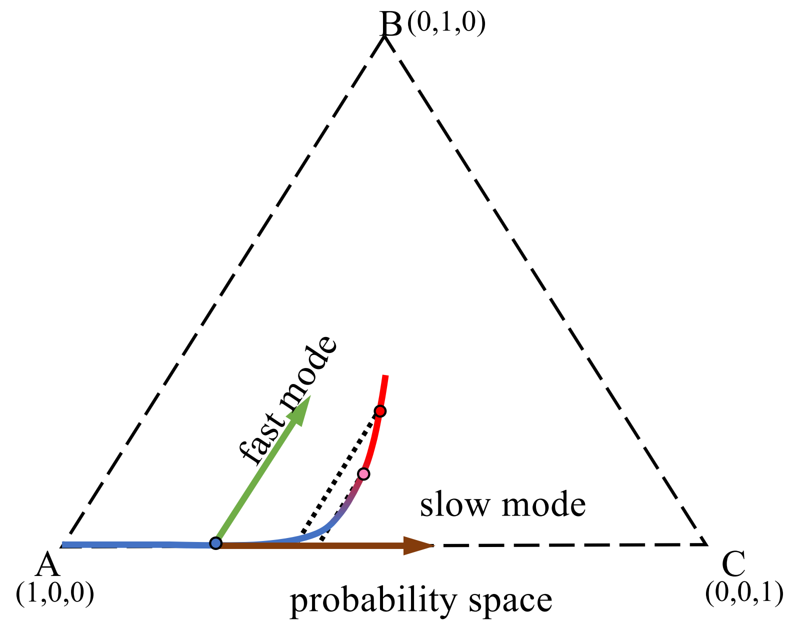
Necessary Condition:



Lu., Z and Raz. O. (2017) PNAS

Take-Home Message in Geometry Perspective

- **Findings:** The Mpemba effect could exist; it contradicts the intuition of near-equilibrium thermodynamics (where dynamics is 1-dmensional).
- **Updated intuition:** Distance does not dictate the relaxation time; it is the distance projected to the slowest relaxation mode.



Lu., Z and Raz. O. (2017) PNAS

Incomplete List of References

Stochastic thermodynamics theory:

- Lu, Z., & Raz, O. (2017). Nonequilibrium thermodynamics of the Markovian Mpemba effect and its inverse. *Proceedings of the National Academy of Sciences*, *114*(20), 5083–5088.
- Klich, I., Raz, O., Hirschberg, O., & Vucelja, M. (2019). Mpemba index and anomalous relaxation. *Physical Review X*, *9*(2), 021060.

Experimental realization:

- Bechhoefer, J., Kumar, A., & Chétrite, R. (2021). A fresh understanding of the Mpemba effect. *Nature Reviews Physics*, *3*(8), 534–535.

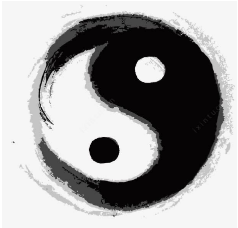
Phase transitions:

- Yang, Z.-Y., & Hou, J.-X. (2022). Mpemba effect of a mean-field system: The phase transition time. *Physical Review E*, *105*(1), 014119.
- Holtzman, R., & Raz, O. (2022). Landau theory for the Mpemba effect through phase transitions. *Communications Physics*, *5*(1), 280.
- Zhang, S., & Hou, J.-X. (2022). Theoretical model for the Mpemba effect through the canonical first-order phase transition. *Physical Review E*, *106*(3), 034131.

Extensions:

- Yang, Z.-Y., & Hou, J.-X. (2020). Non-Markovian Mpemba effect in mean-field systems. *Physical Review E*, *101*(5), 052106.
- Degünther, J., & Seifert, U. (2022). Anomalous relaxation from a non-equilibrium steady state: An isothermal analog of the Mpemba effect. *Europhysics Letters*, *139*(4), 41002.
- Chatterjee, AK, Takada, S, & Hayakawa, H. (2023). Quantum Mpemba effect in a quantum dot with reservoirs. *Physical Review Letters* 131(8), 080402.

Non-equilibrium Control Shortcuts beyond Mpemba Effect



Claim: The Mpemba effect is a special-case example of a general class of non-equilibrium shortcuts.

反る者は道の動なり (老子 第四十章)

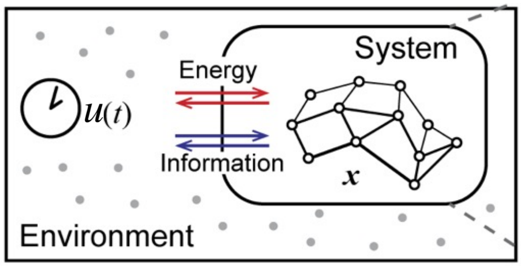
Key Question:
What type of systems are prone to have interesting non-equilibrium shortcuts?

Answer:
Systems with <u>separation of timescales</u> and <u>non-trivial eigenmodes</u> (geometry).

Reference: Chittari SS, & **L. Z.** (2023) Geometric approach to nonequilibrium hasty shortcuts. *The Journal of Chemical Physics*. 159(8).

Supraja Chittari

System under External Control: master equation with parameter u(t)



System under control u

Master equation under control parameter u(t):

$$\frac{d\vec{p}(u)}{dt} = \hat{R}(u) \cdot \vec{p}(u)$$

General solution to the master equation **at constant u**:

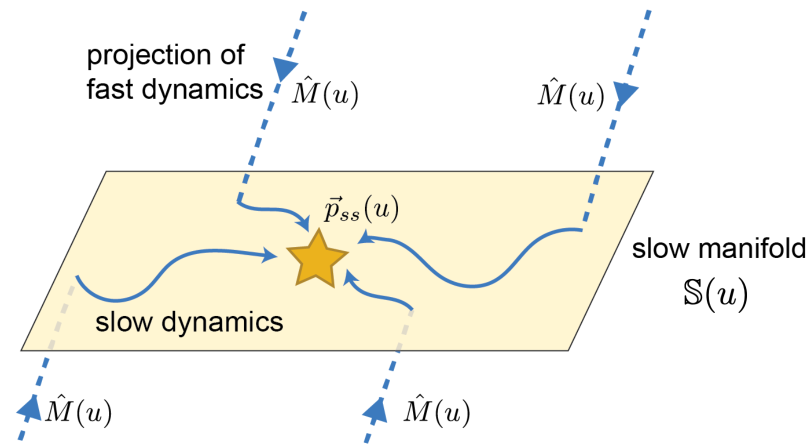
$$\vec{p}(t) = \sum_i c_i \vec{v}_i e^{\lambda_i t}$$

