Anomalous thermal relaxation
in a colloidal system

NSERC CRSNG

YSF-YITP Symposium 45
August 3, 2023

John Bechhoefer

SFU

Anomalous thermal relaxation
in a colloidal system

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Outline

I. **Anomalous thermal relaxation and the Mpemba effect**

II. **Feedback traps & virtual potentials**

III. **Mpemba effect:** Can a hot system cool faster than a warm one?

IV. **Inverse Mpemba:** Can a cold system heat faster?

V. **What potentials lead to a Mpemba effect?**

Exponential relaxation at long times

Thermal relaxation of an extended body

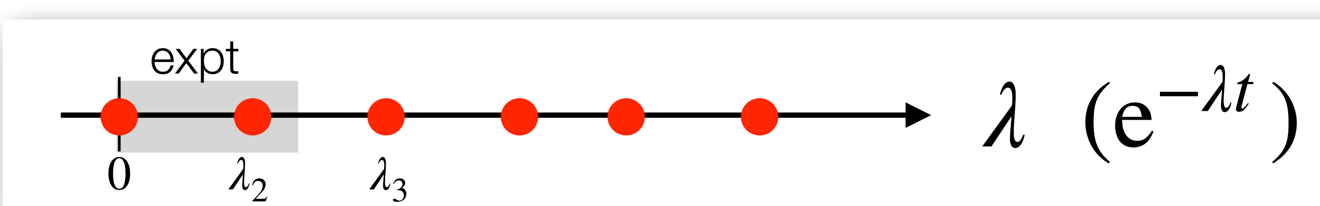
$$\partial_t T = \kappa \nabla^2 T$$

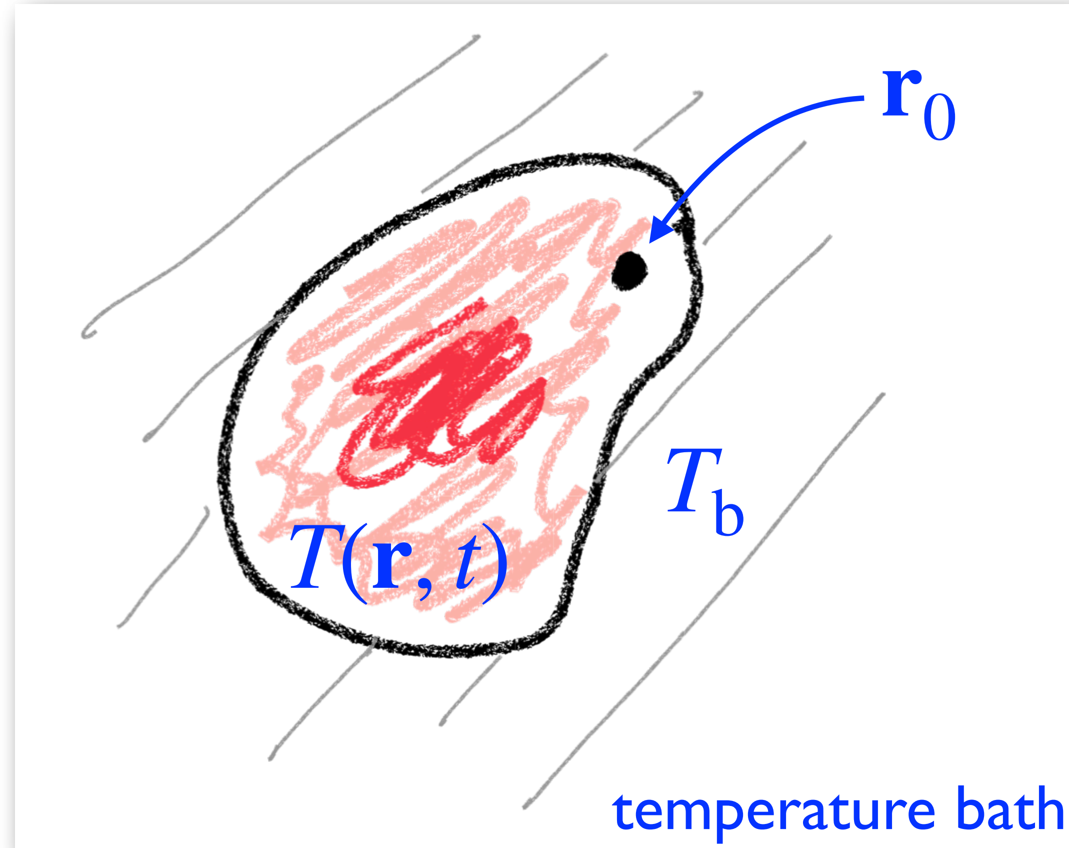
$$T(\mathbf{r}, t) = T_\mathrm{b} + \sum_{m=2}^{\infty} a_m v_m(\mathbf{r})\, \mathrm{e}^{-\lambda_m t}$$

