Anomalous thermal relaxation of physical systems

Nonequilibrium shortcuts to thermal relaxation

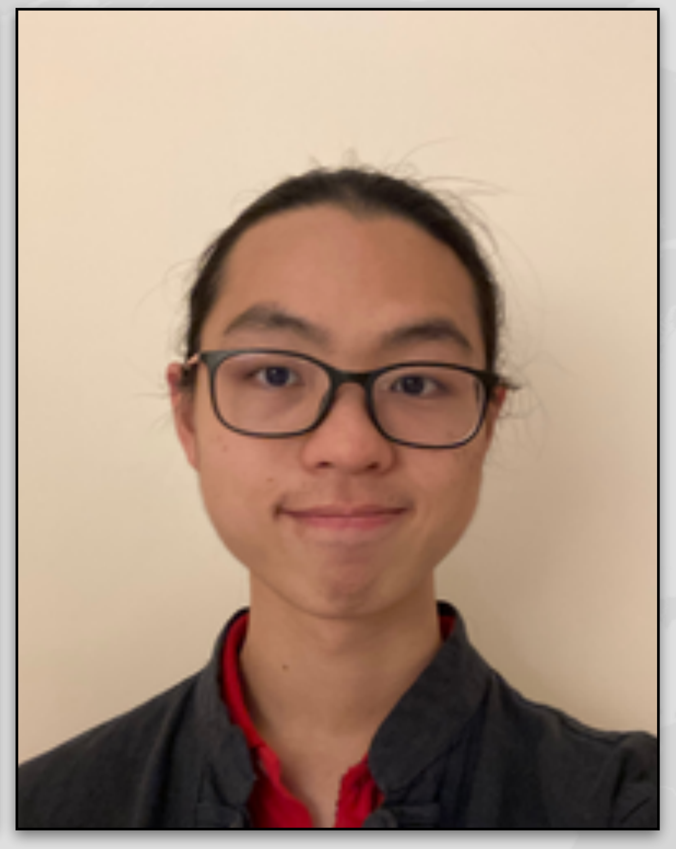
Marija Vucelja
University of Virginia

July, 2024, Frontiers of Nonequilibrium Statistical Physics, Kyoto

Anomalous Thermal Relaxations of Physical Systems

Graduate students


Matthew R. Walker


Gene Chen

Undergraduate alumni

Olivia Goodrich
Matthew R.Walker
Austin Chen
Nicholas Clifford
Jacob Goudeau
Peter Manto

Graduate alumni


Saikat Bera

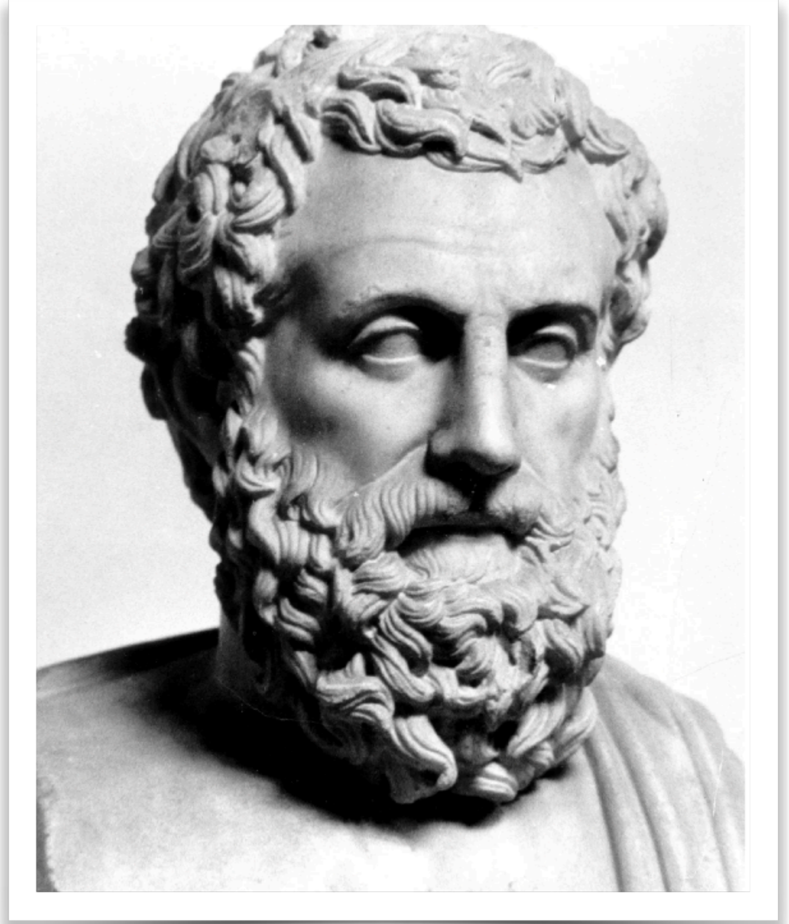
Publications in this talk

S. Bera, M. R. Walker, & MV, arXiv: 2308.04557
M. R. Walker, S. Bera & MV, arXiv:2307.16306
M. R. Walker & MV, arXiv:2022.07496 (under review in PRL)
M. R. Walker & MV, J. Stat. Mech., 2021
I. Klich, O. Raz, O. Hirschberg, & MV, PRX, 2019
MV, O. Raz, J. Bechhoefer, A. Lasanta & G. Teza, Phys. Reports (to appear)

This material is based upon work supported by the NSF under Grant No. DMR-1944539.

The phenomenon

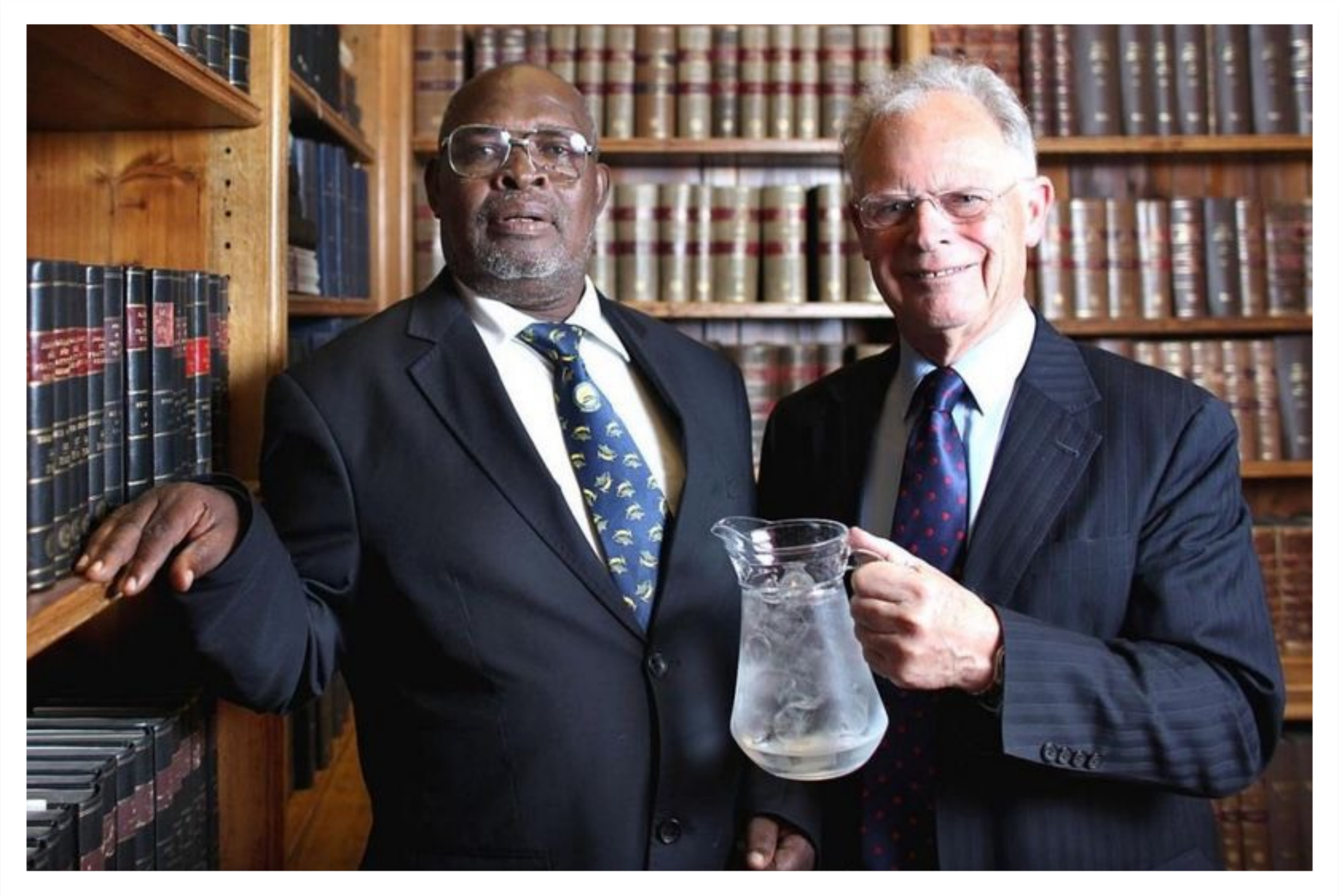
Water



Aristotle

Francis Bacon

René Descartes



Erasto Mpemba and Denis Osborne

"The fact that water has previously been warmed contributes to its freezing quickly; for so it cools sooner. Hence many people, when they want to cool hot water quickly, begin by putting it in the sun. . ."

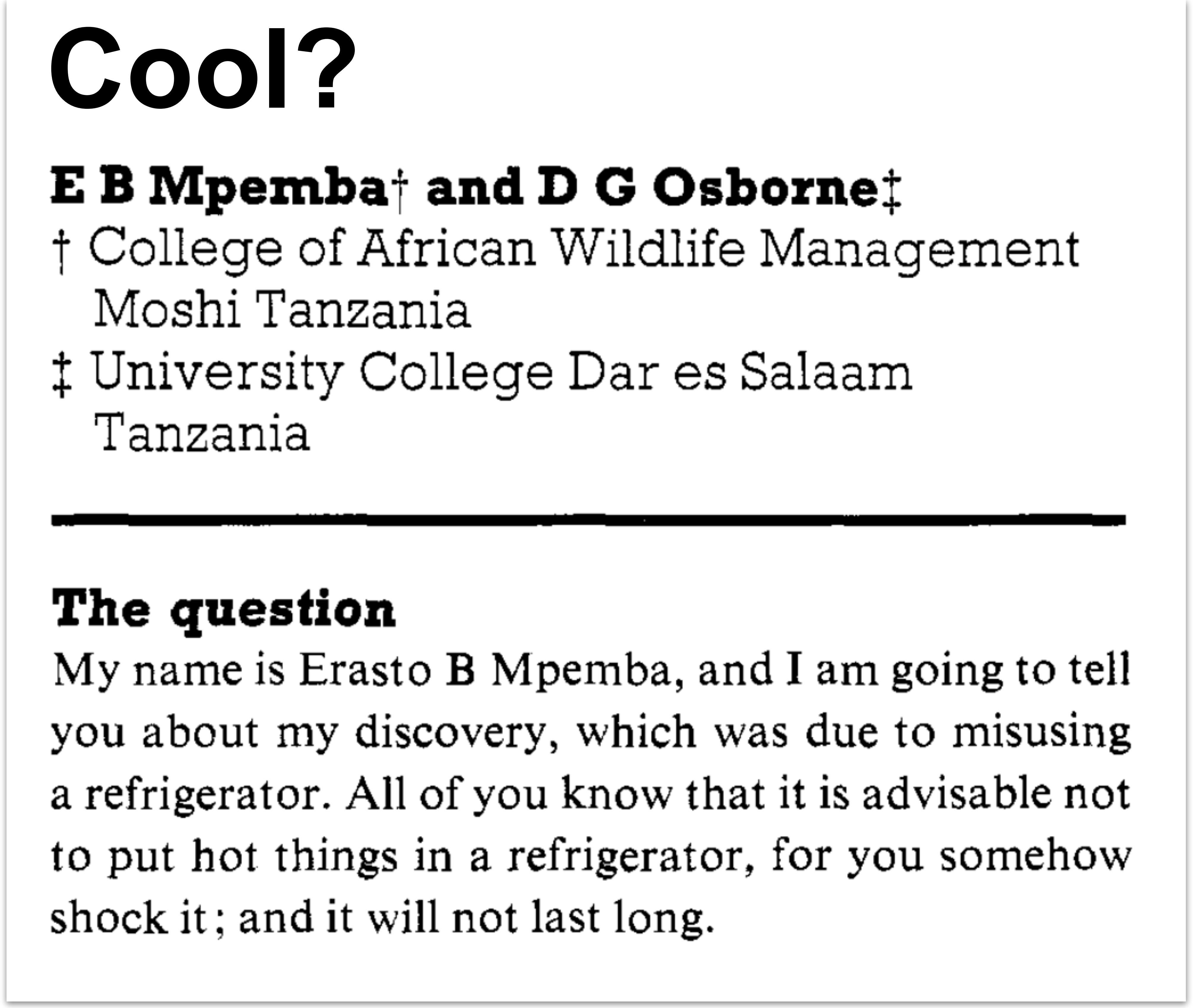
"slightly tepid water freezes more easily than that which is utterly cold."

"One can see by experience that water that has been kept on a fire for a long time freezes faster than other, the reason being that those of its particles that are least able to stop bending evaporate while the water is being heated."

Mpemba B. E. & Osborne D. Phys. Edu., 1969

1963 Mpemba observes the effect while making ice cream

Mpemba B. E. & Osborne D. Phys. Edu., 1969

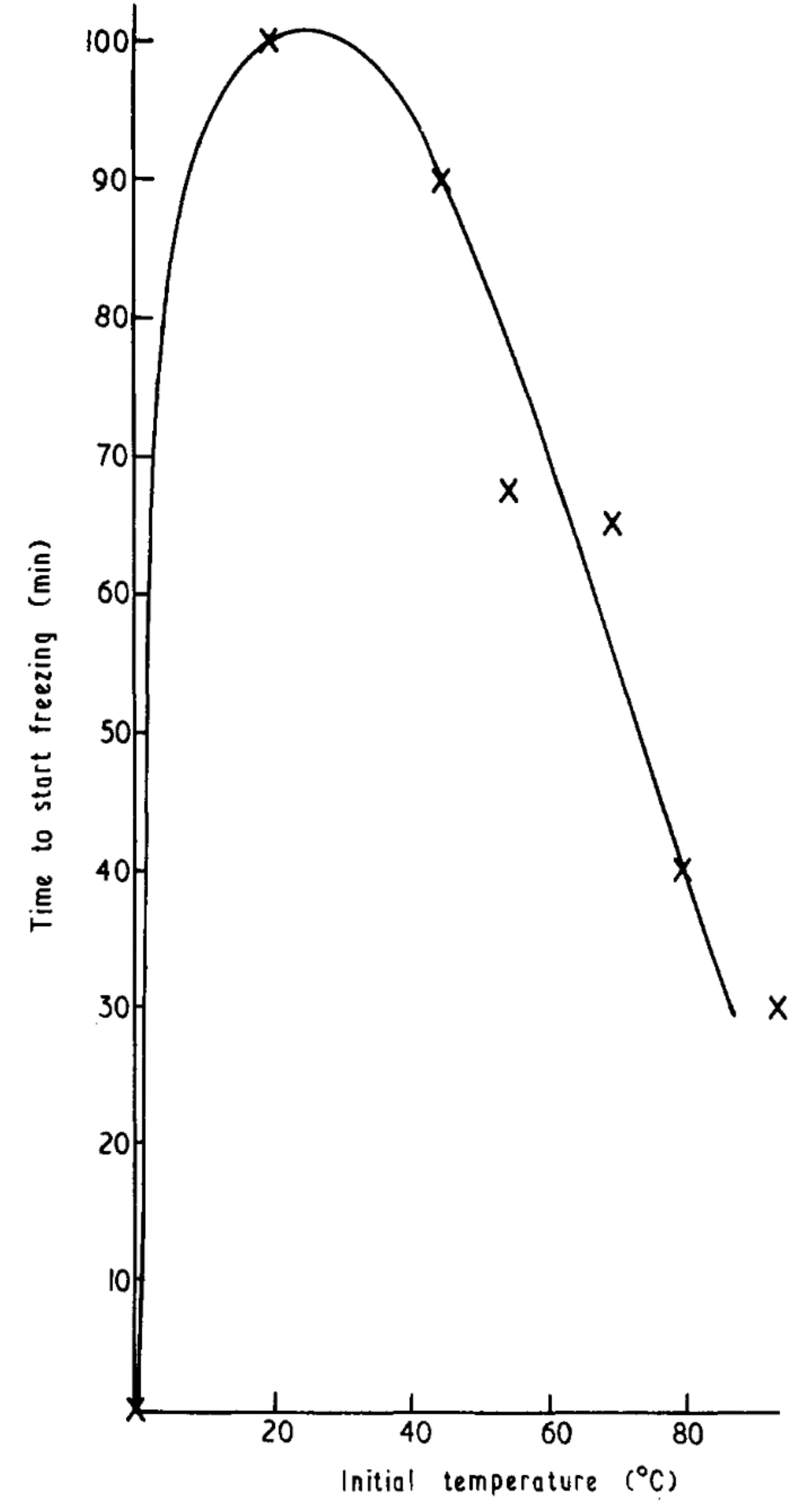


Cool?

E B Mpemba† and D G Osborne‡
† College of African Wildlife Management
Moshi Tanzania
‡ University College Dar es Salaam
Tanzania

The question

My name is Erasto B Mpemba, and I am going to tell you about my discovery, which was due to misusing a refrigerator. All of you know that it is advisable not to put hot things in a refrigerator, for you somehow shock it; and it will not last long.



Time to start freezing as a function of initial sample temperature

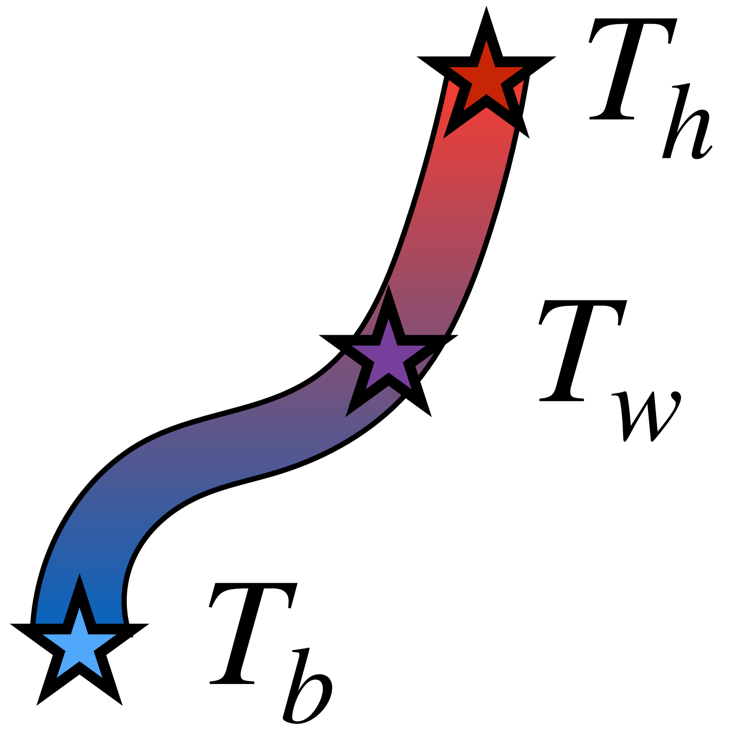
70 cm^3 of water in 100 cm3 Pyrex beakers in a domestic freezer chest
insulation on bottom and side — all loss from the top
pre-boiling (eliminates dissolved gasses)

Mpemba effect

inspired by Mpemba's water experiments

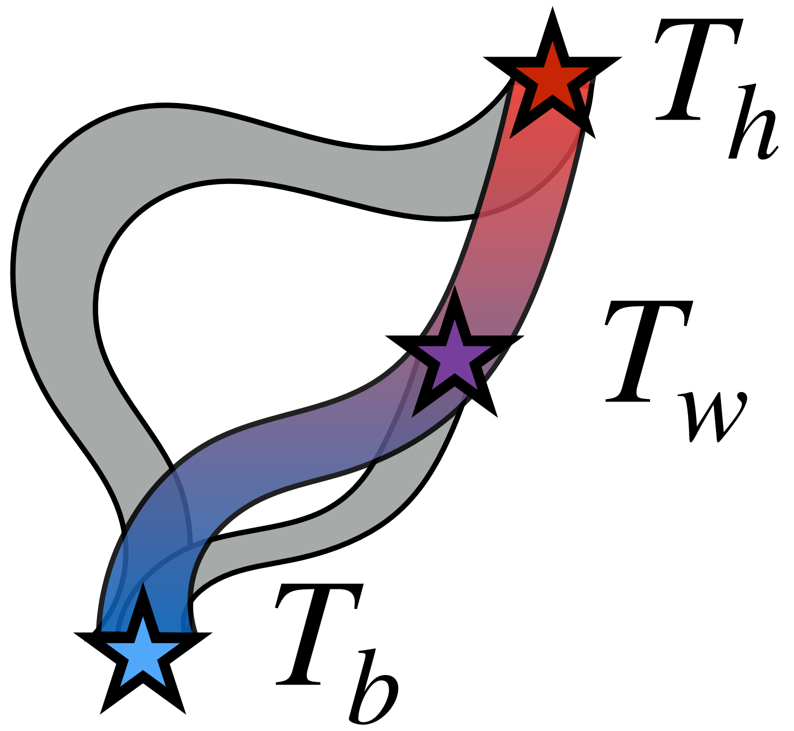
Cooling: Identical systems prepared at T_h and T_w, and coupled to a bath with T_b

$$T_h \geq T_w \geq T_b$$



quasistatic

along the trajectory a system is always close to a equilibrium



quench

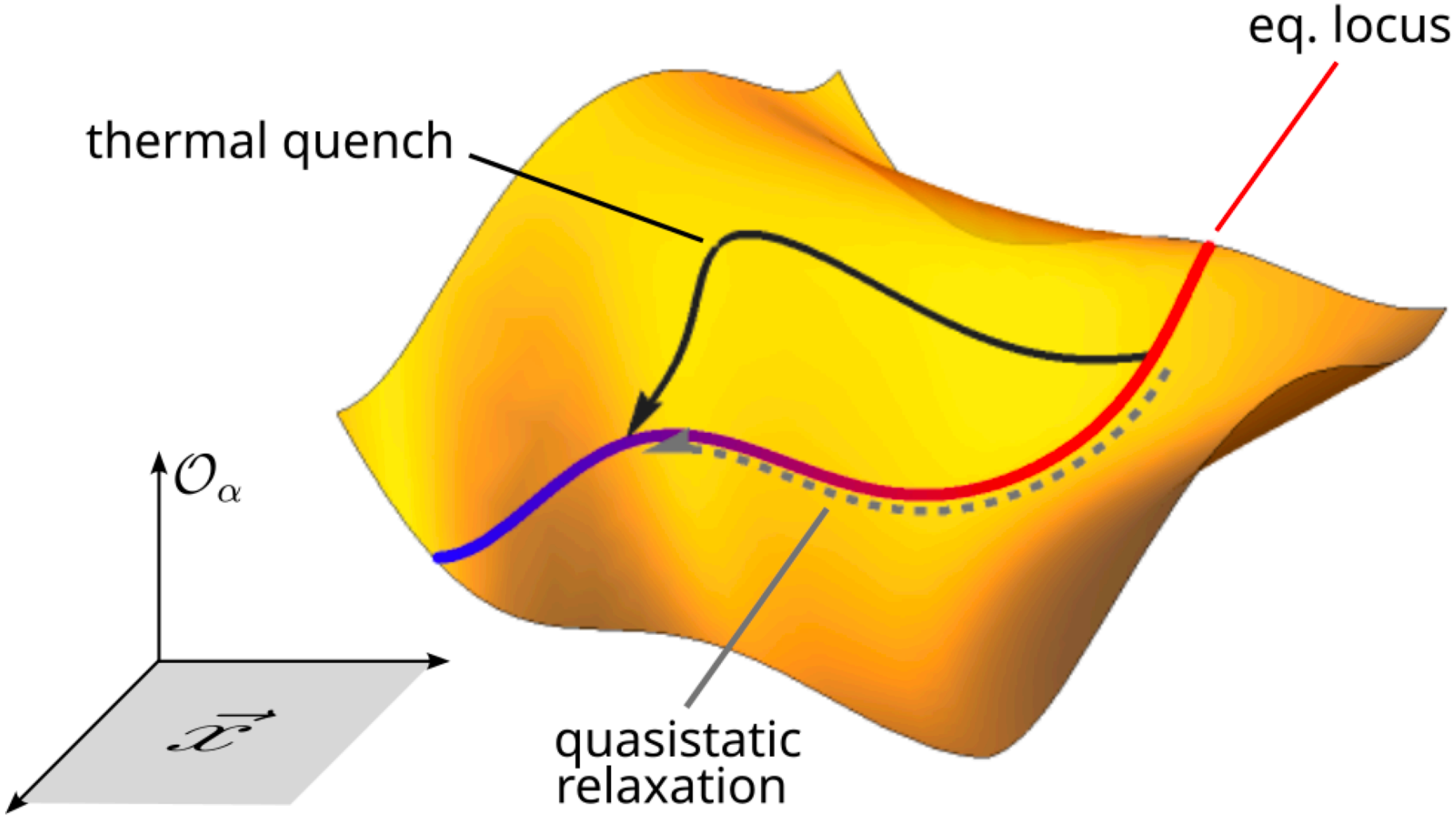
along the trajectory the system generically is out of equilibrium