Eigenvalues with a gap between λ_c and λ_{c+1}

$$\lambda_1, \lambda_2, \cdots \lambda_c, \lambda_{c+1}, \cdots, \lambda_n$$

Separation of timescale!!!!!

$$\frac{1}{|\lambda_{c+1}|} \ll \tau \ll \frac{1}{|\lambda_c|}$$



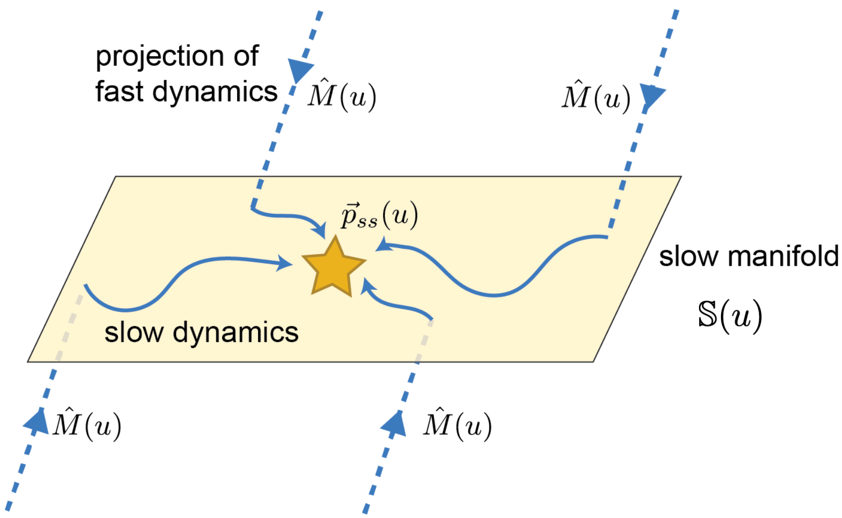
The star is the stationary probability at the chosen "u".

Warm-up Geometric Quiz: Which system is more responsive (top or bottom)?

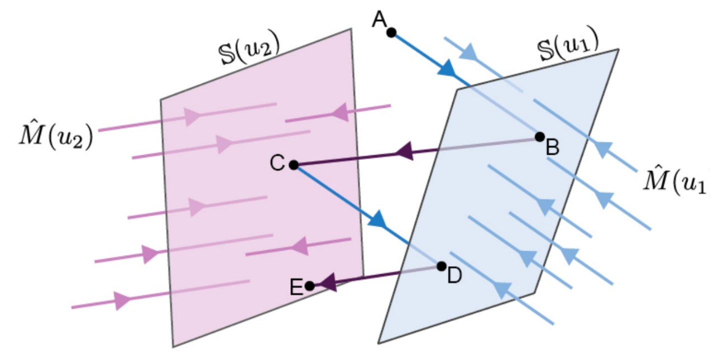
Fast dynamics projects initial distributions onto a slow manifold, which is spanned by the c slow eigenvectors:

$$\vec{p}(\tau) = \hat{T}_\tau \vec{p}_0 = \hat{V} e^{\hat{\Lambda}\tau} \hat{V}^{-1} \vec{p}_0$$

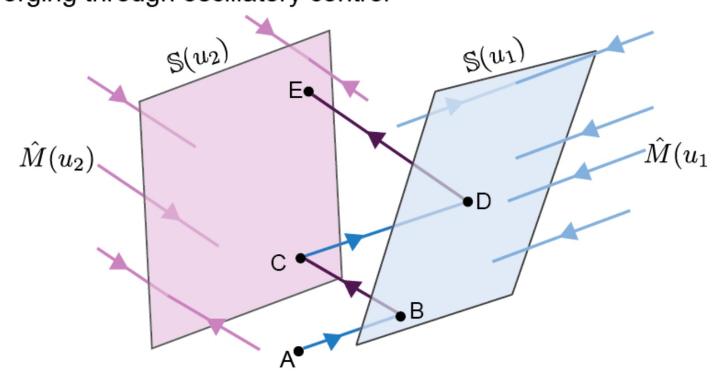
$$\hat{M}_\tau = \hat{V} \hat{D}_{01} \hat{V}^{-1}$$



Converging through oscillatory control

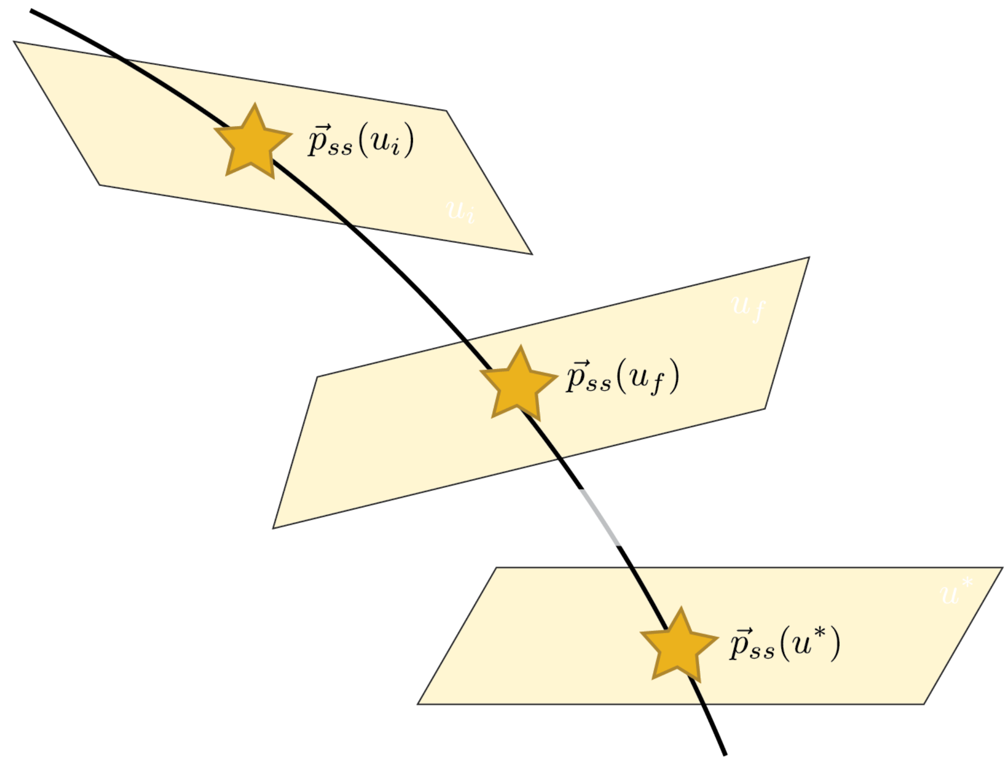


Diverging through oscillatory control



Now let us consider a continuous range of parameter “u”:

- At each value of u, there is one steady state, one slow manifold (base), and one fast projection map (fibers toward base).
- The set of all steady states for each “u” forms a black curve (1-dim u).
- **As a result:**
  > There is a family of slow manifolds parameterized by “u” (yellow planes).
  > Each plane receives projection from (fast dynamics) that are typically not perpendicular to the base.

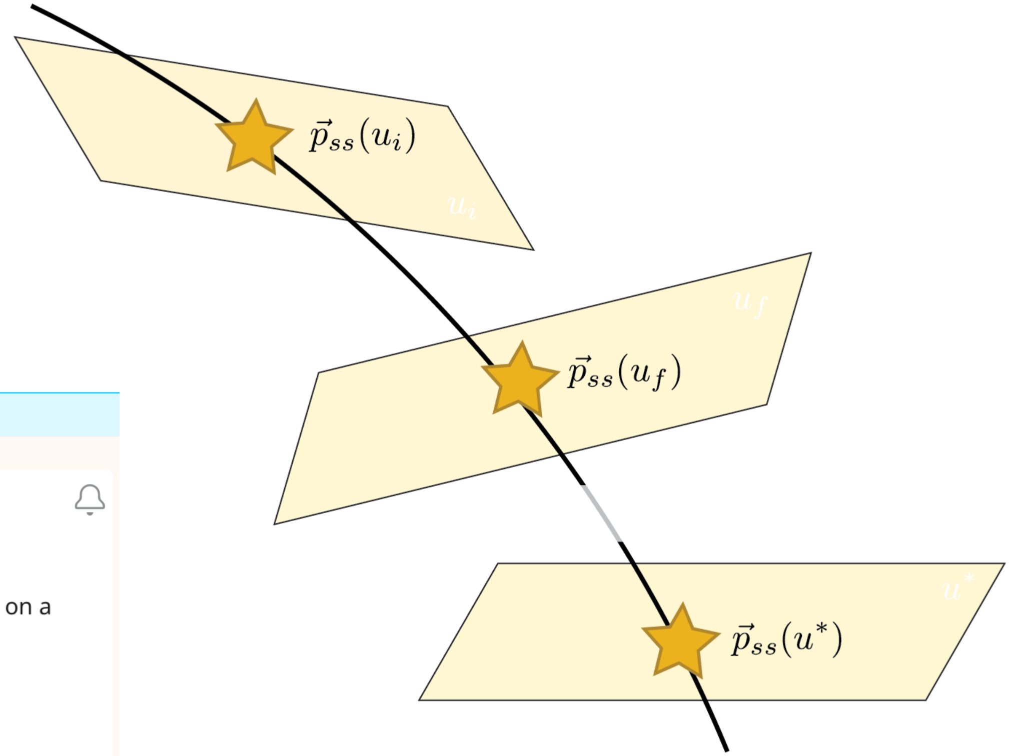


Black curve is the steady-state locus (made of stars).

What do we mean by **Non-equilibrium Hasty Shortcut**?

Goal:

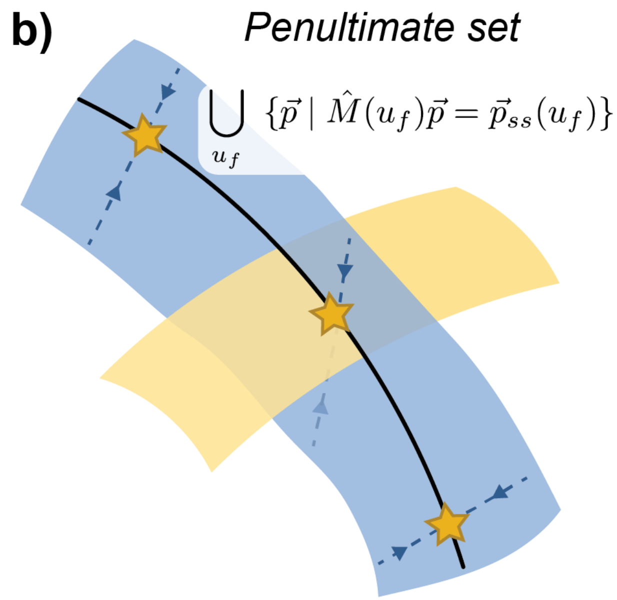
Starting at an initial steady state for initial u_i, how to control $u(t)$ to steer the system into the final steady state corresponding to the value of u_f without involving any slow dynamics?



Black curve is the steady-state locus consisting of stars.

Toward the Design Principle of **Hasty Shortcut – When Can It Exist?**

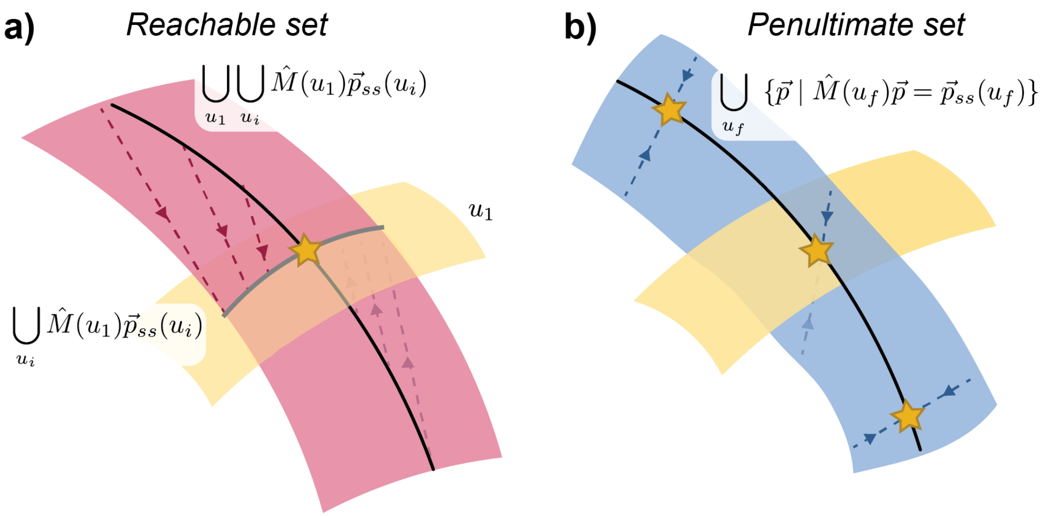
Attn Audiences: Please remind me to twist my arm.