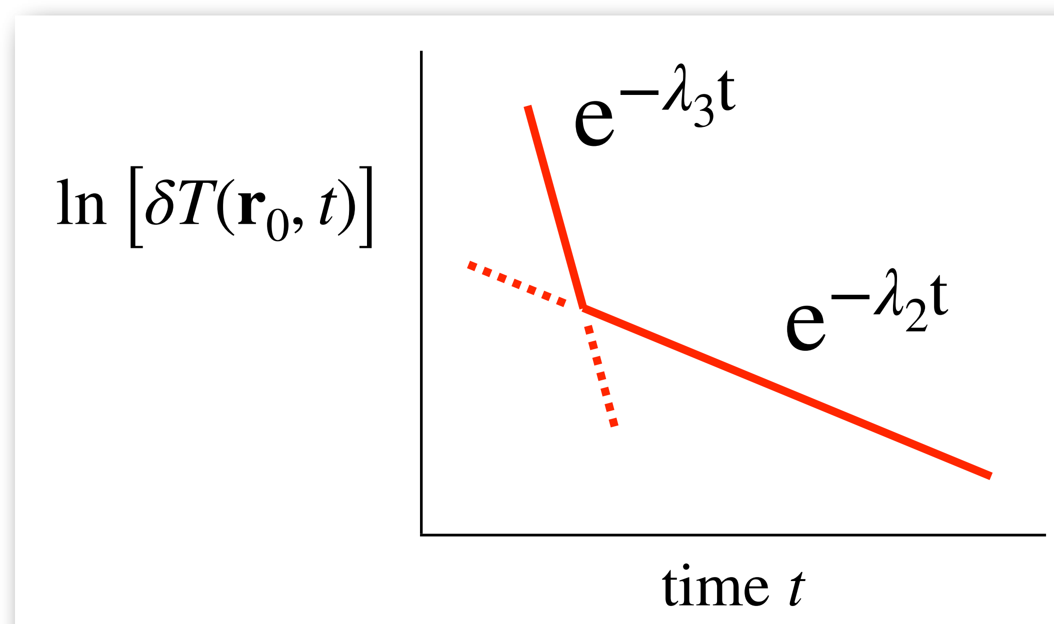
At long times $t \gg \lambda_3^{-1}$

temperature at one point relaxes exponentially

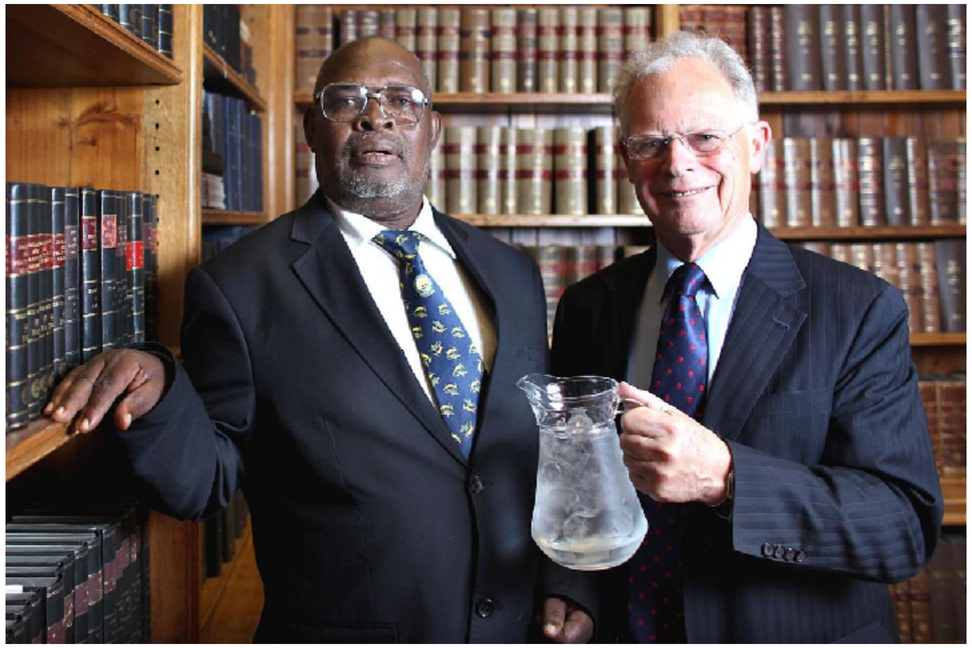
$$T(\mathbf{r}, t) \approx T_\mathrm{b} + a_2 v_2(\mathbf{r})\, \mathrm{e}^{-\lambda_2 t}$$





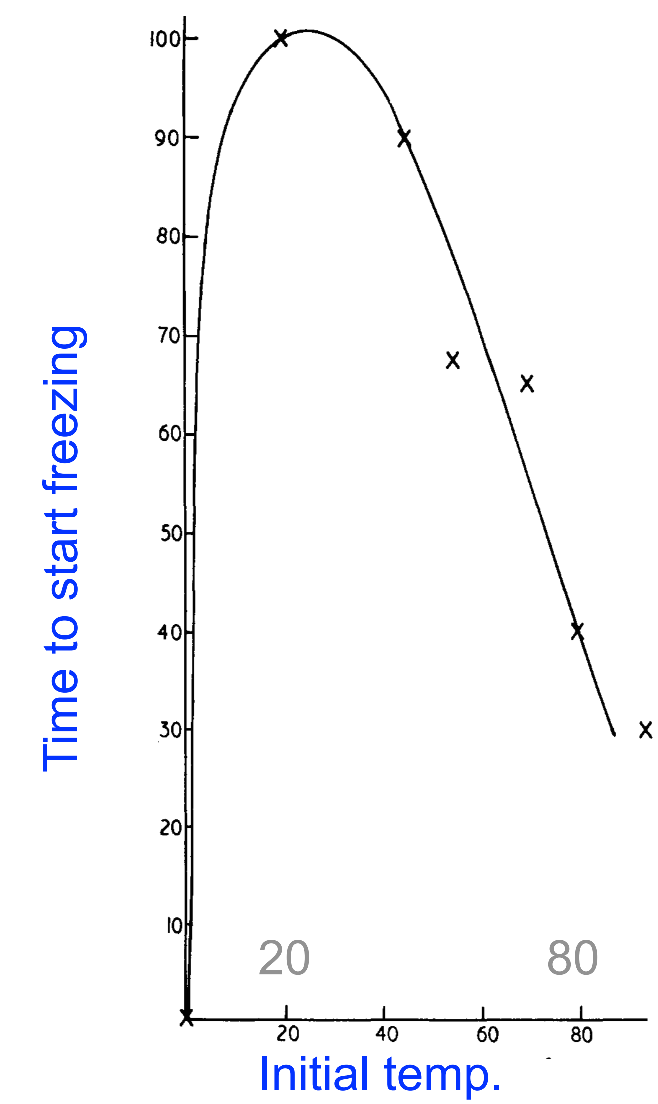


Mpemba effect



Erasto Mpemba & Denis Osborne 2013 (*Phys. Educ.* 1969)

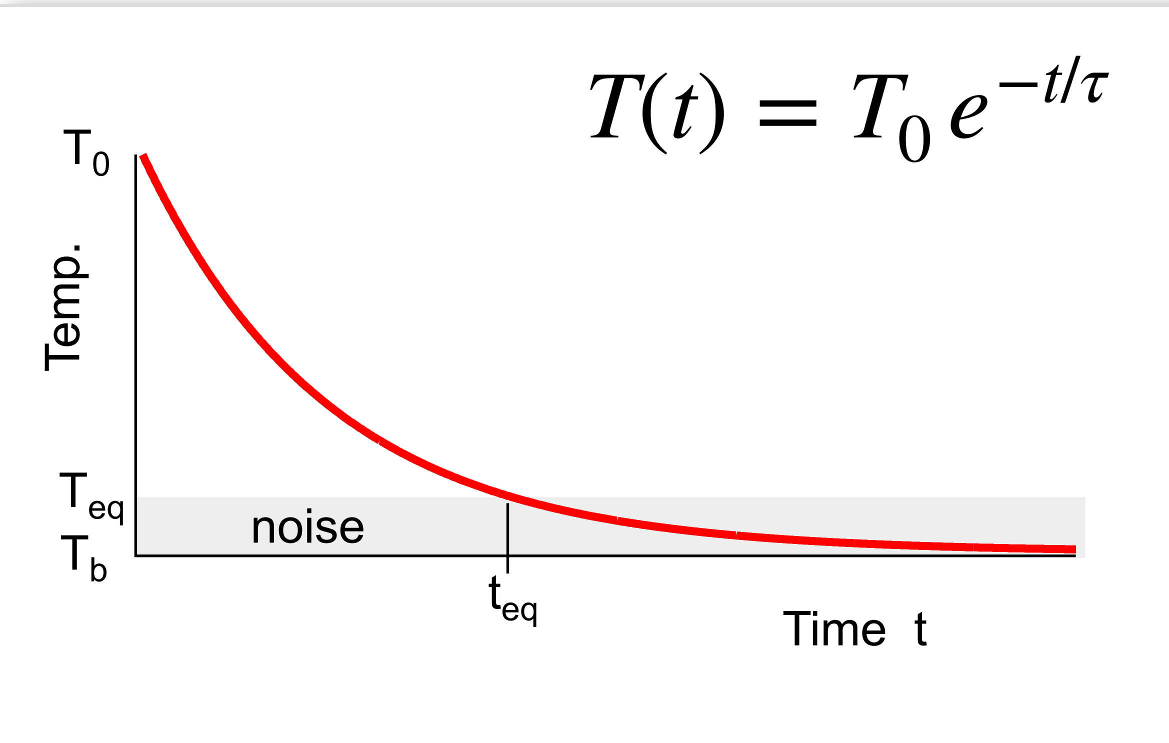
'If you take two similar containers with equal volumes of water, one at 35°C and the other at 100°C, and put them into a refrigerator, the one that started at 100°C freezes first. Why?'