Mpemba effect

System prepared at T_h "overtakes" the system prepared at T_w and "cools down faster" to T_b

Heating - analog effect: *Z. Lu & O. Raz, PNAS 2016; A. Kumar, R. Chétrite, & J. Bechhoefer, PNAS 2022*

Thermal quench



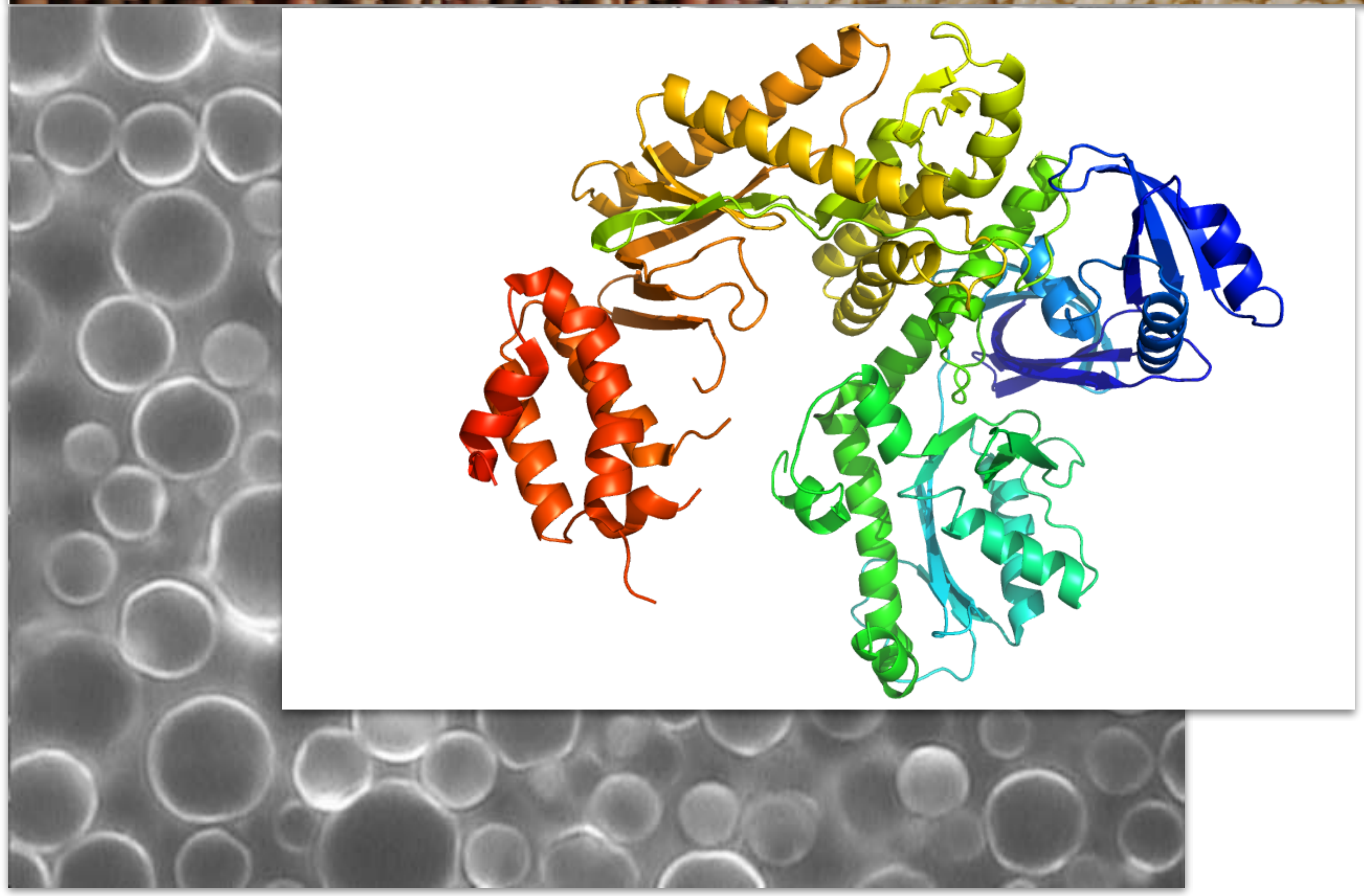
$\mathcal{O}(\vec{x})$ observable

review: MV, O. Raz, J. Bechhoefer, A. Lasanta & G. Teza, Phys. Reports (to appear)

Observations

Experiment
water
clathrate hydrates
granular fluids
colloids in optical lattices
polymers
magnetic alloys
qubits

Numerics
granular fluids
spin glasses
polymers
quantum systems
nanotube resonators
cold gasses
magnetic systems
systems with no equipartition
molecular dynamics of water molecules
molecular gasses

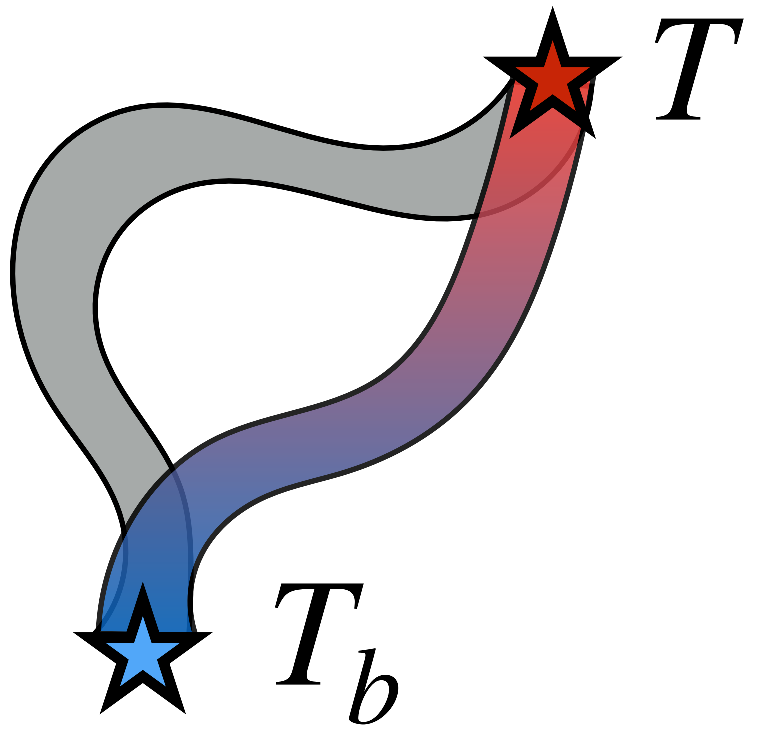


With water: it is complicated

How to think about the Mpemba effect?

General physical system: relaxation dynamics

mathematical description



Master eq.

$$\partial_t \mathbf{p} = R\,\mathbf{p}$$

$p_x(t)$ probability of the system to be at a phase space point x at time t

R relaxation rate matrix

Detailed Balance

$$R_{xy}\pi_y^{T_b} = R_{yx}\pi_x^{T_b}$$

Boltzmann distribution: $\pi_x^{T_b} \propto e^{-\beta_b E_x}$

equilibration: $\lim_{t\to\infty} \mathbf{p}(t) = \boldsymbol{\pi}^{T_b}$

initial condition: $\mathbf{p}(t=0) = \boldsymbol{\pi}^{T}$

(details will depend on the system: Liouville eq., Fokker-Planck eq., Master eq.)

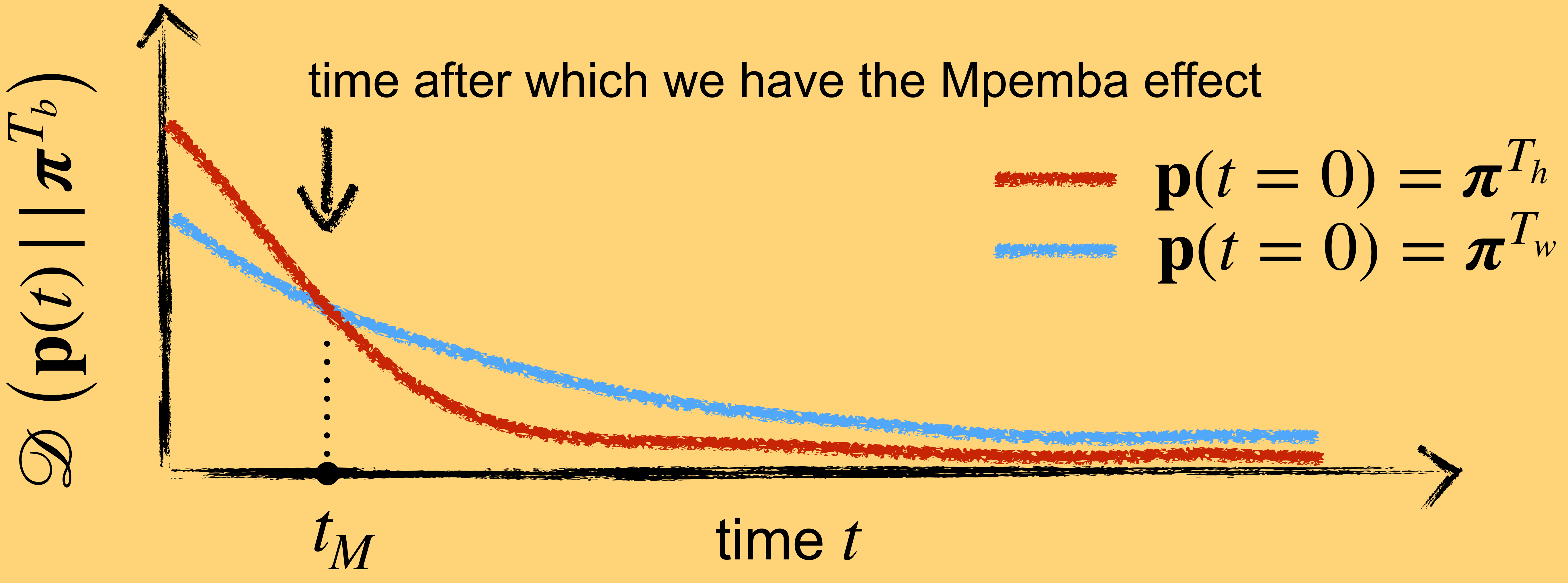
How to measure the effect?

A measure of how close the system is to equilibrium

Kullback-Leibler divergence

$$\mathscr{D}\left(\mathbf{p}(t)\,||\,\boldsymbol{\pi}^{T_b}\right) \equiv \sum_x p_x \ln\left(\frac{p_x}{\pi_x^{T_b}}\right) = \Sigma(\infty) - \Sigma(t)$$

$\Sigma(t)$ total amount of entropy produced at t


time after which we have the Mpemba effect

Eigenvalue problem

relaxation rate matrix $R(T_b)$

$$R\,\mathbf{v}_\mu = \lambda_\mu \mathbf{v}_\mu \qquad \mathbf{u}_\mu R = \lambda_\mu \mathbf{u}_\mu \qquad \lambda_1 = 0 > \lambda_2 \geq \lambda_3 \geq \dots$$

$$\mathbf{p}(t) = \boldsymbol{\pi}^{T_b} + \sum_{\mu>1} a_\mu \mathbf{v}_\mu e^{\lambda_\mu t}$$

$$a_\mu(T, T_b) = \frac{\mathbf{u}_\mu \cdot \boldsymbol{\pi}^T}{\mathbf{u}_\mu \cdot \mathbf{v}_\mu}$$

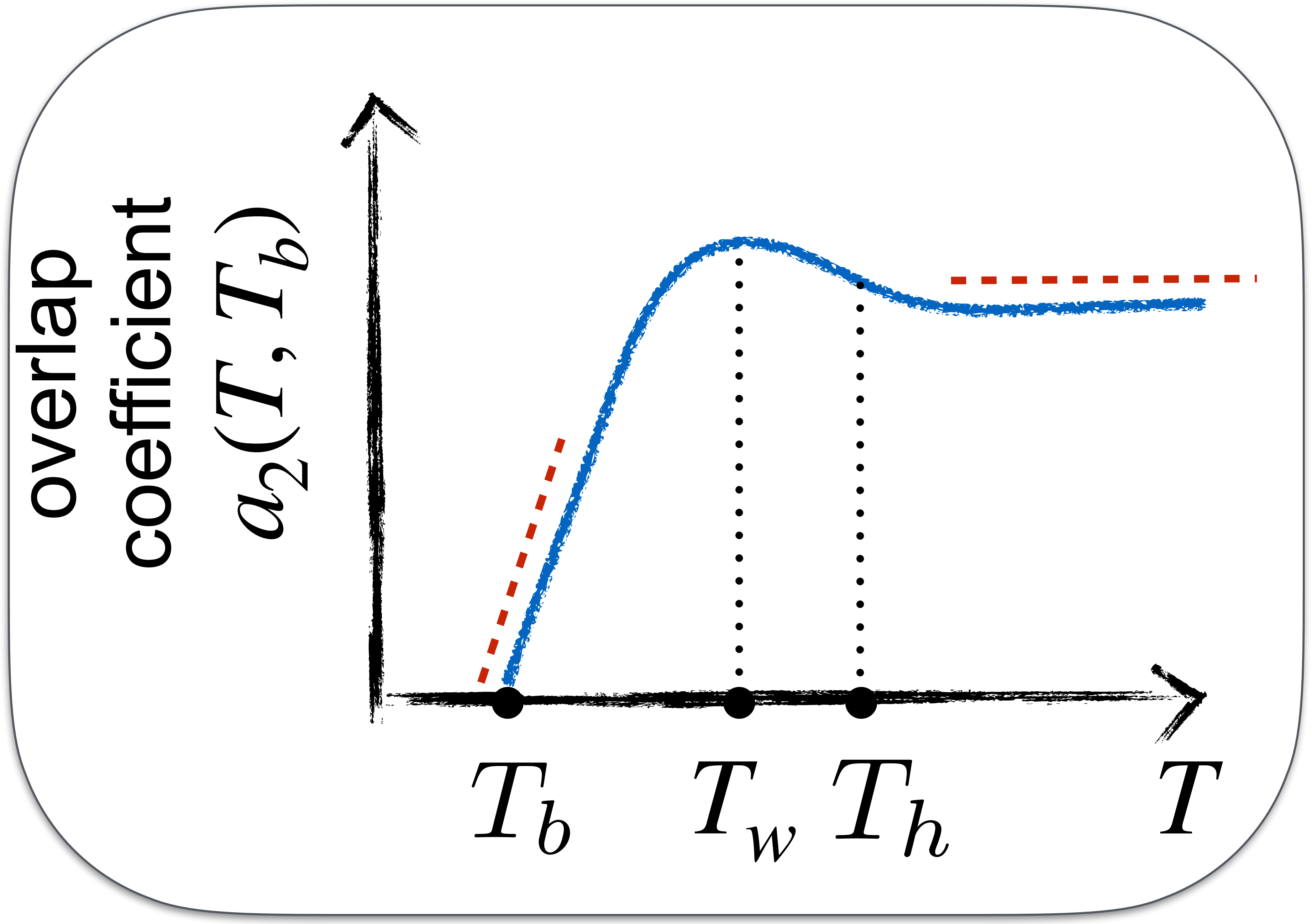
initial condition $\boldsymbol{\pi}^T$

assumption: $\lambda_2 > \lambda_3$

long time limit: $\mathbf{p}(t) \approx \boldsymbol{\pi}^{T_b} + a_2 \mathbf{v}_2 e^{\lambda_2 t}$

Mpemba effect condition: $|a_2(T_h)| < |a_2(T_w)|$

Z. Lu & O. Raz, PNAS 2016



Our questions

- How often does the effect happen?

  Why should we care?

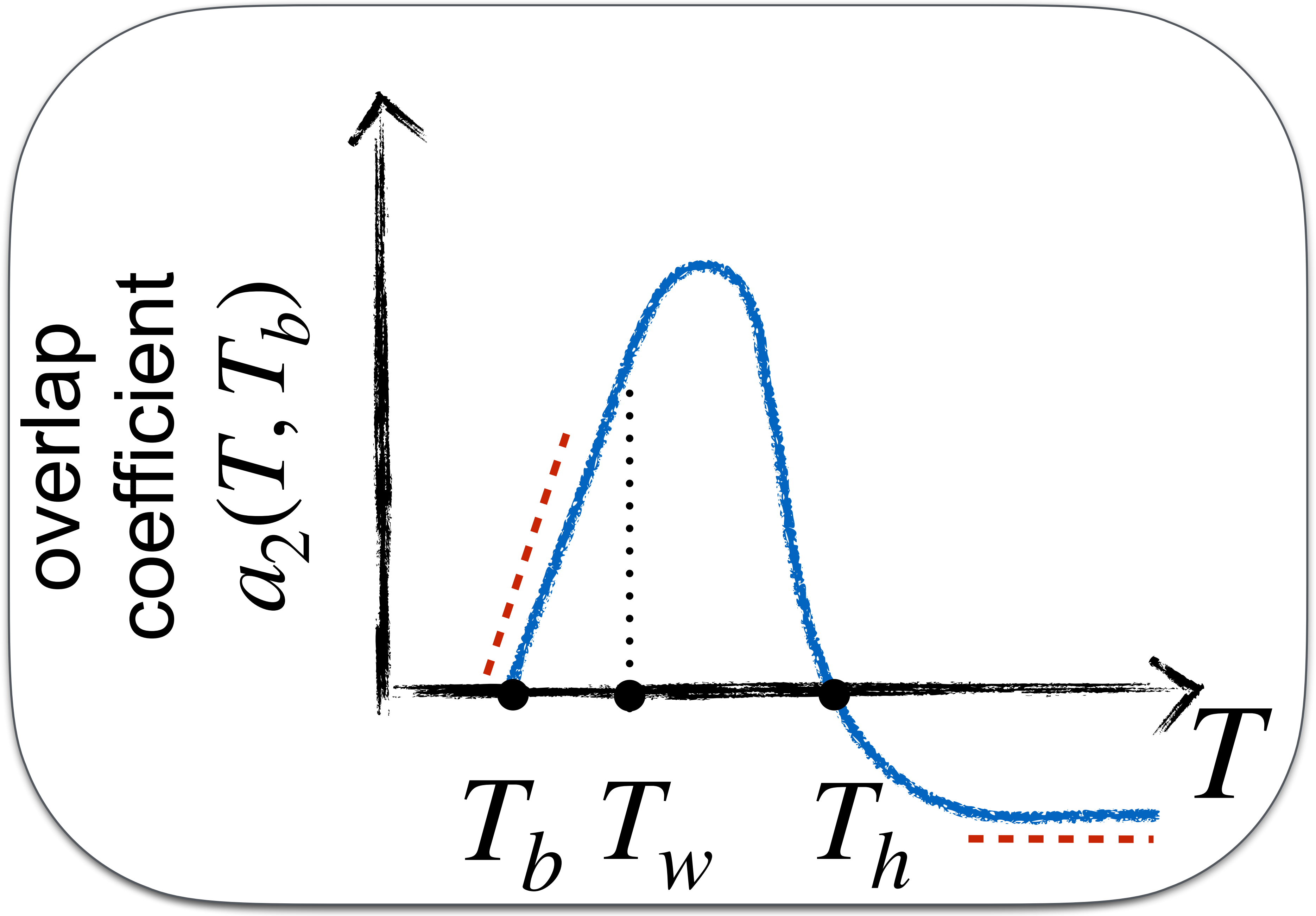
- Does the effect happen in thermodynamic limit?

  Or is it a finite size effect?

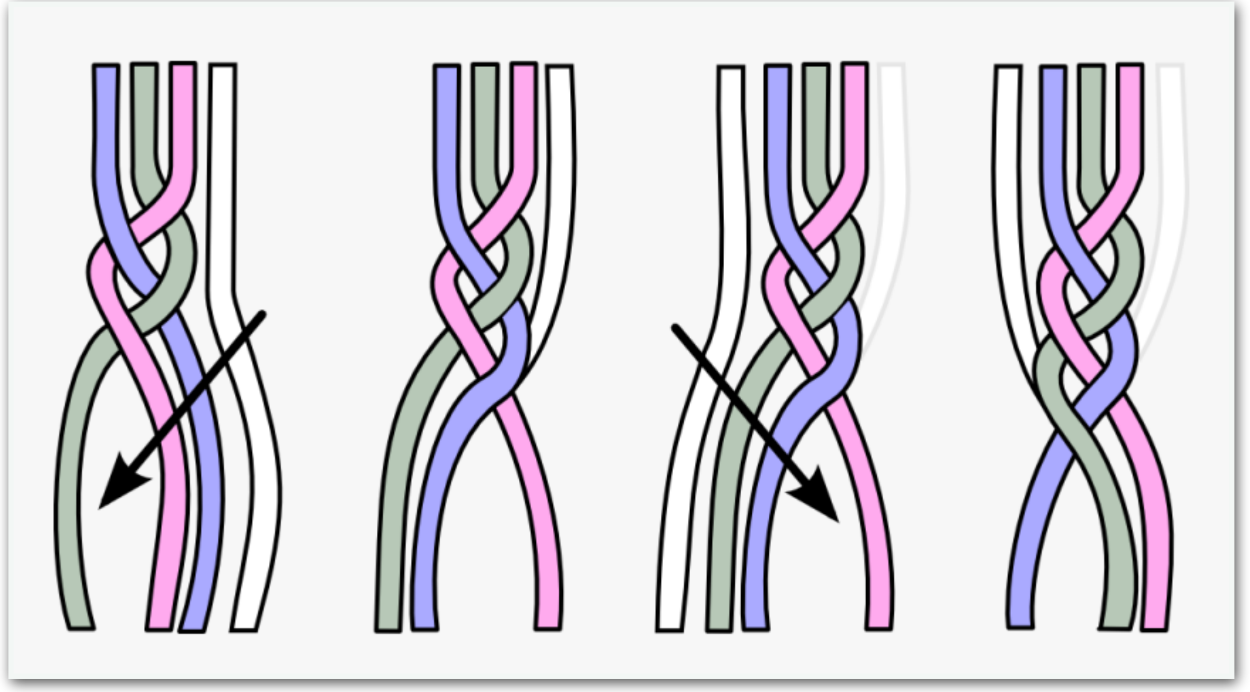
- Intuition

  When does the Mpemba effect happen?

New regime — exponential faster cooling



- relaxation time shortens from $-\lambda_2^{-1}$ to $-\lambda_3^{-1}$
- topological properties

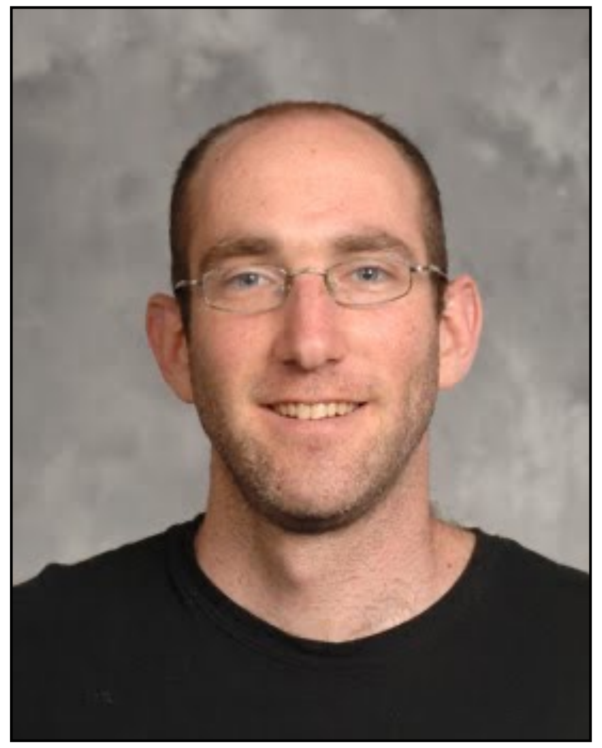


STRONG MPEMBA EFFECT

theoretical prediction *I. Klich, O. Raz, O. Hirschberg, & MV, PRX, 2019*

first experimental observation *Kumar A. & Bechhoefer J., Nature, 2020*

Israel Klich



Oren Raz
WIS

Ori Hirschberg
NYU

How often does the effect happen?

