The Mpemba index and anomalous relaxation

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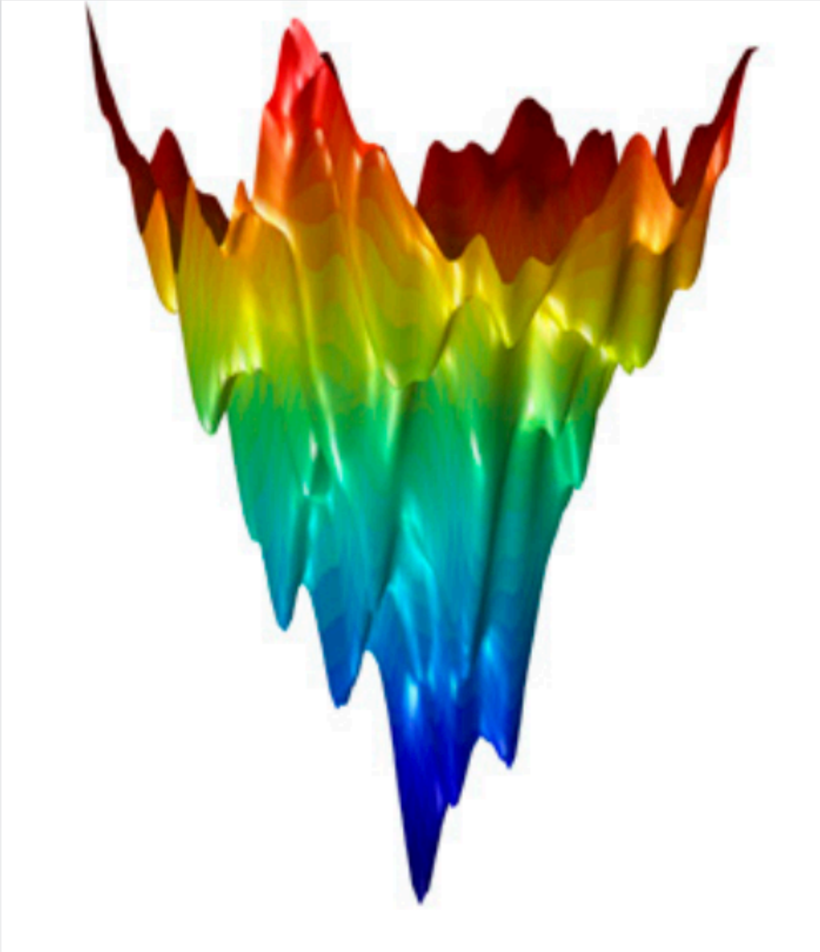
KITP, January 2018

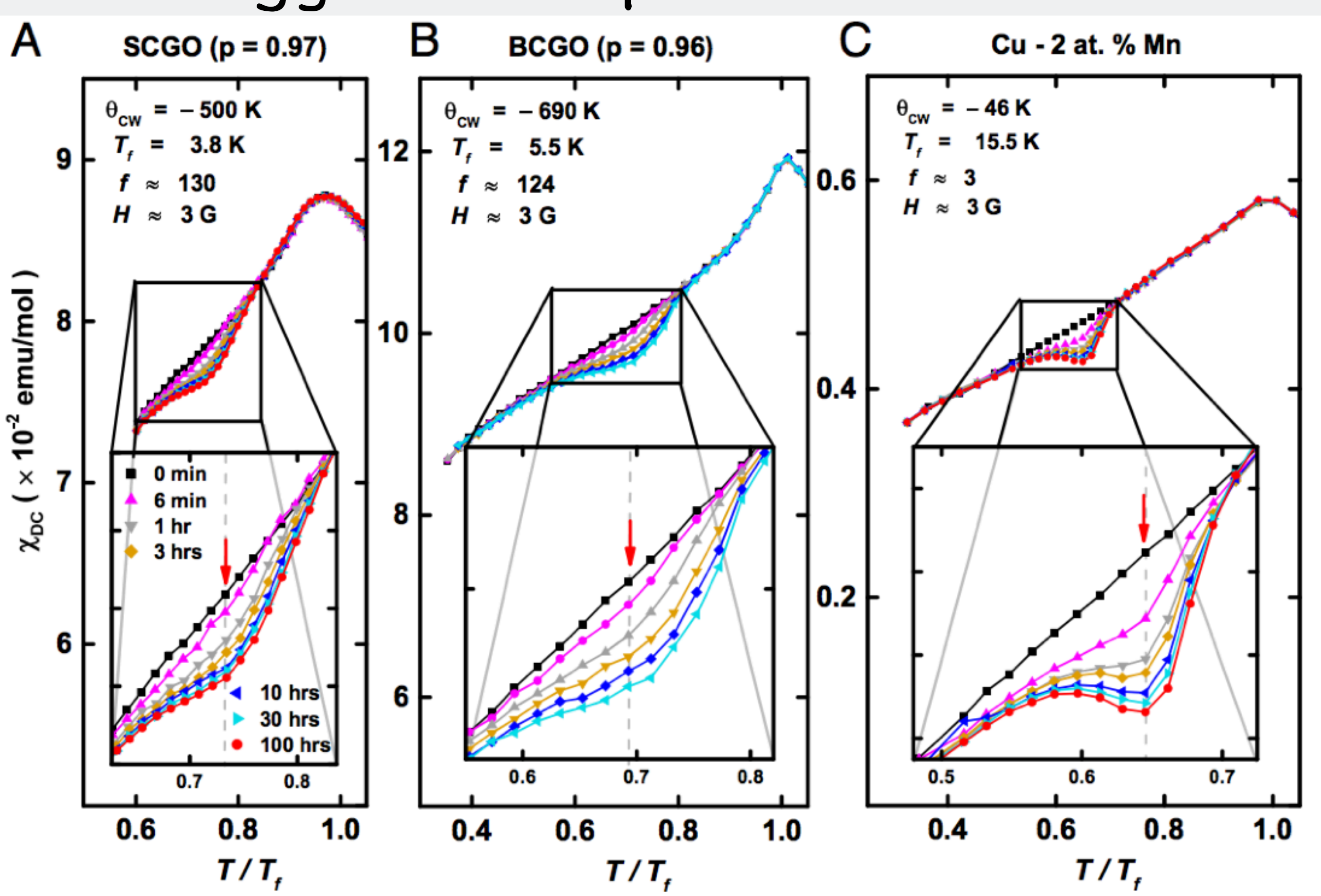


Energy landscape

Relations to memory, aging and rejuvenation

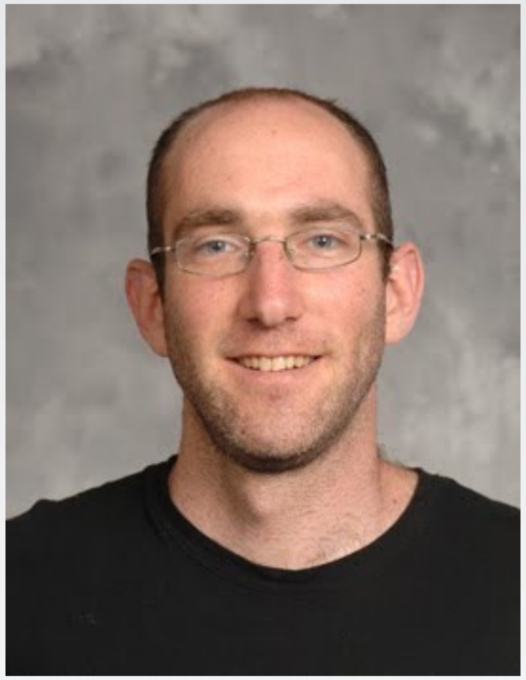
Mpemba effect:

- Property of dynamics
- Present in out-off equilibrium processes
- Interplay of energy levels and transition barriers



Susceptibility

joint work with

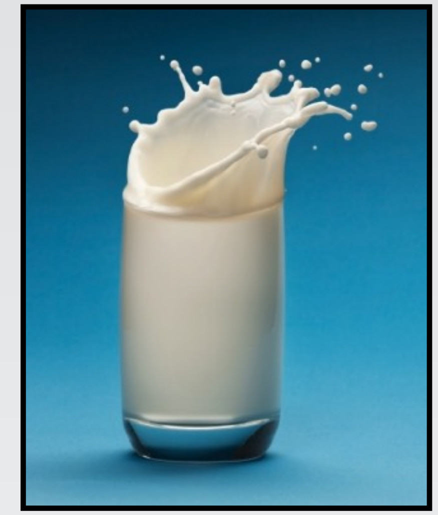


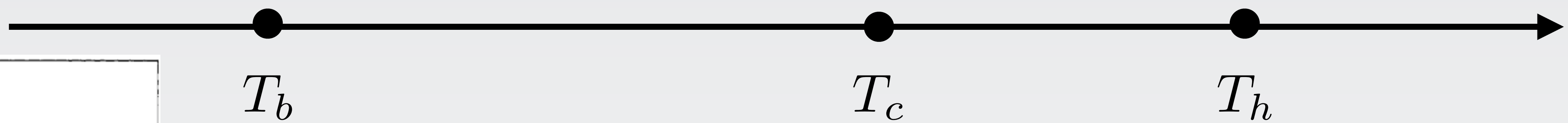
Oren Raz
WIS

Israel Klich
UVa

Ori Hirschberg
NYU

Mpemba Effect — warm water freezes faster than cool





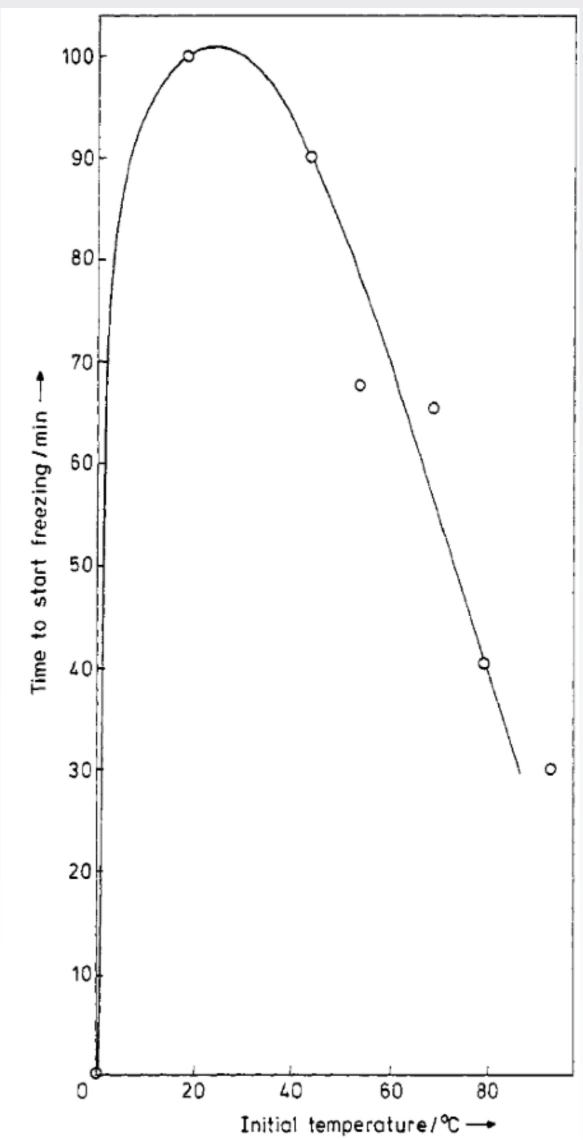
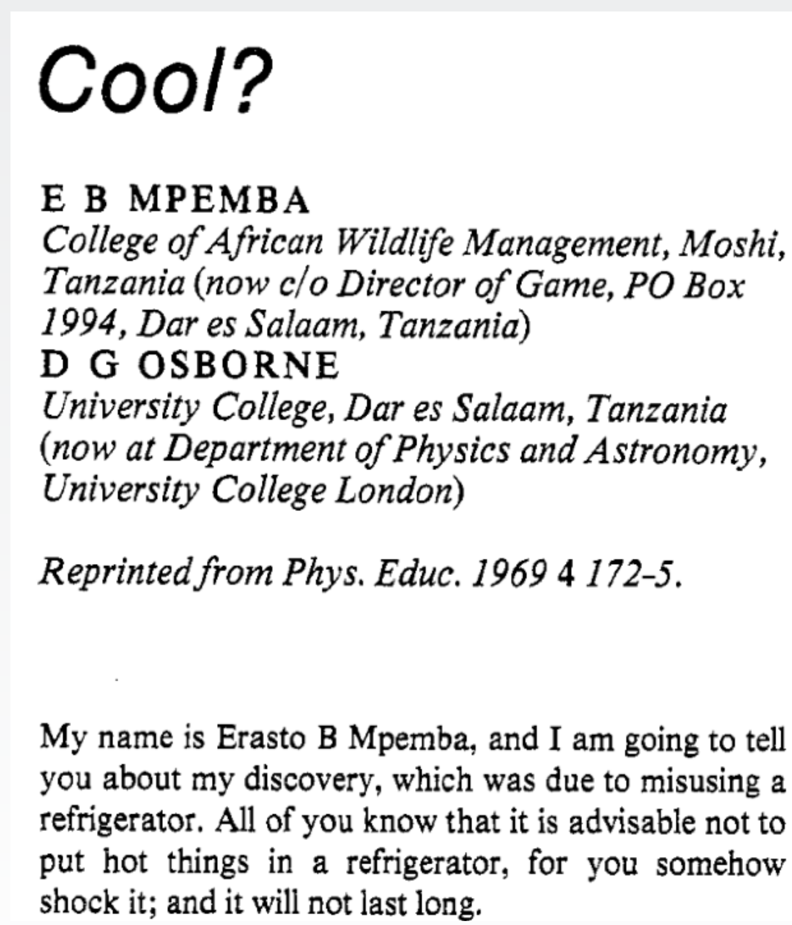


Figure 1 Plot of time for water to start freezing against initial temperature of water



Cool?

E B MPEMBA
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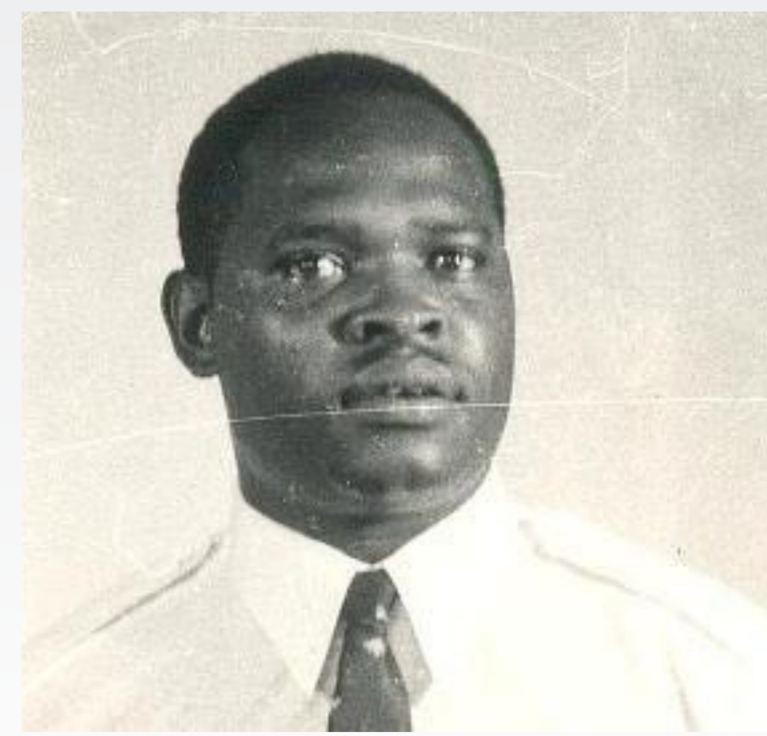
Reprinted from Phys. Educ. 1969 **4** *172–5.*

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.



Erasto Bartolomeo Mpemba

OPEN

Questioning the Mpemba effect: hot water does not cool more quickly than cold

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Henry C. Burridge[1,2] & Paul F. Linden[1]

The Mpemba effect is the name given to the assertion that it is quicker to cool water to a given temperature when the initial temperature is higher. This assertion seems counter-intuitive and yet references to the effect go back at least to the writings of Aristotle. Indeed, at first thought one might consider the effect to breach fundamental thermodynamic laws, but we show that this is not the case. We go on to examine the available evidence for the Mpemba effect and carry out our own experiments by cooling water in carefully controlled conditions. We conclude, somewhat sadly, that there is no evidence to support meaningful observations of the Mpemba effect.