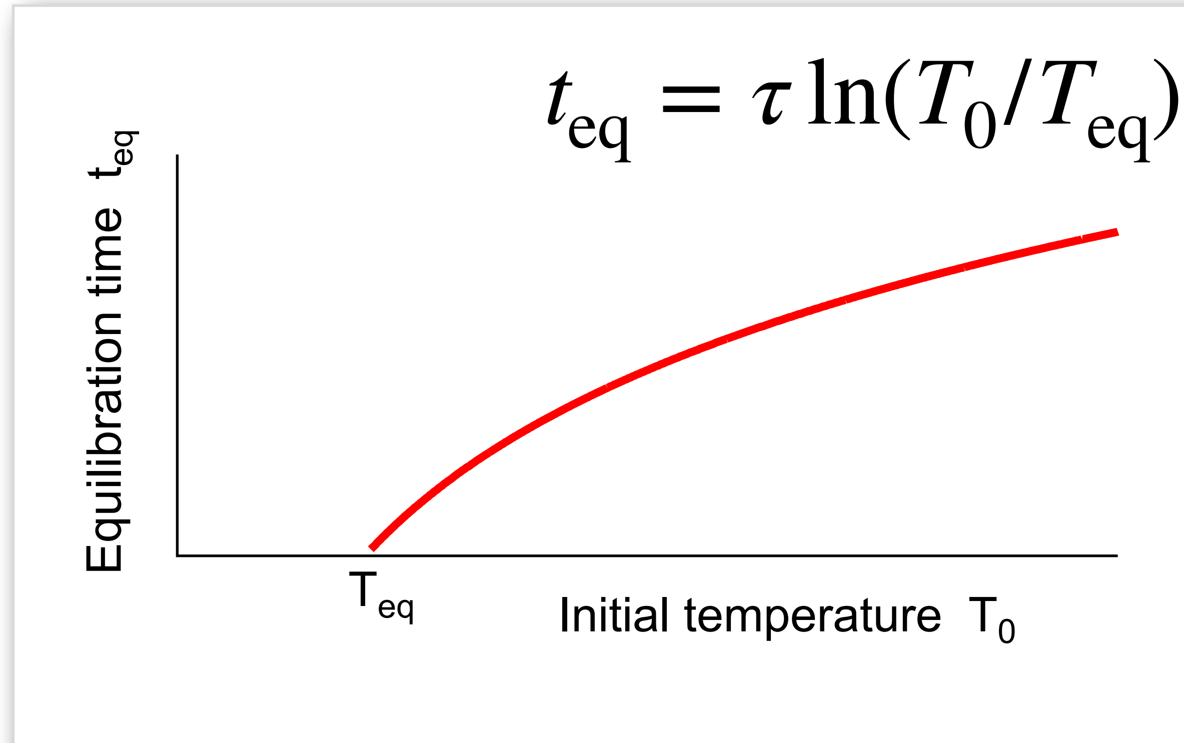
Hot water can freeze faster than warm water.
when quenched in the same (supercooled) bath.

Mpemba effect

For slow cooling, temperature decreases through all intermediate values.



Exponential relaxation



Equilibration time increases monotonically

Mpemba effect

(Too Many) Explanations for Water → Ice

- Evaporation
- Supercooling
- Dissolved gasses
- Convection
- Heat exchange with environment

Mpemba effect

Is there a universal / general / illuminating explanation?

(Too Many) Explanations for Water → Ice

- Evaporation
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Mpemba effect

Explanations?

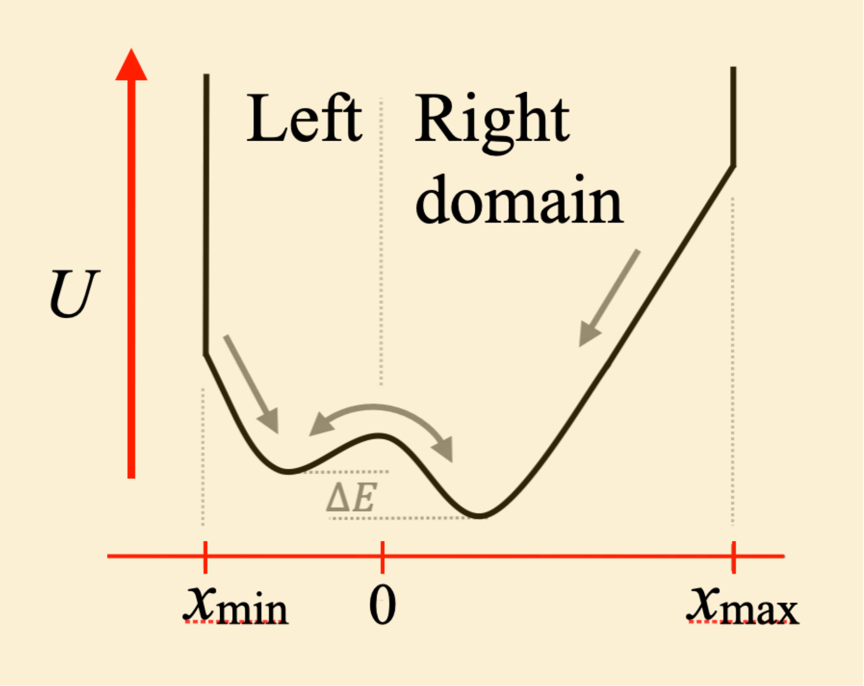
Is there a universal / general / illuminating explanation?