Condition: Shortcuts exist if and only if the reachable set and the penultimate set intersects beyond the black curve. (**non-trivial intersection**)

Geometry Allowing for Non-trivial Intersection

Attn Audiences: Please remind me to twist my arm.



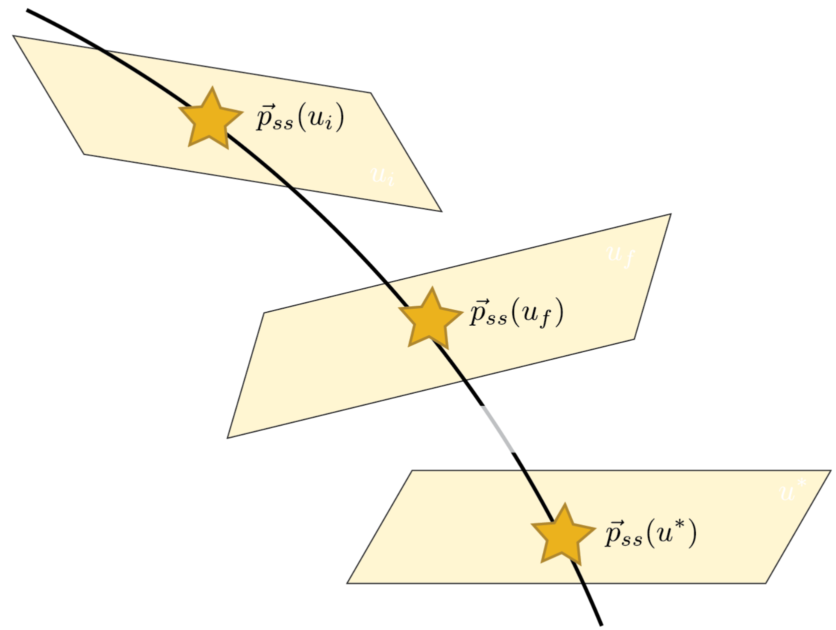
- **The steady-state locus is better bent than straight.**
- **The reachable manifold is better bent than flat.**
- **The penultimate manifold is also better bent than flat.**

What does the geometric requirement "bent" mean in terms of the property of the family of rate matrix $\hat{R}(u)$?

Optional Slide: Geometric Intuition for Eigen-analysis

Assuming that each transition rates are continuous and smooth functions of u.

Eigenvalues and eigenvectors are smooth functions, and thus these objects may change smoothly with u. ☹

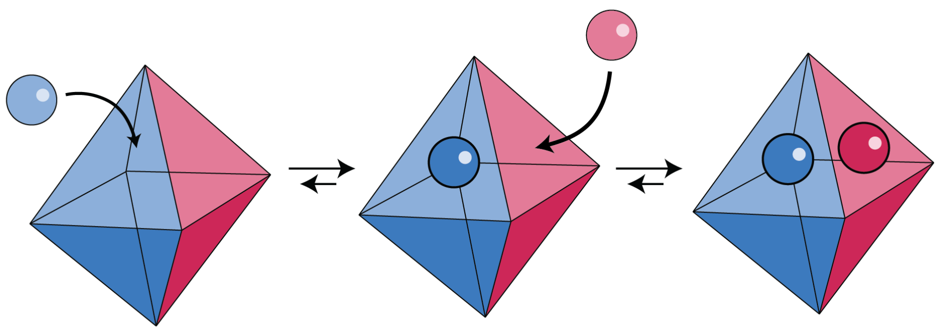


However, if eigenvalues as functions of u cross each other at certain critical values of u^*, or has avoided crossing, then the orientation of the slow manifold has a "jump" at the u^*. Similar jump occurs for the directions of the fast projection (sudden fiber-direction change). ☺

Eigenvalue gap and eigenvalue crossing at certain u^*'s could allow for the non-trivial geometry for the hasty shortcut.

Demo by Chemical Systems: Shortcut to Self-Assembly

Control parameter: c_s



$$E(\mathbf{s}) = h\sum_k s_k + J\sum_{<l,m>} s_l s_m$$

$F_s = E_s - T\ln(g_s)$

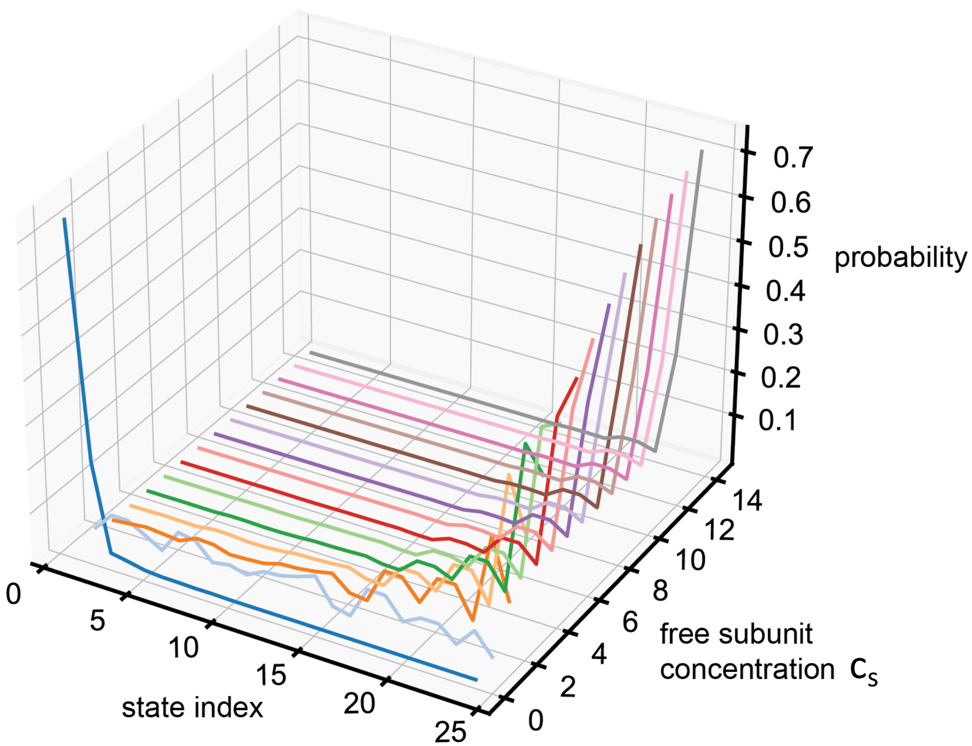
g_s: configuration degeneracy.