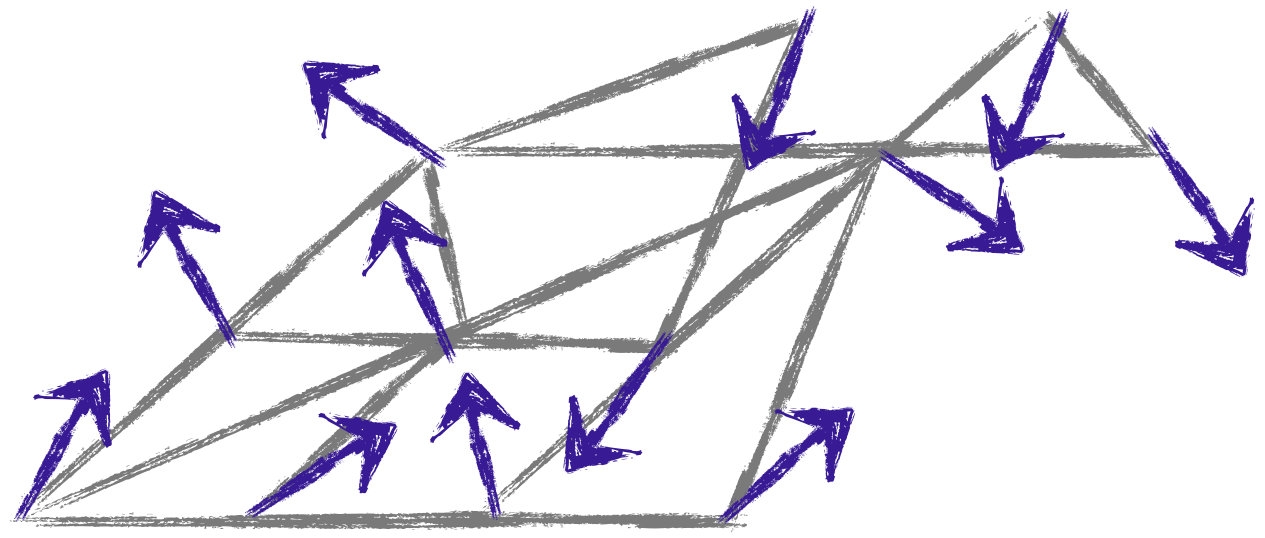
Why should we care?

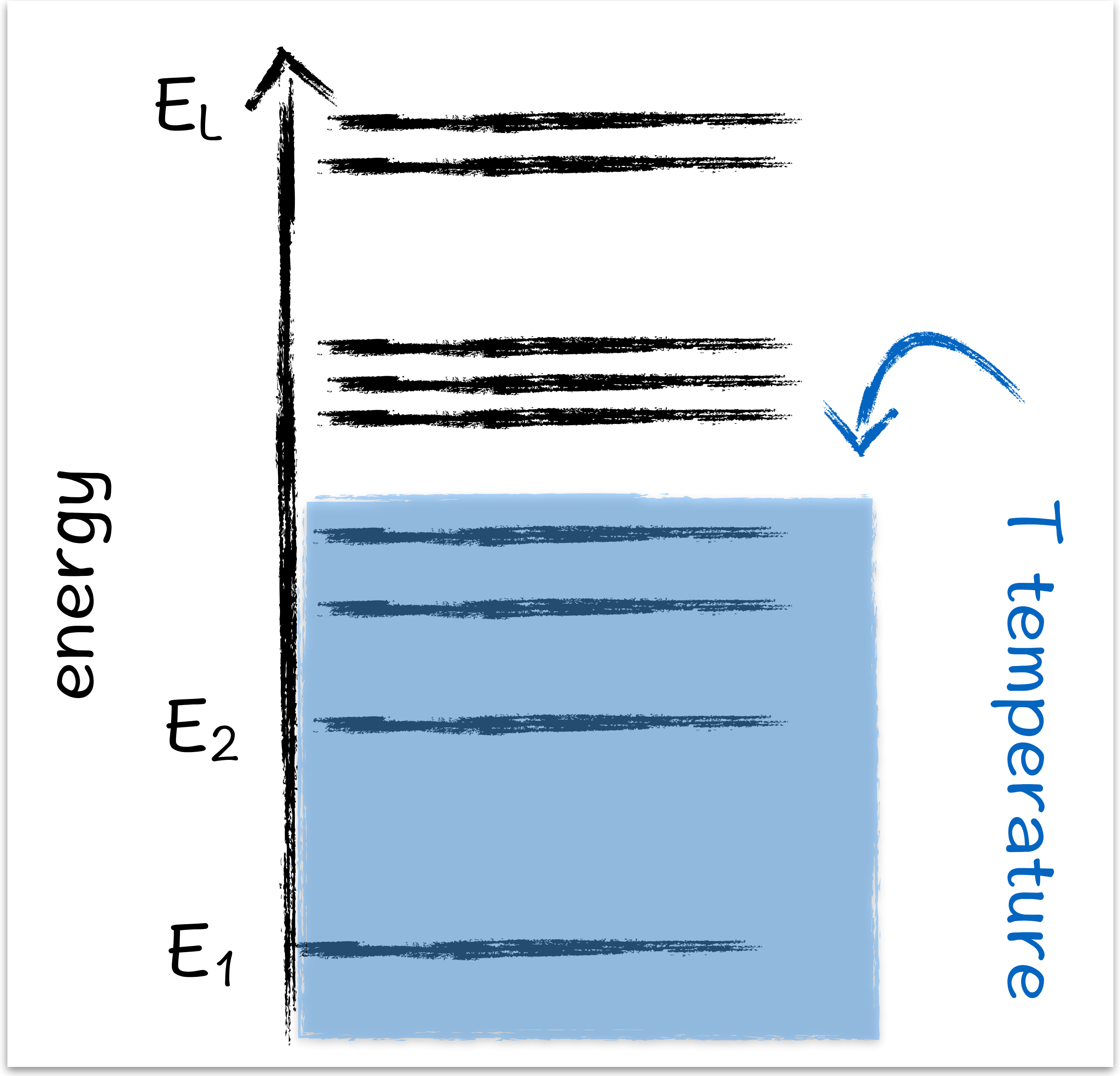
Random Energy Model

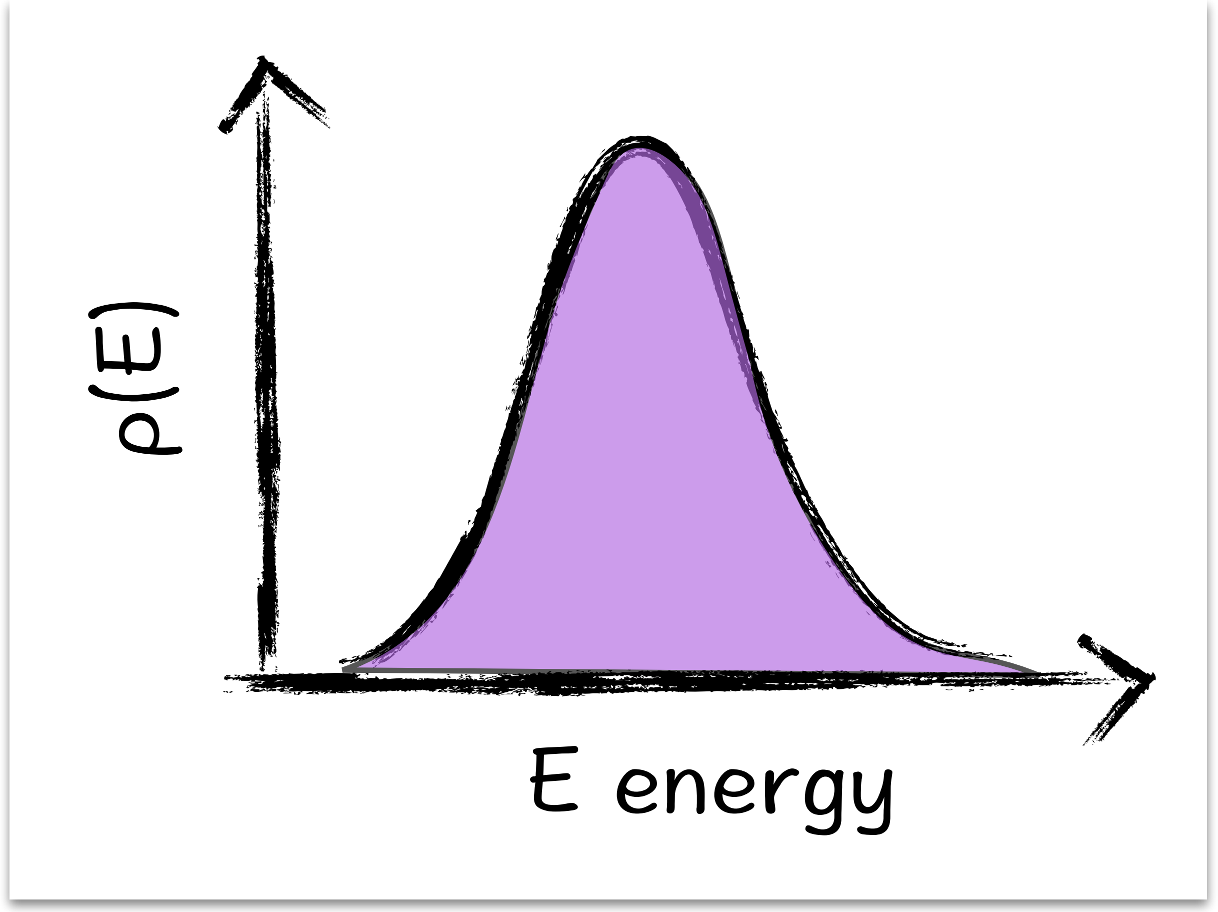
B. Derrida 1981; D. Gross & M. Mezard, 1984

simple model of a disordered system

spin glass
disordered spins with often frustrated interactions





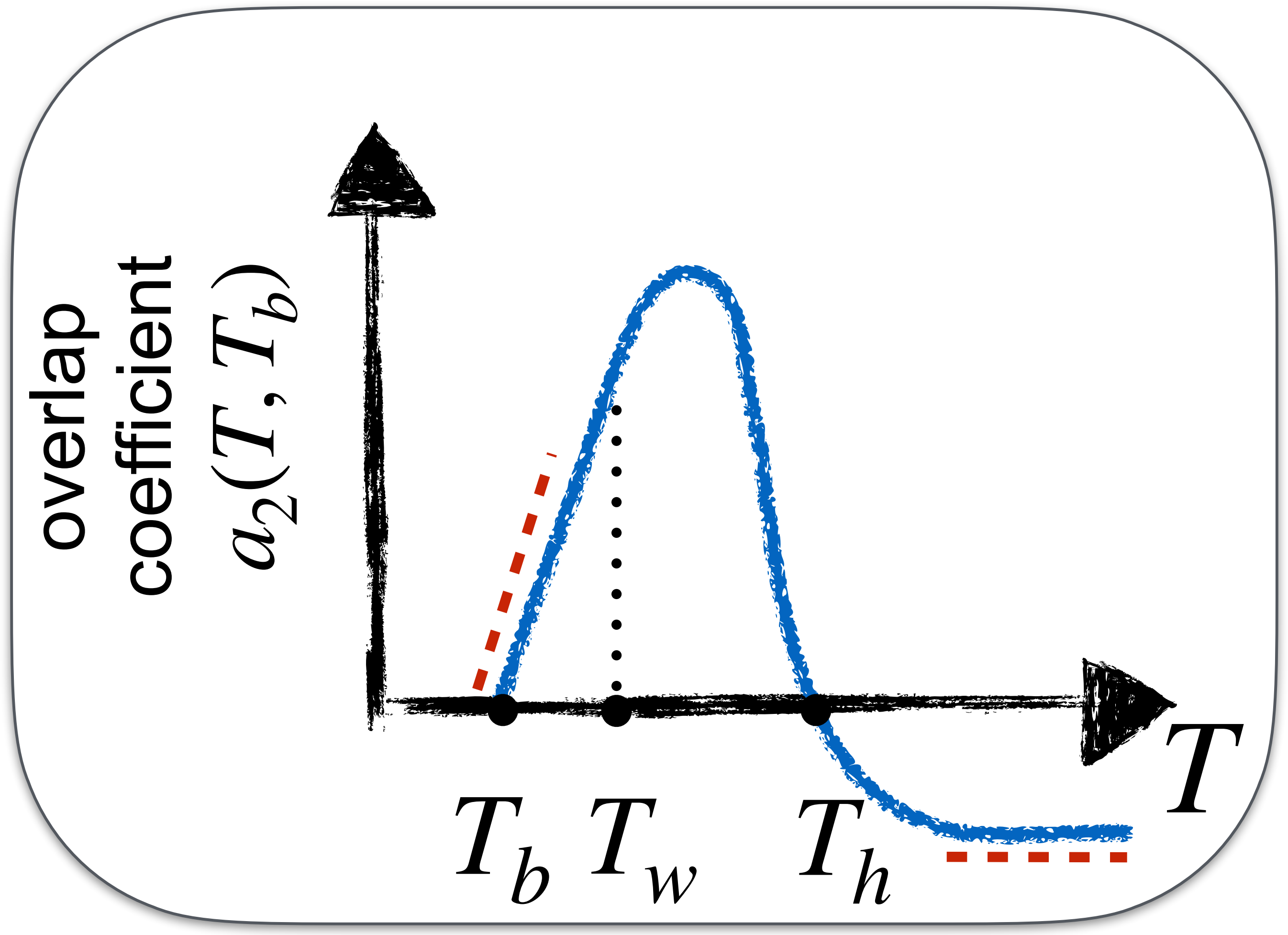


- energies $\{E_i\}$ — random variables drawn from $\rho(E)$
- “sample” — a particular realization

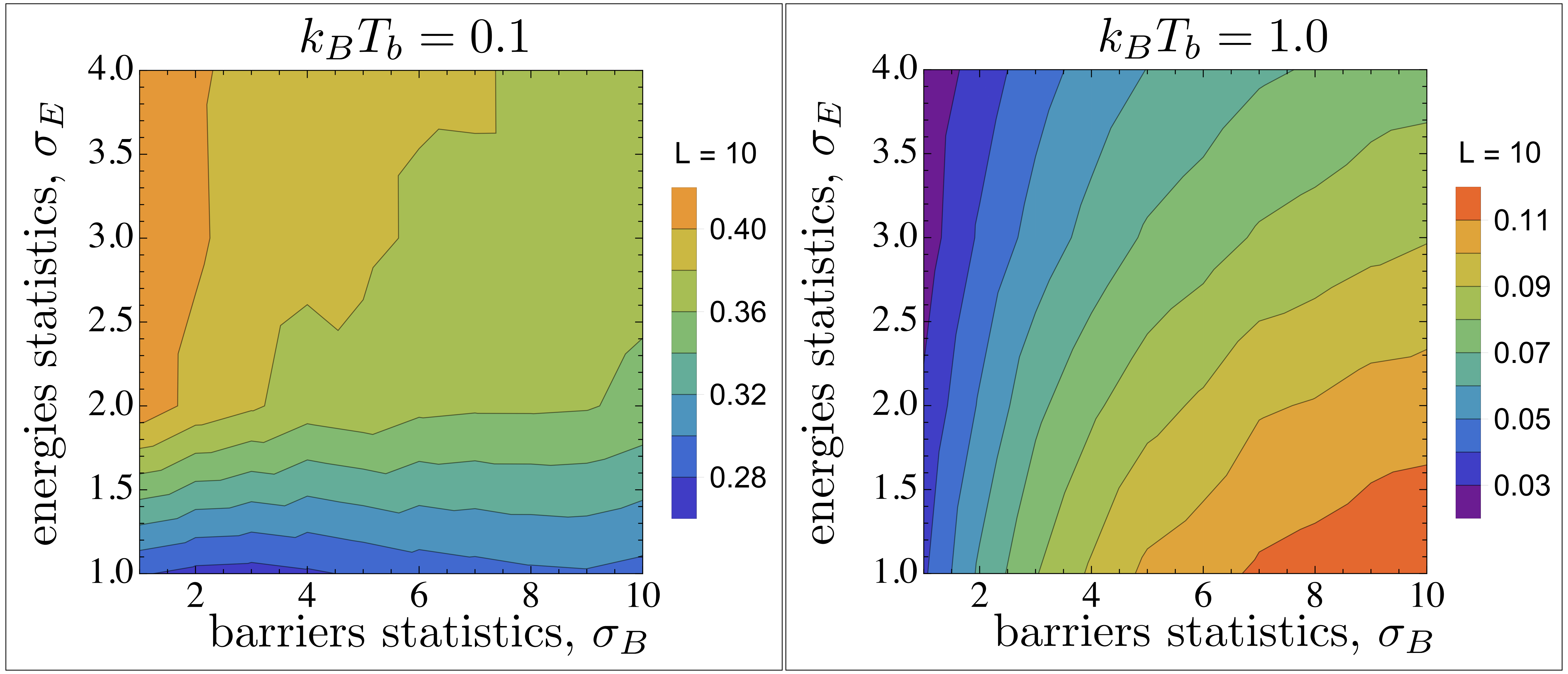
Likelihood of the Mpemba effect in Random Energy Model

$$R_{ij} \propto e^{-\beta_b(B_{ij}-E_j)}$$

energies E_j and “barriers” B_{ij}



Lower bound for the Mpemba effect: Prob $\left(-\partial_T a_2|_{T=T_b} a_2(T=\infty) > 0\right)$



each point is averaged over 10^5 realizations, number of levels: $L = 10$, energies E_j and “barriers” B_{ij} chosen from distributions $\mathcal{N}(0,\sigma_E^2)$ and $\mathcal{N}(0,\sigma_B^2)\theta(B_{ij})$

I. Klich, O. Raz, O. Hirschberg, & MV, PRX, 2019

Dauntingly hard disorder to average over barriers

rate matrix:

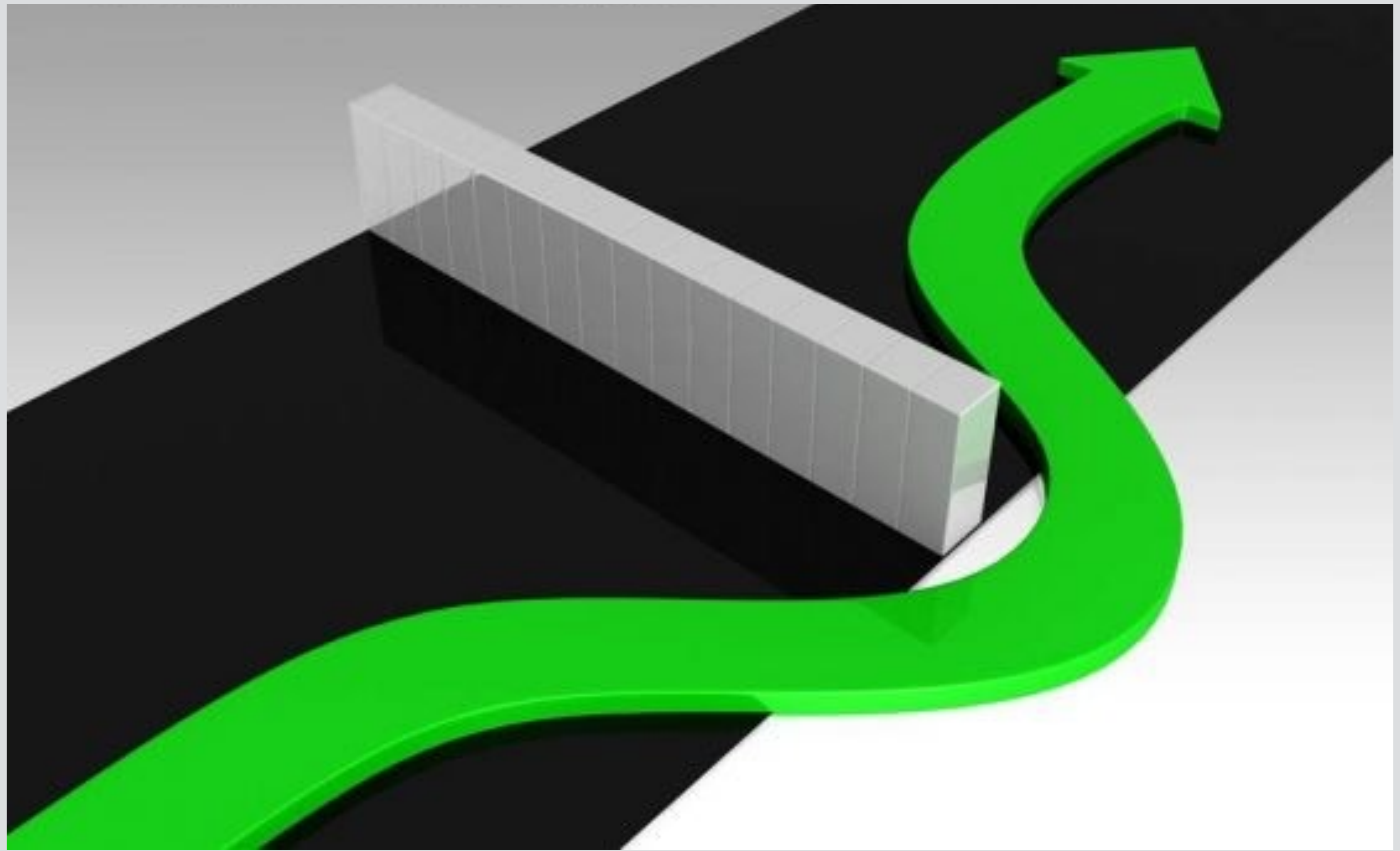
$$R_{ij} e^{-\beta_b E_j} = R_{ji} e^{-\beta_b E_i}$$

$$R_{ij} = \begin{cases} e^{-\beta_b (B_{ij} - E_j)} & i \neq j \\ -\sum_{k \neq j} R_{kj} & i = j \end{cases}$$

$$B_{ij} = B_{ji}$$

One needs to know the 2nd eigenvector of $R(T_b)$ for an ensemble of B_{ij}

However, we can try something ORTHOGONAL!