Single colloidal particle in a potential, in water

Stochastic thermodynamics

- Small systems are cleaner settings to explore
- General theory for finite-state systems,
  heuristic for continuous-state systems

Zhiyue Lu and Oren Raz, *PNAS* 2017



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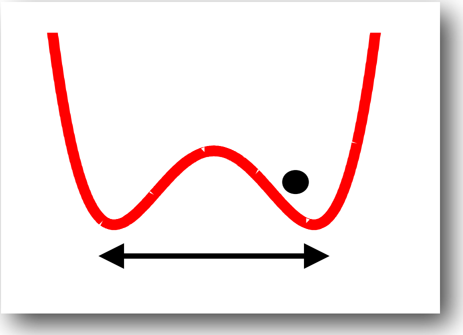
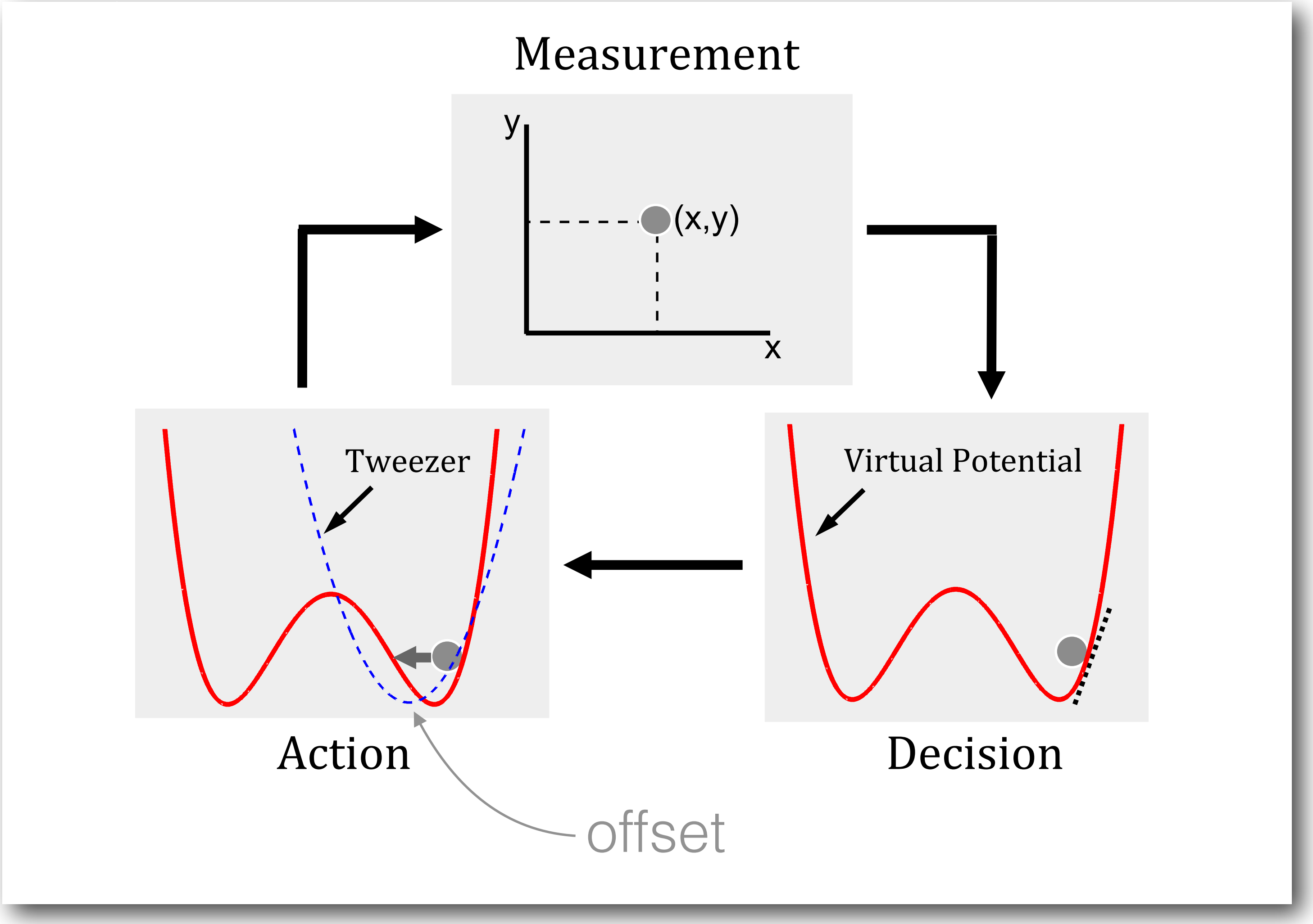
Feedback trap