$$\frac{d\vec{p}(t)}{dt} = \hat{R}\cdot\vec{p}(t)$$

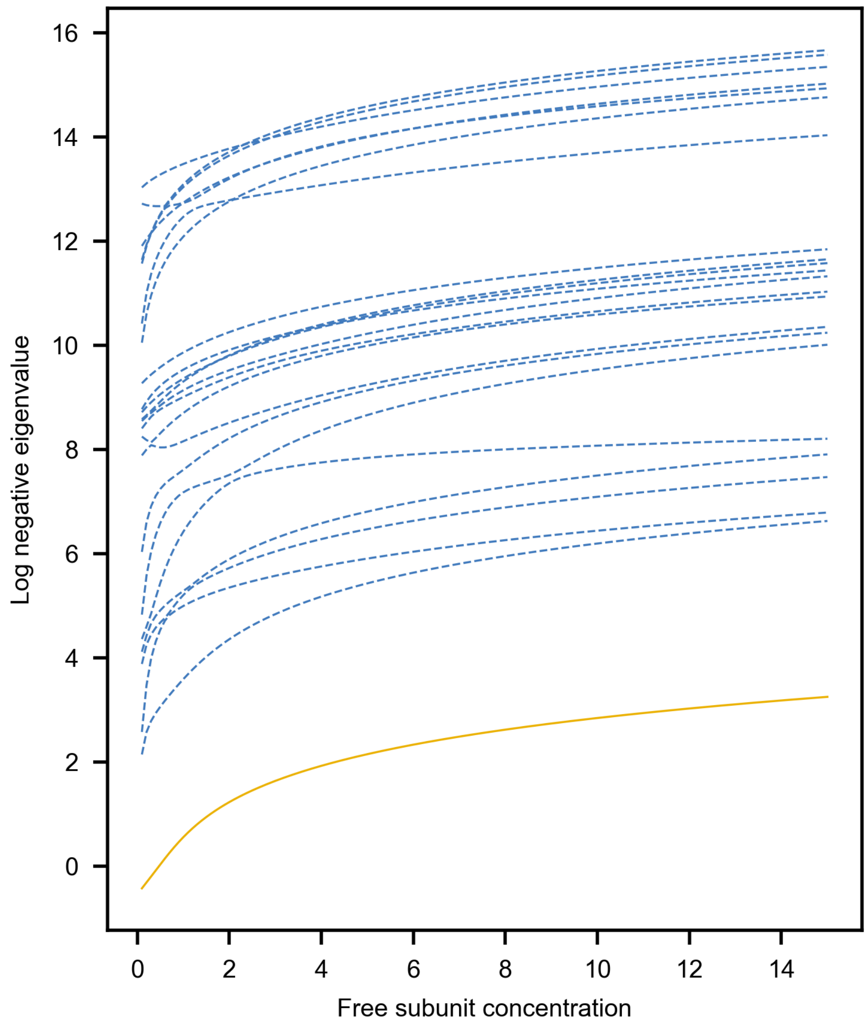
$$R_{ji} = c_s e^{\beta\frac{F_j - F_i}{2} + \beta C\eta(i,j)}$$ binding rate

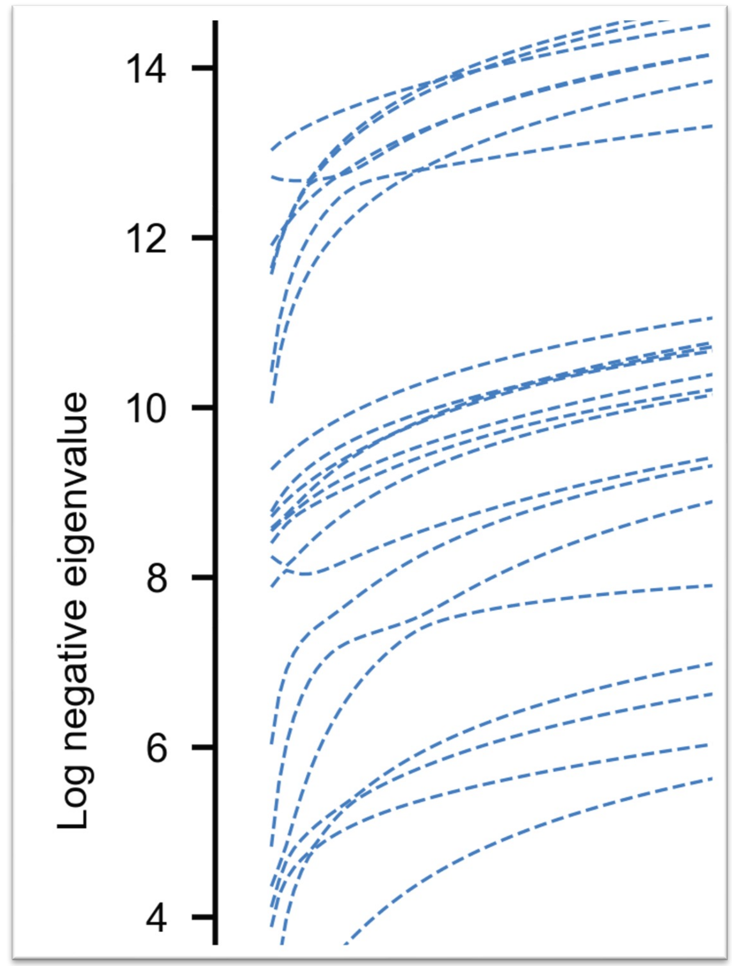
$$R_{ji} = e^{\frac{F_j - F_i}{2} + \beta C\eta(i,j)}$$ unbinding rate