2nd eigenvector candidate:

$$\vec{f}_2(\vec{X}) = \vec{X} - \frac{\vec{X} \cdot \vec{f}_1}{||\vec{f}_1||^2} \vec{f}_1$$

random vector $\vec{X}$ with x_i iid Gaussian

Strong Mpemba effect - at least two zeros of a_2

$$a_2(T) = \frac{\vec{f}_2 \cdot F^{1/2} \vec{\pi}(T)}{\vec{f}_2 \cdot \vec{f}_2}$$

estimating the lower bound for the Mpemba Index

$$-\partial_T a_2 |_{T=T_b} a_2(T = \infty) \propto (\vec{X} \cdot \vec{u})(\vec{X} \cdot \vec{w})$$

$\vec{u}, \vec{w}$ depend on energy levels only

Averaging over random vectors $\overrightarrow{X}$ with Gaussian

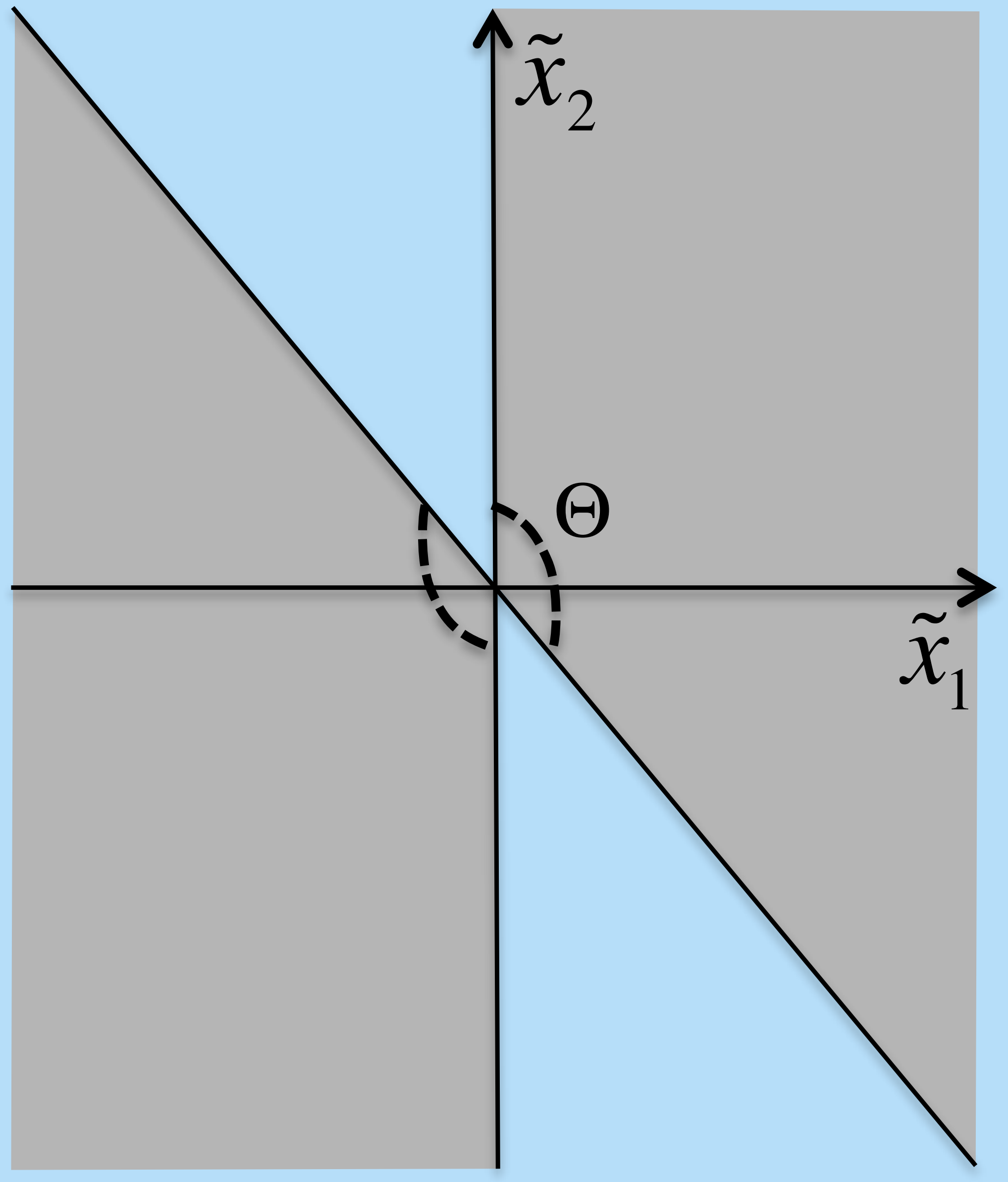
Isotropic ensemble

$$X = \tilde{x}_1 u + \tilde{x}_2 \frac{w - \frac{(u\cdot w)}{||u||^2} u}{\sqrt{||w||^2 - \frac{(w\cdot u)^2}{||u||^2}}} + \text{orthogonal terms to } u, w$$

$$\text{Prob}\left((X\cdot u)(X\cdot w) > 0\right) =$$

$$\text{Prob}\left(\tilde{x}_1^2 (u\cdot w) + \tilde{x}_1 \tilde{x}_2 |u\cdot w| K > 0\right)$$

$$K \equiv \sqrt{\frac{||u||^2 ||w||^2}{(w\cdot u)^2} - 1}$$



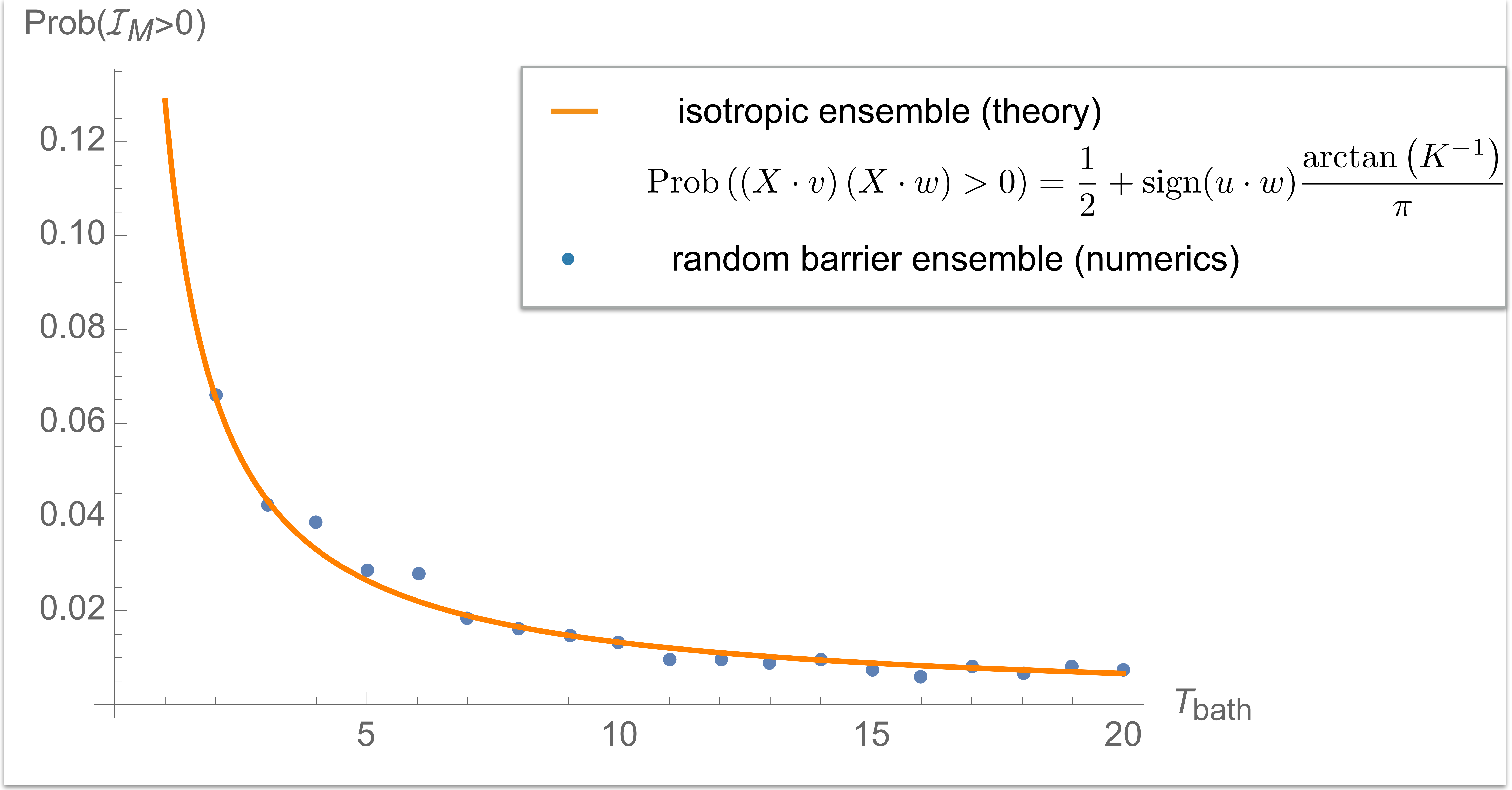
the grey area over the total area:

$$\text{Prob}\left((X\cdot v)(X\cdot w) > 0\right) = \frac{1}{2} + \text{sign}(u\cdot w)\frac{\arctan\left(K^{-1}\right)}{\pi}$$

Probability of the strong Mpemba effect

a particular energy realization, n=10 energy levels,

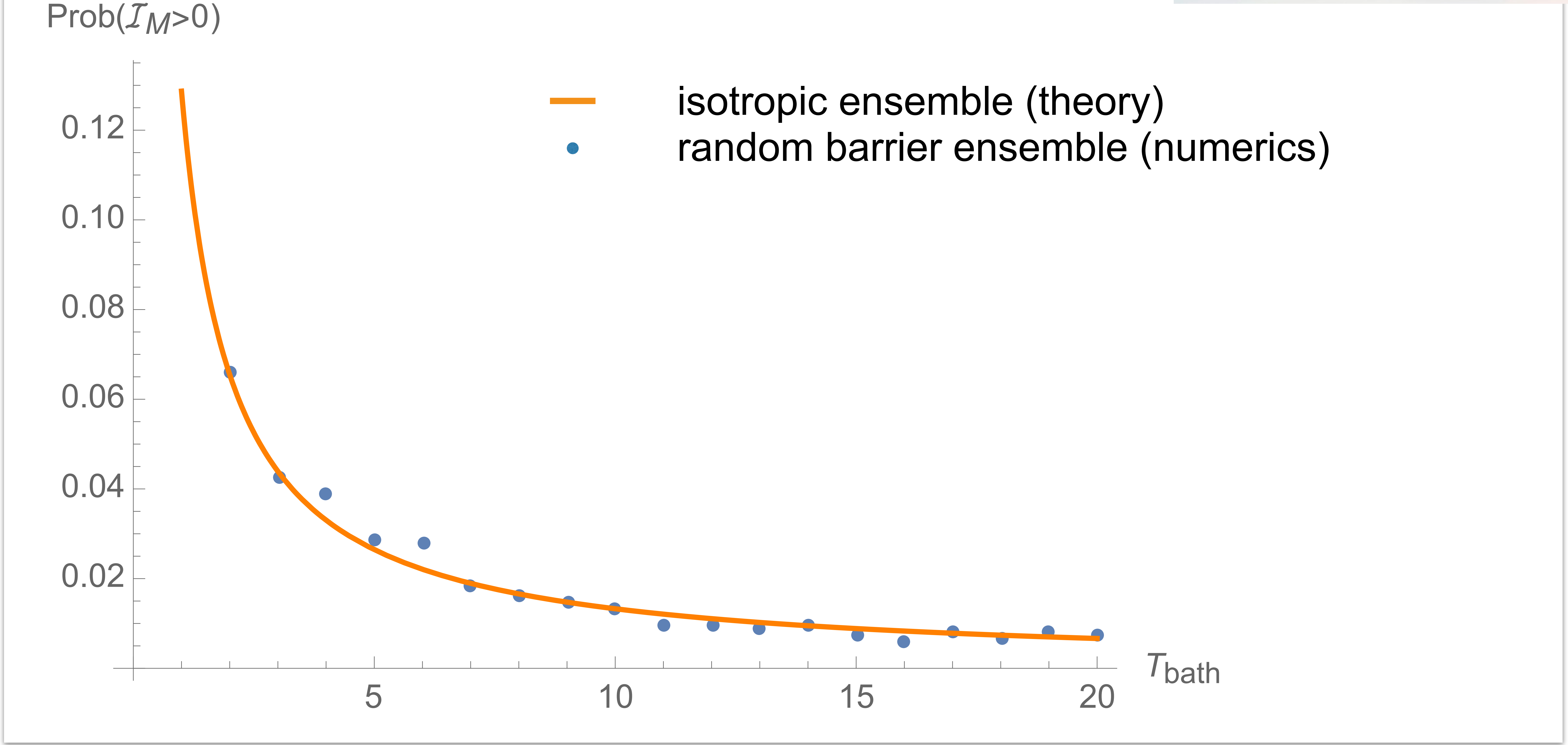
(random barriers with N(0,25), each point 4000 realizations)



works well: pdf of barriers is wider then pdf of energies, T higher then energy spread

Note!

two very different ensembles, yet they match well in not-so-low T range, for wide barrier distribution.



large T limit: $\text{Prob}(\mathcal{I}_M > 0) \sim \dfrac{C_E}{T_b}$

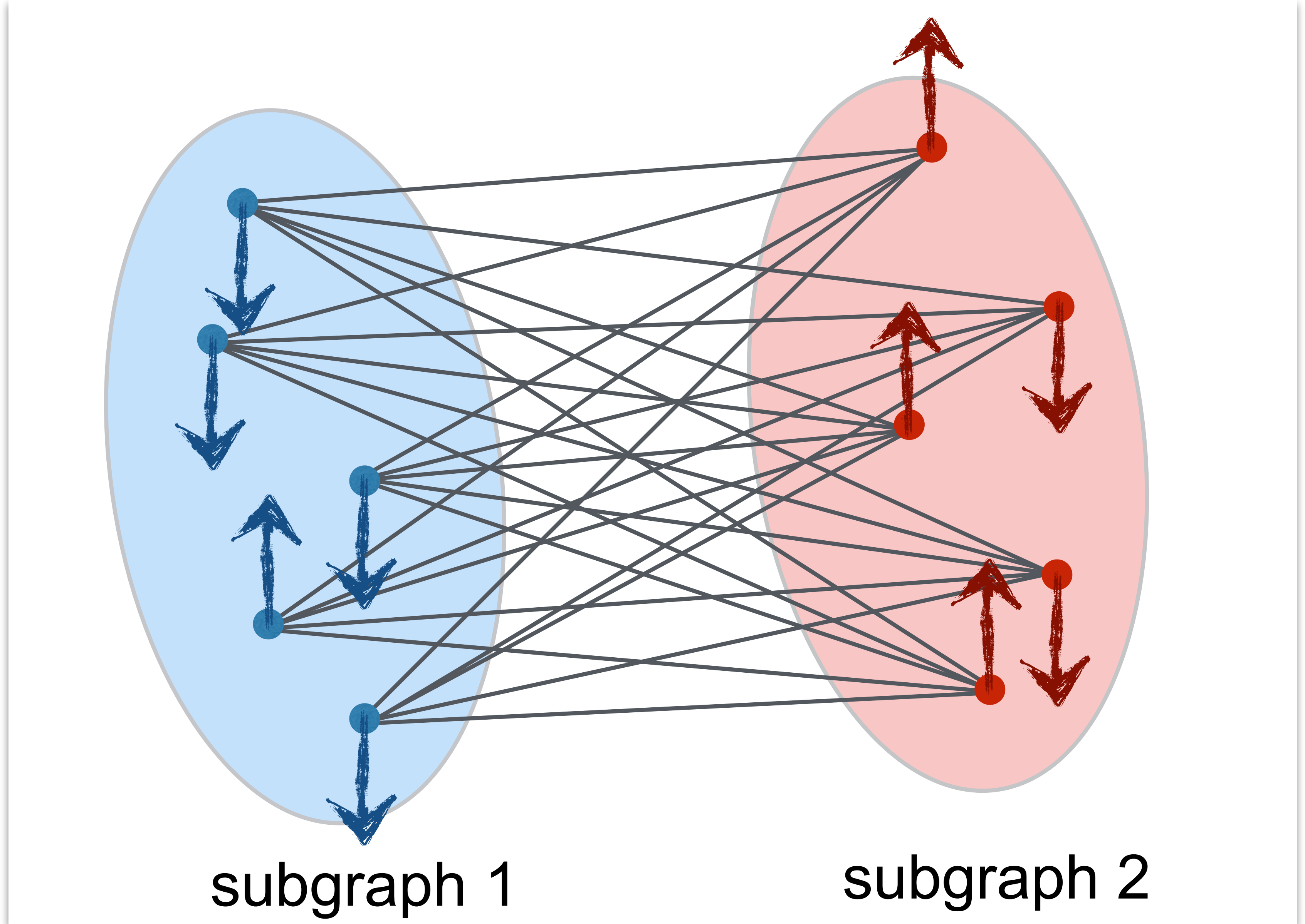
$$C_E = \frac{1}{\pi|(\bar{E}^2 - \overline{E^2})|}\left(8\bar{E}^6 - 24\bar{E}^4\overline{E^2} + 20\bar{E}^2\overline{E^2}^2 - 5\overline{E^2}^3 + 4\bar{E}^3\overline{E^3} - 2\bar{E}\overline{E^2E^3} - \overline{E^3}^2 - \bar{E}^2\overline{E^4} + \overline{E^2E^4}\right)^{1/2}$$

Does the effect happen in thermodynamic limit?

Or is it a finite size effect?

Mean field antiferromagnet

N Ising spins (states ± 1)



Hamiltonian

$$\mathscr{H}(x_1, x_2) = -\frac{N}{2}\left[Jx_1x_2 + \mu H(x_1 + x_2)\right]$$

H magnetic field
$J \equiv -1$interaction strength
$\mu \equiv 1$ magnetic moment
x_i magnetization on subgraph i

Glauber dynamics

- choose a spin at random
- only transitions to neighboring states are allowed

$$R^{u_1}(x_1, x_2) = \frac{1 - x_1}{2\left[1 + e^{-2\beta_b(x_2 + H)}\right]}$$ flip a spin up in subgraph 1

$$R^{u_2}(x_1, x_2) = \frac{1 - x_2}{2\left[1 + e^{-2\beta_b(x_1 + \mu H)}\right]}$$ flip a spin up in subgraph 2

$$R^{d_1}(x_1, x_2) = \frac{1 + x_1}{2\left[1 + e^{2\beta_b(x_2 + \mu H)}\right]}$$ flip a spin down in subgraph 1

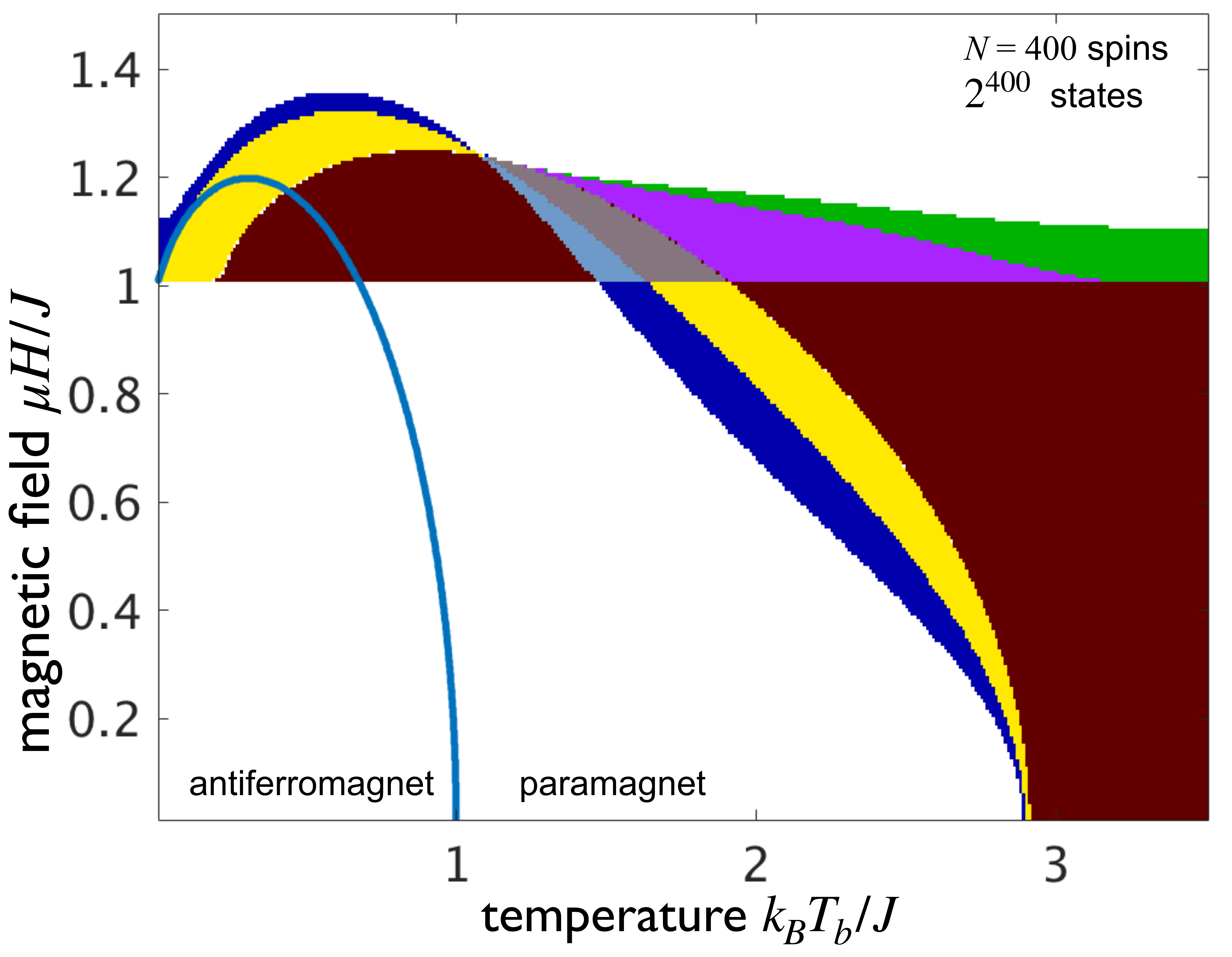
$$R^{d_2}(x_1, x_2) = \frac{1 + x_2}{2\left[1 + e^{2\beta_b(x_1 + \mu H)}\right]}$$ flip a spin down in subgraph 2

Mpemba effect phase diagram for the antiferromagnet

I. Klich, O. Raz, O. Hirschberg, & MV, PRX, 2019

$\mathscr{I}^h_M =$ # of zeros below T_b

$\mathscr{I}^c_M =$ # of zeros above T_b



- ⬜ No effect
- 🟦 Weak effect cooling & no effect heating,
- 🟩 Strong effect heating $\mathscr{I}^h_M = 1$ & Weak effect cooling
- 🟫 Strong effect heating $\mathscr{I}^h_M = 1$ & no effect cooling
- 🟪 Weak effect heating & no effect cooling
- 🔵 Strong effect heating $\mathscr{I}^h_M = 2$ & no effect cooling
- ◼ Strong effect heating $\mathscr{I}^h_M = 1$ & Strong effect cooling $\mathscr{I}^c_M = 1$
- 🟨 Strong effect cooling $\mathscr{I}^h_M = 1$ & Weak effect heating

Weak Mpemba effect — nonmonotonic $a_2(T, T_b)$ as function of T

Strong Mpemba effect — zero of $a_2(T, T_b) = 0$

Relaxation trajectories in thermodynamics limit

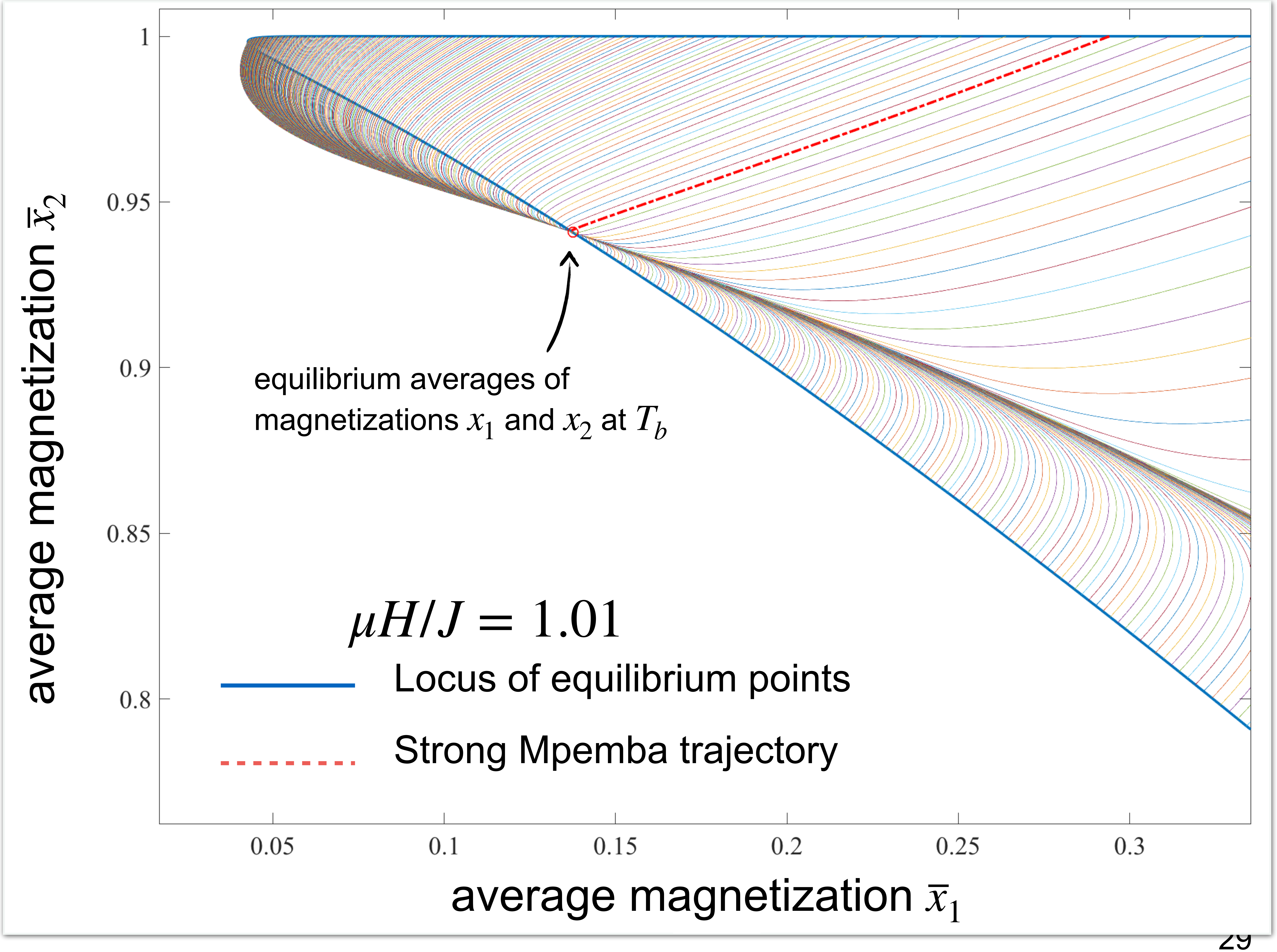
x_i magnetization on subgraph i

$$\partial_t p = \partial_{x_1}\left[\left(R^{d_1} - R^{u_1}\right)p\right] + \partial_{x_2}\left[\left(R^{d_2} - R^{u_2}\right)p\right]$$