ABEL = AntiBrownian ELectrokinetic

Put a diffusing particle in a virtual potential

micron-scale silica bead, in water

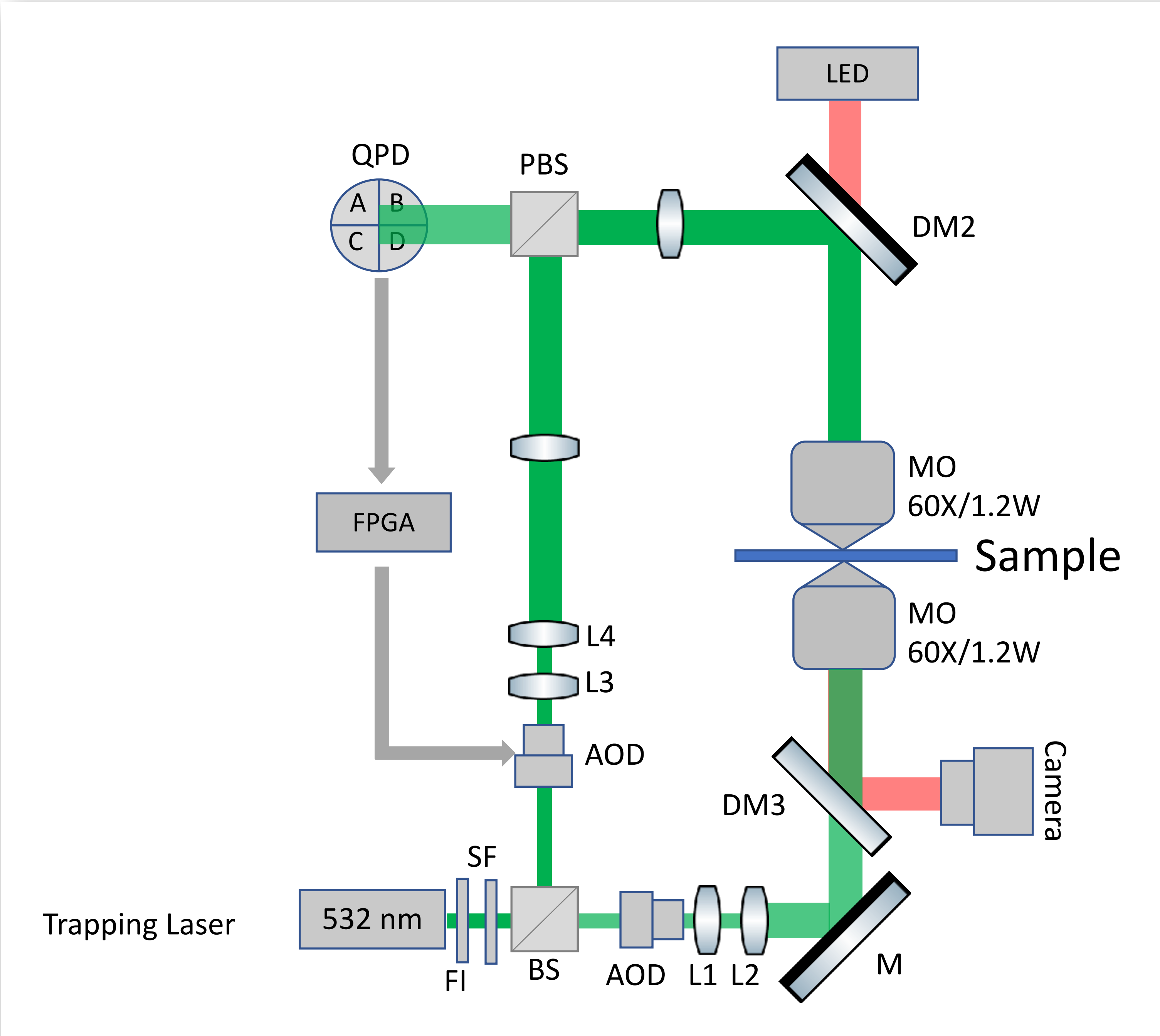




Here: offset optical tweezers
"source the force"