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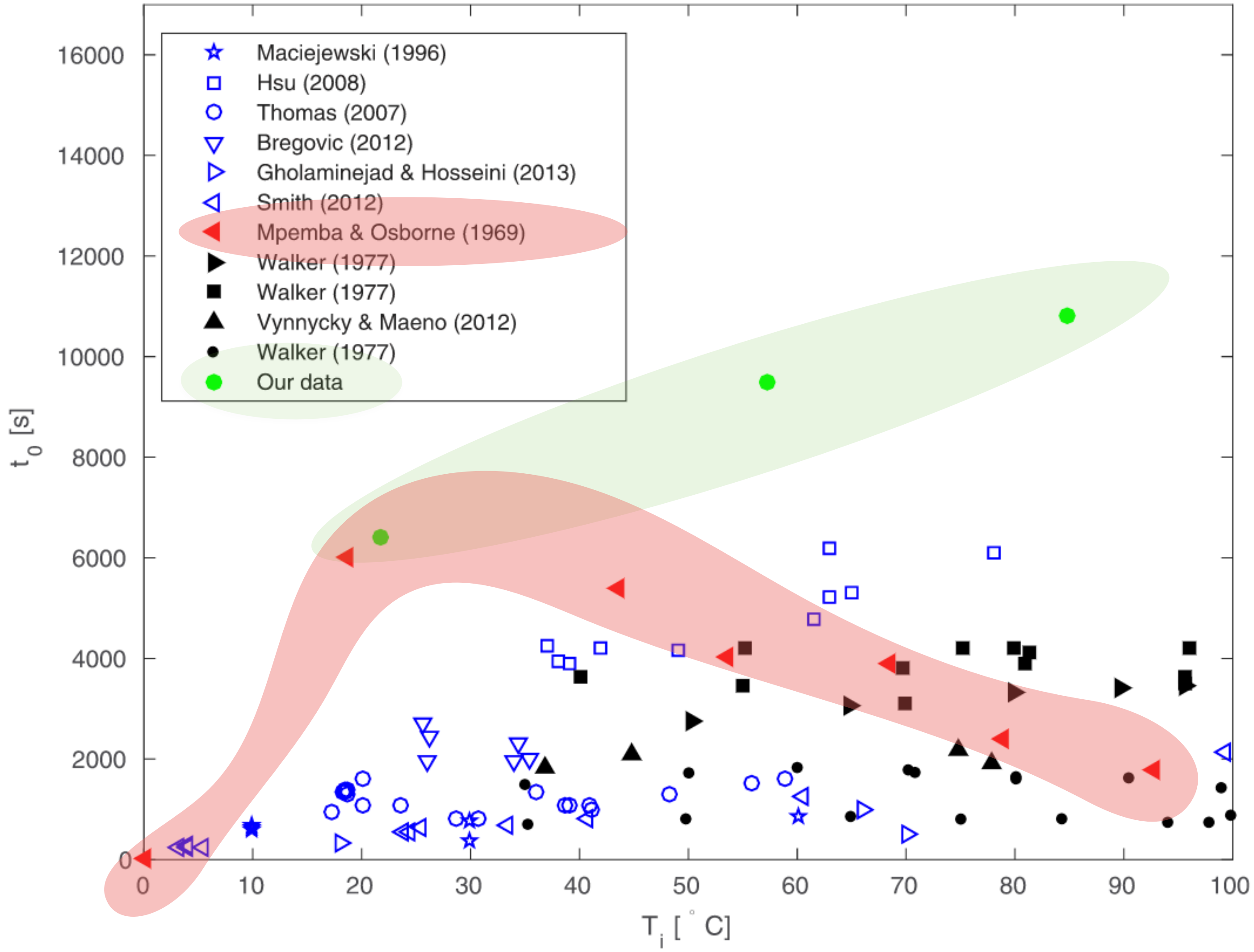
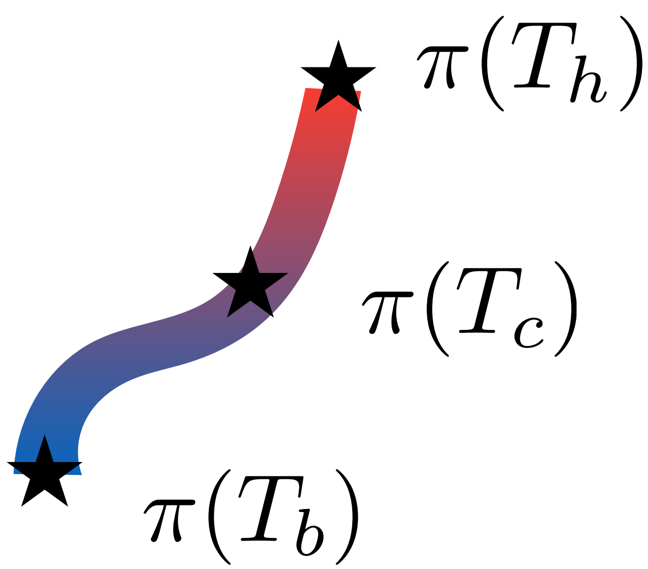


Figure 1. The time t_0 to cool to 0 °C, plotted against the initial temperature, T_i for the 'Mpemba-type' experiments. The data show a broad trend of increasing cooling time with increasing initial temperature, with the notable exception being the data of Mpemba & Osborne[8].

Cooling

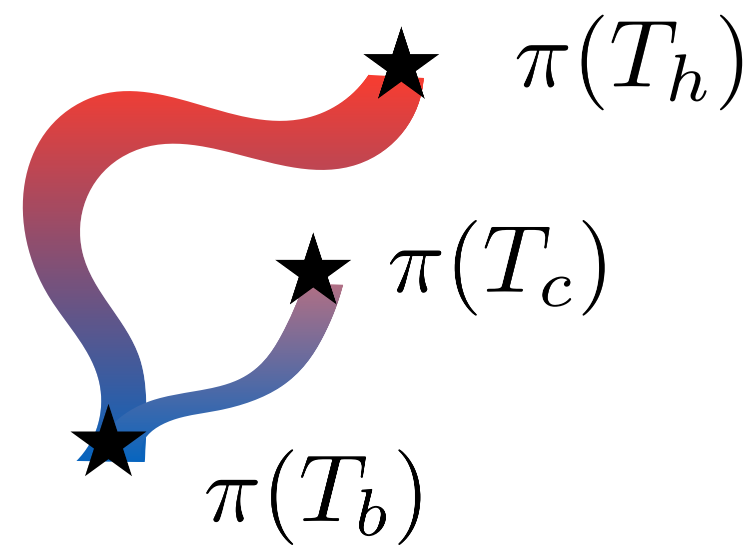
Look at 3 systems $T_b < T_c < T_h$

Gibbs distribution $\pi_i = \dfrac{e^{-\beta E_i}}{Z}$



quasistatic

along the trajectory the system is always in equilibrium



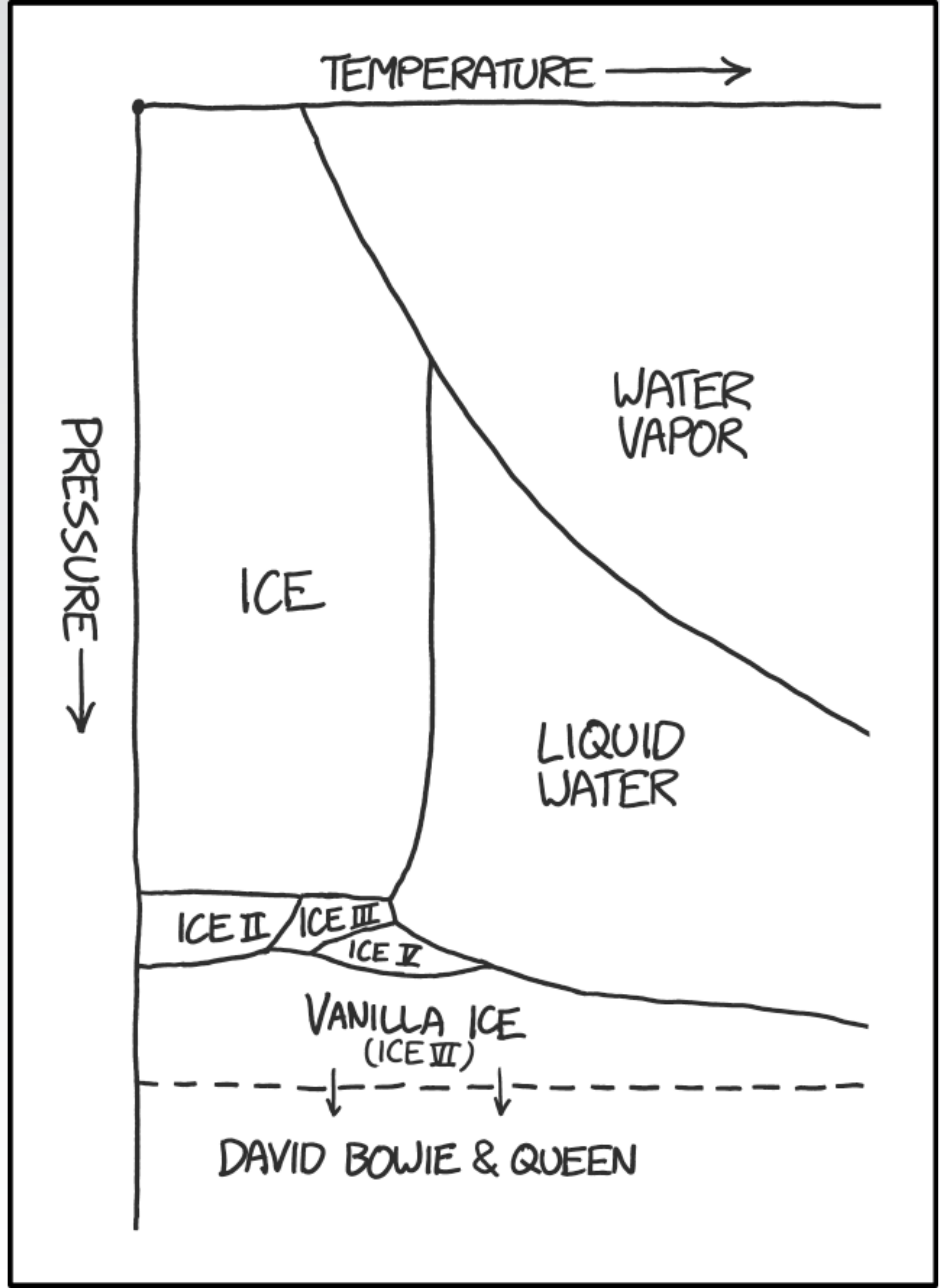
quench

along the trajectories the system generically is out of equilibrium

* likewise we can have the Inverse Mpemba effect - when heating the system

Water phase diagram

Is the Mpemba effect special to water?



xkcd

Moving away from water — in a general system:

- What are the minimal ingredients for an Mpemba effect?
- How generic is the Mpemba effect?

Let's specify the relaxation dynamics

$$\partial_t |p\rangle = R(T_b) |p\rangle$$

initial condition $|p(T, t=0)\rangle = |\pi(T)\rangle$

at large time limit $|p(T, t \to \infty)\rangle = |\pi(T_b)\rangle$

Gibbs distribution $\pi_i = \frac{e^{-\beta E_i}}{Z}$

Note: R depends only on the bath temperature T_b

Specifying the rate matrix R:

- No-memory of the past, Markovian process, local in time relaxation
- Convergence to the bath T_b — detailed balance is sufficient (global balance is necessary).

at T_b: $R_{ij}\pi_j = R_{ji}\pi_i$

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

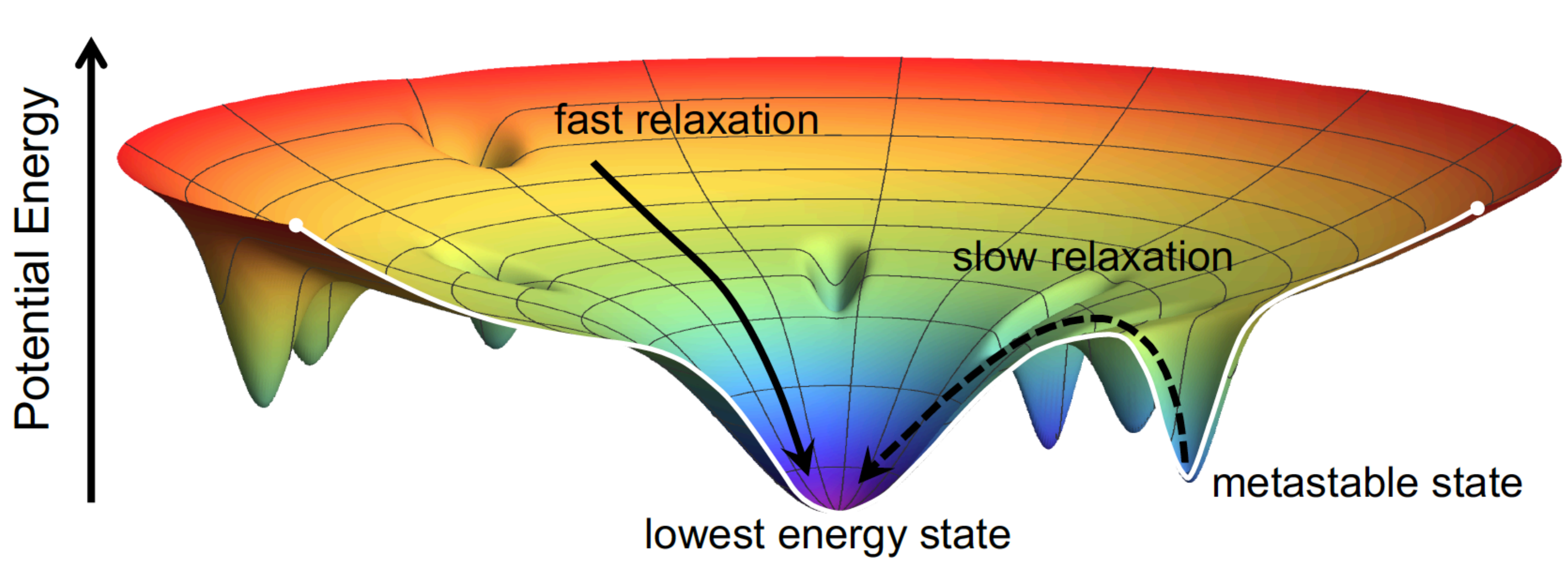
$$B_{ij} = B_{ji}$$

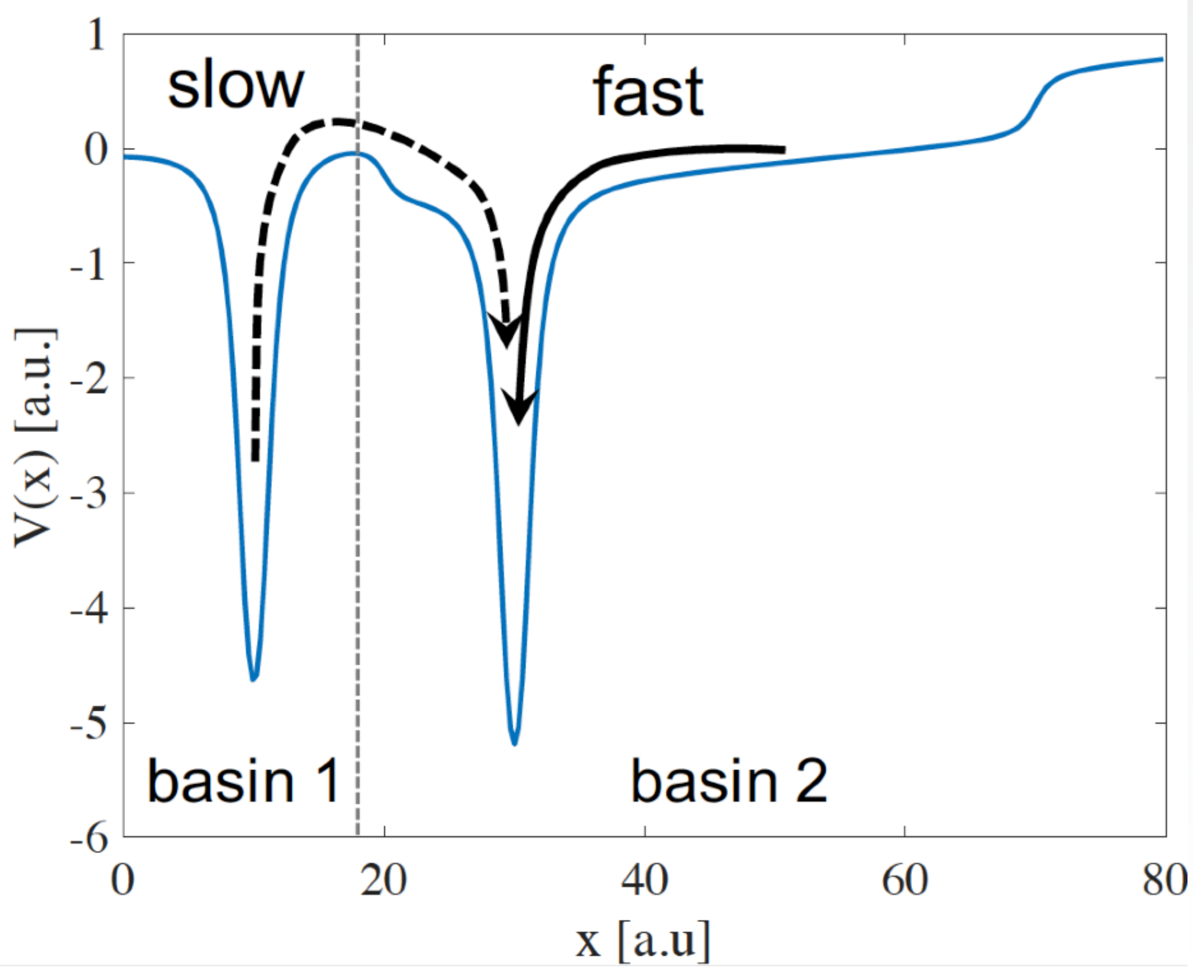
Metropolis

$$B_{ij} = \max(E_i, E_j) \qquad R(j \to i) = \min\left(1, \frac{\pi_i}{\pi_j}\right)$$

Example where Mpemba effect happens

Lu &Raz, arXiv:1609.05271v1 PNAS





Fokker-Planck eq.

$$\partial_t p(x,t) = \partial_x(\mu(\partial_x V) + D\partial_x)p(x,t)$$

$$D = \mu k_B T$$

The slowest relaxation mode corresponds to transition from one well to another

How to measure the Mpemba effect?