Equilibrium configuration probability distributions under various c_s

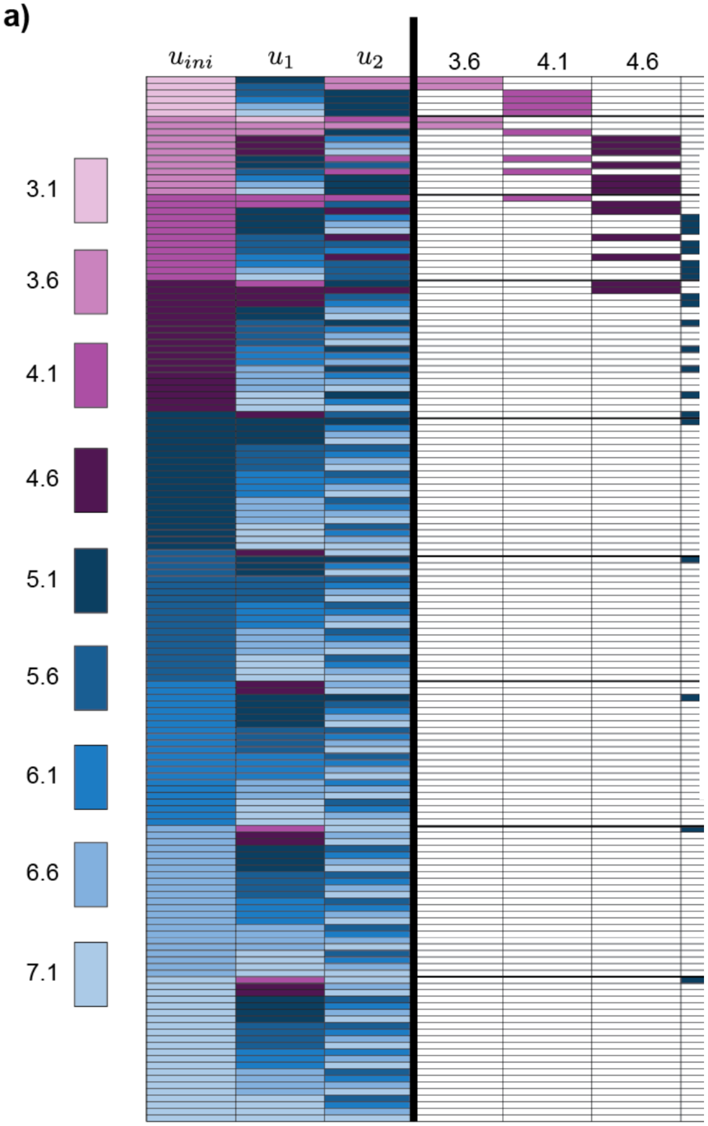


Eigenvalue Crossings and Avoided Crossings (c_s from 0 to 3)

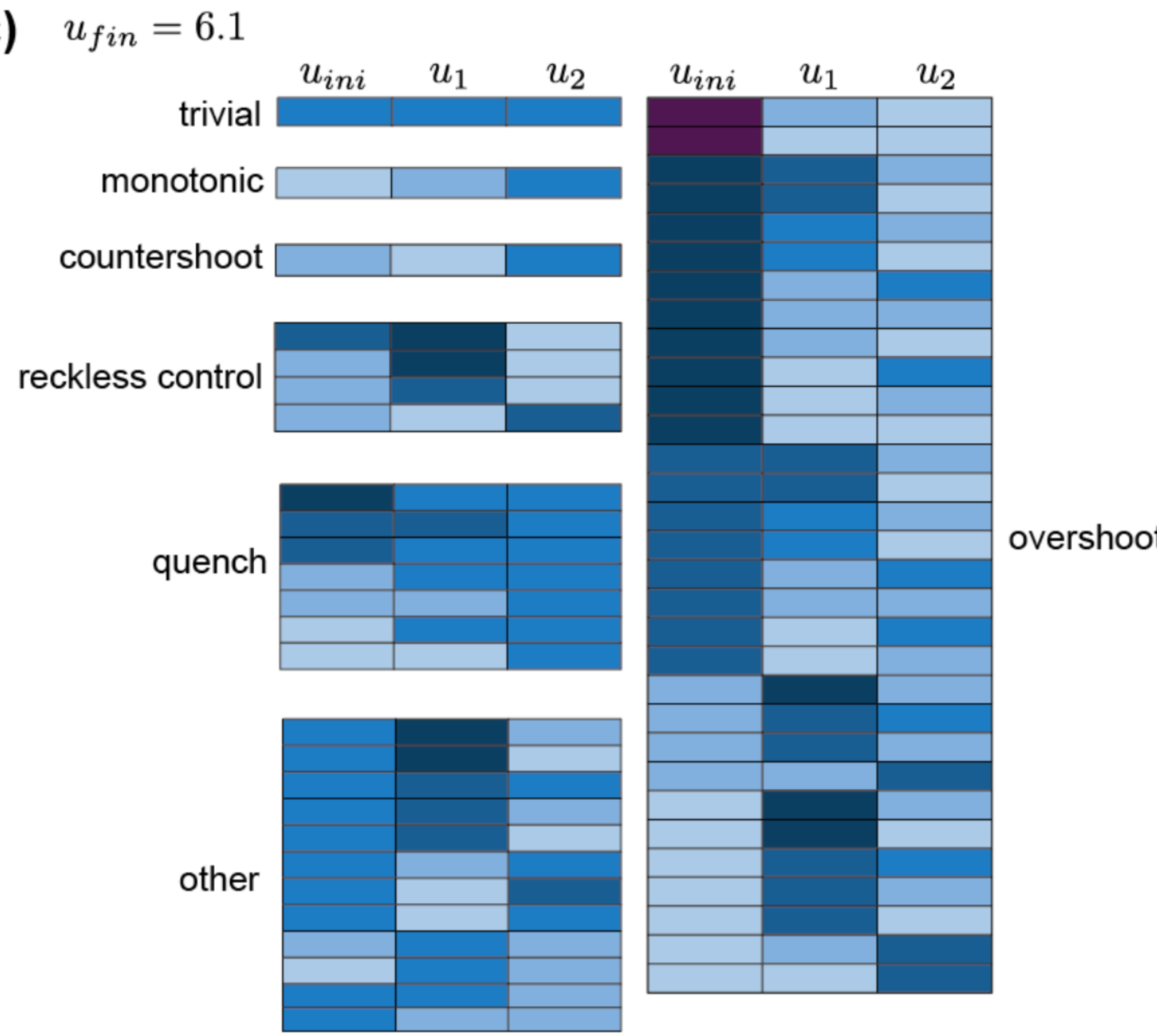




a)


u_{ini}
u_1
u_2
3.6
4.1
4.6
3.1
3.6
4.1
4.6
5.1
5.6
6.1
6.6
7.1

c)