A. E. Cohen and W. E. Moerner *APL* 2005
original version used applied E-field for force

Feedback trap



feedback loop
rate: 100 kHz

A. Kumar & J. Bechhoefer, *Appl. Phys. Lett.* 2018

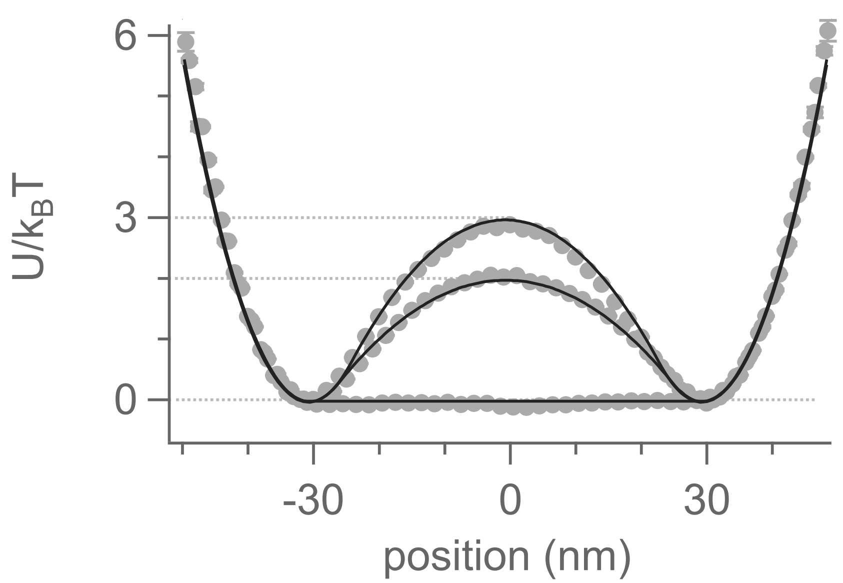
Feedback trap

The right tool for this experiment

- ~ arbitrary potential shapes

Change barrier height

fix well spacing, curvature



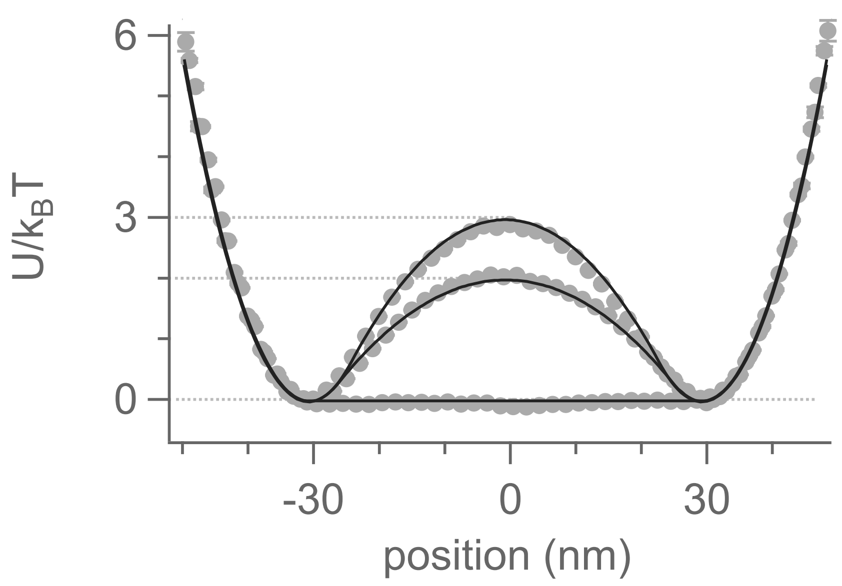
Feedback trap

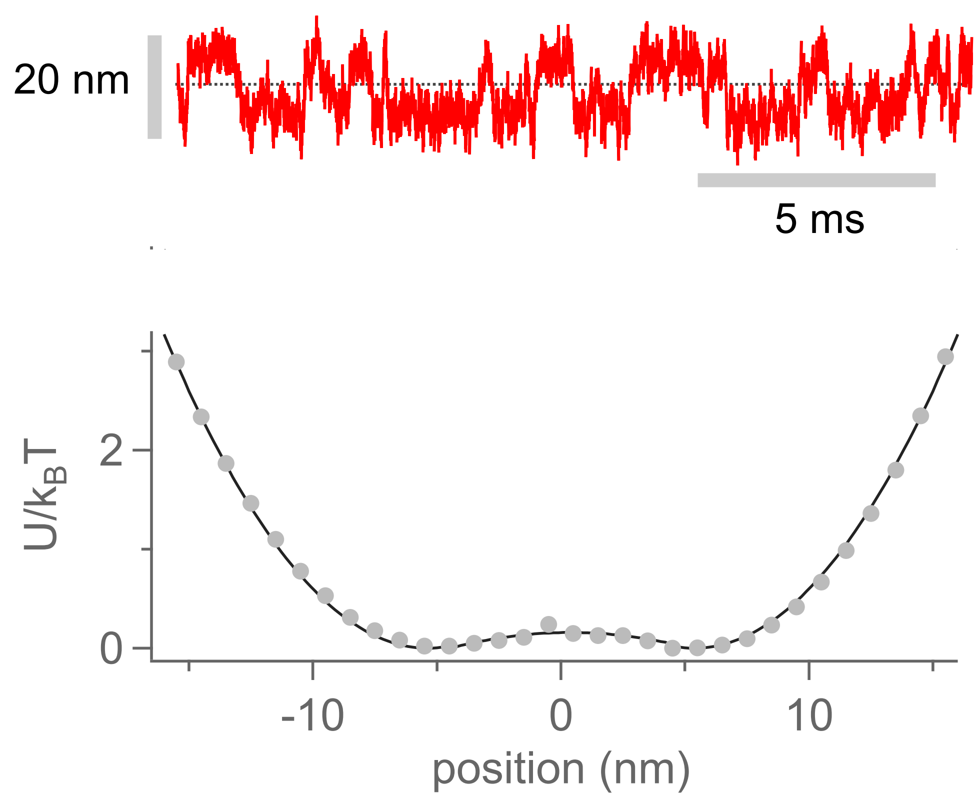
The right tool for this experiment

- ~ arbitrary potential shapes
- small length scales → fast dynamics

Change barrier height

fix well spacing, curvature





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Mpemba effect

Traditional definition: initially hotter system cools and freezes more quickly

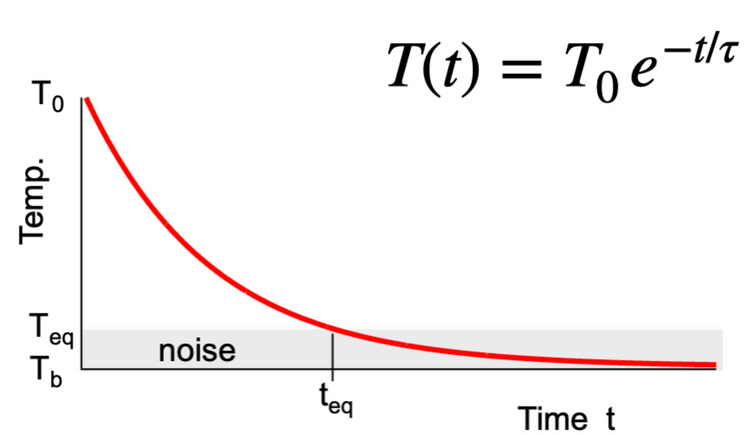
Ambiguities: nucleation (to initiate freezing) a sensitive stochastic process

Mpemba effect exists if $t_h < t_w$

t_h: time to cool a hot system

t_w: time to cool a warm system

- Initial and final states in thermal equilibrium with a heat bath.
- Cooling time: time elapsed between initial and final equilibrium states.

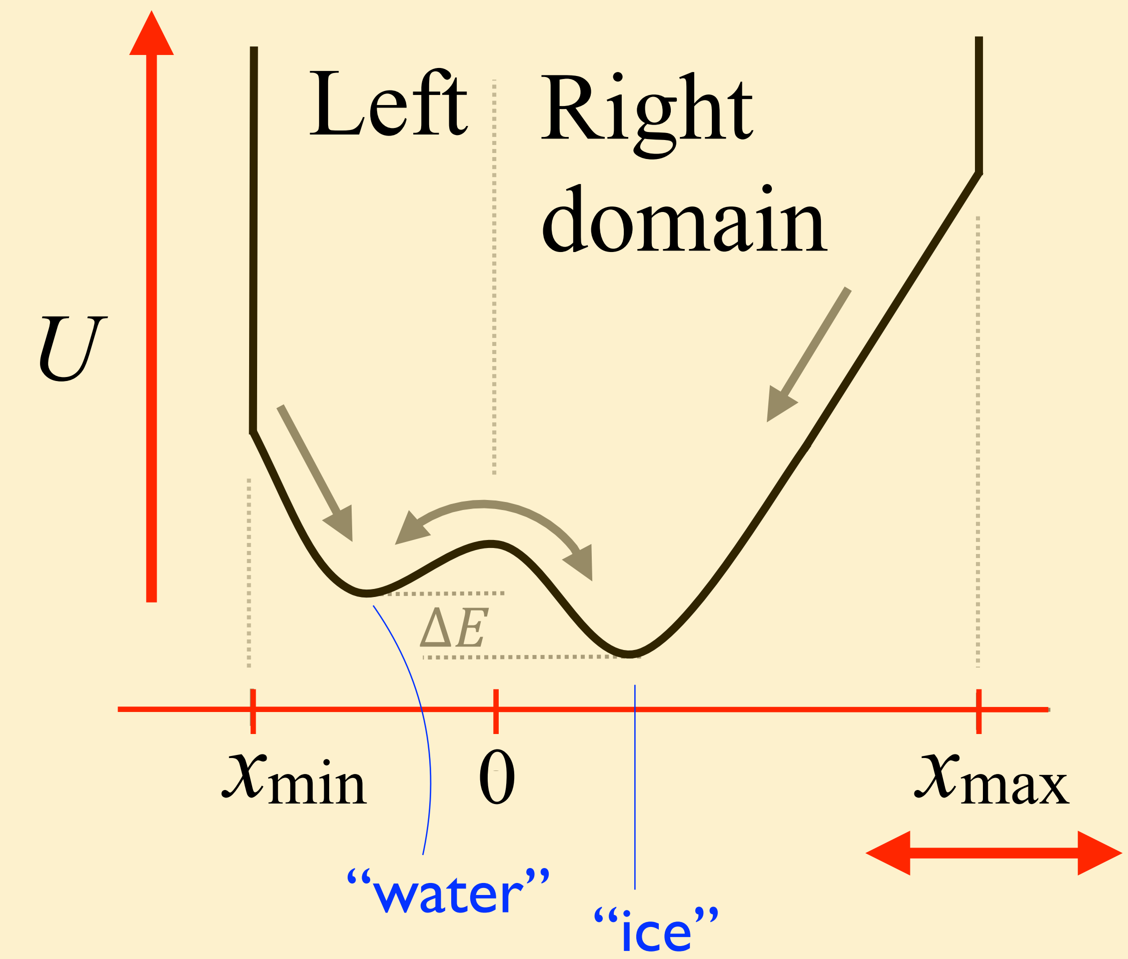


Equilibrium states are well defined.

Phase transition not a part of def.