Solution for the probability distribution

$$|p(T,t)\rangle = \sum_i a_i e^{-|\lambda_i|t} |v_i\rangle$$

$$R|v_i\rangle = \lambda_i |v_i\rangle \qquad \lambda_1 = 0 \geq \lambda_2 \geq \lambda_3 \geq \ldots$$

Define a distance function (e.g. free energy difference)

$$D(p(T,t),\pi_b) = \frac{F(p) - F(\pi_b)}{T_b}$$

At large times things are simpler

suppose we started at temperature T

$$|p(T,t)\rangle \approx |\pi(T_b)\rangle + a_2(T)\,|v_2\rangle\, e^{-|\lambda_2|t}$$

a_2 (T) depends on the initial state

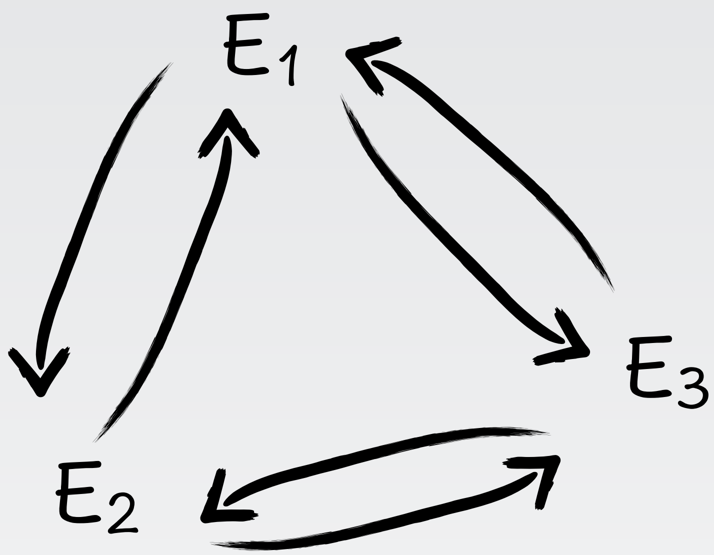
$T_b < T_c < T_h$

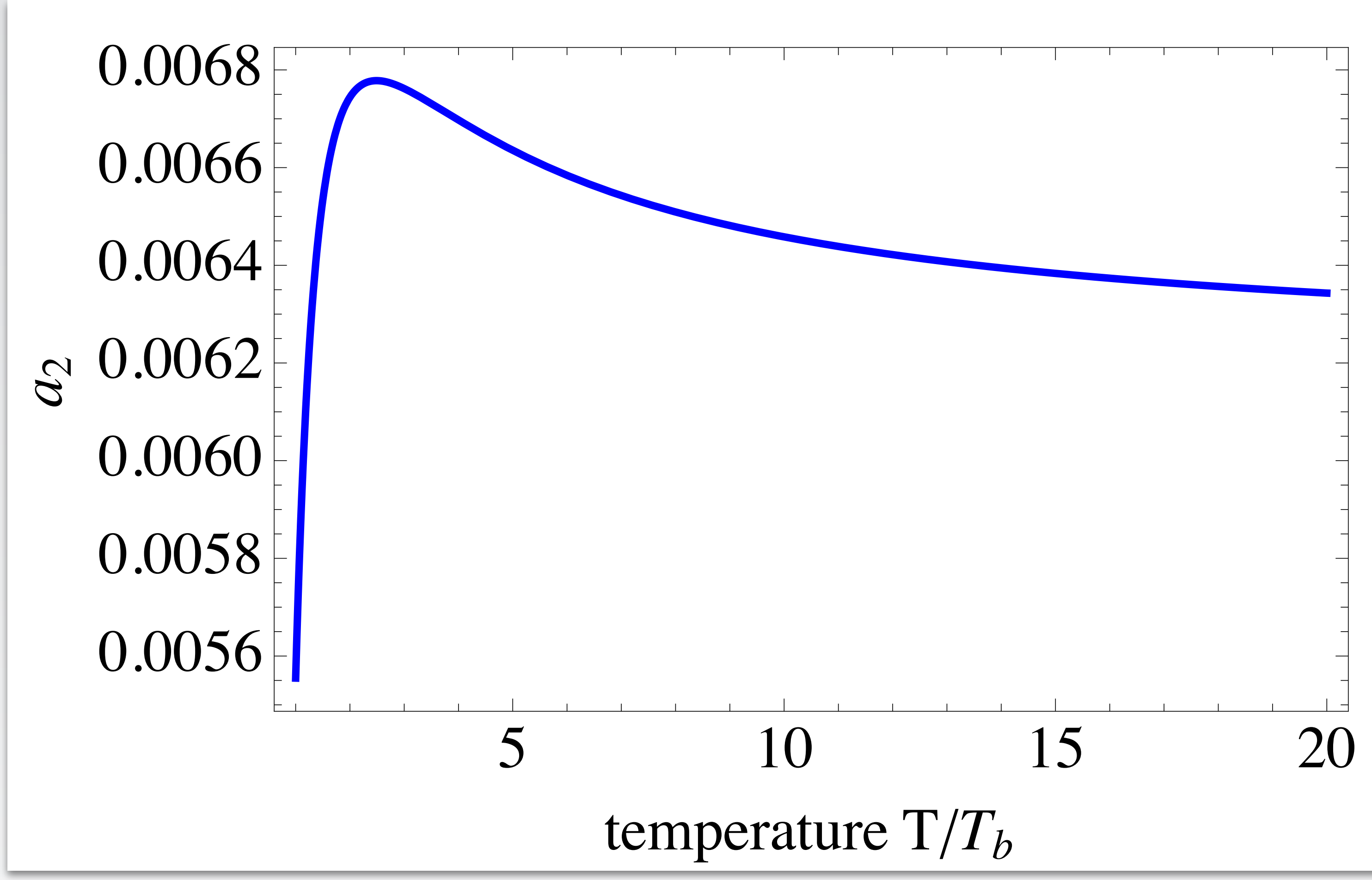
We have an Mpemba effect for

$$|a_2(T_h)| < |a_2\,(T_c)|$$

3 level system

E_i, B_{ij} random real numbers between [0,1]





Energies

$$\begin{pmatrix} E_1 \\ E_2 \\ E_3 \end{pmatrix} = \begin{pmatrix} 0.390102 \\ 0.977556 \\ 0.439562 \end{pmatrix}$$

Barriers

$$B = \begin{pmatrix} & 0.696996 & 0.328845 \\ 0.696996 & & 0.825929 \\ 0.328845 & 0.825929 & \end{pmatrix}$$

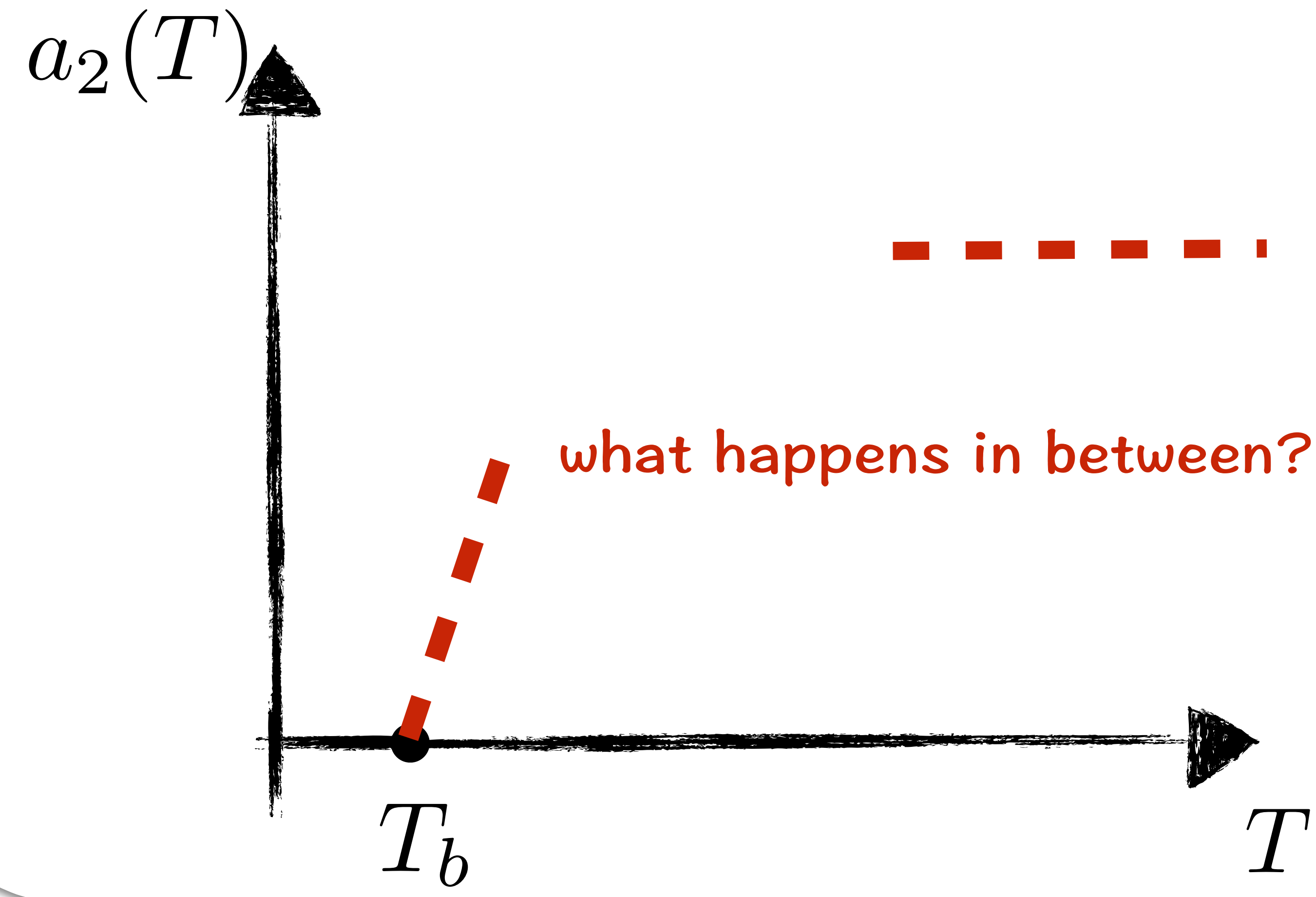
What do we know about a_2?

$$a_2(T) = \frac{\langle v_2| F |\pi(T)\rangle}{\langle v_2| F |v_2\rangle} \qquad F = \mathrm{diag}(e^{\beta_b E_1}, ..., e^{\beta_b E_N})$$

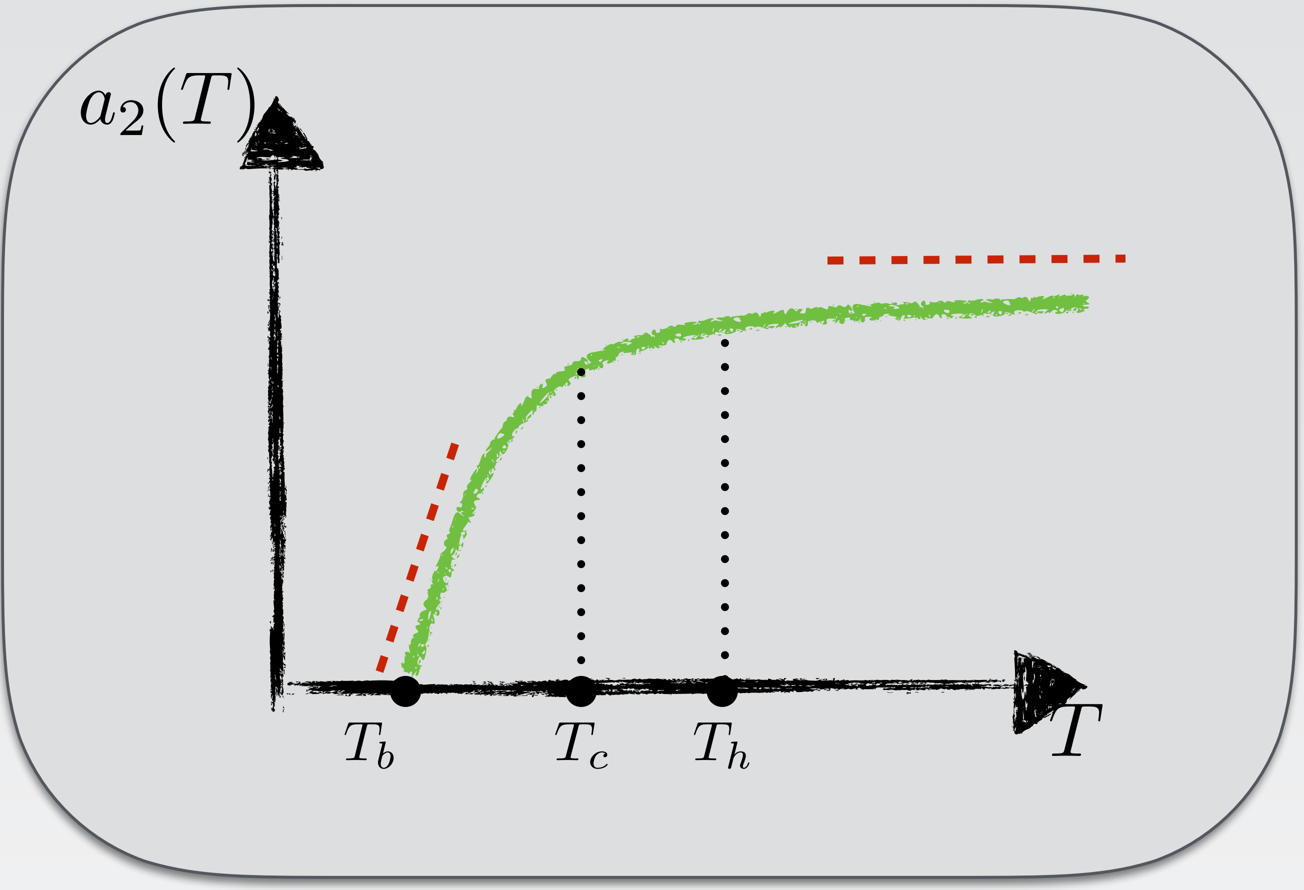
two special points:

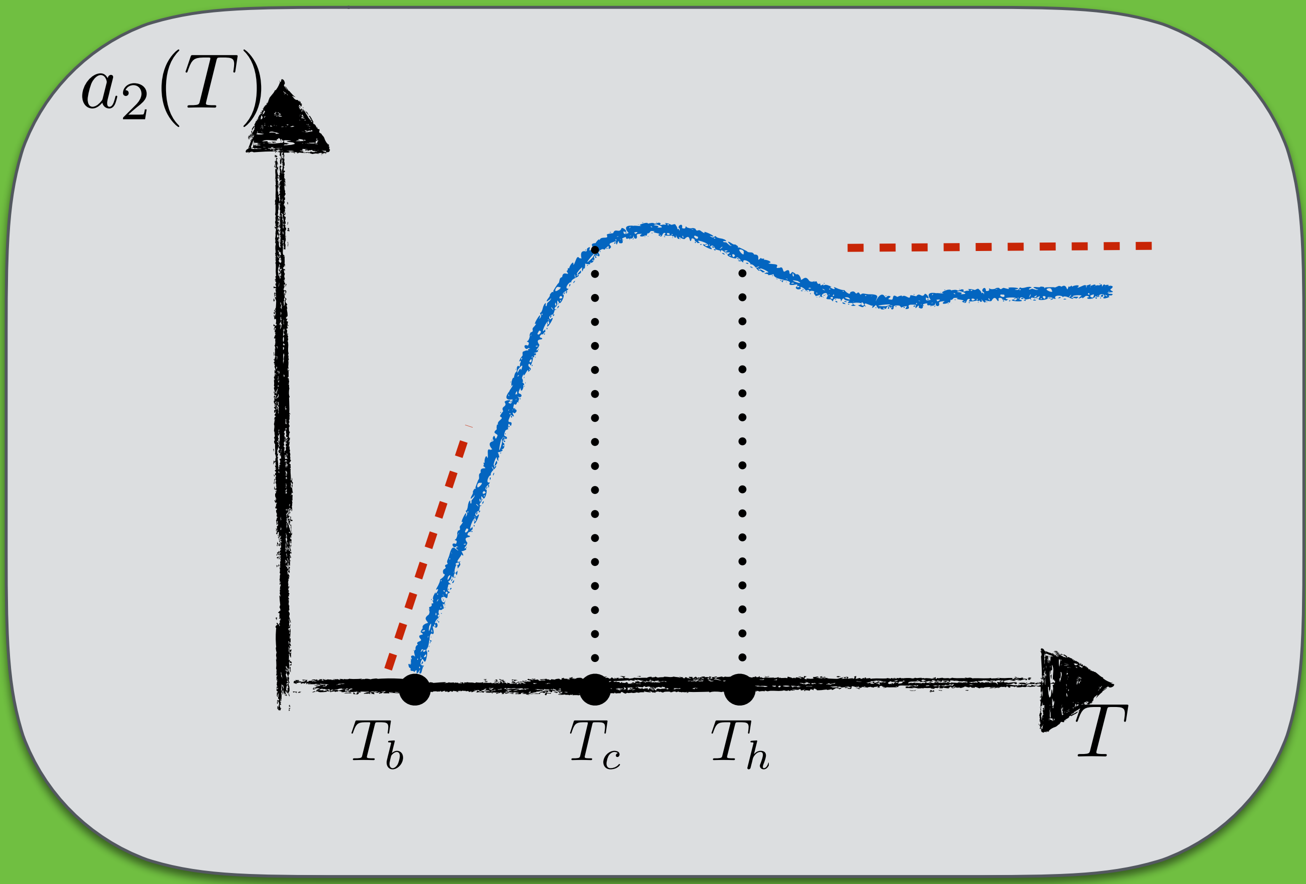
$a_2(T_b) = 0$

$a_2(T \to \infty) = \mathrm{const}$ since: $|\pi(T \to \infty)\rangle = \frac{1}{N}(1, ..., 1)$



Is there Mpemba effect?