$u_{fin} = 6.1$
u_{ini}
u_1
u_2
trivial
monotonic
countershoot
reckless control
quench
other
overshoot

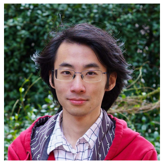
Take-home messages

- We find the geometric requirement of the hasty shortcut to manipulate a thermodynamic system from one steady state to another.

Open questions

- Is it generally true that hasty shortcuts typically need to cross critical control values where eigenvalues cross?
- What does "eigenvalue crossing" for the classical master equation imply in the physical system? Especially at the thermodynamic limit?
- What are other mechanisms of the hasty shortcut beyond eigenvalue crossing? (e.g., **hub-states** & **bend black curve?**)

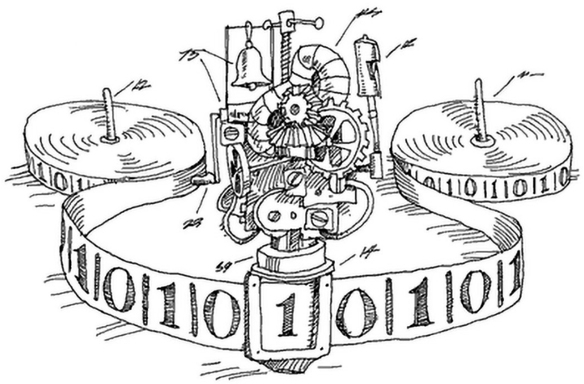
Bonus: Non-equilibrium Manipulation of an Ising-like Polymer into a Memory & Computer

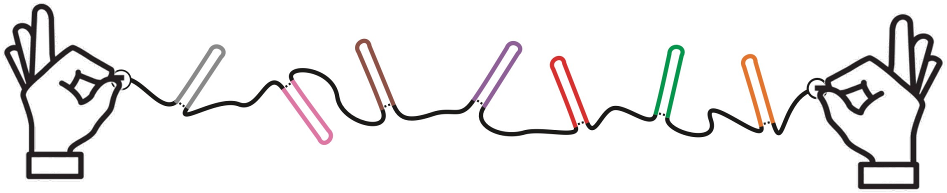


Dr. Zhongmin Zhang

Poster week #2

Single Molecular Automaton





Temporal protocol recognition: “smart” polymer that discerns temporal patterns of mechanical force signal. It is a “memory register” that records the historical mechanical information into its meta-stable configurations.

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Z. Zhang, **Z. Lu**, in prep.

Outline

I. **Counter-intuitive effects where systems evolve beyond stationarity**

-- from Mpemba effect to non-equilibrium shortcuts

II. **Meditation on Geometry: Bird's-Eye View of Thermodynamic Theory**

III. **Geometry & Non-equilibrium Theory Beyond Steady States:**

-- energy rectification, information transduction, response theory…

Nonequilibrium Thermodynamics Beyond Steady States

I. **Counter-intuitive effects where systems evolve beyond stationarity**

-- from Mpemba effect to non-equilibrium shortcuts

II. **Meditation on Geometry: Bird's-Eye View of Thermodynamic Theory**

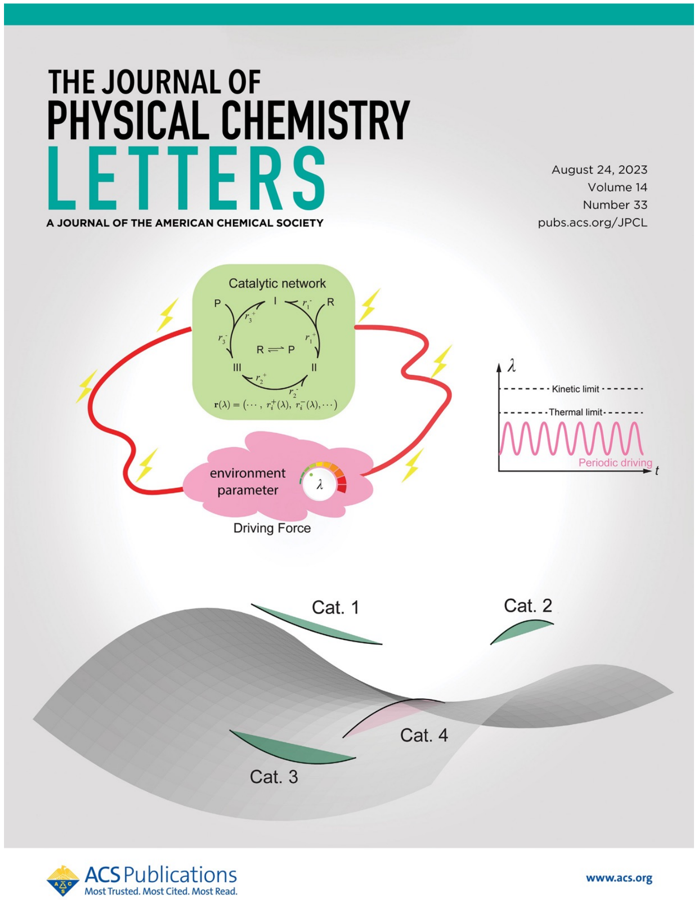
III. **Geometry & Non-equilibrium Theory Beyond Steady States:**

-- a) Geometric design principle for energy rectifying molecular machines;
-- b) Mpemba-like response in biological information sensors;
-- c) Information Geometry and non-stationary response theory;

and many more…

Part II and III are very short and aim to inspire discussions after the session.