Mpemba effect

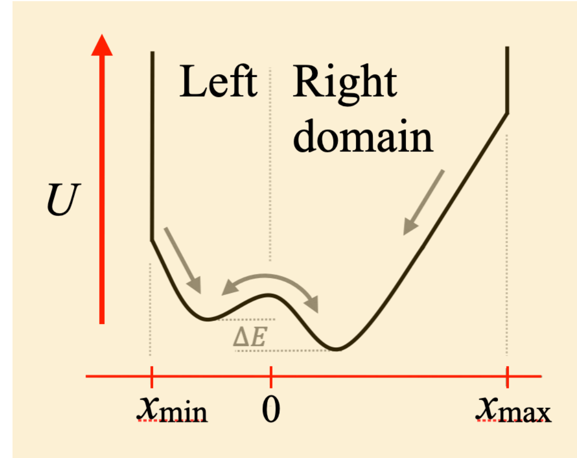
- **Colloidal particle in a potential**
  - in water at bath temperature
- **A tilted double-well potential**
  - metastable & stable macrostates
    "water" "ice"
  - Asymmetric domain
  - Small spatial dimension 200–800 nm
  - Fast equilibration time ≈ 0.1 s
  - 1,000–10,000 trials vs. ~10



"inspired by a true story"

$$\alpha = \frac{|x_{\max}|}{|x_{\min}|}$$ Aspect ratio

Mpemba effect

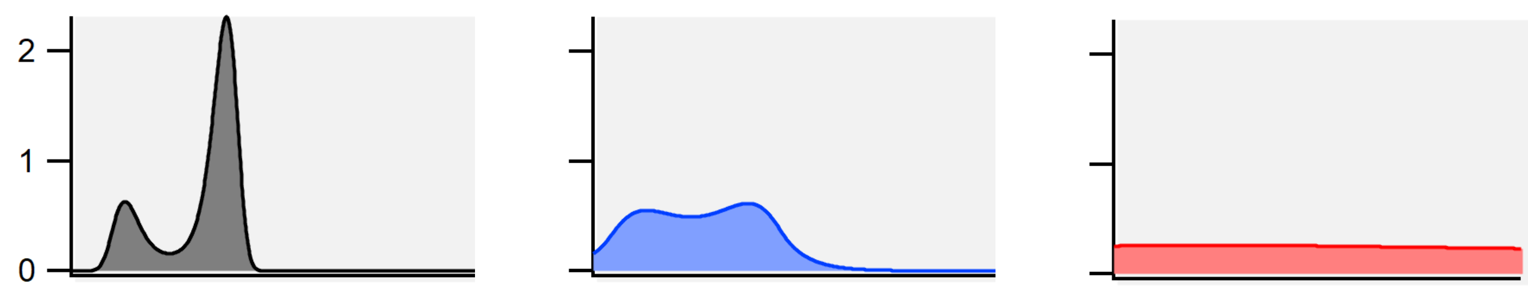


Quenching protocol

- Prepare systems at different initial temperatures: $T_b < T_0 < 1000\, T_b$

Boltzmann PDF

cold | warm | hot



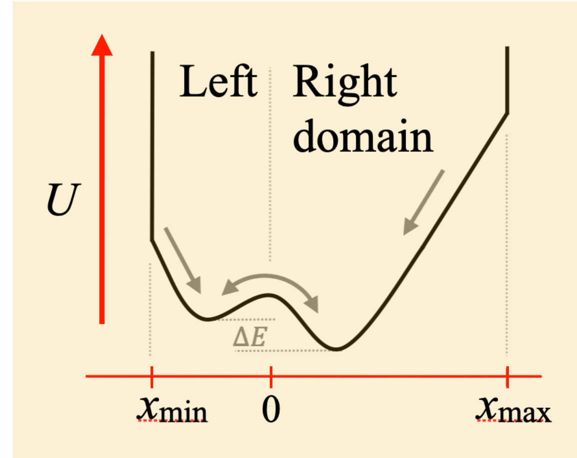
$T_0 = T_b$ | $12\, T_b$ | $1000\, T_b$

- Instantaneous quench in bath

Release particle at position x_0 sampled from equilibrium at T_0

- Let cool from $T_0 \to T_b$
- Repeat process many times to get ensemble estimate of $p(x, t)$

Mpemba effect



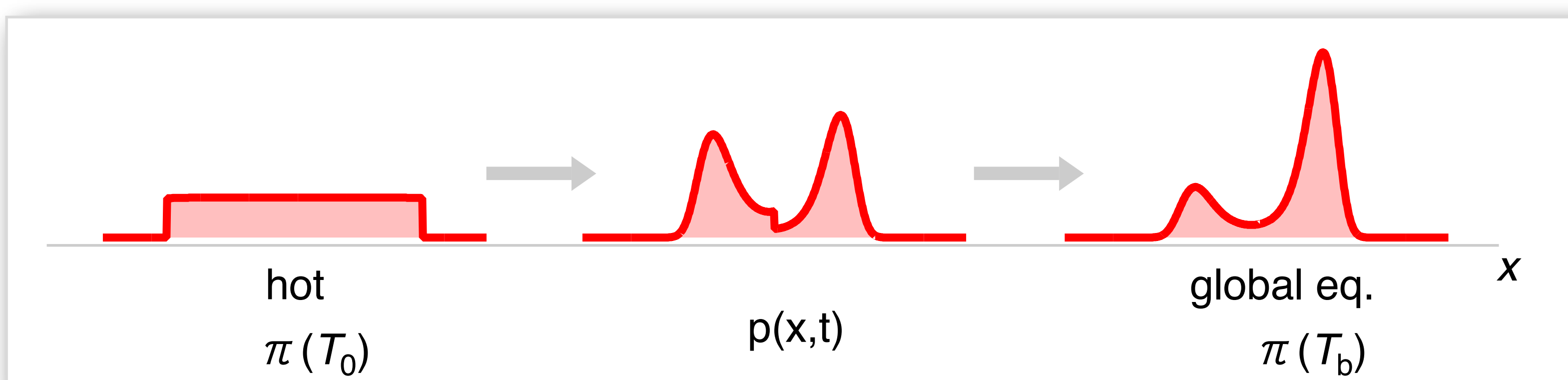
Measurement process

$p(x, t)$ Boltzmann, T_b

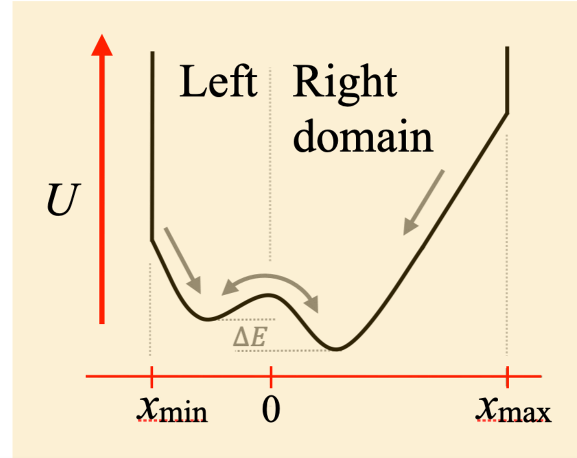
$$\mathscr{D} \approx \sum_{i=1}^{N_b} |p_i - \pi_i|$$