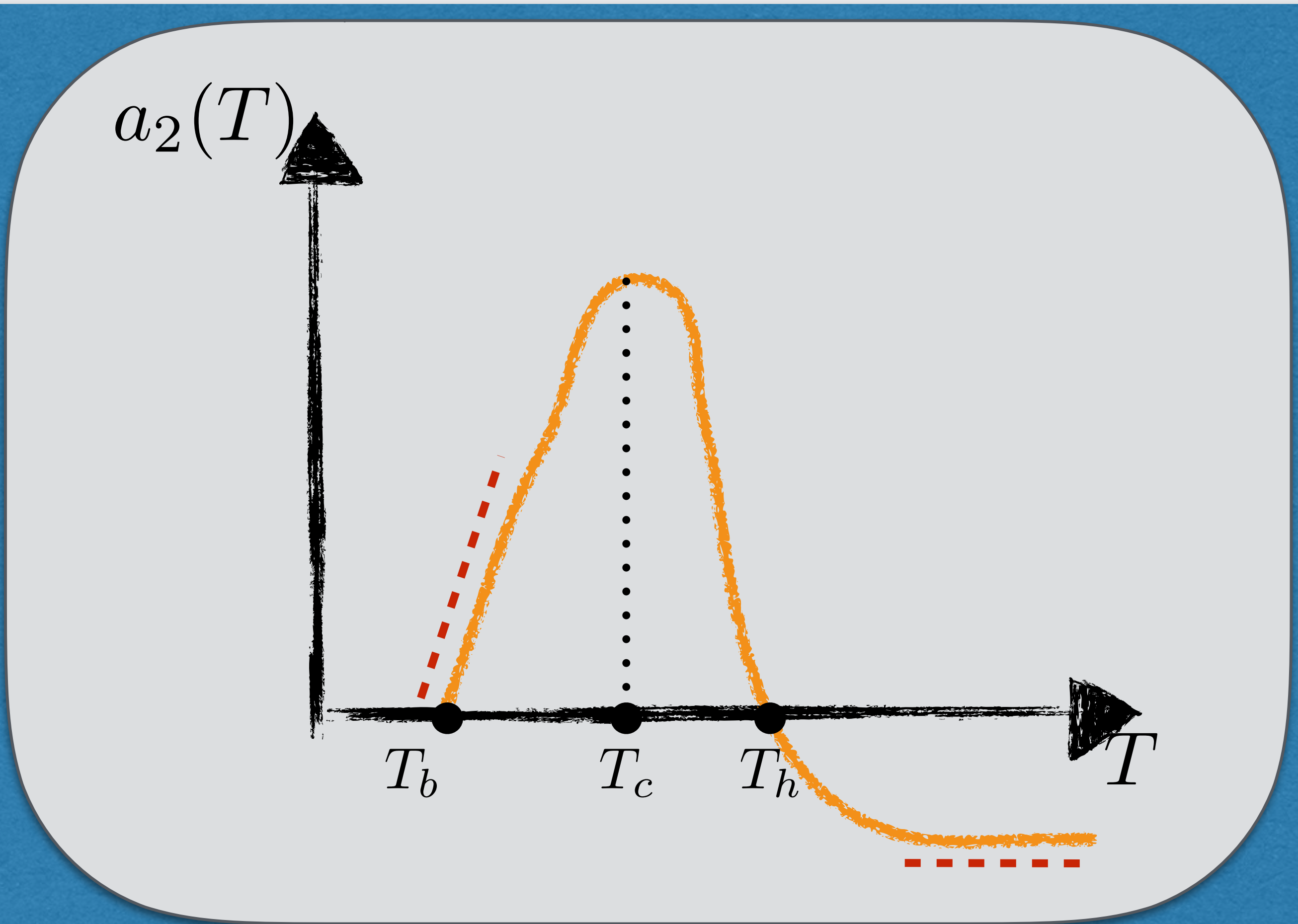


No

Yes

Can we have a more dramatic effect?

Yes

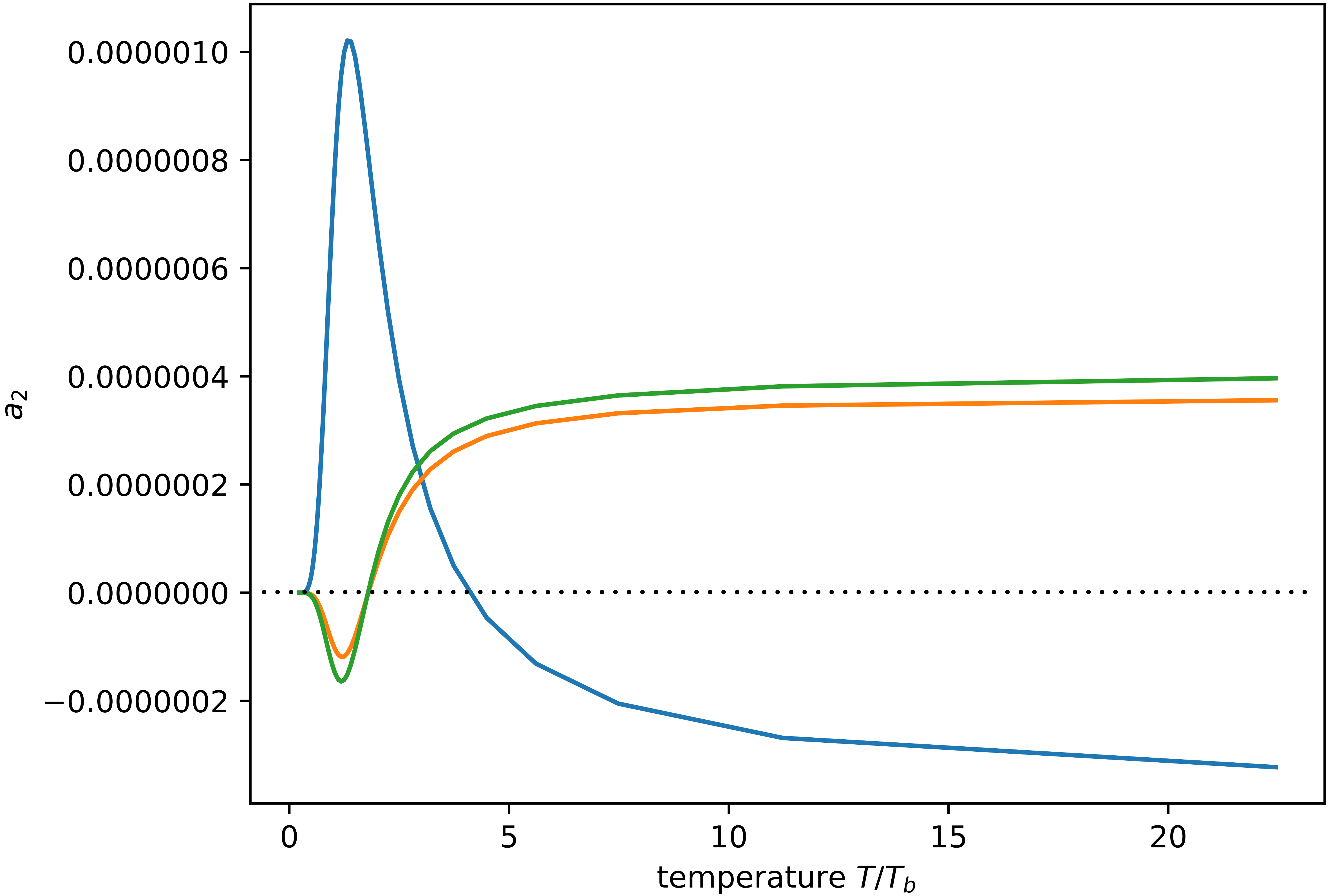


relaxation time jumps from $\frac{1}{\lambda_2}$ to $\frac{1}{\lambda_3}$

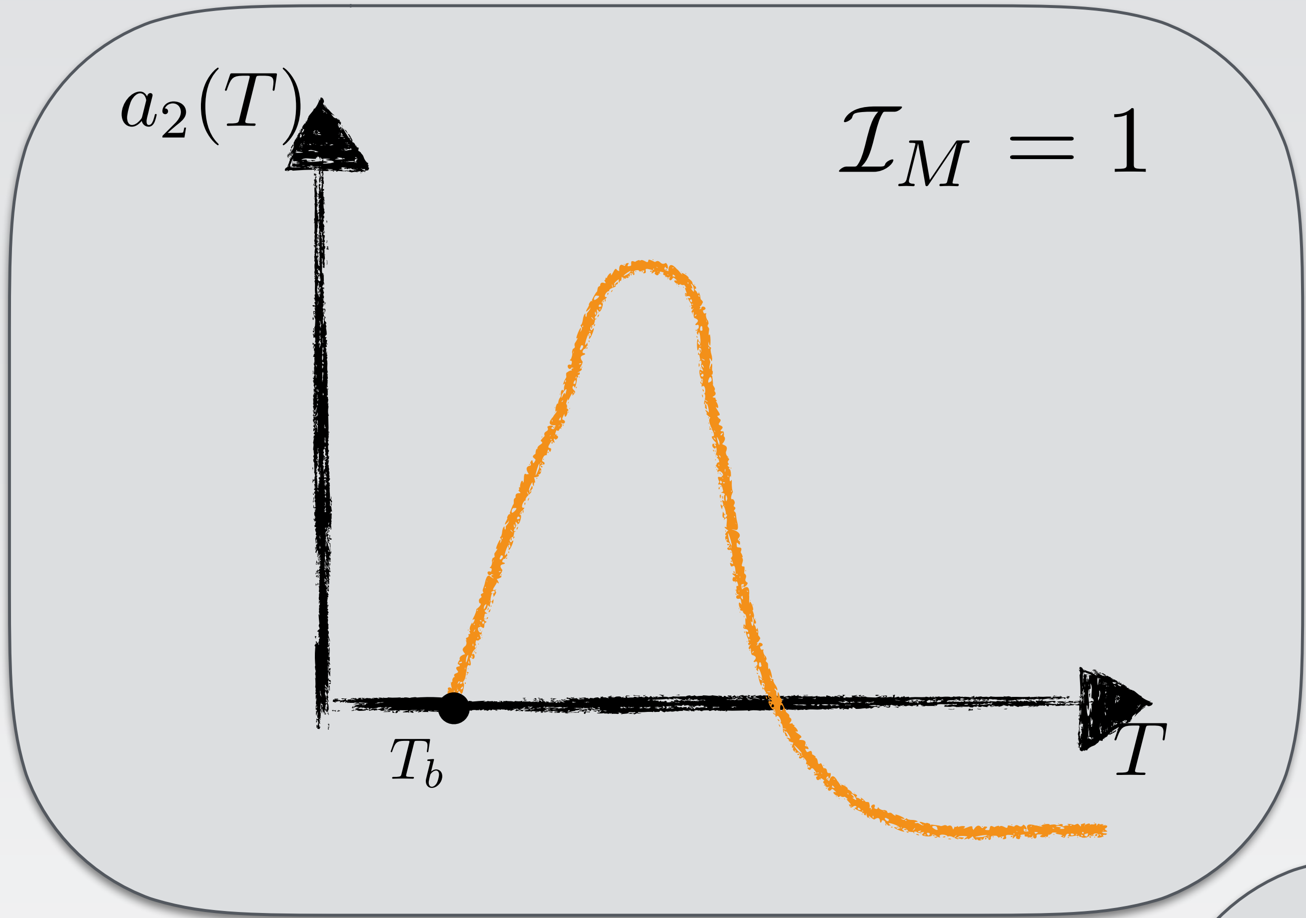
We call this the STRONG MPEMBA EFFECT

Random Energy Model

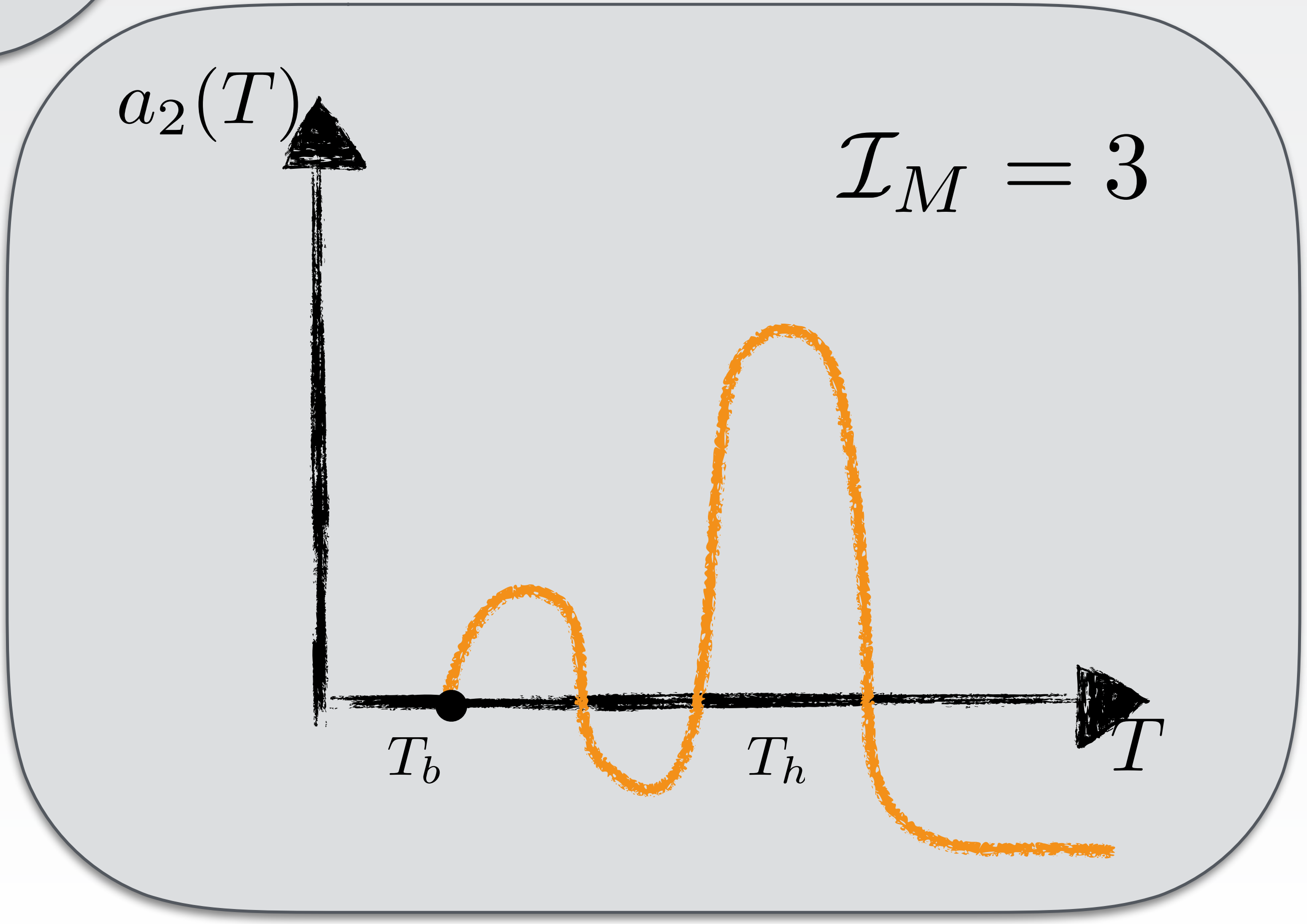
128 energy levels, $p(E_i) = N(0,4)$, $p(B_{ij}) = N(0,4)$, $\beta_b = 4.5$