a) Geometry can be Useful for Designing Molecular Machines



Theory for Oscillation-Driven Molecular Machine

1. What is the theoretical limit of pumped performances?
2. What type of performance can(not) be pumped?

Practical Design Principles for such Machines

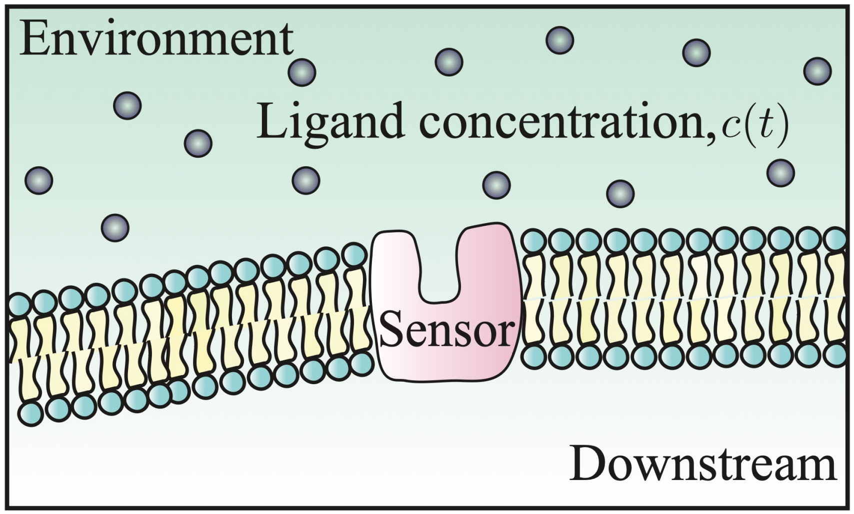
1. What is the optimal catalyst for desired performance?
2. What is the optimal protocol to pump a catalyst?

Z. Zhang, **ZL**, JPCL 2023

Z. Zhang, Vincent Du, **ZL**, PRE 2023

b) Information Transduction Far From Steady States

Asawari
Pagare



Refs:
A. Pagare, SH. Min, **Z. Lu**. "Theoretical upper bound of multiplexing in biological sensory receptors" Physical Review Research, 5 (2023): 023032.
A. Pagare, **Z. Lu**. "Information Benchmark for Biological Sensors Beyond Steady States -- **Mpemba-like sensory withdrawal effect**" under review at PRX Life, see also arXiv:2406.04304 (2024)

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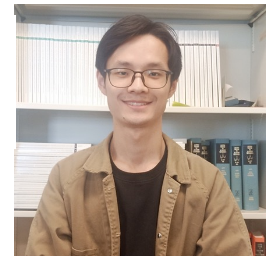
c) Response Theory for non-steady process

Poster week #2



Jiming Zheng

- Linear response:

  Rep Kubo. *Reports on progress in physics* 29.1 (1966): 255.

- Nonequilibrium Steady State (NESS) sensitivity:

  Jeremy A. Owen, Todd R. Gingrich, Jordan Horowitz. *PRX* 10.1 (2020): 011066. [Graph Theory]
  Pedro E. Harunari, Sara Dal Cengio, Vivien Lecomte, Matteo Polettini. *arXiv: 2402.13193*. [Graph Theory]
  Timur Aslyamov, Massimiliano Esposito. *PRL* 132.3 (2024): 037101. [Linear Algebra]
  Timur Aslyamov, Massimiliano Esposito. *arXiv:* 2402.13990. [Linear Algebra]

- Non-stationary sensitivity:

  Andreas Dechant, Shin-ichi Sasa. *PNAS* 117 (12) 6430-6436 (2020).
  Pedro E. Harunari, Sara Dal Cengio, Vivien Lecomte, Matteo Polettini. *arXiv:* 2402.13193.

$$|\partial_{R_{e\pm}}\langle Q\rangle| \leq \sqrt{\mathrm{Var}[Q]}\cdot\frac{\sqrt{A_{e\pm}}}{R_{e\pm}}$$

sensitivity relation

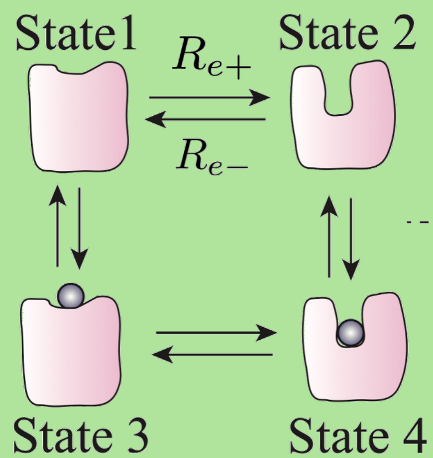
$$|\langle Q\rangle' - \langle Q\rangle| \leq 2\max_{X_\tau}|Q|\cdot\sin(G_{e\pm})$$

finite response relation

This work: J. Zheng, **Z. Lu**, "Information Geometry and Universal Bounds on Non-stationary Responsiveness of Markov Dynamics", arXiv:2403.10952 (2024)

How Do General Non-equilibrium Systems Respond to Stimuli?

environmental
parameters
(T, p, c, etc.)

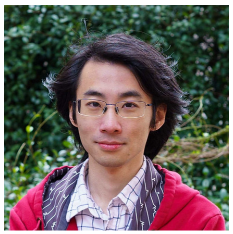


$\langle Q \rangle$

What is the biological observable Q?
How to improve sensitivity?
How to improve robustness?
Which kinetic path matters more?
How to use the response to design drugs?
...

How does any arbitrary quantity Q(t) respond to changes in environmental parameters?
Can general understanding be obtained for arbitrary systems independent of system's detail?

Acknowledgements



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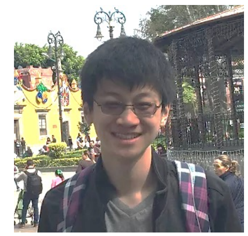
Jiming Zheng

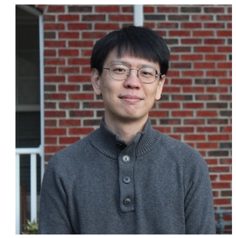
Supraja Chittari

Asawari Pagare

Chase Slowey



Vincent Du



Dr. Sa Hoon Min

^^^ Please contact Dr. Zhang if your department looks for new talented faculty colleagues!!!

Collaborators & Friends: Prof. Hong Qian & Prof. Oren Raz

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