$p(x_1, x_2, t)$ probability for the system to be at (x_1, x_2) at t

average magnetization

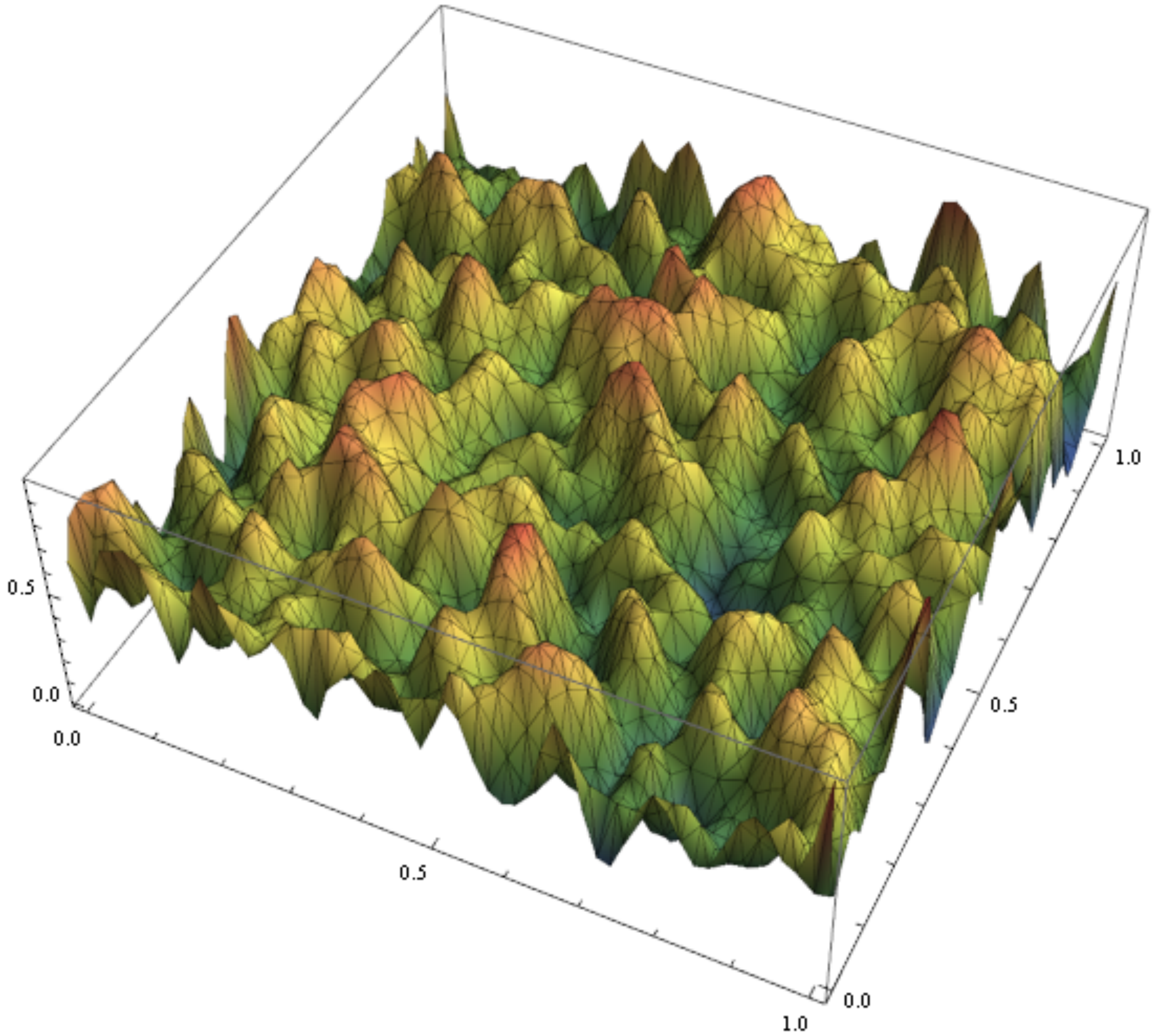
$$\bar{x}_i \equiv \iint x_i\, p(x_1, x_2, t)dx_1 dx_2$$

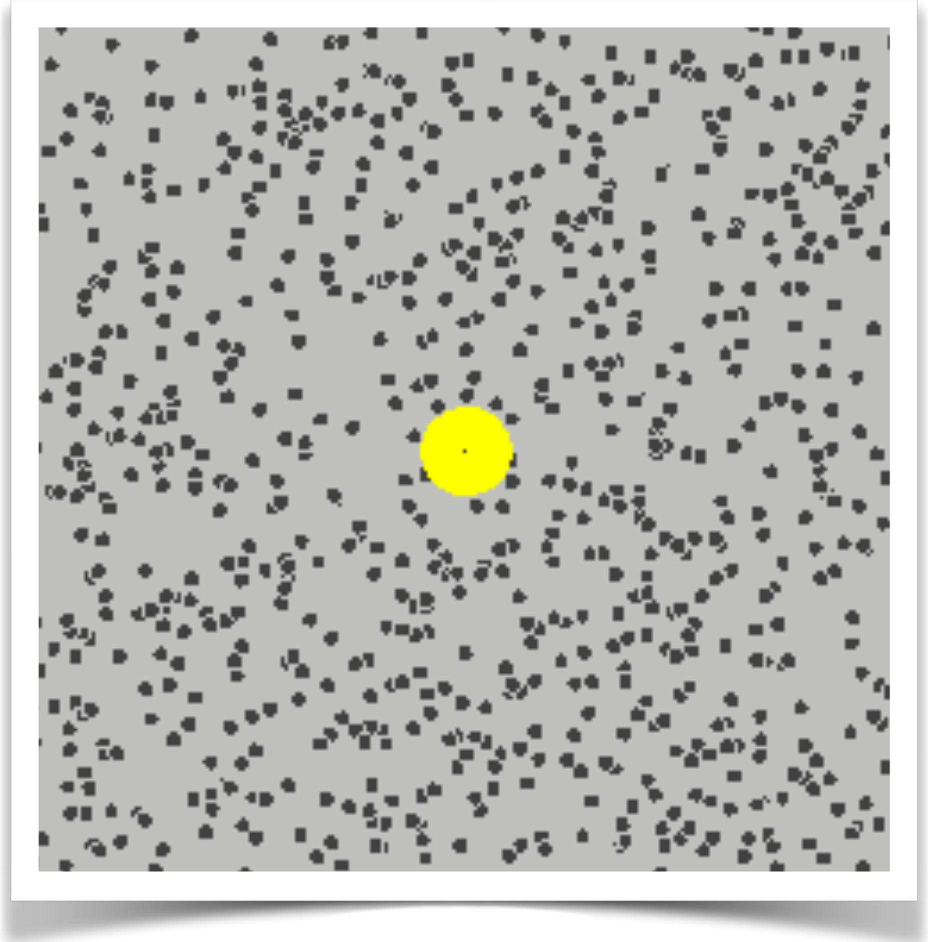


Intuition

When does the Mpemba effect happen?

Particle diffusion on a potential landscape





Brownian particle
wikipedia

Matthew R. Walker

overdamped Langevin eq.

$$\cancel{m\ddot{x}} - \gamma\dot{x} = -\,U'[x] + \xi(t)$$

thermal noise: $\langle \xi(t) \rangle = 0$

$$\langle \xi(t)\xi(t') \rangle = \gamma D(T_b)\delta(t - t')$$

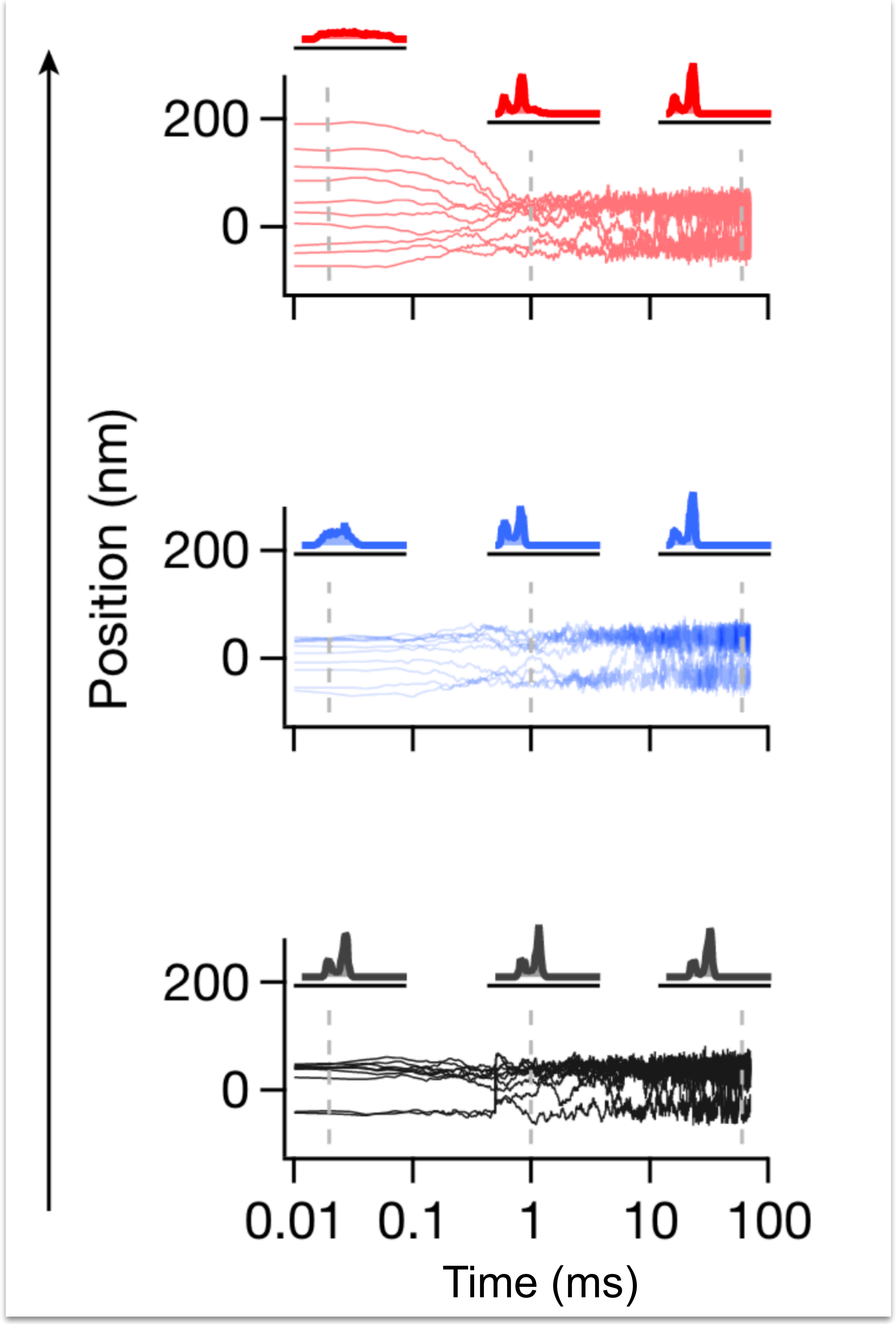
Fokker-Planck eq. $$\partial_t p(x,t) = \frac{\partial}{\partial x}\left(\frac{1}{\gamma}U'(x)p(x,t)\right) + D(T_b)\frac{\partial^2}{\partial x^2}p(x,t)$$

diffusion coefficient $D(T_b) = \frac{k_B T_b}{\gamma m}$

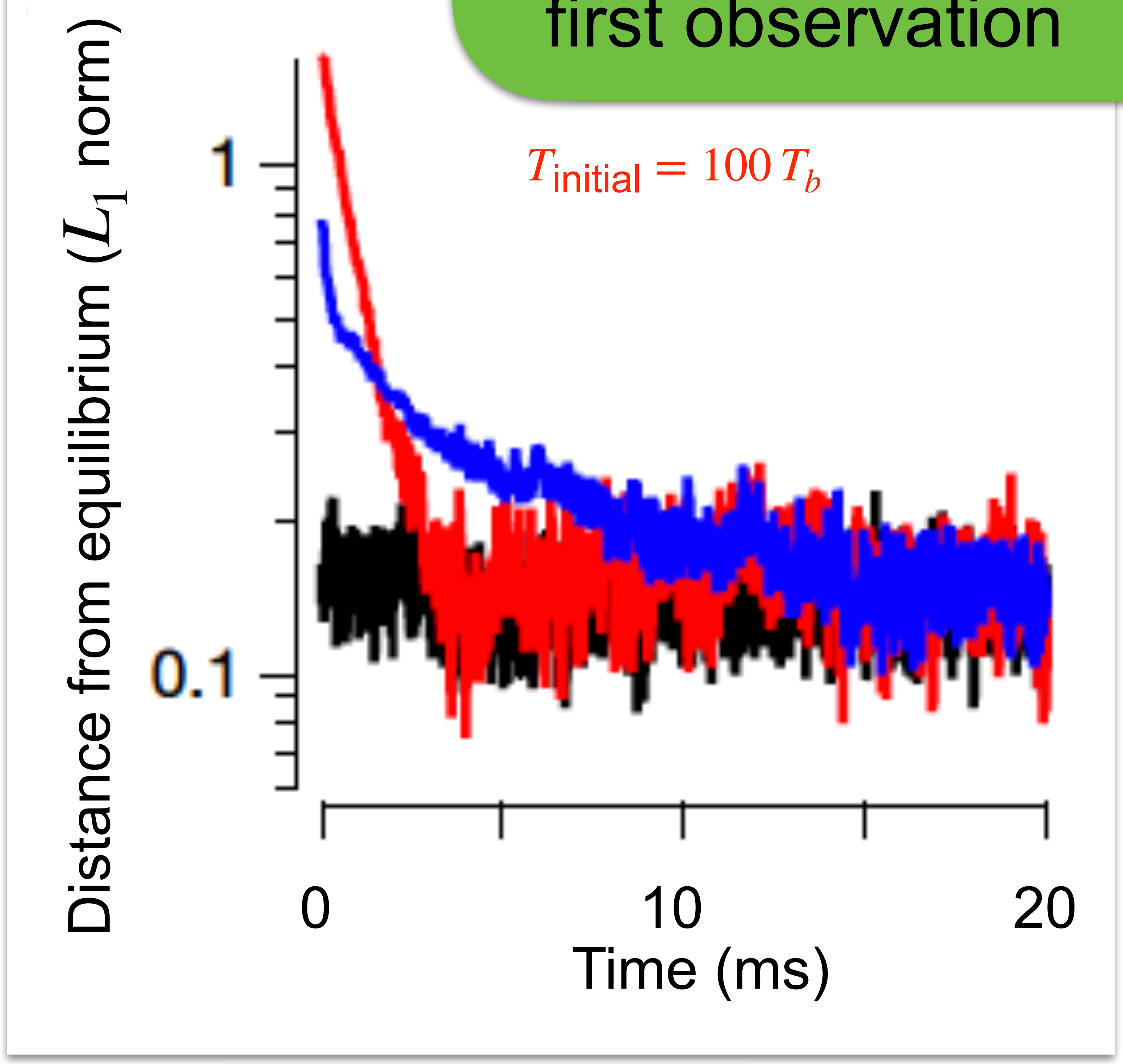
initial condition: $p(0,x) \propto e^{-\frac{U(x)}{k_B T}}$