Mpemba index $\mathcal{I}_M$



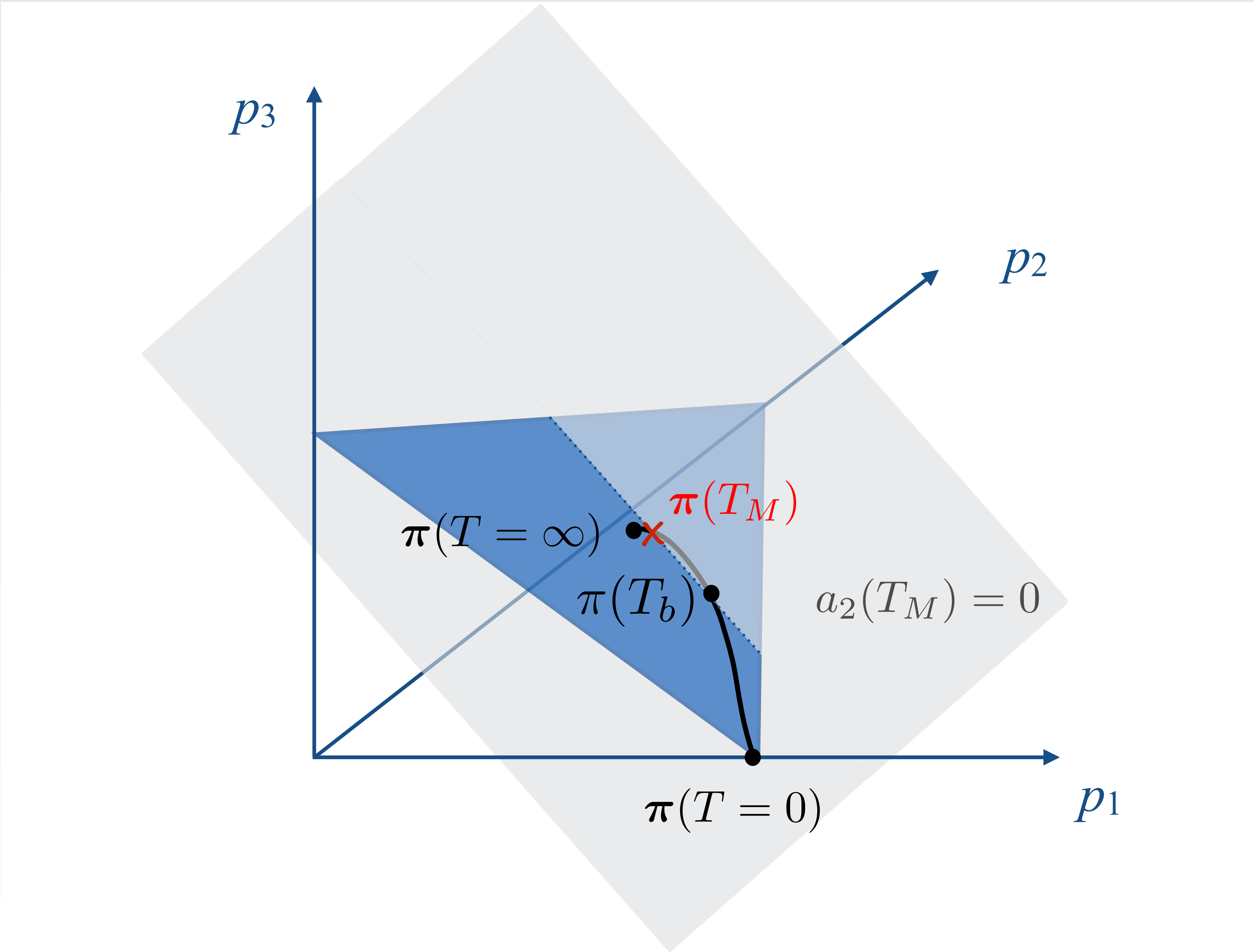
Number of time the trajectory crosses zero for $T > T_b$



the index has topological nature

To have the Strong Mpemba effect the trajectory crosses zero at least once for $T > T_b$

illustration for 3 states



How generic is the strong Mpemba effect?

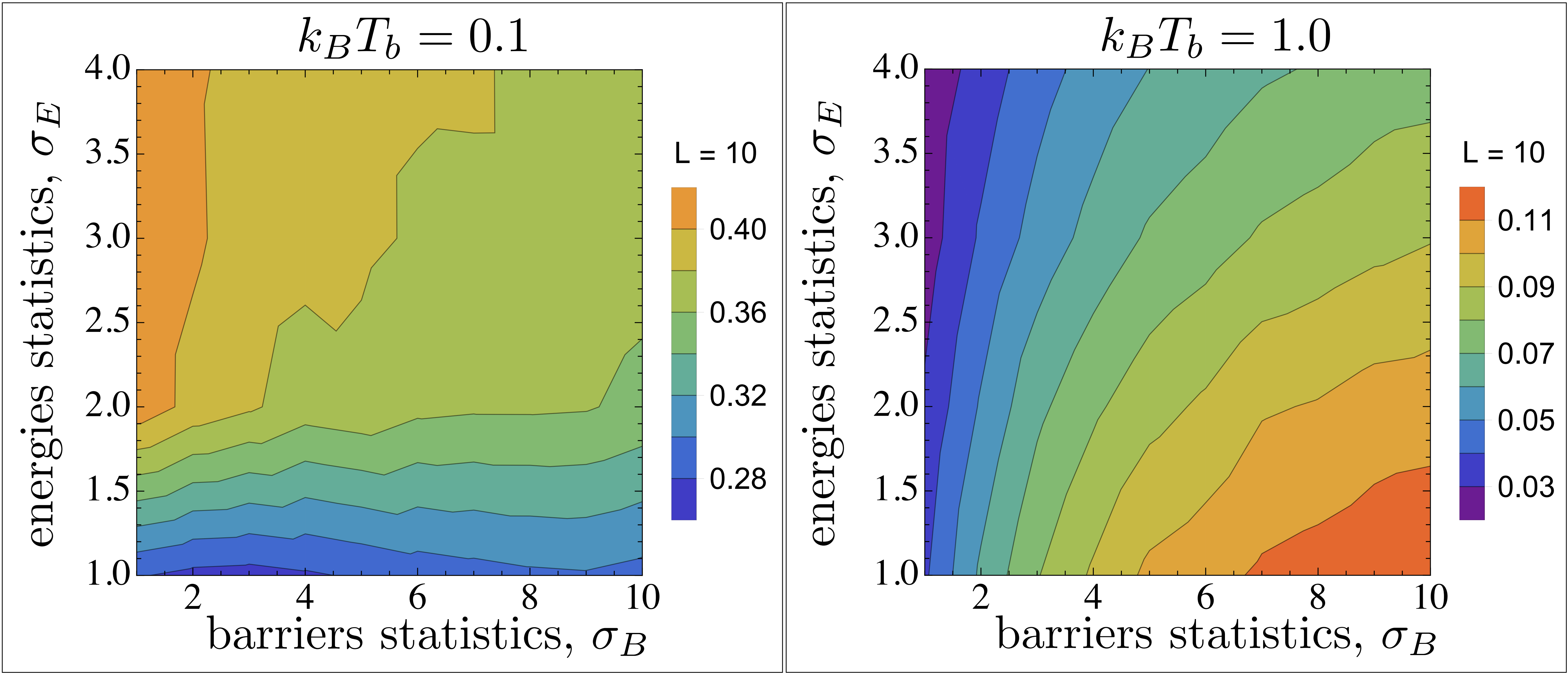
Random Energy Model

each point is averaged over 10^5 realizations,

energies $\mathcal{N}(0, \sigma_E^2)$, barriers $\mathcal{N}(0, \sigma_B^2)$

density map:

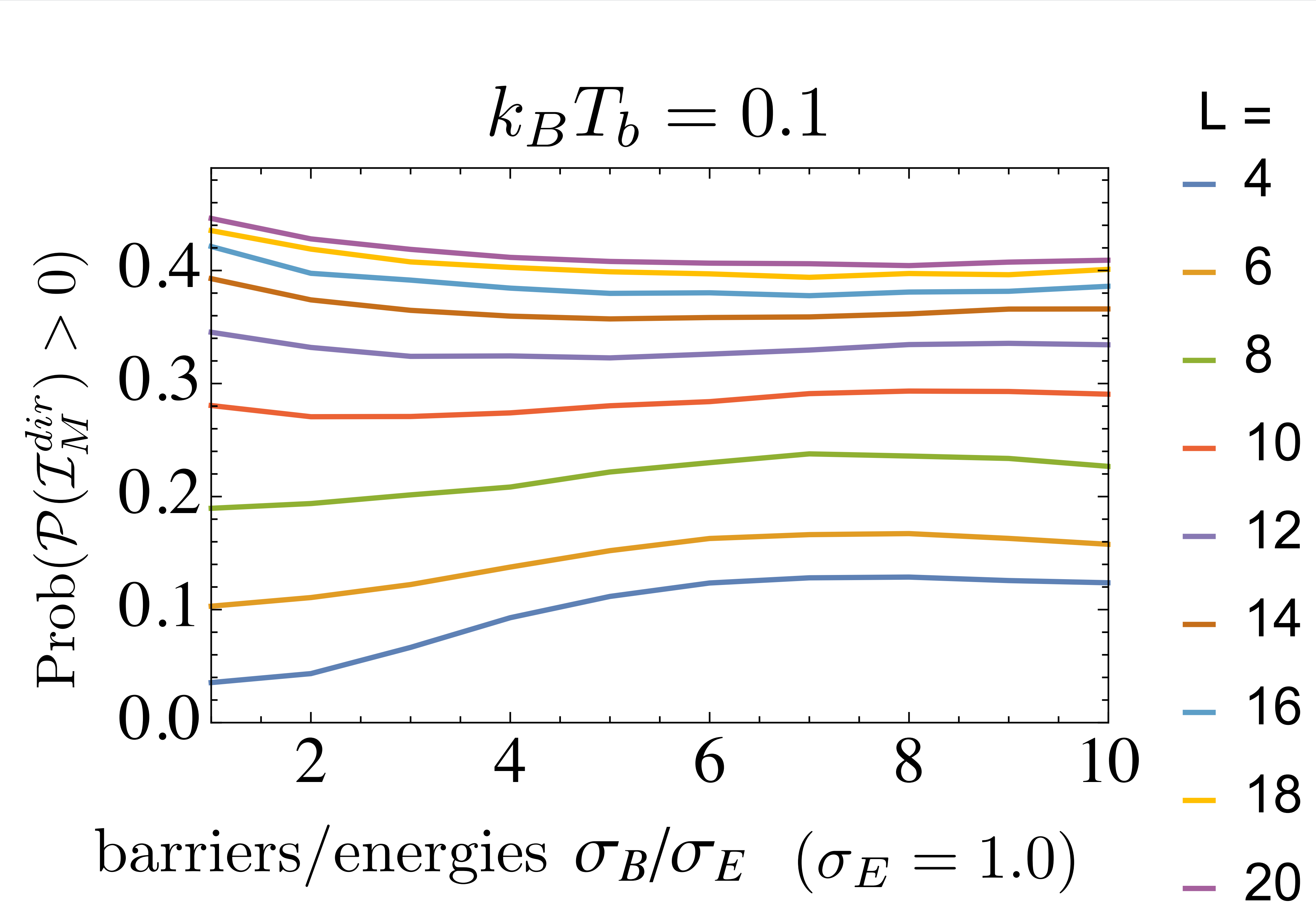
Probability of Parity of direct Mpemba Index $\mathrm{Prob}(\mathcal{P}(\mathcal{I}_M^{dir}) > 0)$



Random Energy Model with Random Barriers

Changing the system size

averaged over 2 x 10^5 realizations



Dauntingly hard disorder average over barriers

rate matrix R:

at T_b: $R_{ij}\pi_j = R_{ji}\pi_i$

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

$B_{ij} = B_{ji}$

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

However, we can try something ORTHOGONAL!

Can we say something about the second eigenvector $|f_2\rangle$?

let's take a random vector $|X\rangle$ with x_i iid Gaussian, make an orthogonal vector to $|f_1\rangle$

$$|f_2(X)\rangle = |X\rangle - \frac{\langle X, f_1\rangle}{||f_1||^2}\,|f_1\rangle$$

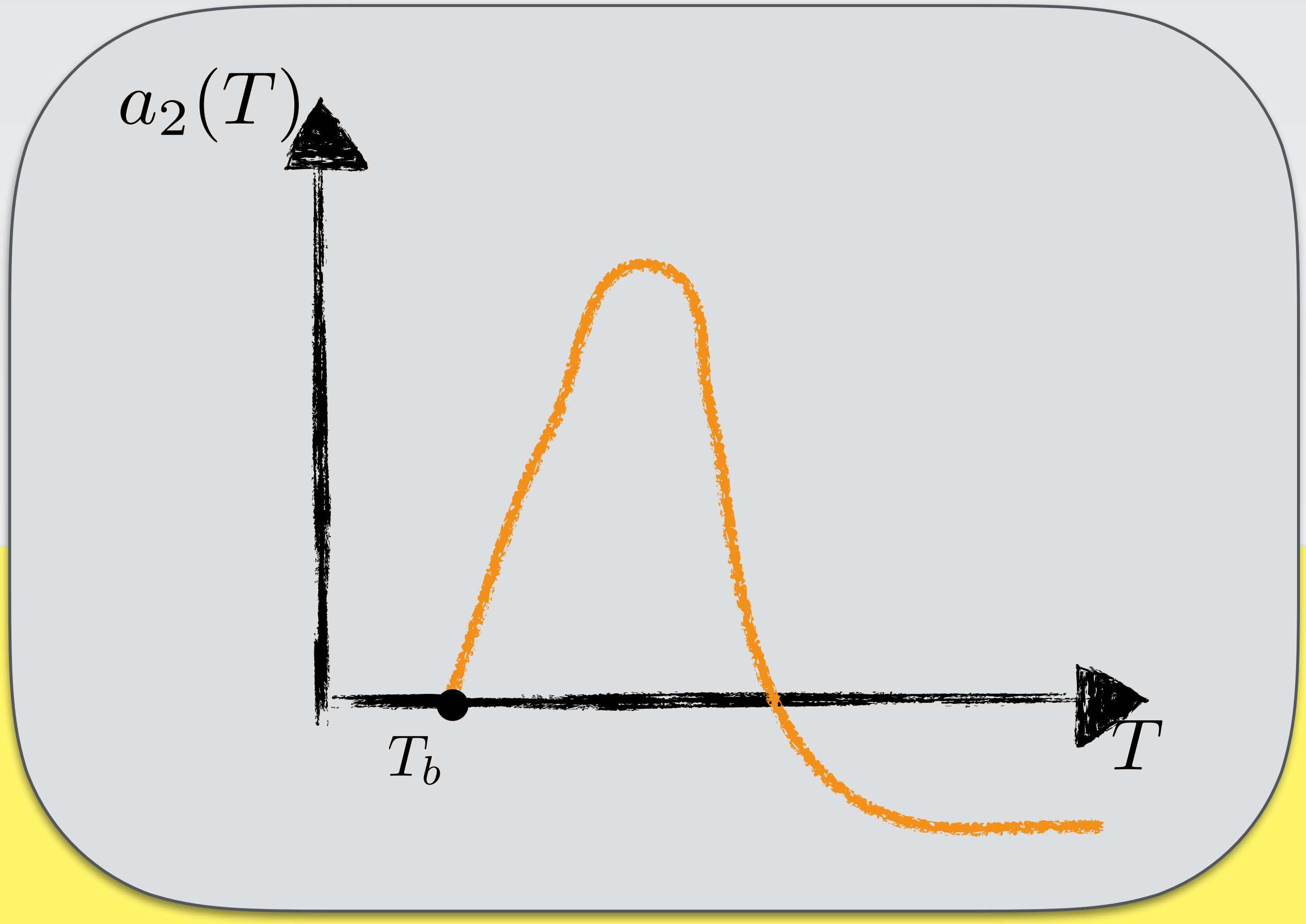
$$\tilde{R} = F^{1/2} R F^{1/2}$$

$$\tilde{R} f_i = \lambda_i f_i$$

$$\langle f_i | f_j\rangle = \delta_{ij}$$

Lower bound for the Mpemba index

Strong Mpemba effect - needs at least two zeros of a_2



look at the sign the product of a_2 infinitesimally close to the T_b and at infinity

$$\Theta(-a_2(T \to \infty)\partial_T a_2|_{T=T_b})$$

detects odd number of crossings

“Isotropic” ensemble

$$|f_2(X)\rangle = |X\rangle - \frac{\langle X, f_1\rangle}{||f_1||^2} |f_1\rangle$$