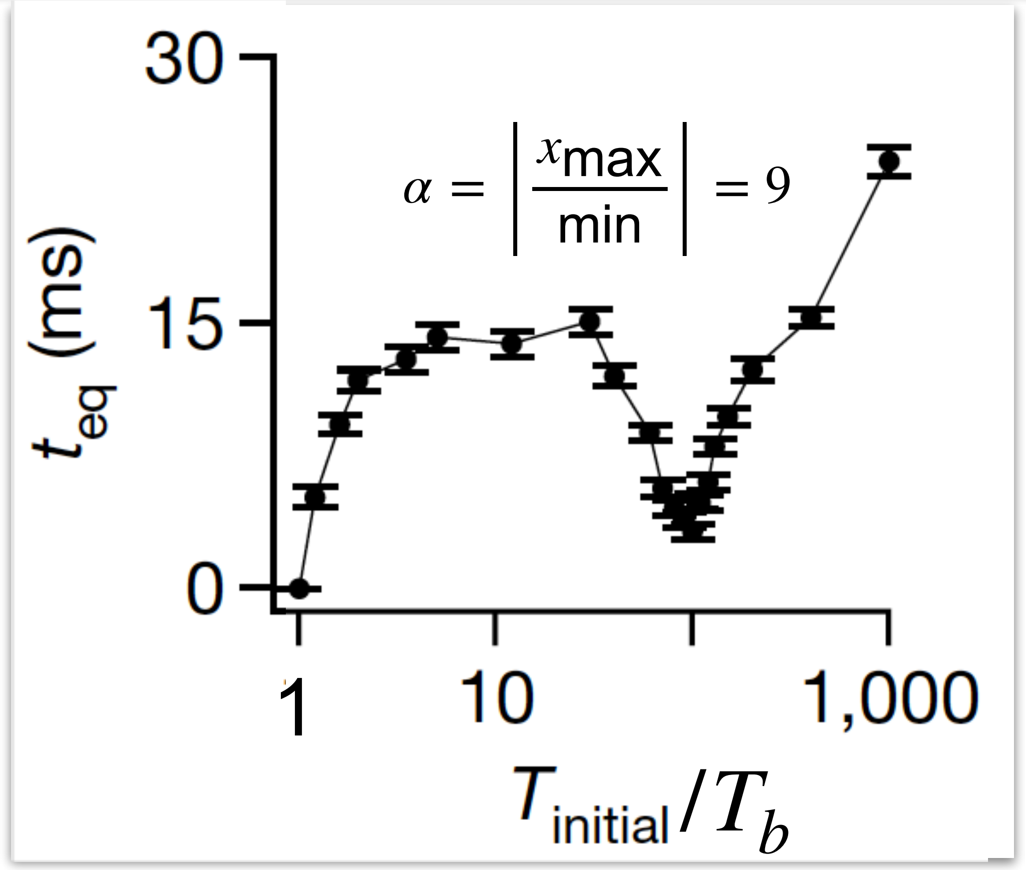
Experiment: Colloid in an optical trap

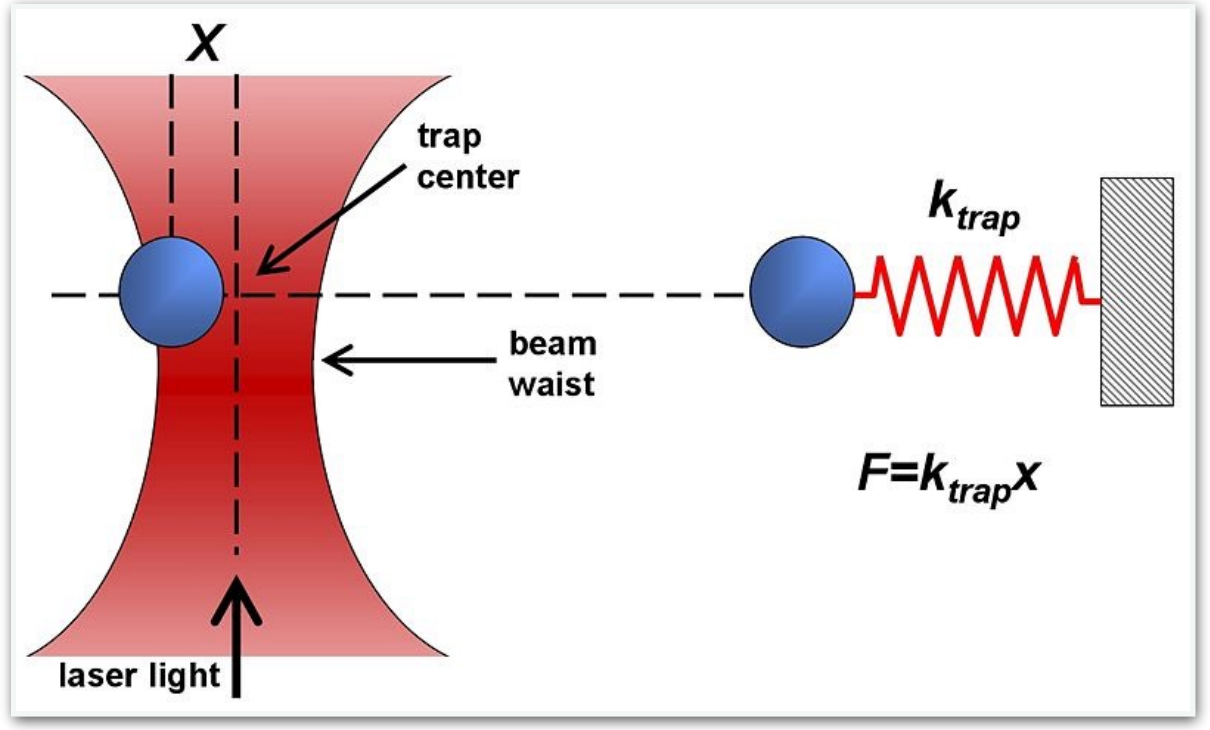
Kumar A. & Bechhoefer J., Nature, 2020

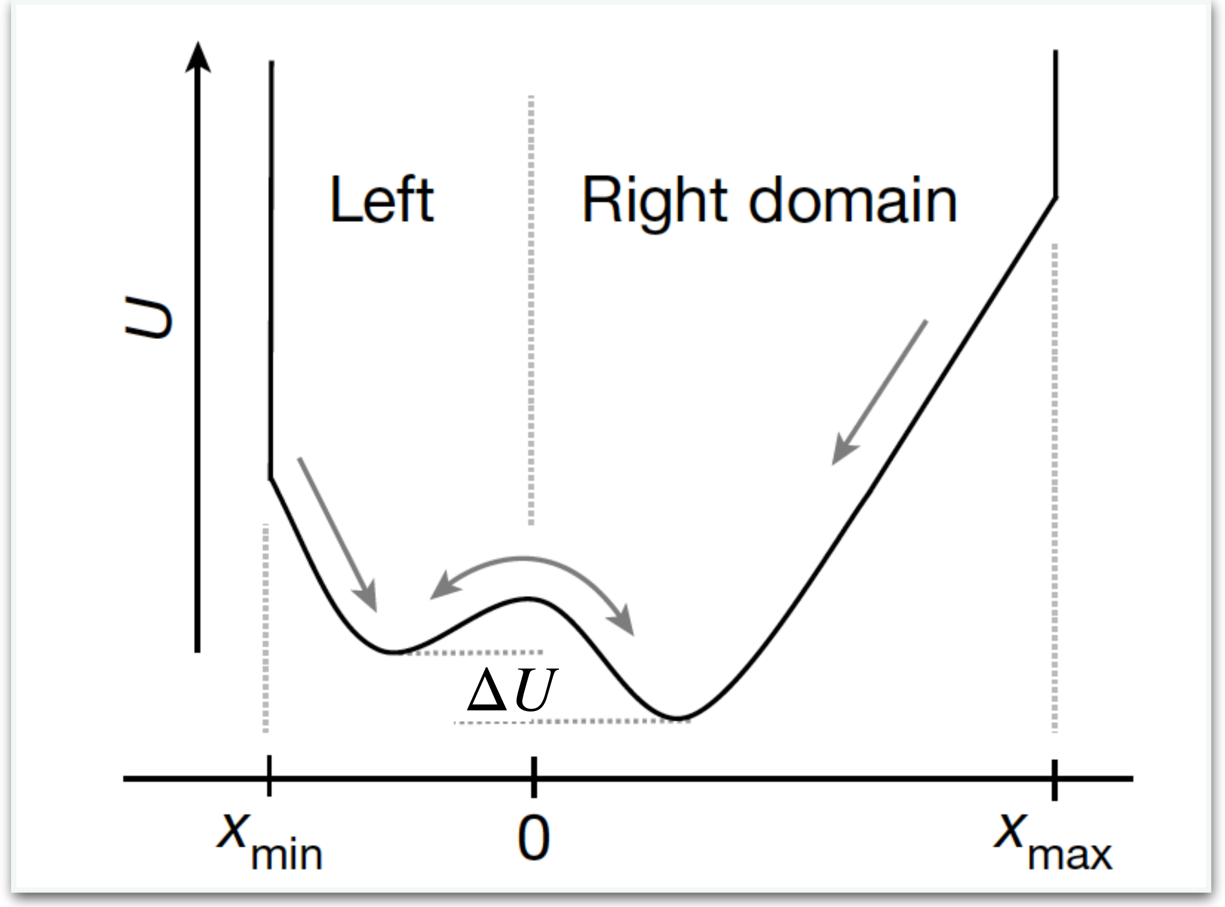


Strong Mpemba effect
first observation



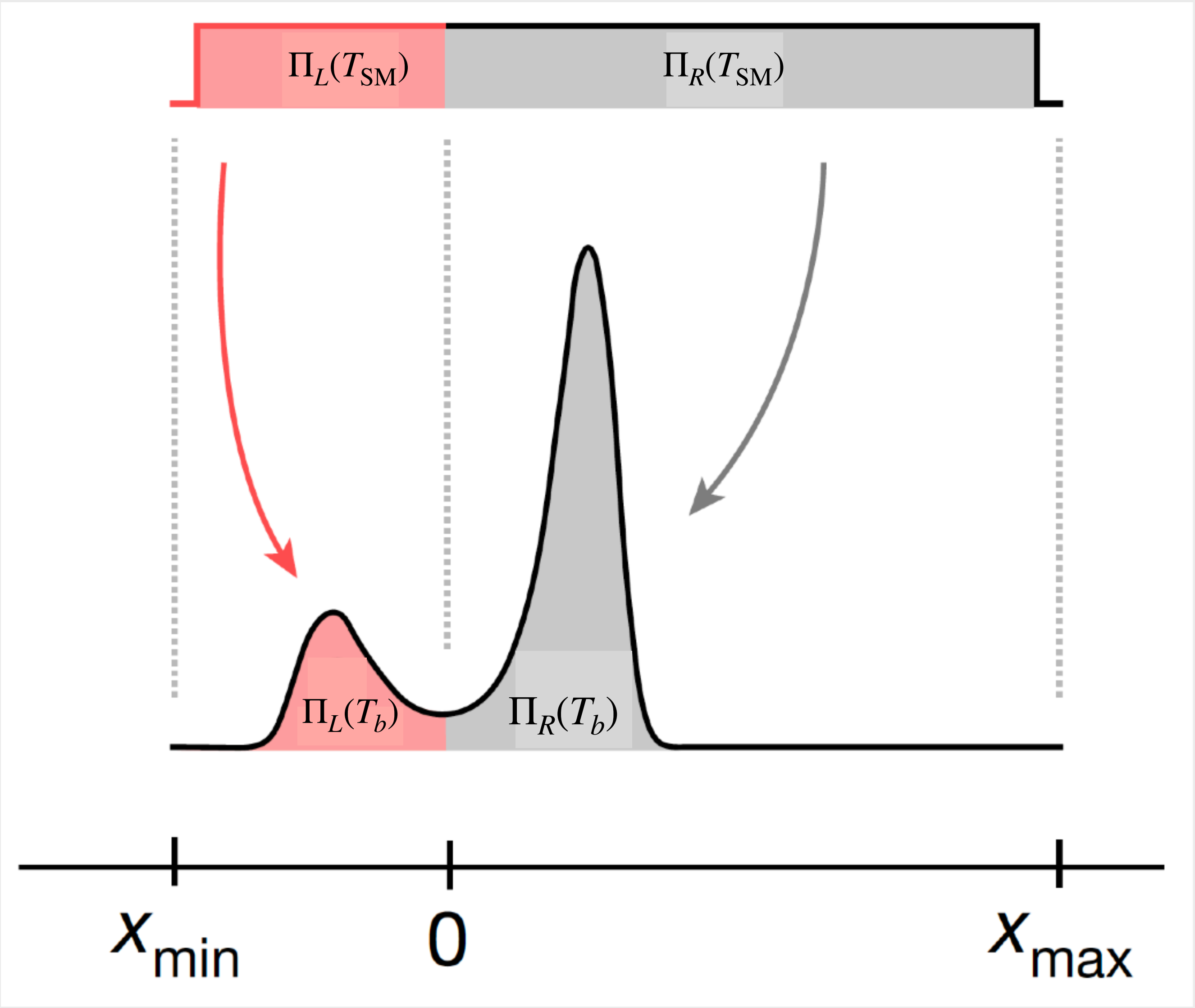






- metastability — separated and deep wells
- geometry $\alpha = \left|\frac{x_{\max}}{x_{\min}}\right|$

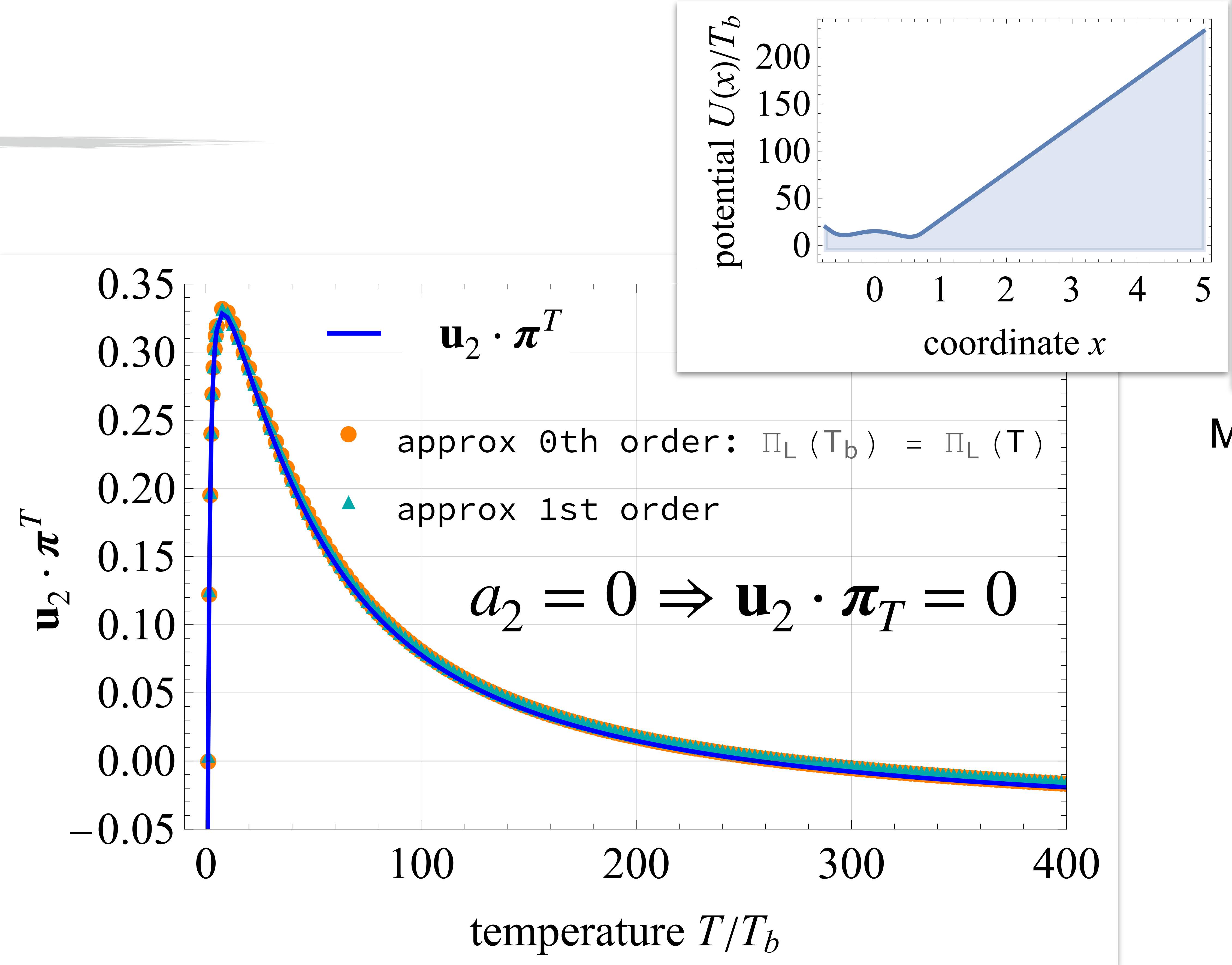
Strong Mpemba effect



$$\Pi_L(T_b) \approx \Pi_L(T_{SM})$$

$$\Pi_L(T) \equiv \int_{\mathscr{D}_L} e^{-\frac{U(x)}{k_B T}} dx$$

Kumar A. & Bechhoefer J., Nature, 2020



Matthew R. Walker

Strong Mpemba effect condition

$$0 = \left(\frac{\Pi_L(T)}{\Pi_L(T_b)} - \frac{\Pi_R(T)}{\Pi_R(T_b)}\right) + \frac{\gamma\lambda_2}{T_b}\left(\langle \mathscr{A}_L \rangle_{L,T} \frac{\Pi_L(T)}{\Pi_L(T_b)} - \frac{\Pi_R(T)}{\Pi_R(T_b)} \langle \mathscr{A}_R \rangle_{R,T}\right)$$

$$\mathscr{A}_L = \frac{T_b}{\gamma}\left[\tau_L(x_{max}) - \tau_L(x_{min})\right]$$

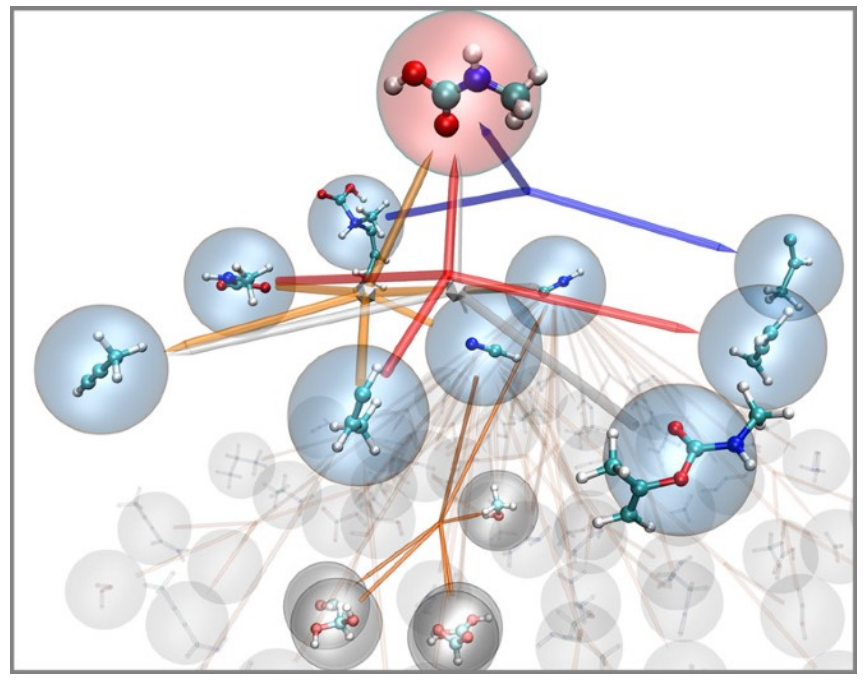
τ_L mean free passage time from left well

M. R. Walker & MV, arXiv:2022.07496 (under review in PRL)

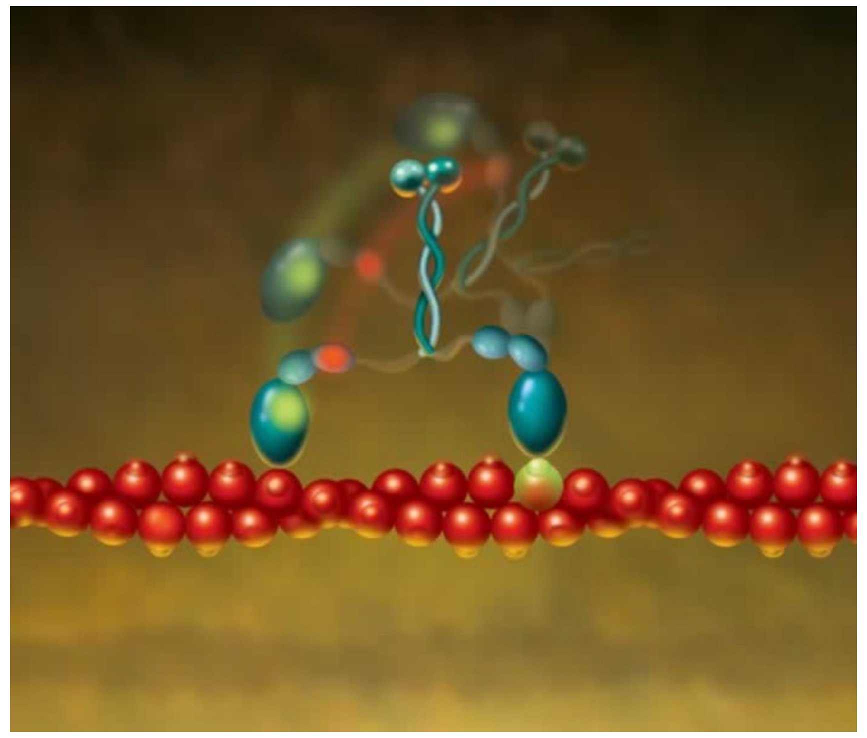
Surprises

Role of dynamics in Mpemba effect

S. Bera, M. R. Walker, & MV, arXiv: 2308.04557



chemical reactions



molecular motors

Linear reaction networks

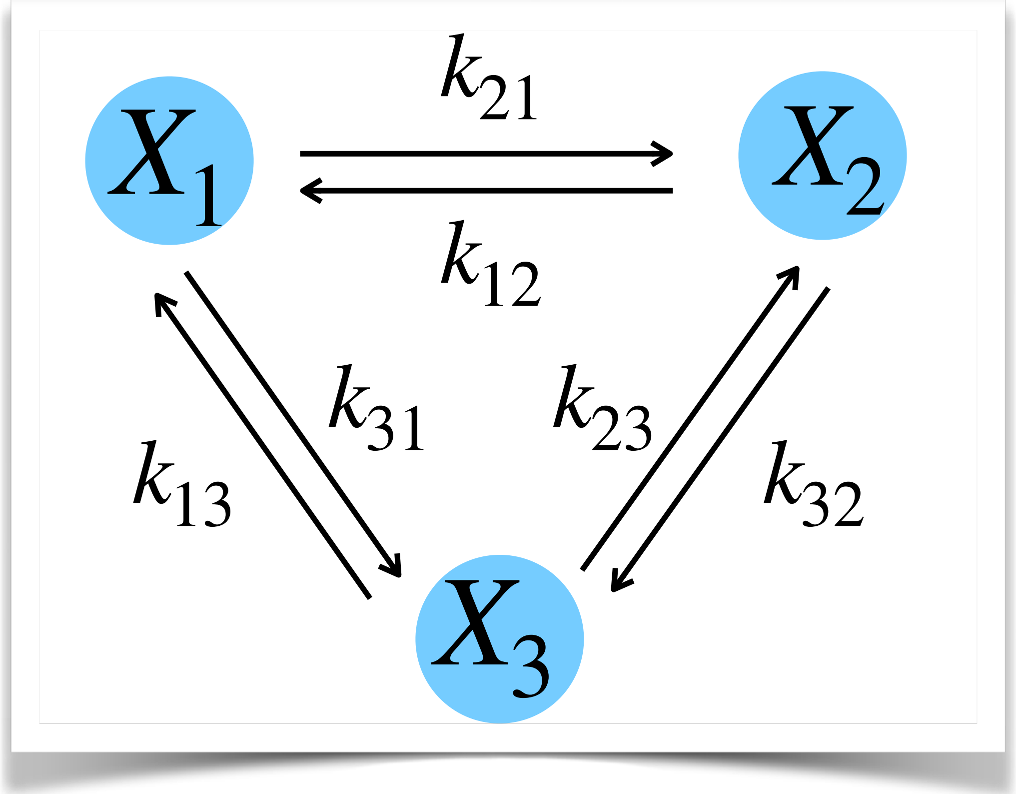
Detailed balance does not specify the dynamics —
it just sets the ratios of rates.

$$\frac{k_{ij}}{k_{ji}} = e^{-\beta_b(\epsilon_i-\epsilon_j)}$$

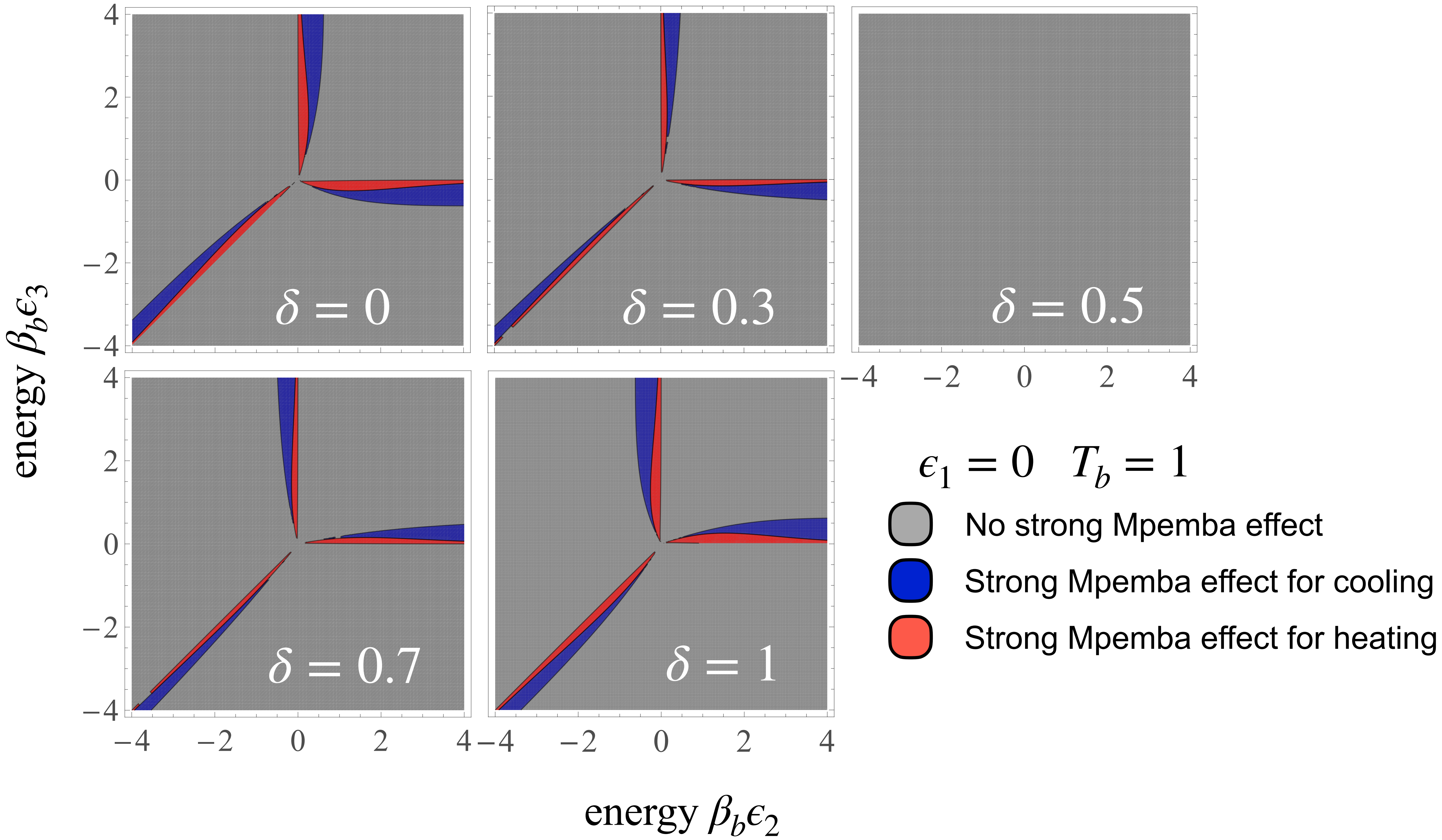
To study dynamics we introduce: load factor δ

Choice of rate constants:

- for $j \to i$ in the clockwise direction: $k_{ij} = e^{-\beta_b(\epsilon_j-\epsilon_i)(1-\delta)}$, $k_{ji} = e^{-\beta_b(\epsilon_j-\epsilon_i)\delta}$ $(\delta \in [0,1])$



X_i reactants
k_{ij} transition rate $j \to i$



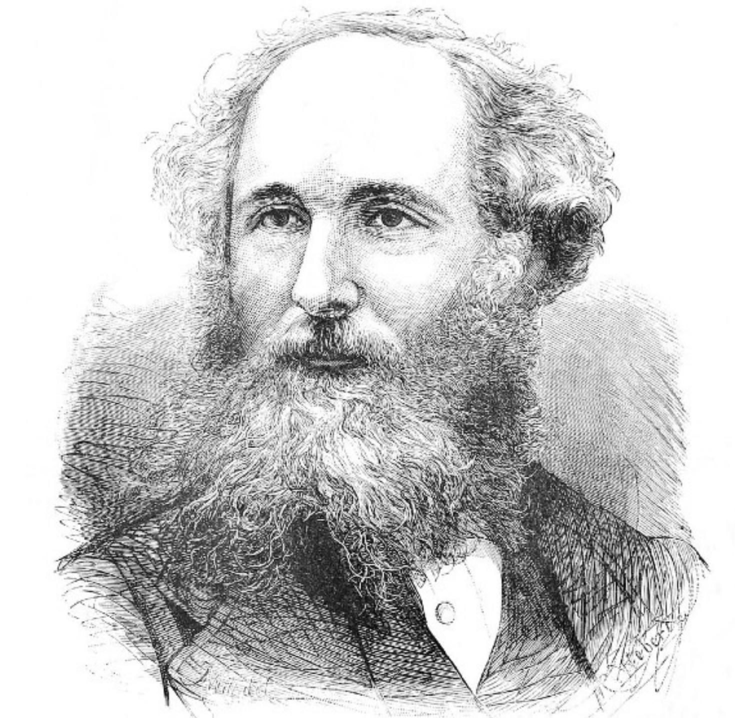
Matthew R. Walker

Saikat Bera

Exchanging information

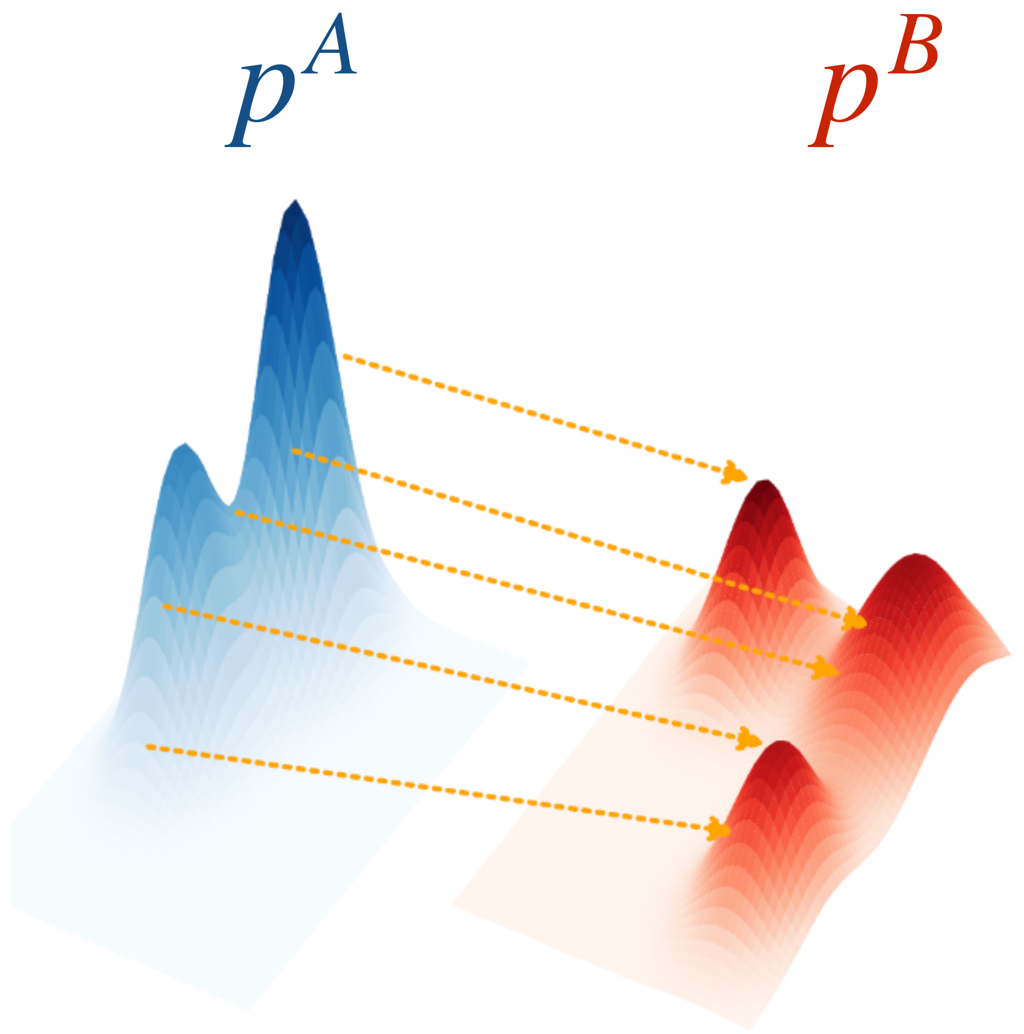
S. Bera, M. R. Walker, & MV, arXiv: 2308.04557

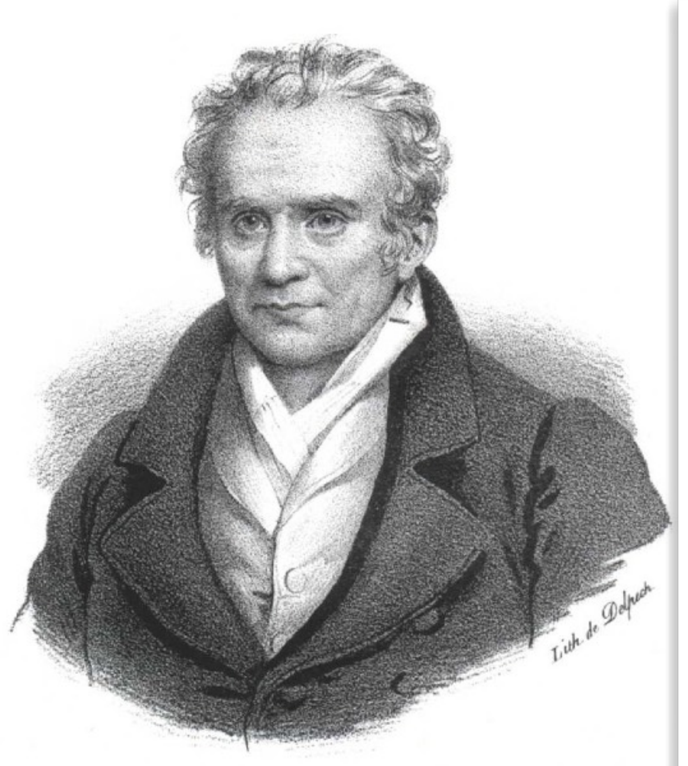
- shorter cycle time
- enhanced power output
- constant efficiency
- stable device

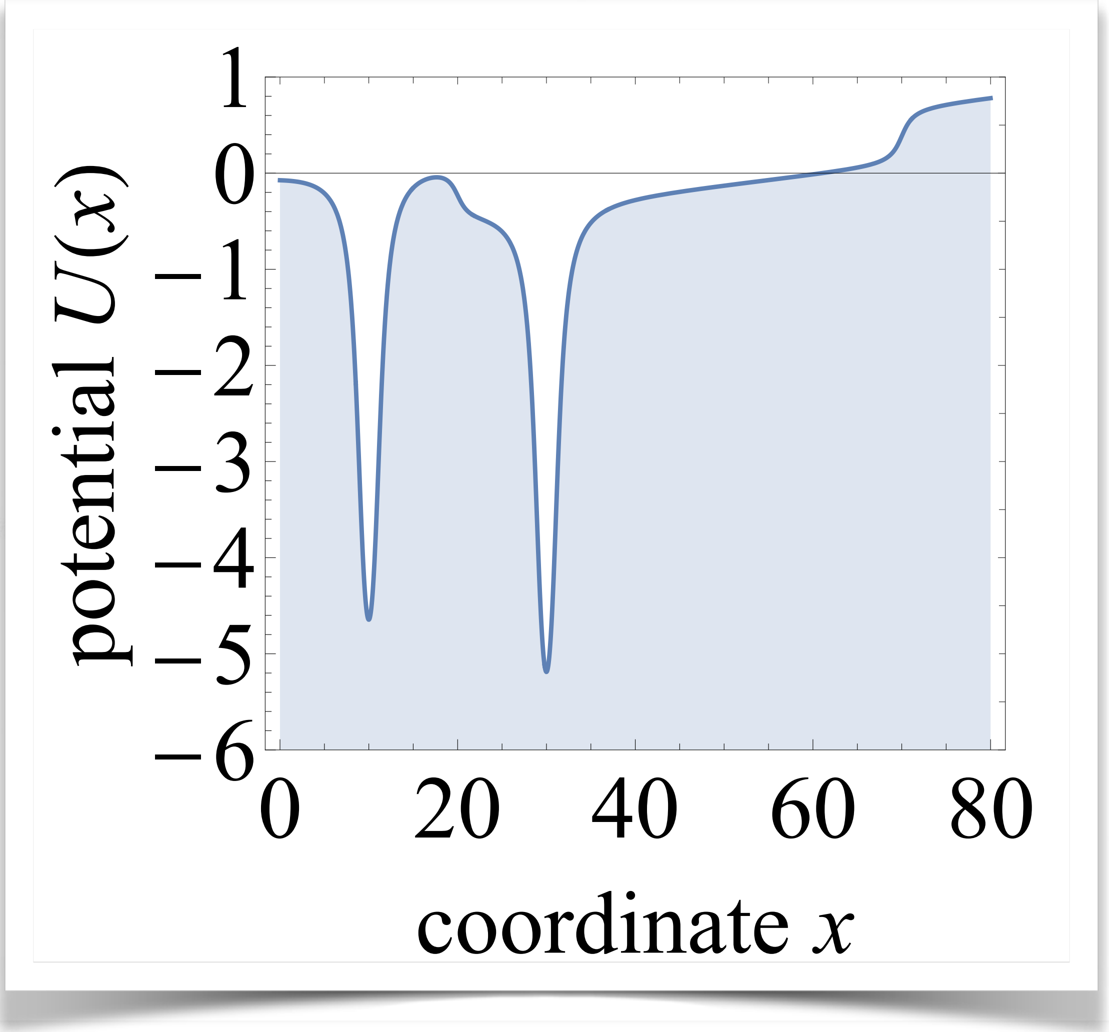


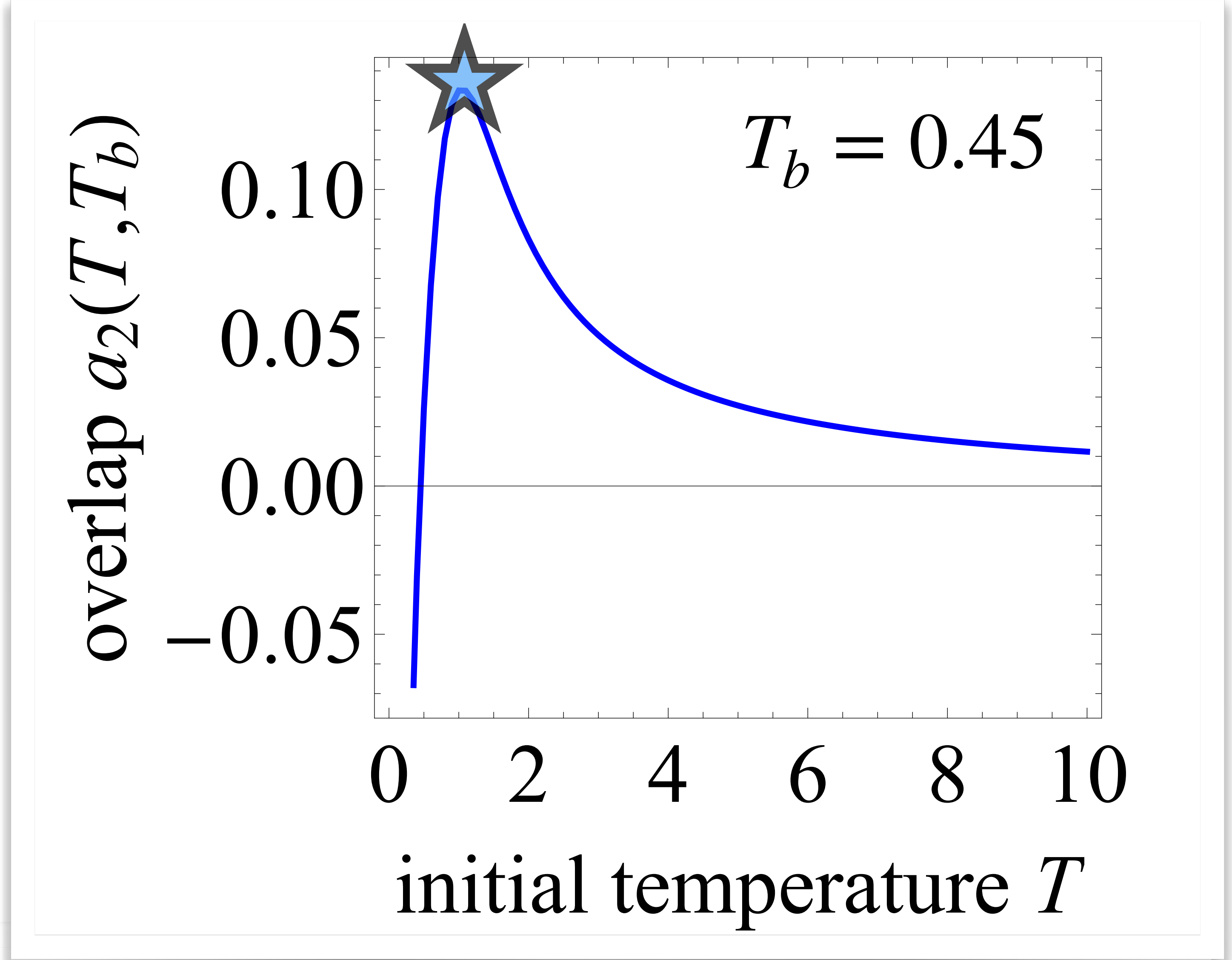
James Clerk Maxwell

Can fast be also optimal?




Gaspard Monge



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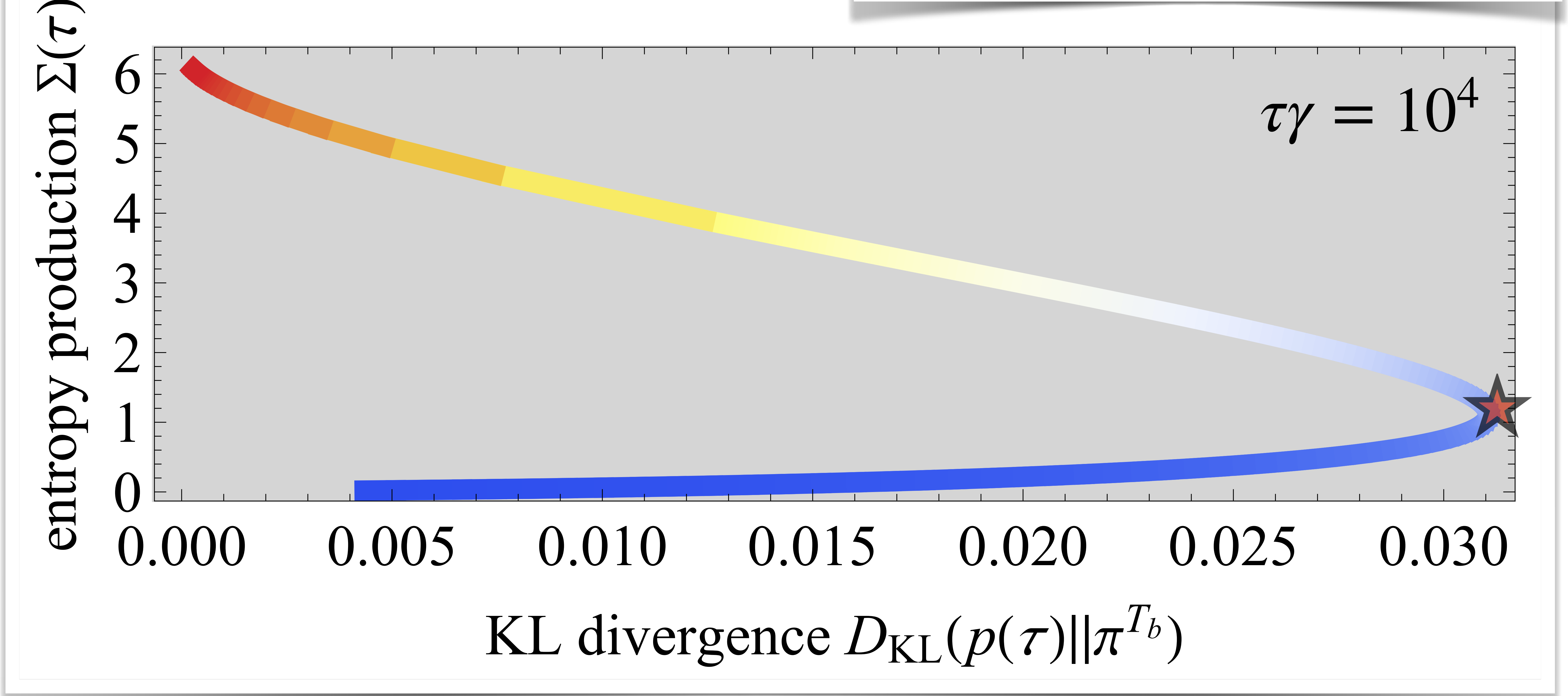
Optimal transport

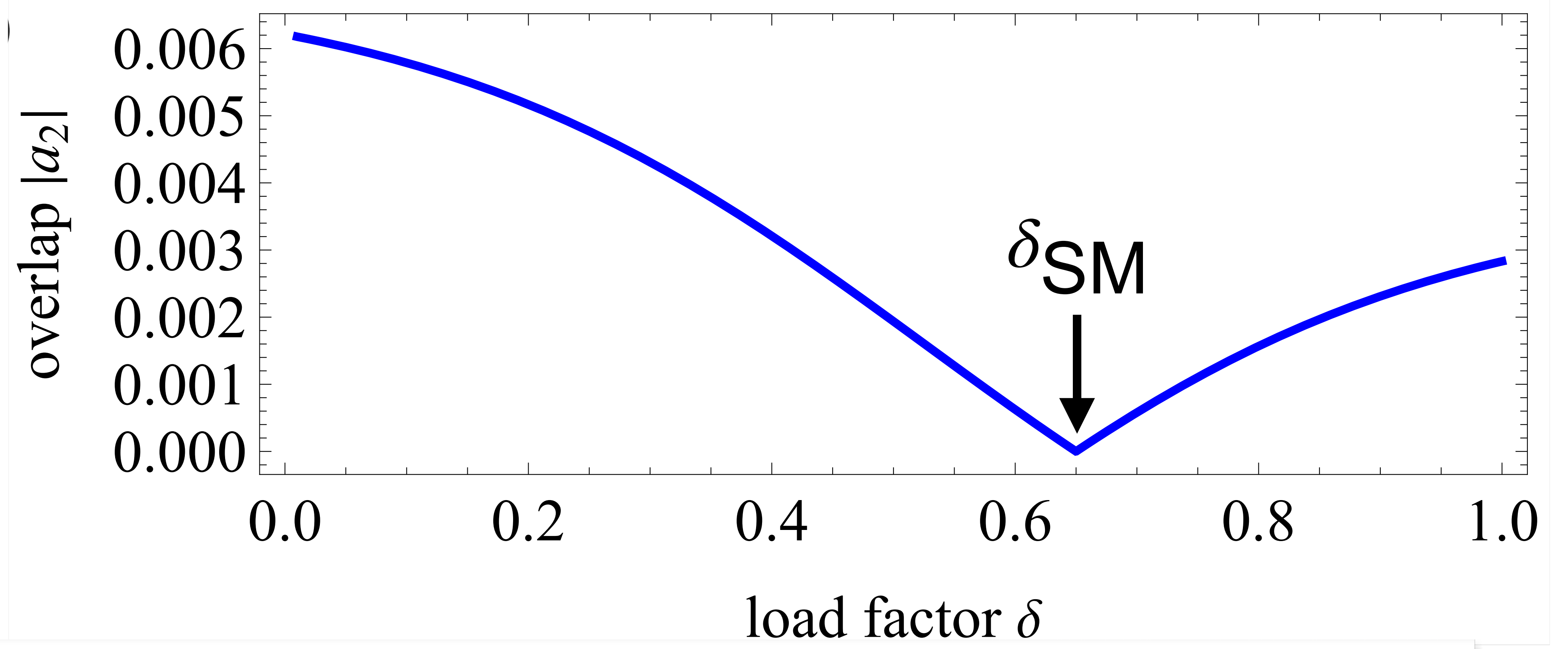
move p^A to p^B in finite time τ

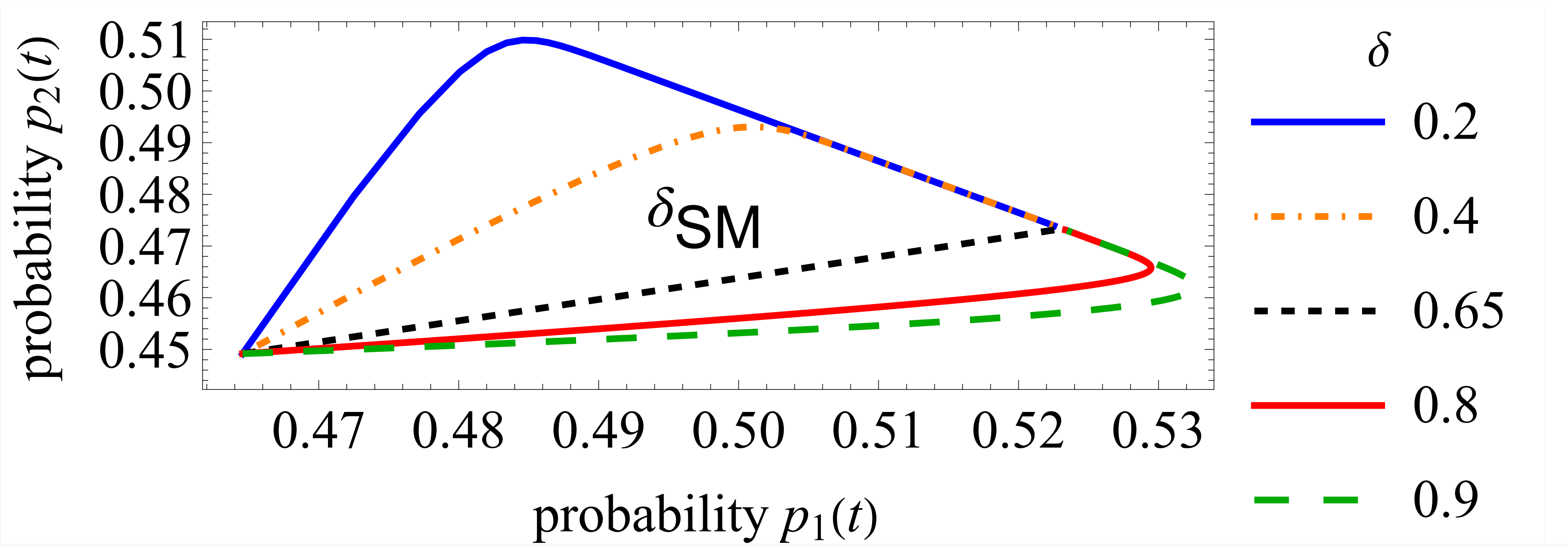
with the least amount of resources (minimal dissipation)