random vector |X> with x_i iid Gaussian

Strong Mpemba effect - two zeros of a_2

$$a_2(T) = \frac{\langle f_2| F^{1/2} |\pi(T)\rangle}{\langle f_2| f_2\rangle}$$

estimating the lower bound for the Mpemba Index

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

u, w depend on energy levels only

Averaging over random vectors |X> with Gaussian iids

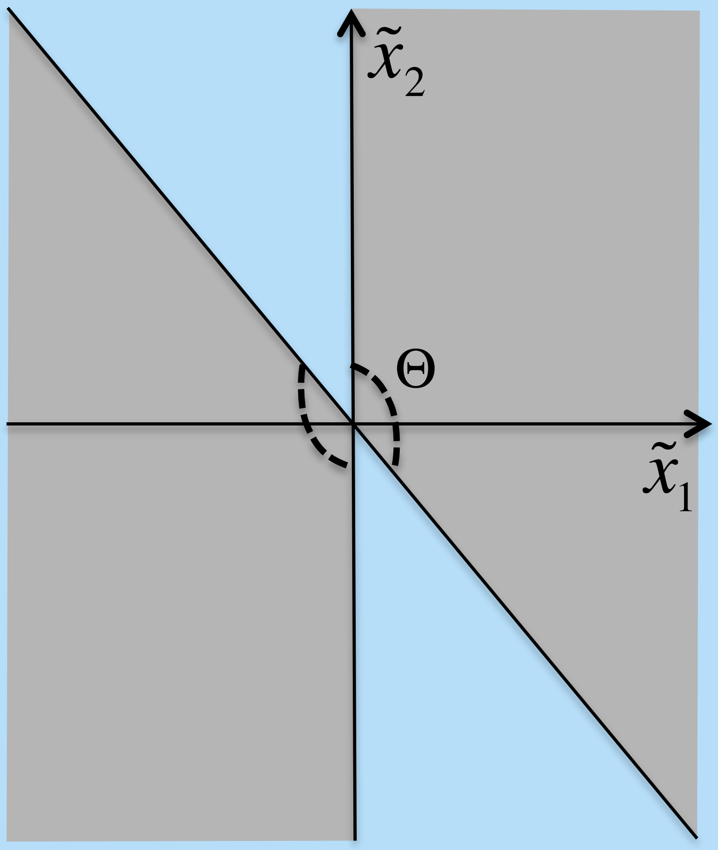
Isotropic ensemble

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

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

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

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

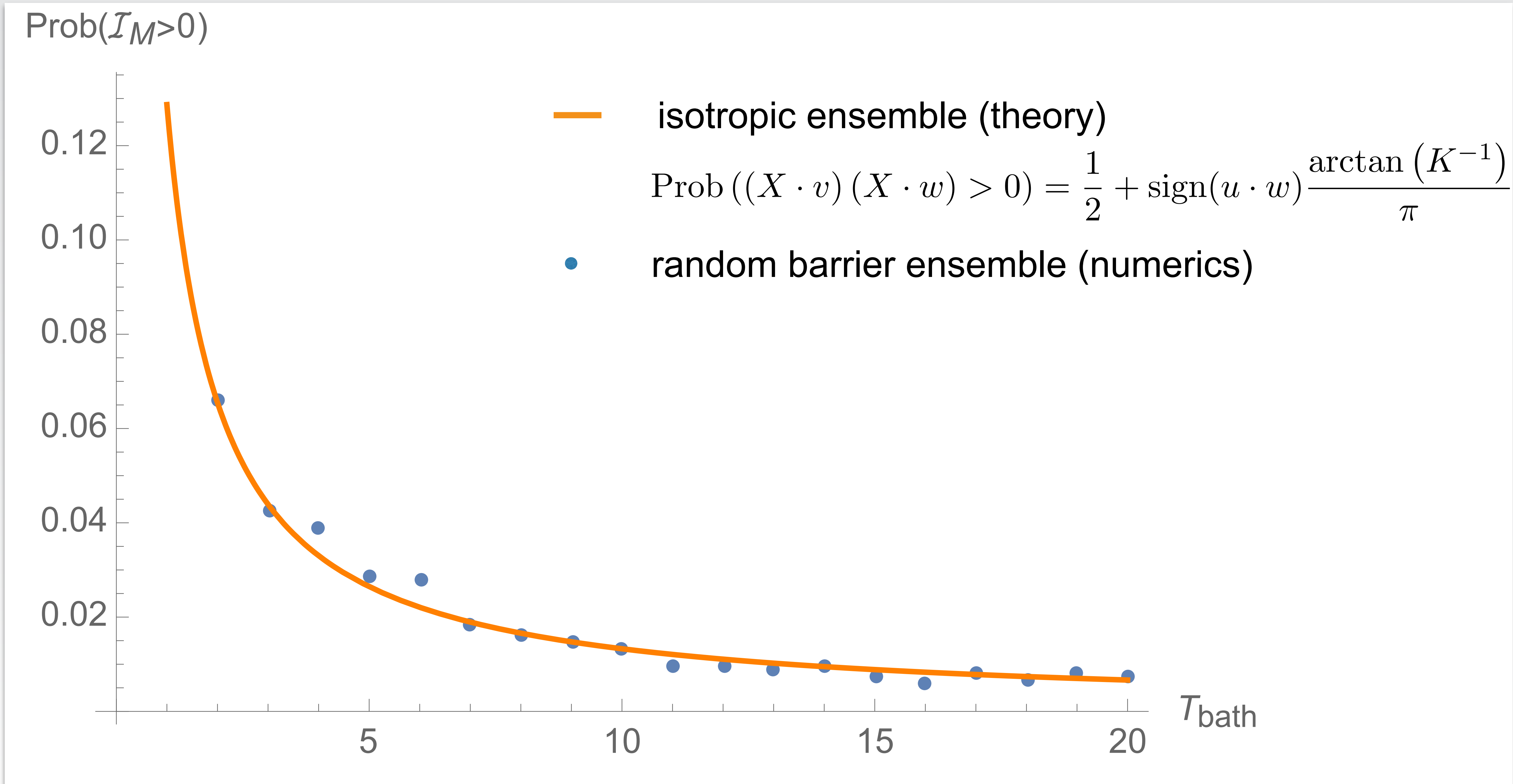


the grey area over the total area:

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

Probability of the strong Mpemba effect

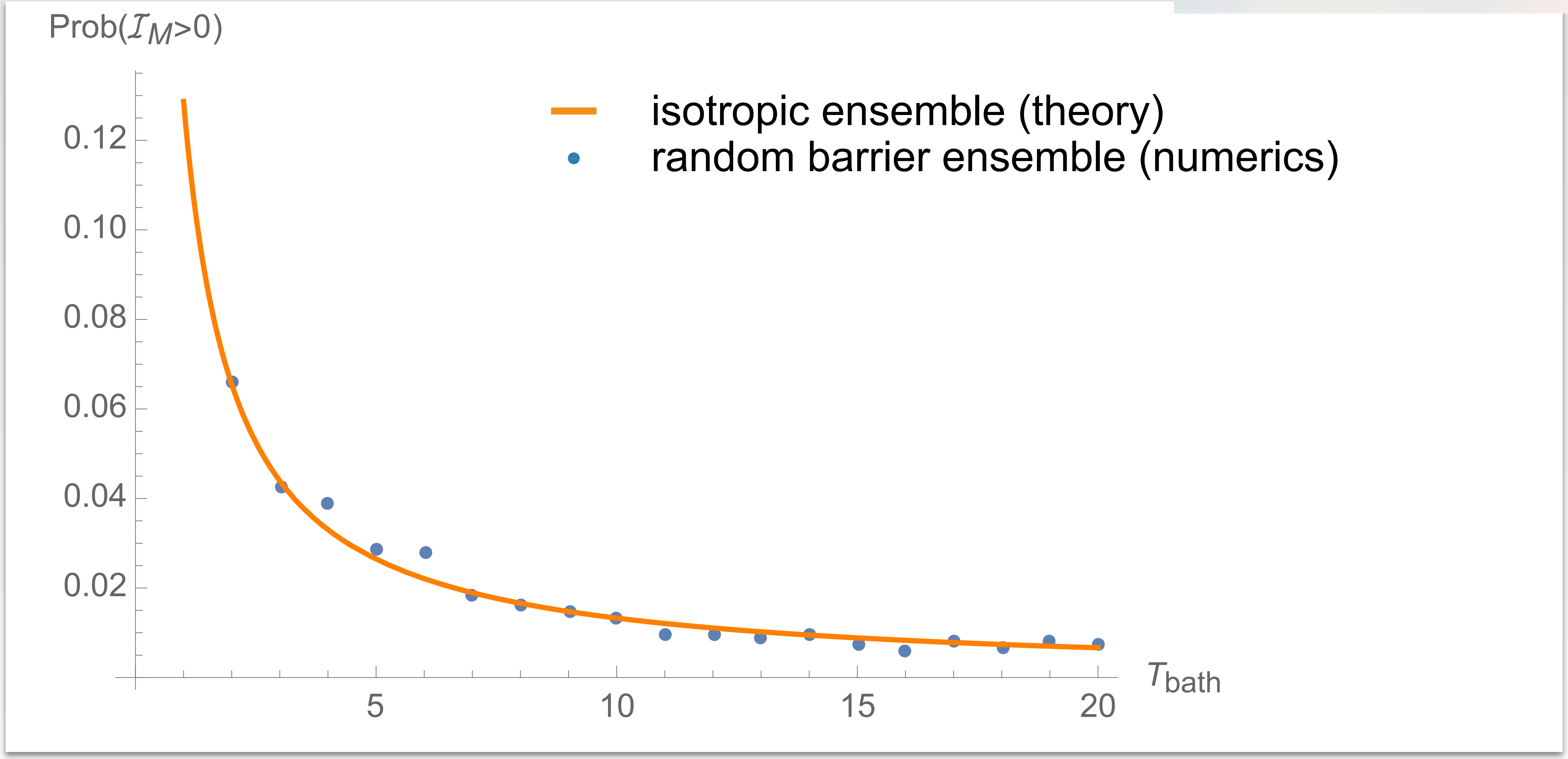
a particular energy realization, n=10 energy levels,
(random barriers with N(0,25), each point 4000 realizations)



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

Note, this is non-trivial!

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



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

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

Glauber dynamics

- only transitions to neighboring states are allowed

This introduces **additional barriers**

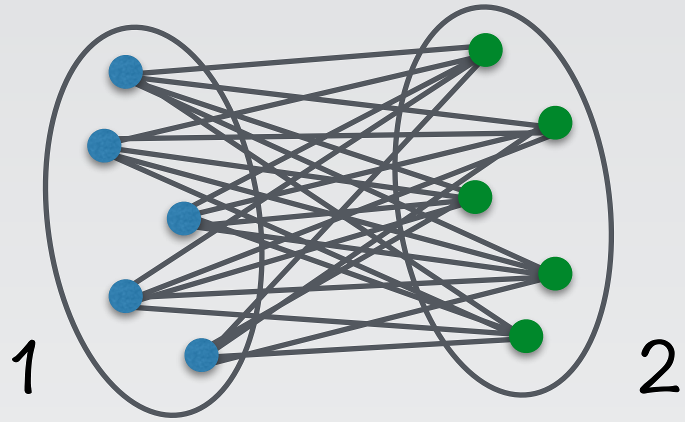
for a system of spins:

$$B_{ij} = \begin{cases} \frac{1}{\pi_i + \pi_j} & \text{single spin flip from } i \text{ to } j \\ \infty & \text{otherwise} \end{cases}$$

Similar results for Metropolis dynamics

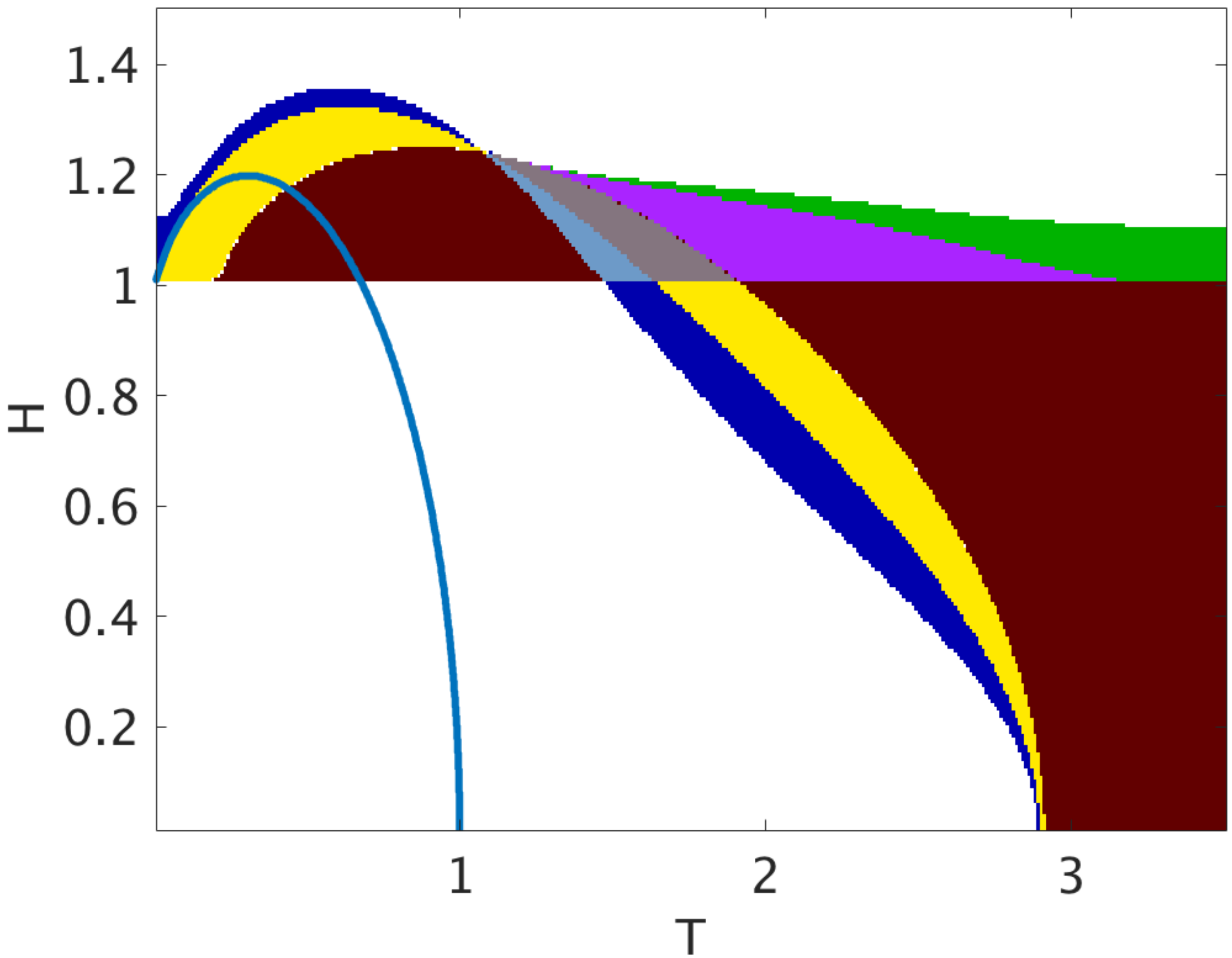
Anti-ferromagnet

complete bipartite graph



N = 140 spins

x_1, x_2 magnetization densities on subgraphs 1 and 2



Energy:

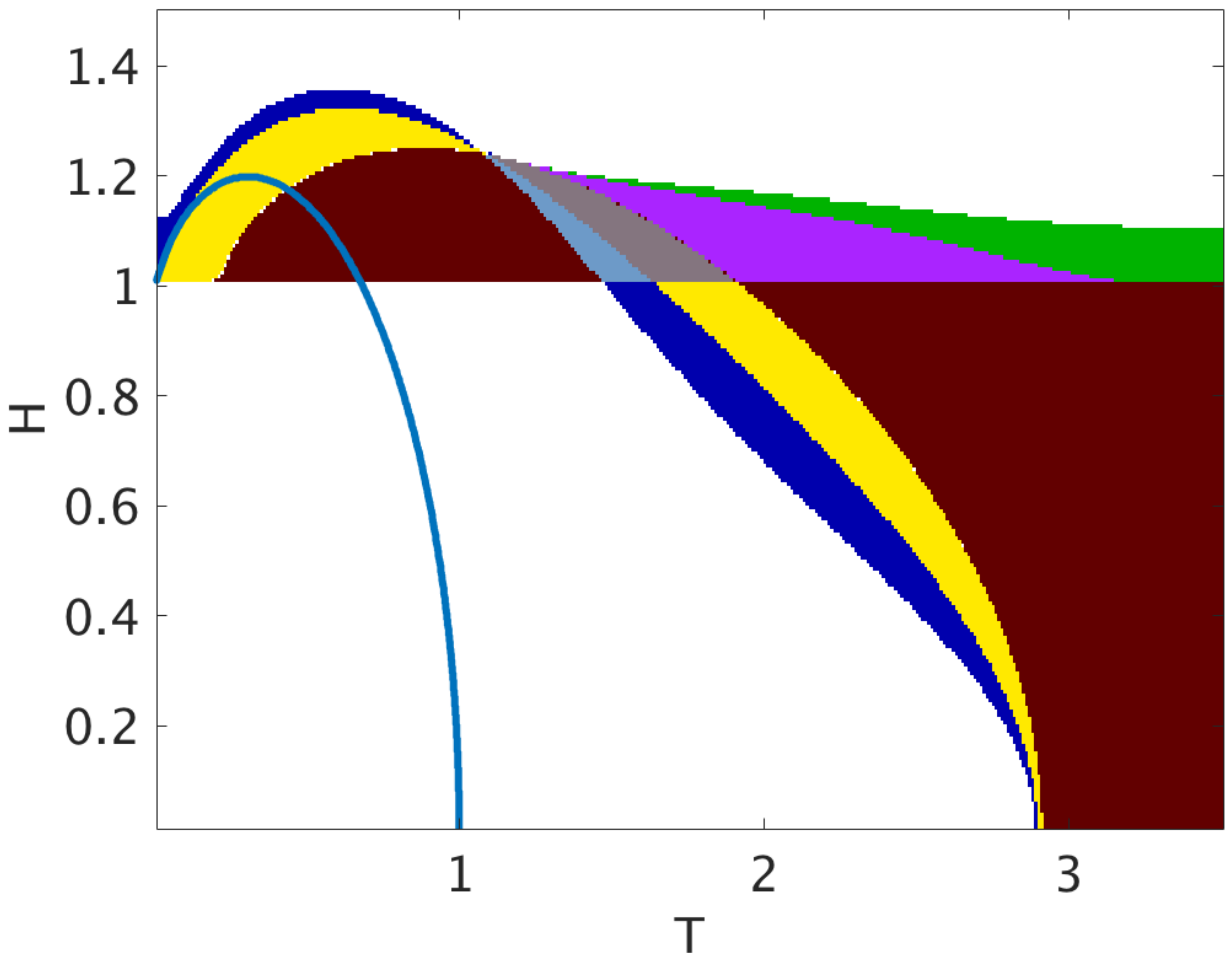
$$\mathcal{H} = \frac{N}{2}\left[-Jx_1x_2 - \mu H(x_1 + x_2)\right],$$

H magnetic field

J interaction strength

μ magnetic moment

Mpemba
Phase diagram



No direct nor inverse effect

Weak direct & no inverse effect

Weak inverse & no direct effect

Strong inverse $I_M=1$ & no direct

Strong inverse $I_M=2$ & no direct

Strong inverse $I_M=1$ & weak direct

Strong inverse $I_M=1$ & strong direct $I_M=1$

Strong direct $I_M=1$ & weak inverse

Thermodynamic limit

Master eq:

$$\partial_t p(x_1,x_2) = R^{u_1}(x_1-\Delta x,x_2)p(x_1-\Delta x,x_2)$$
$$+ R^{u_2}(x_1,x_2-\Delta x)p(x_1,x_2-\Delta x)$$
$$+ R^{d_1}(x_1+\Delta x,x_2)p(x_1+\Delta x,x_2)$$
$$+ R^{d_2}(x_1,x_2+\Delta x)p(x_1,x_2+\Delta x)$$
$$- \Big[R^{u_1}(x_1,x_2) + R^{d_1}(x_1,x_2)$$
$$+R^{u_2}(x_1,x_2) + R^{d_2}(x_1,x_2)\Big]\, p(x_1,x_2)$$

Continuum limit: Fokker-Planck eq. with force terms

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

All captured by evolution of average x1 and x2

$$\overline{x_1}(t) \equiv \int x_1 p(x_1, x_2) dx_1 dx_2,$$

$$\overline{x_2}(t) \equiv \int x_2 p(x_1, x_2) dx_1 dx_2,$$

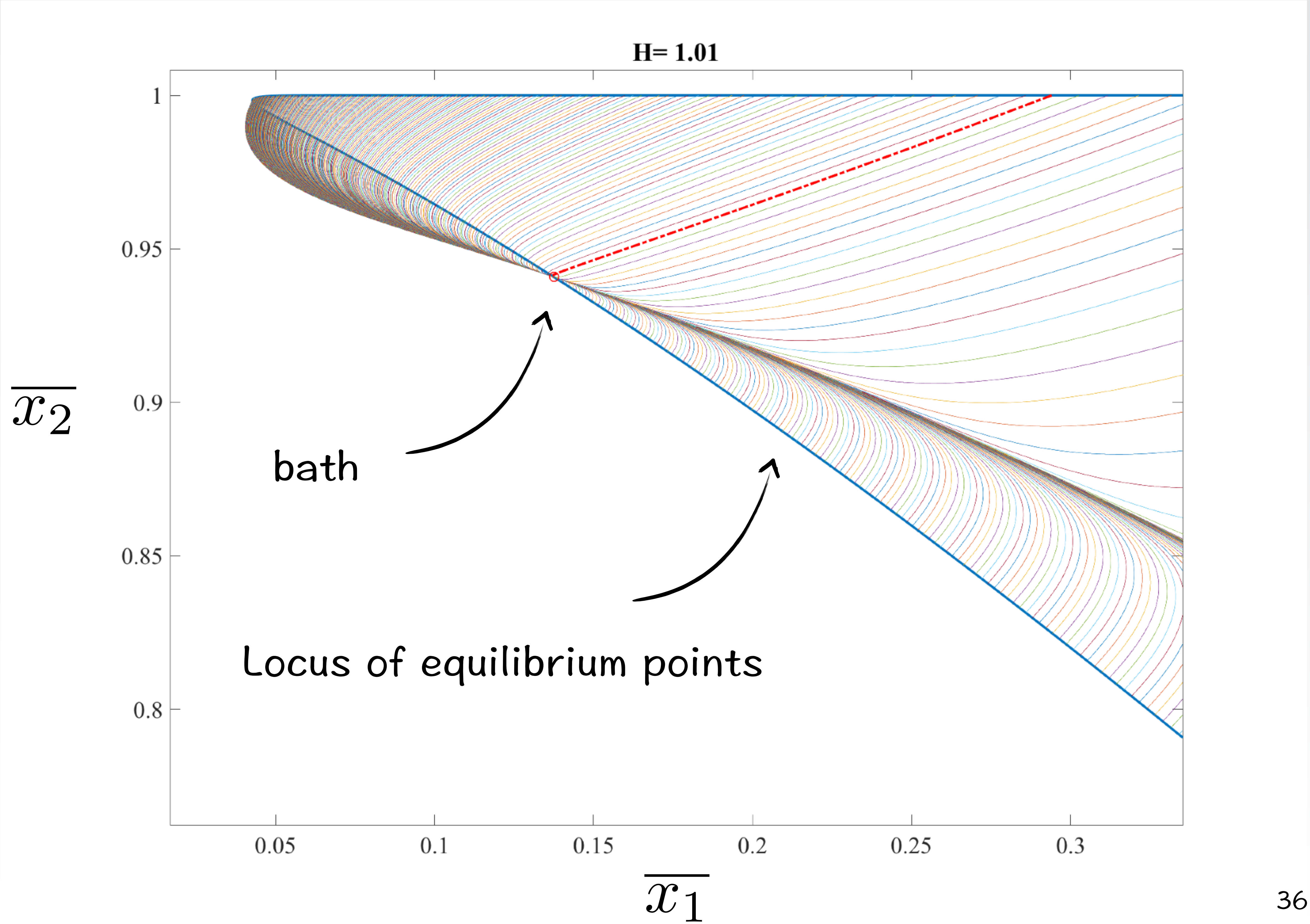
Eqs. of motion of the averages

$$\dot{\overline{x_1}} = \frac{1}{2}\left(\tanh \beta_b \left(H - \overline{x_2}\right) - \overline{x_1}\right)$$

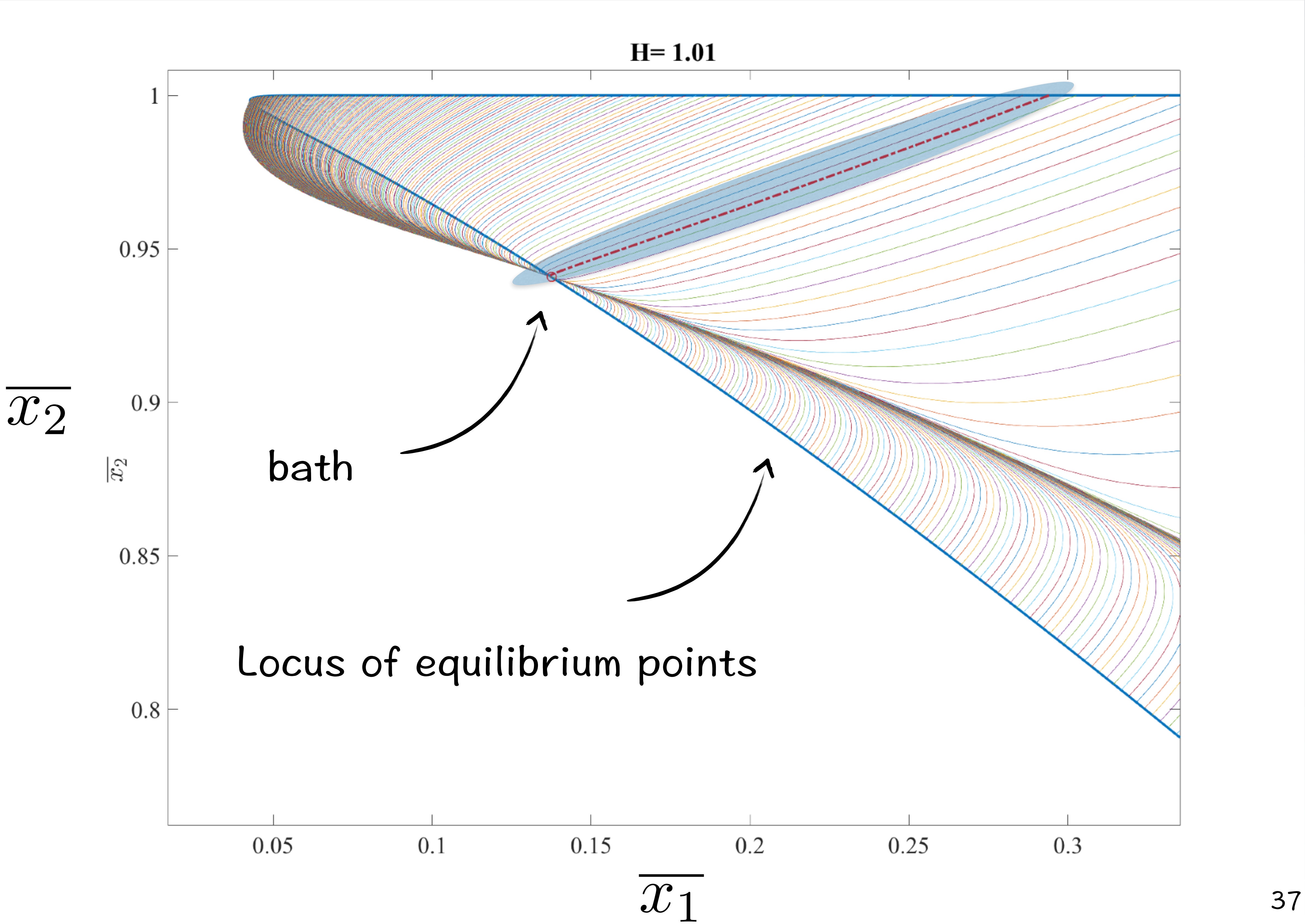
$$\dot{\overline{x_2}} = \frac{1}{2}\left(\tanh \beta_b \left(H - \overline{x_1}\right) - \overline{x_2}\right)$$