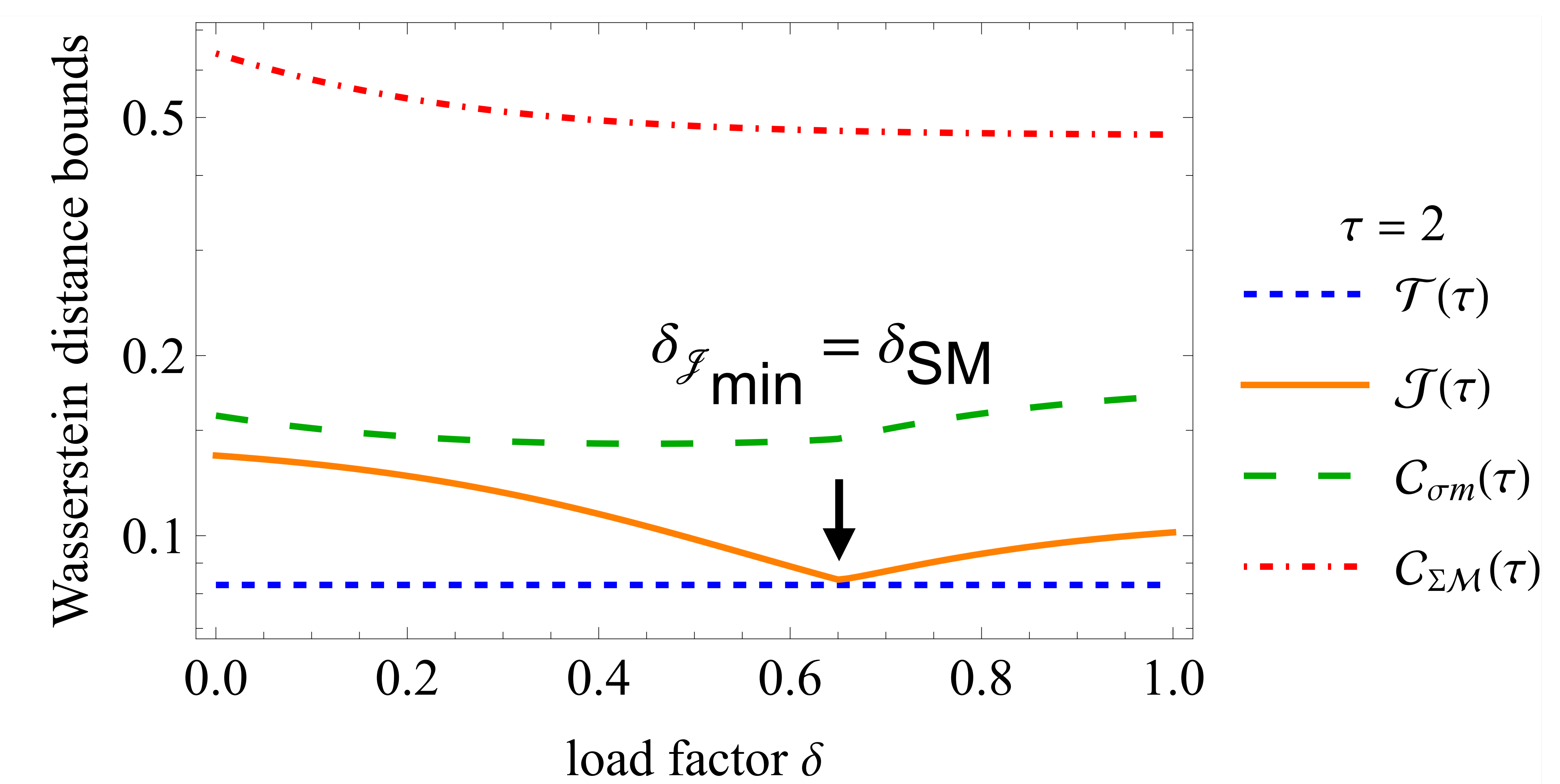


Fast and optimal

M. R. Walker, S. Bera & MV, arXiv:2307.16306





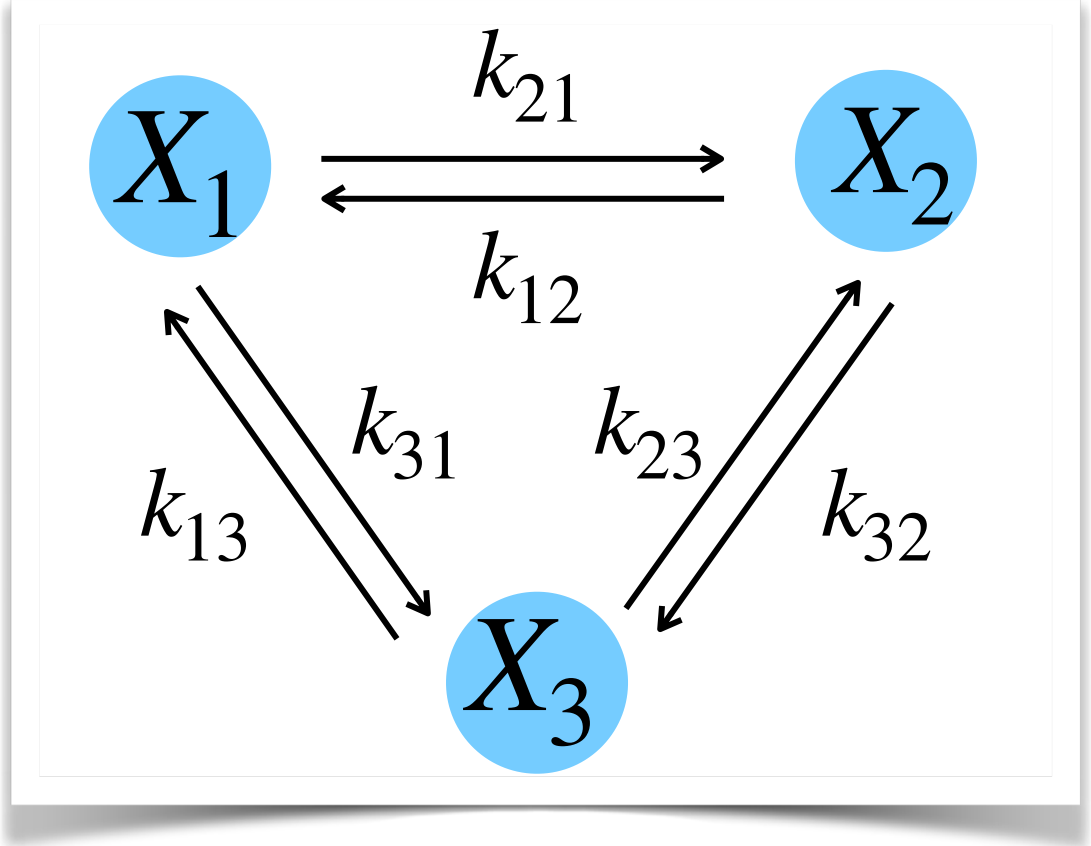


δ_{SM} dynamics with Strong Mpemba effect

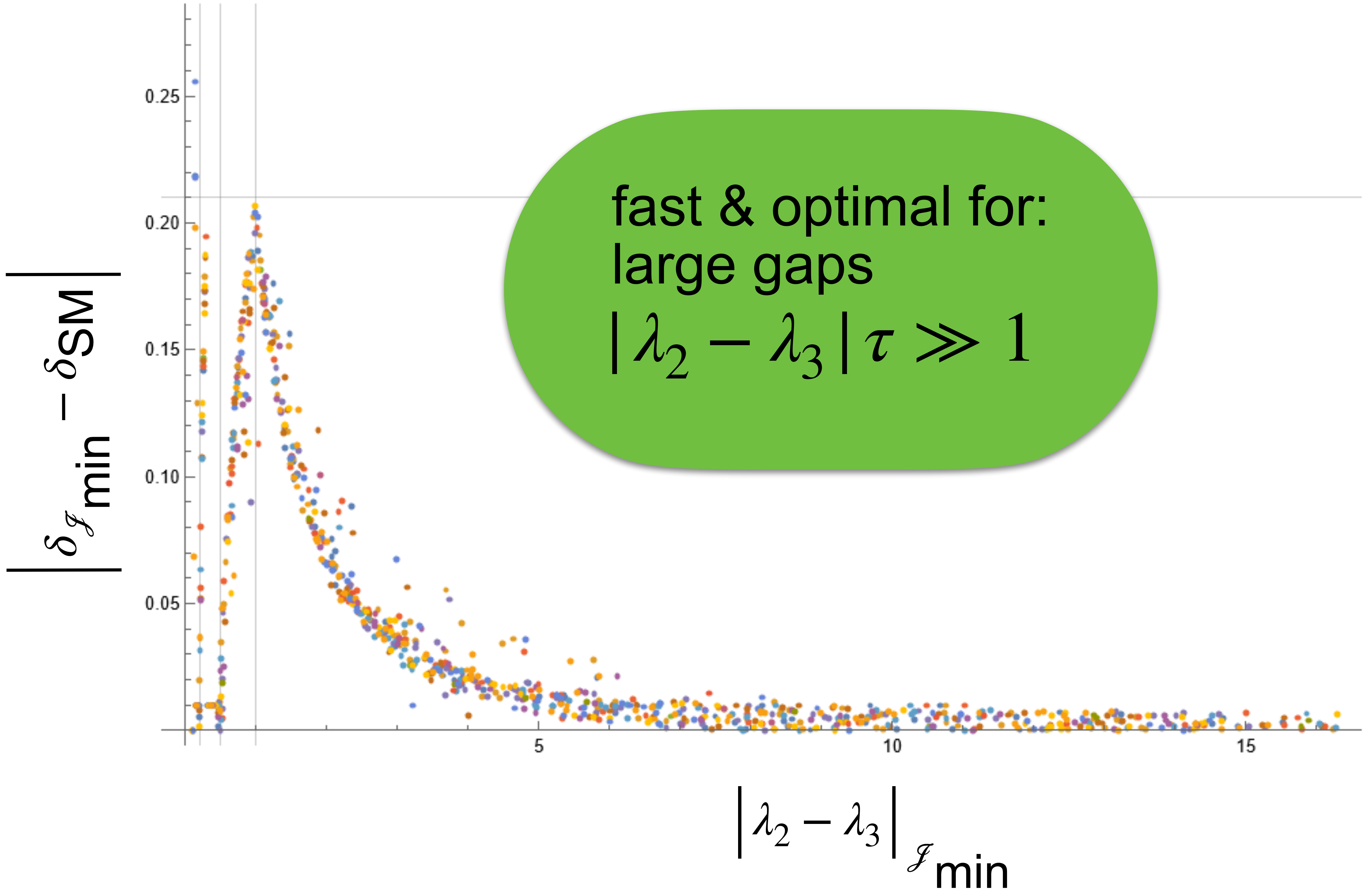
"flow cost"

$$\mathcal{J}(\tau) \equiv \int_0^\tau \sum_{x>y} |j_{xy}(t)|\, dt$$

$$j_{xy} = R_{xy}p_y - R_{yx}p_x$$ net current



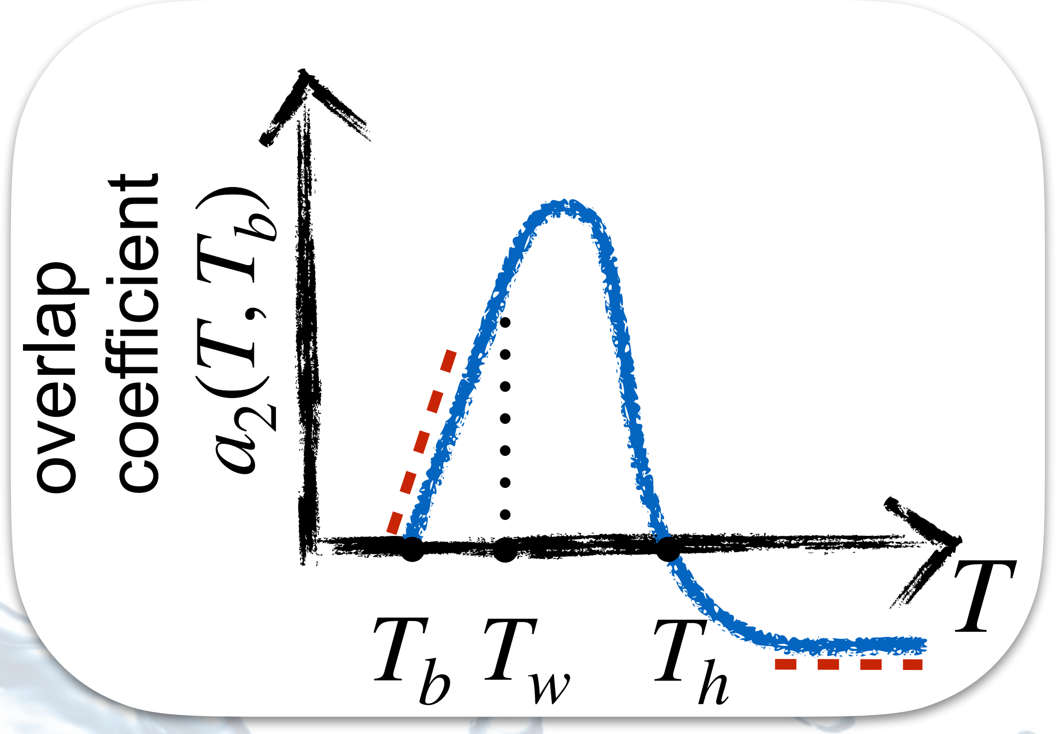
$k_{23}(\delta), k_{32}(\delta)$

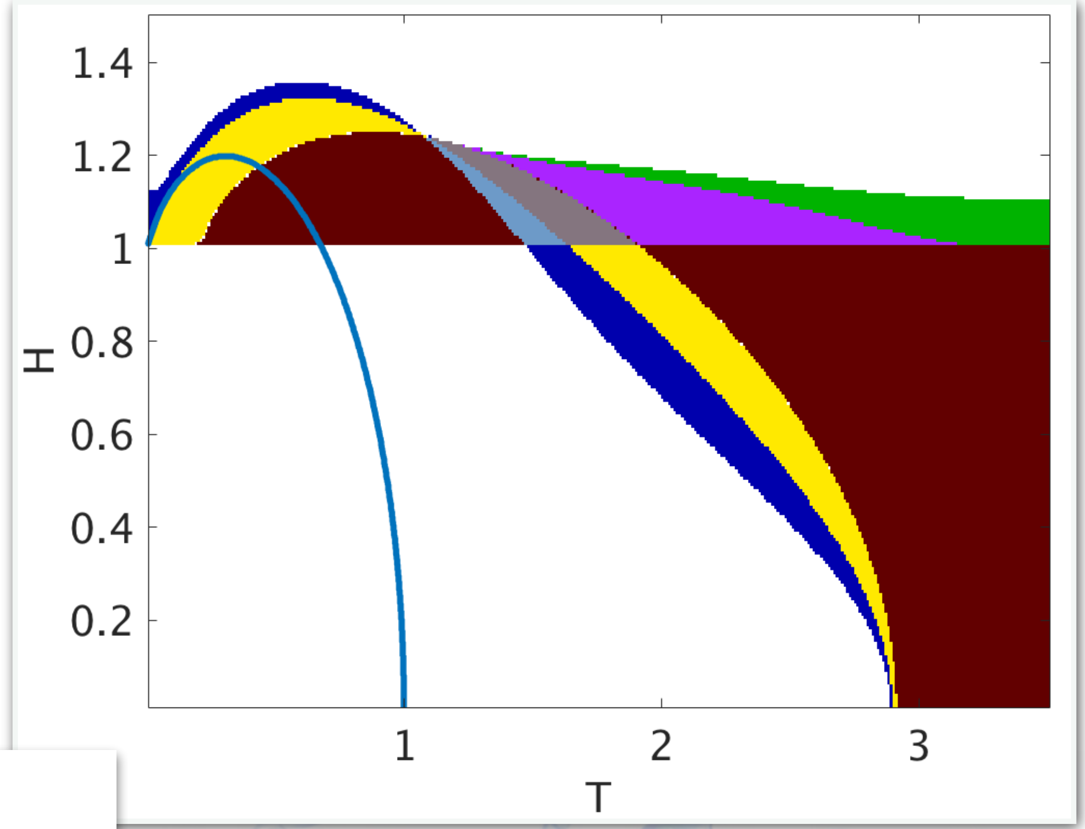


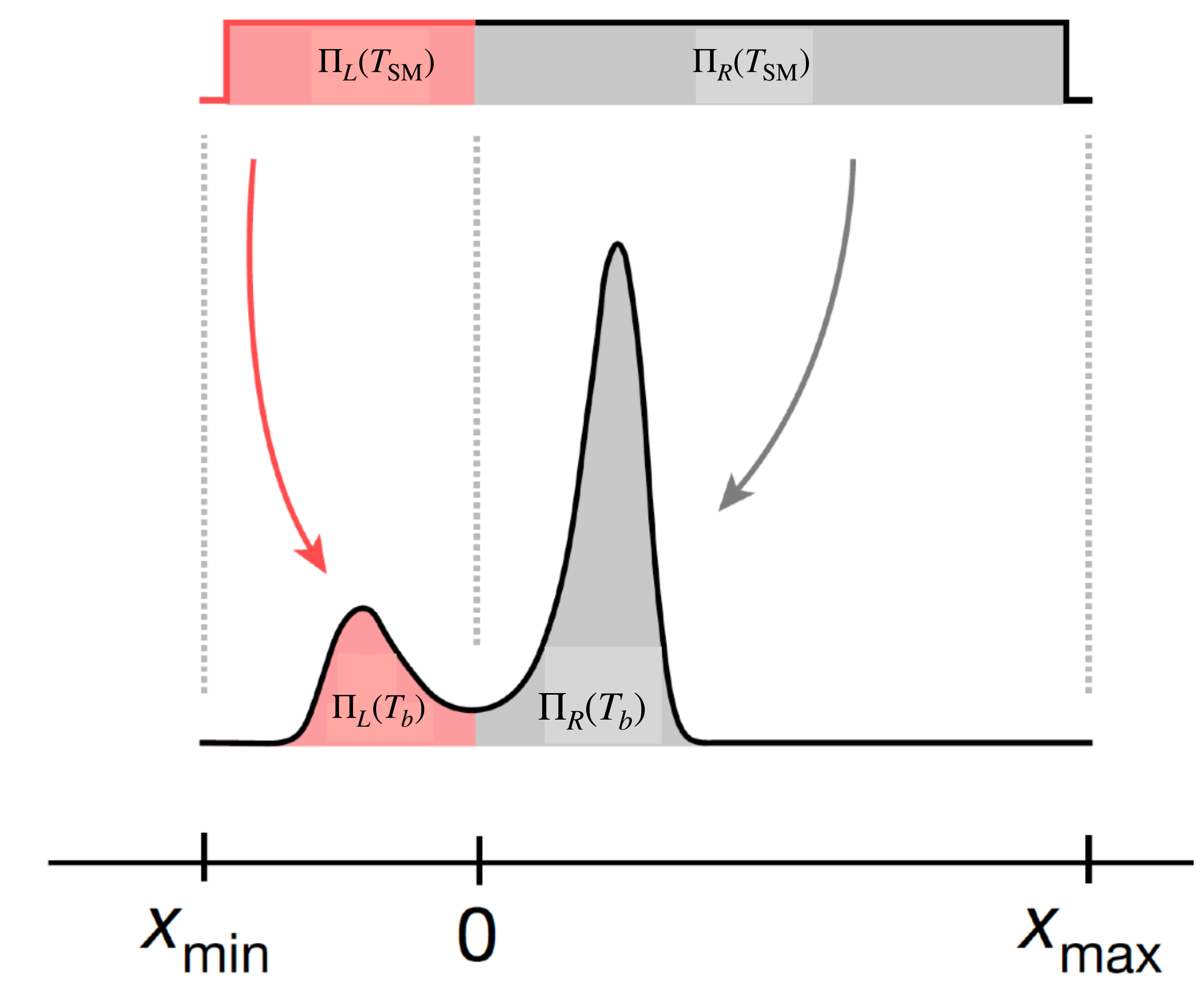
fast & optimal for:
large gaps
$|\lambda_2 - \lambda_3|\tau \gg 1$

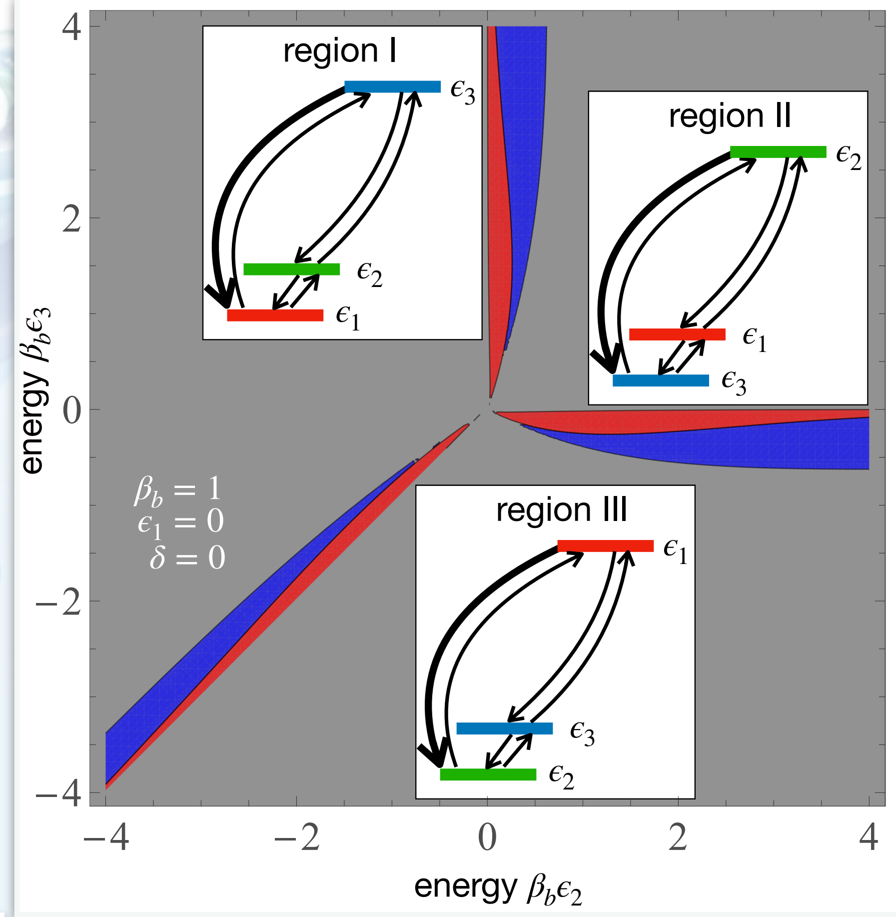
Summary

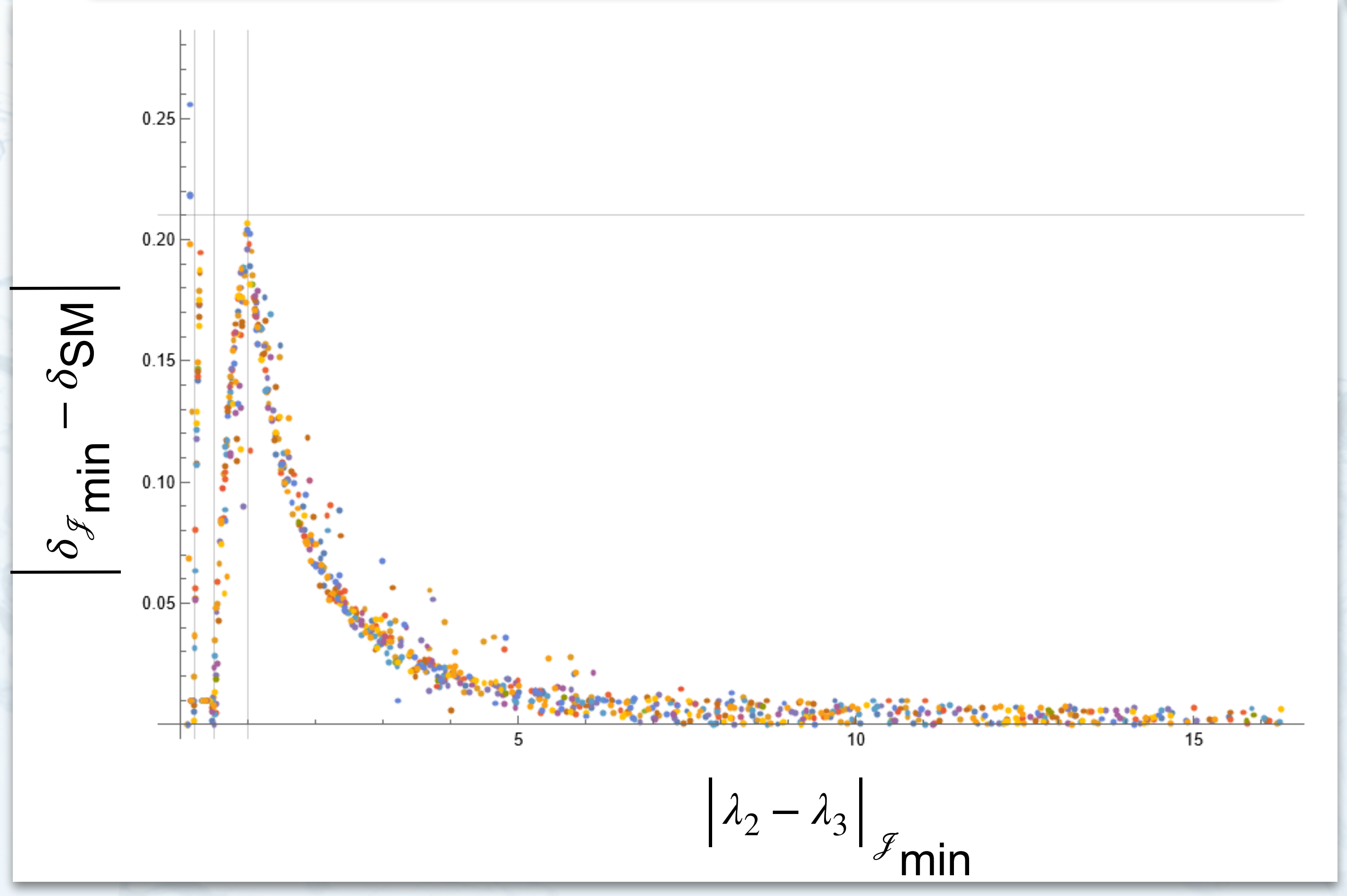
- Mpemba effect is a general phenomenon
- New regime: Strong Mpemba effect (exponentially faster relaxation; topological features)
- Intuition:
    - Metastable states are important, but not necessary*
    - Geometry of domain and potential matter
    - Dynamics matter:
        - Exchange information is affected by presence of Strong Mpemba effect — such as shorter cycles, enhanced power
        - Fast and optimal can happen for the same dynamics

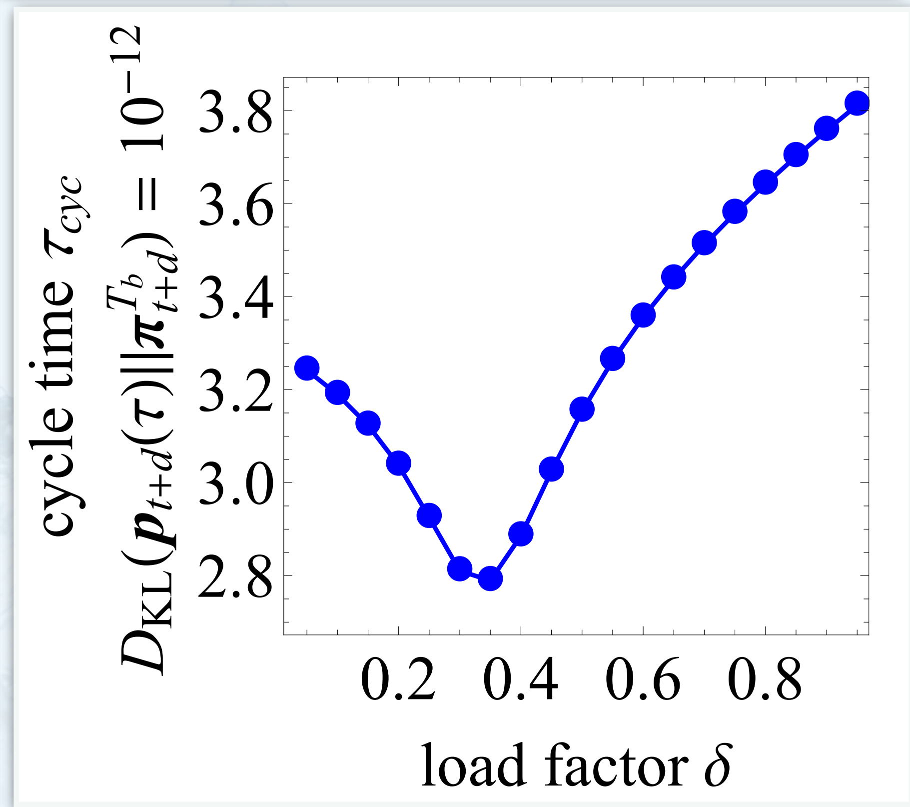












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*M. R. Walker & MV, J. Stat. Mech., 2021

Thank you!