Magnetization densities plane at H = 1.01

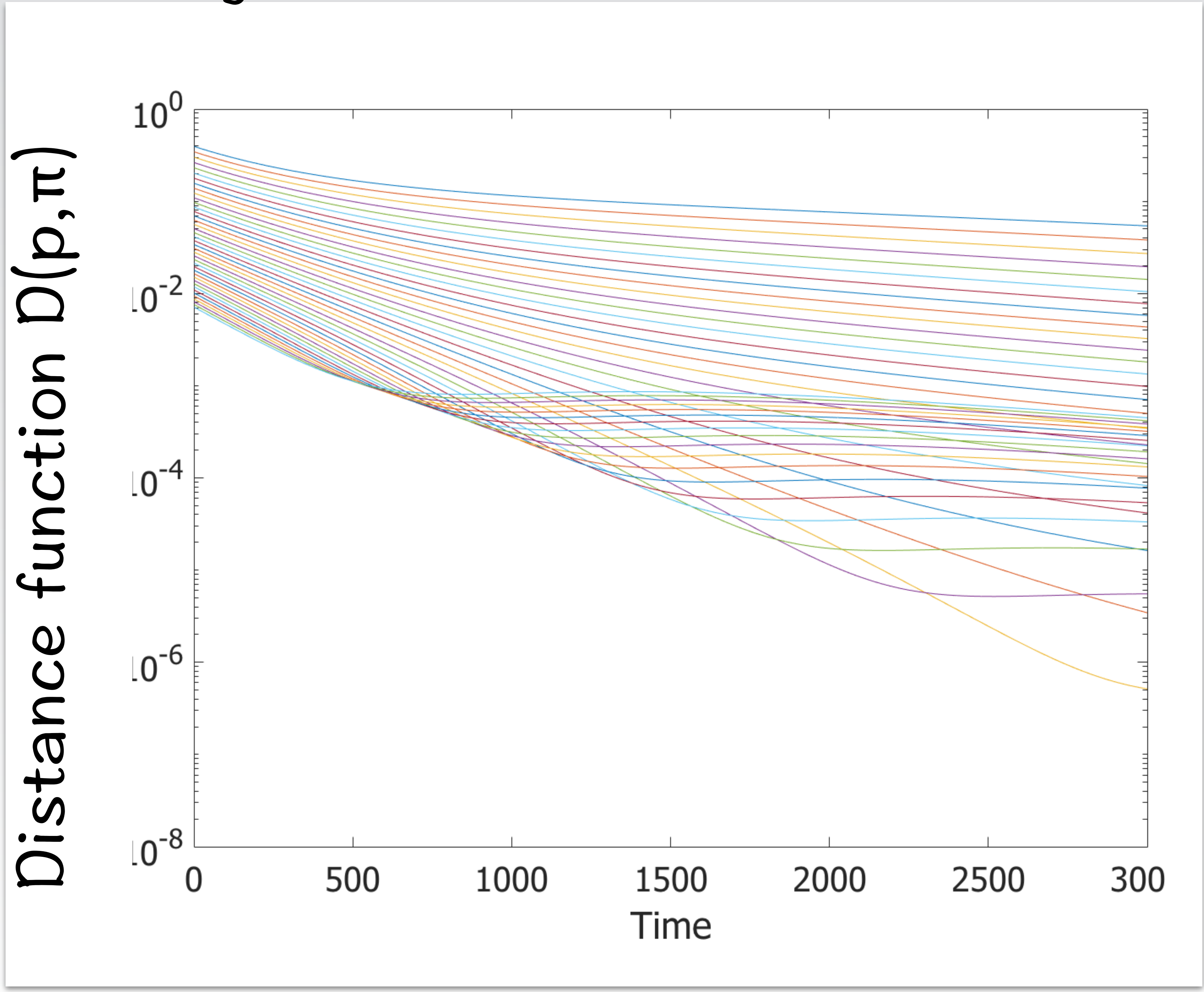
Relaxation trajectories



Strong Mpemba trajectory

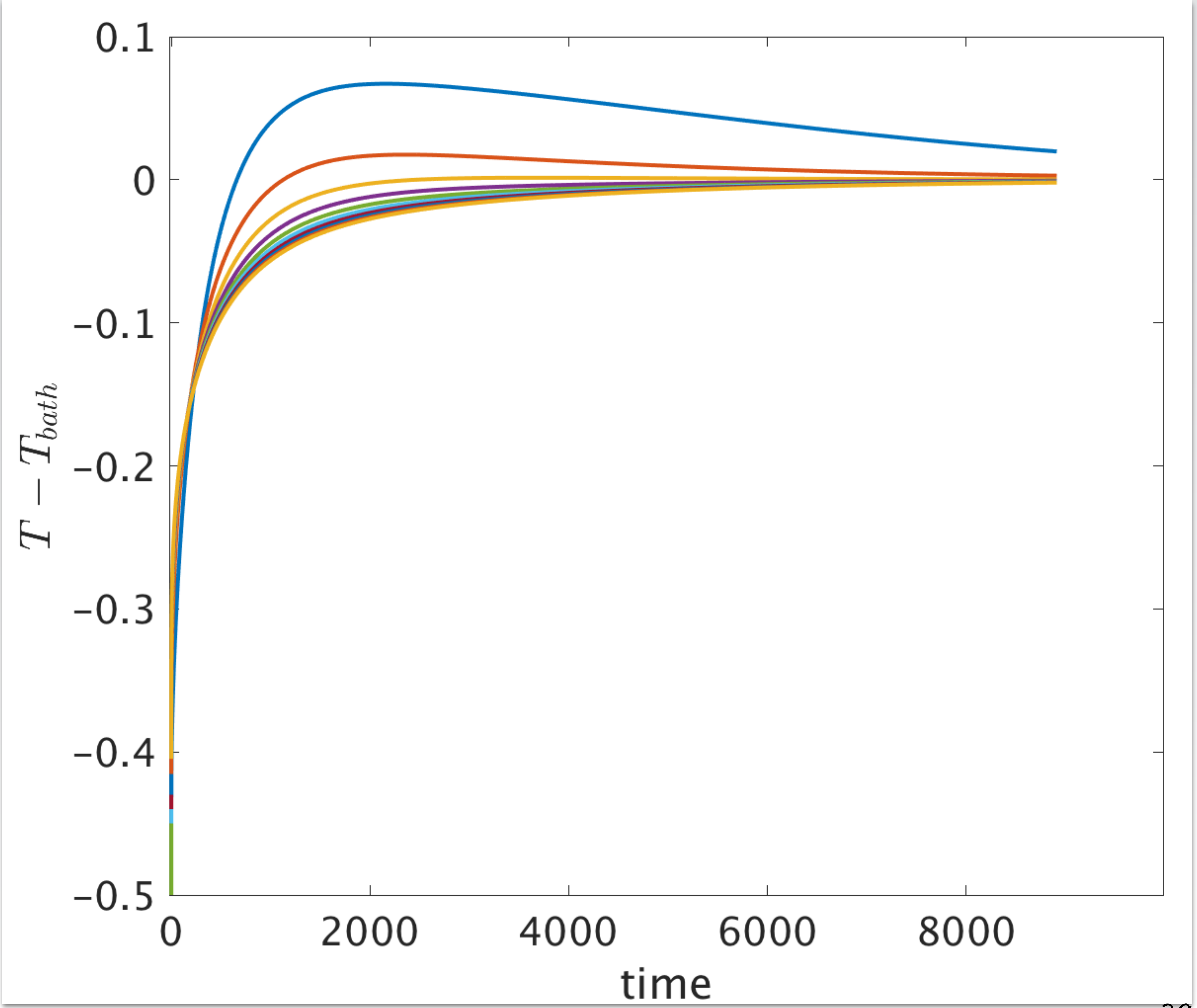


Mpemba effect — weak & strong whenever we have crossing trajectories



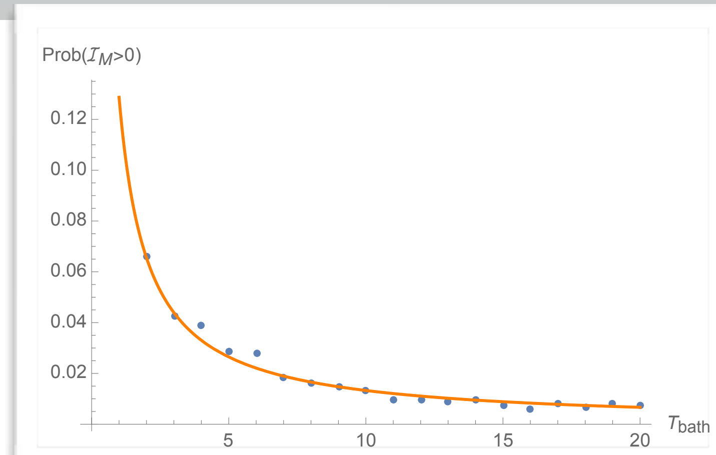
$$D(p(T,t),\pi_b) = \frac{F(p) - F(\pi_b)}{T_b}$$

Thermal overshoot

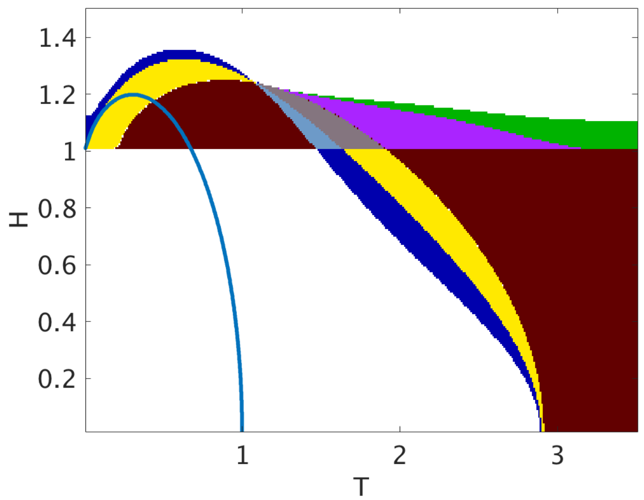


Summary

- Mpemba effect for general systems
  - Weak Mpemba effect
  - Strong Mpemba effect; Mpemba index
- Isotropic ensemble (random vector orthogonal to bath equilibrium) gives good estimate for Prob(Strong Mpemba)



- Metropolis on a complete graph - NO Mpemba effect
- Anti-ferromagnet with Glauber dynamics and single-spin flips — phase diagram of Strong Mpemba Effect



A. Samarakoon, T. J. Sato, T. Chen, G.-W. Chern, J. Yang, I. Klich, R. Sinclair, H. Zhou, and S.-H. Lee, Proceedings of the National Academy of Sciences 113, 11806 (2016)

Significance

Our bulk susceptibility and Monte Carlo simulation study of aging and memory effects in densely populated frustrated magnets (spin jam) and in a dilute magnetic alloy (spin glass) indicates a nonhierarchical landscape with a wide and nearly flat but rough bottom for the spin jam and a hierarchical rugged funnel-type landscape for the spin glass.

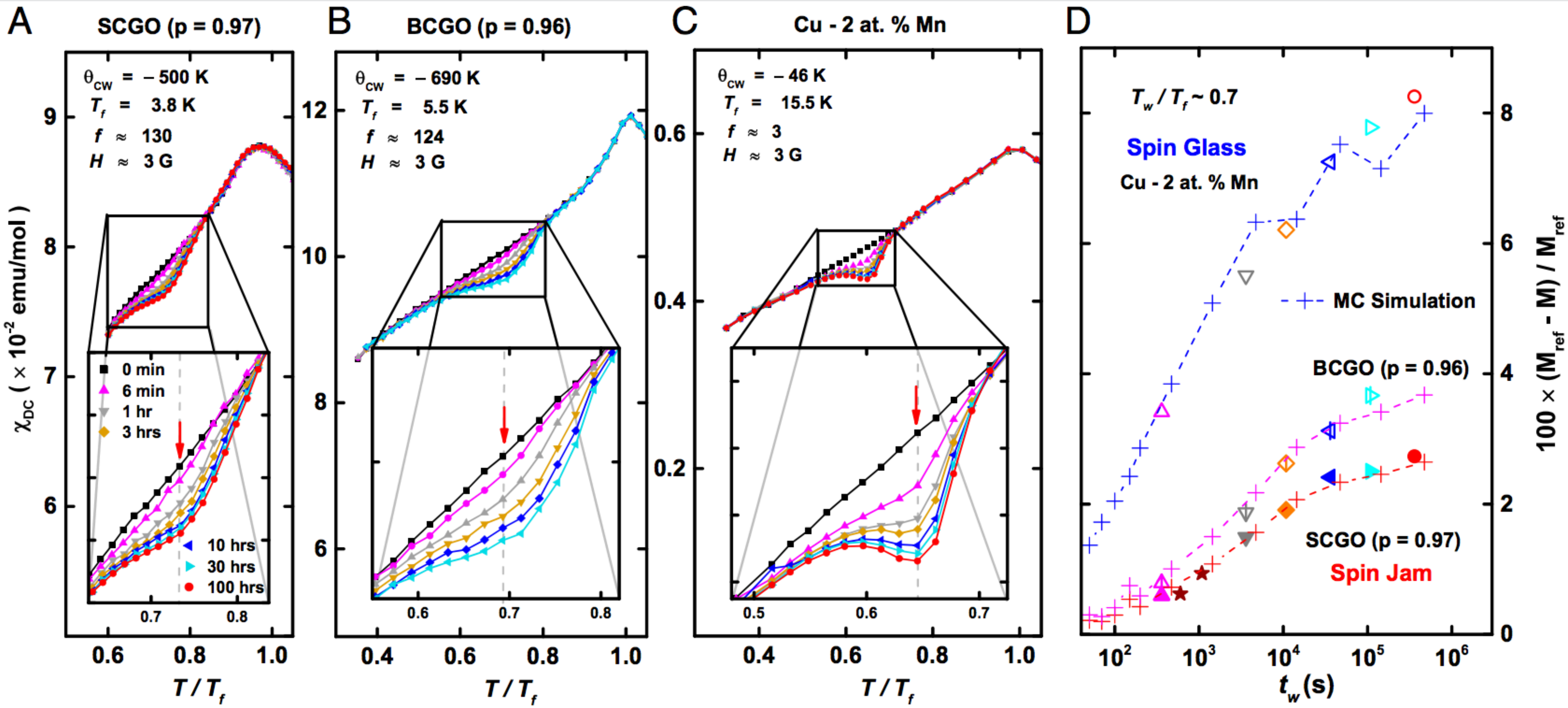
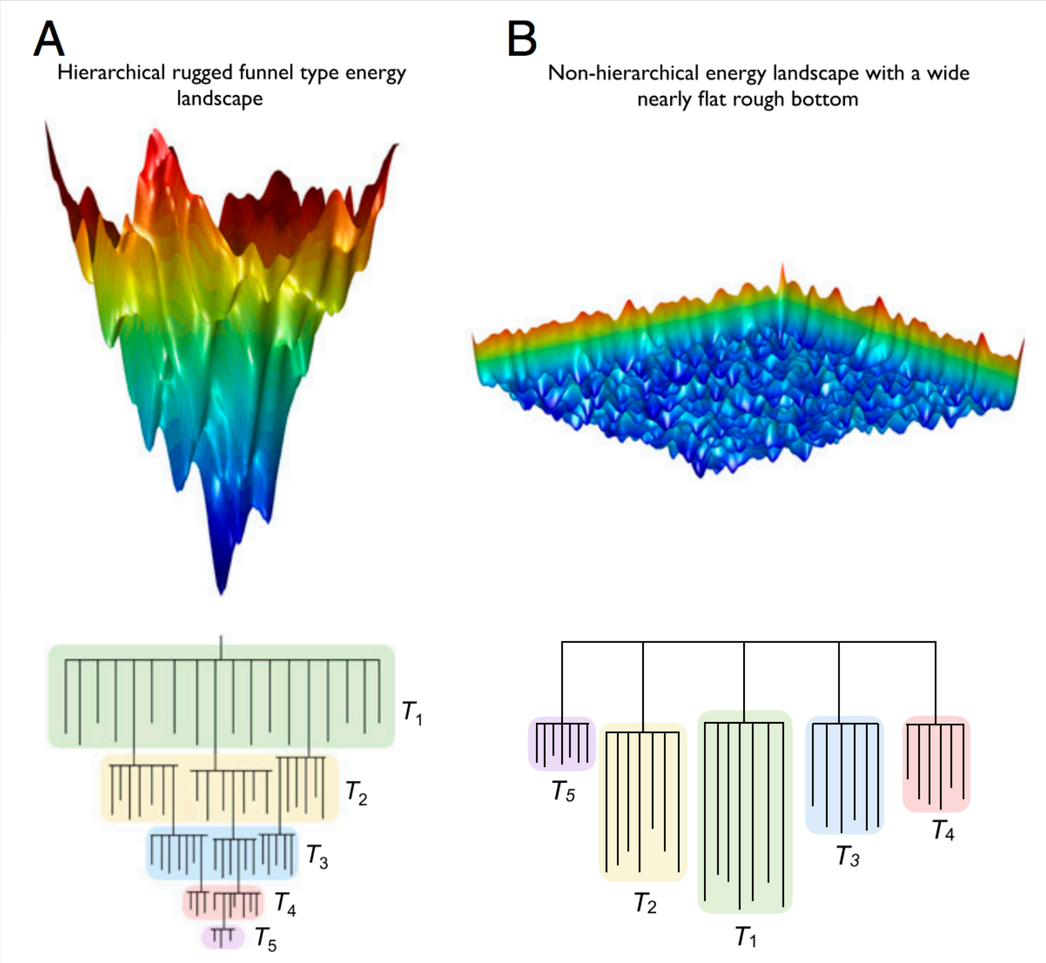
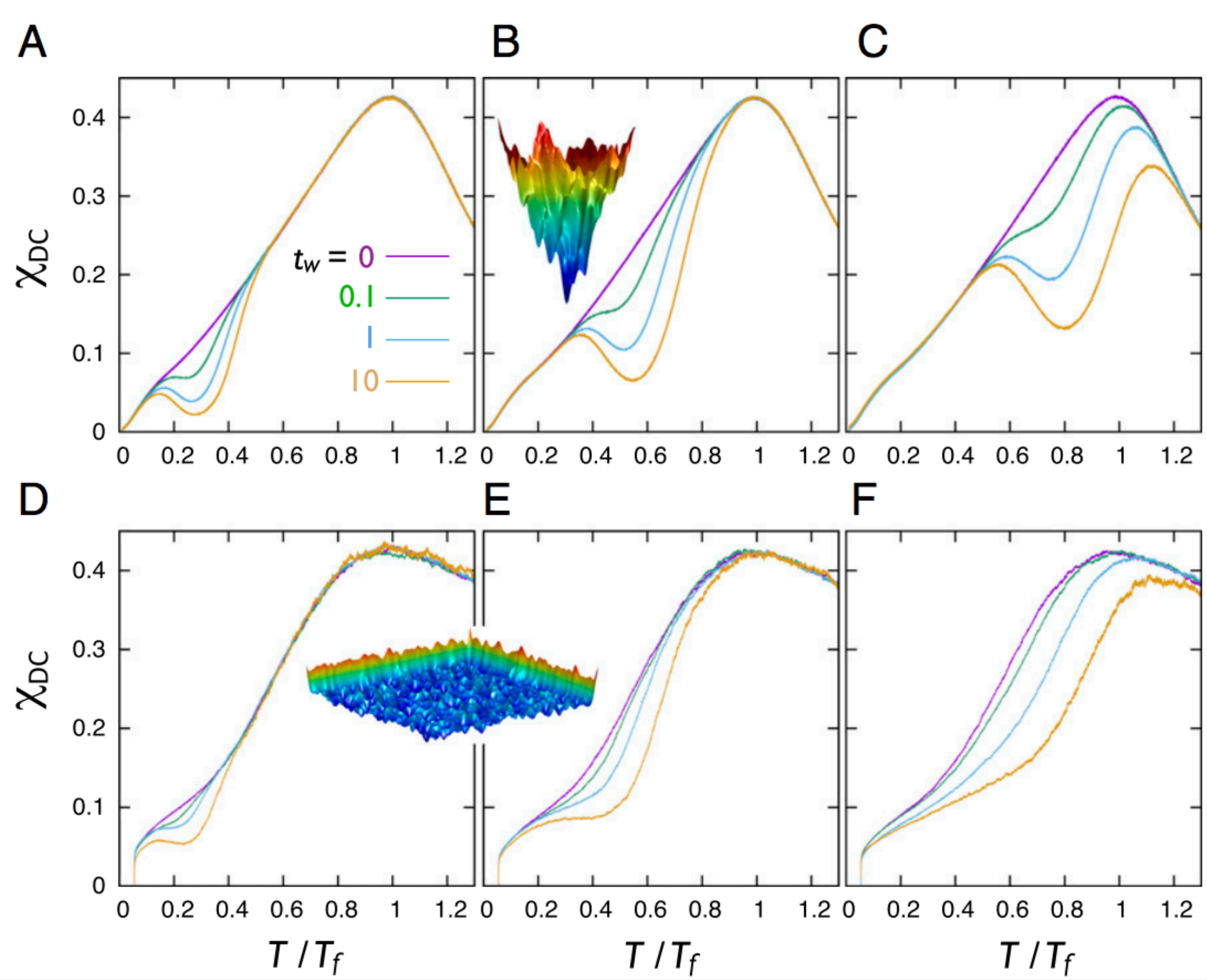


Fig. 2. (*A*–*C*) Bulk susceptibility, $\chi_{DC} = M/H$, where *M* and *H* are magnetization and applied magnetic field, respectively, obtained from (*A*) SCGO($p = 0.97$), (*B*) BCGO($p = 0.96$), and (*C*) a spin glass *CuMn2%*, with $H = 3$ G. Symbols and lines with different colors indicate the data taken with different waiting times, t_w, ranging from 0 h to 100 h, at $T_w/T_f \sim 0.7$, where T_w and T_f are the waiting and the freezing temperature, respectively. (*D*) From the data shown in *A*–*C*, the aging effect was quantified for the three systems by $(M_{ref} - M)/M_{ref}$, where M_{ref} is the magnetization without waiting, and it was plotted as a function of t_w in a log scale. The "+" symbols mark the results of our MC simulations. Details of the simulations can be found in *Supporting Information*.

Relations to memory, aging and rejuvenation





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"…plumbers talk about it all the time".