L_1 distance

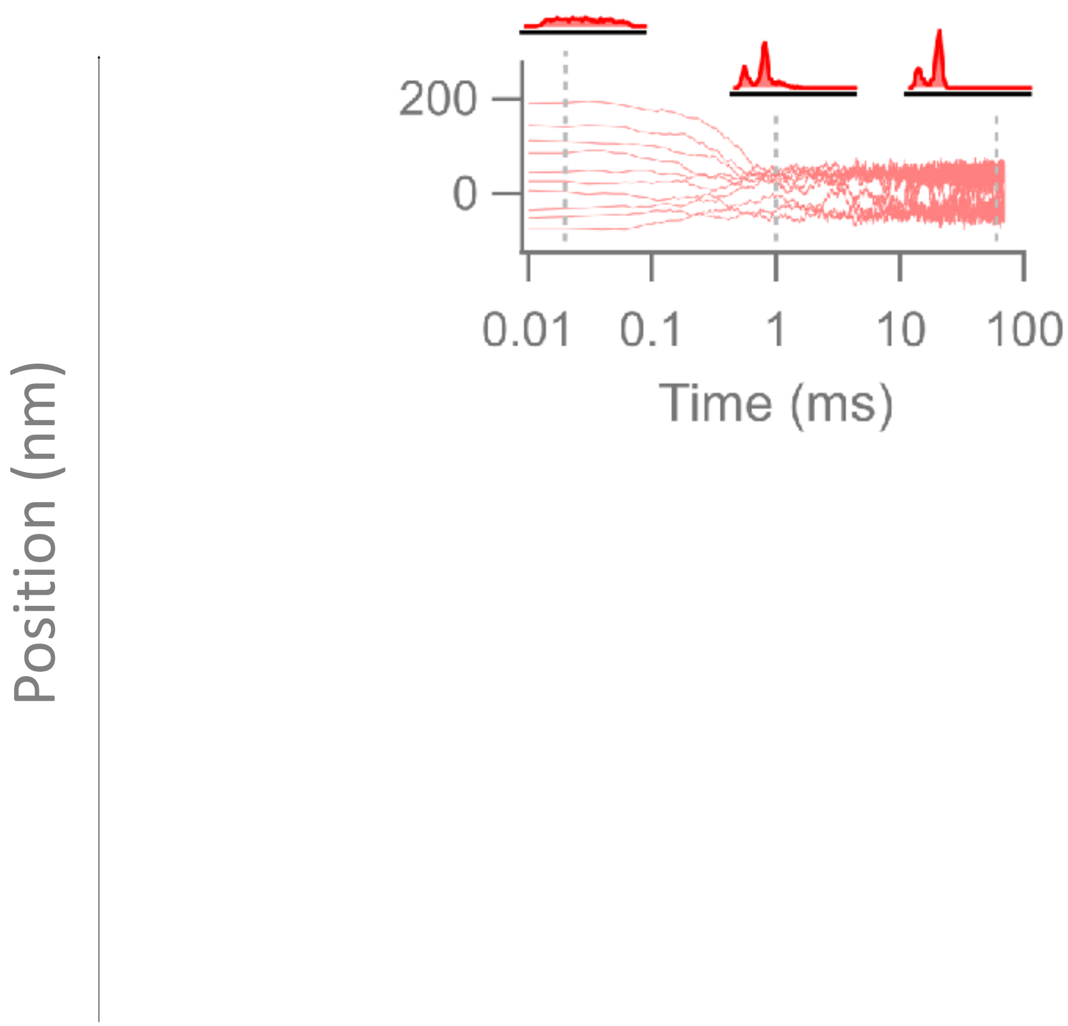
- System temperature well defined at beginning (T_0) and end (T_b)
- At intermediate times, $p(x,t)$ is not a Boltzmann dist. for any effective temperature
- Use metric / divergence between pdf's
  L_1, L_2, Kullback-Leibler, …
- see Mpemba in one, see in all*

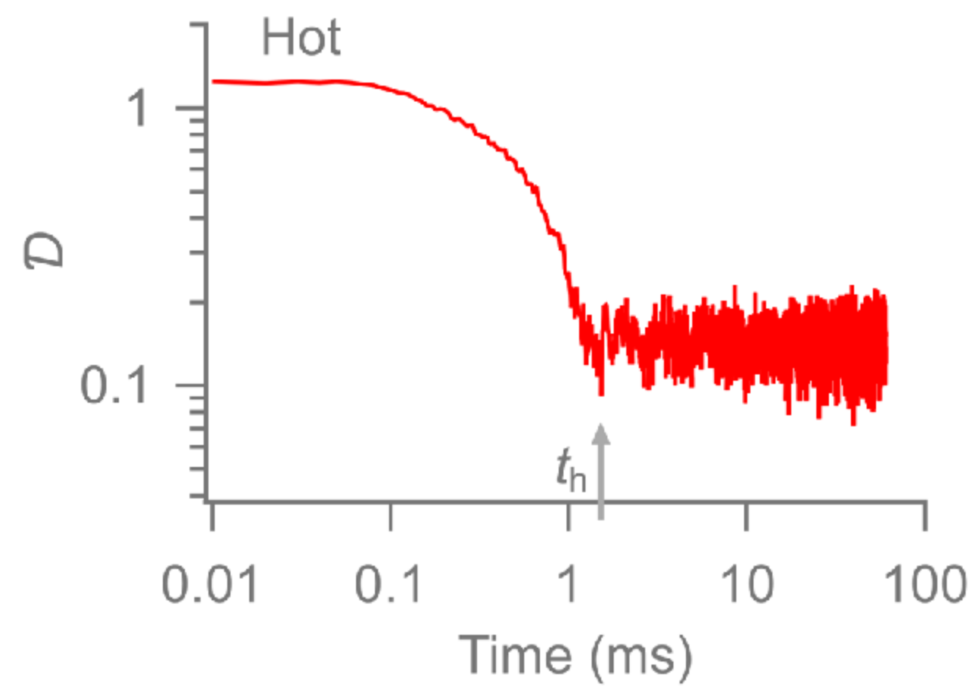


Mpemba effect



Measurement process

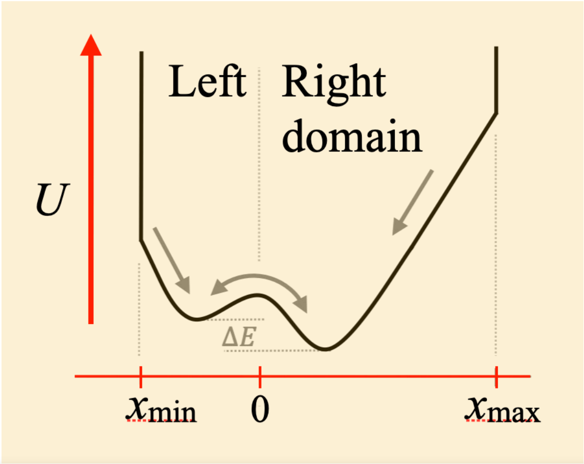




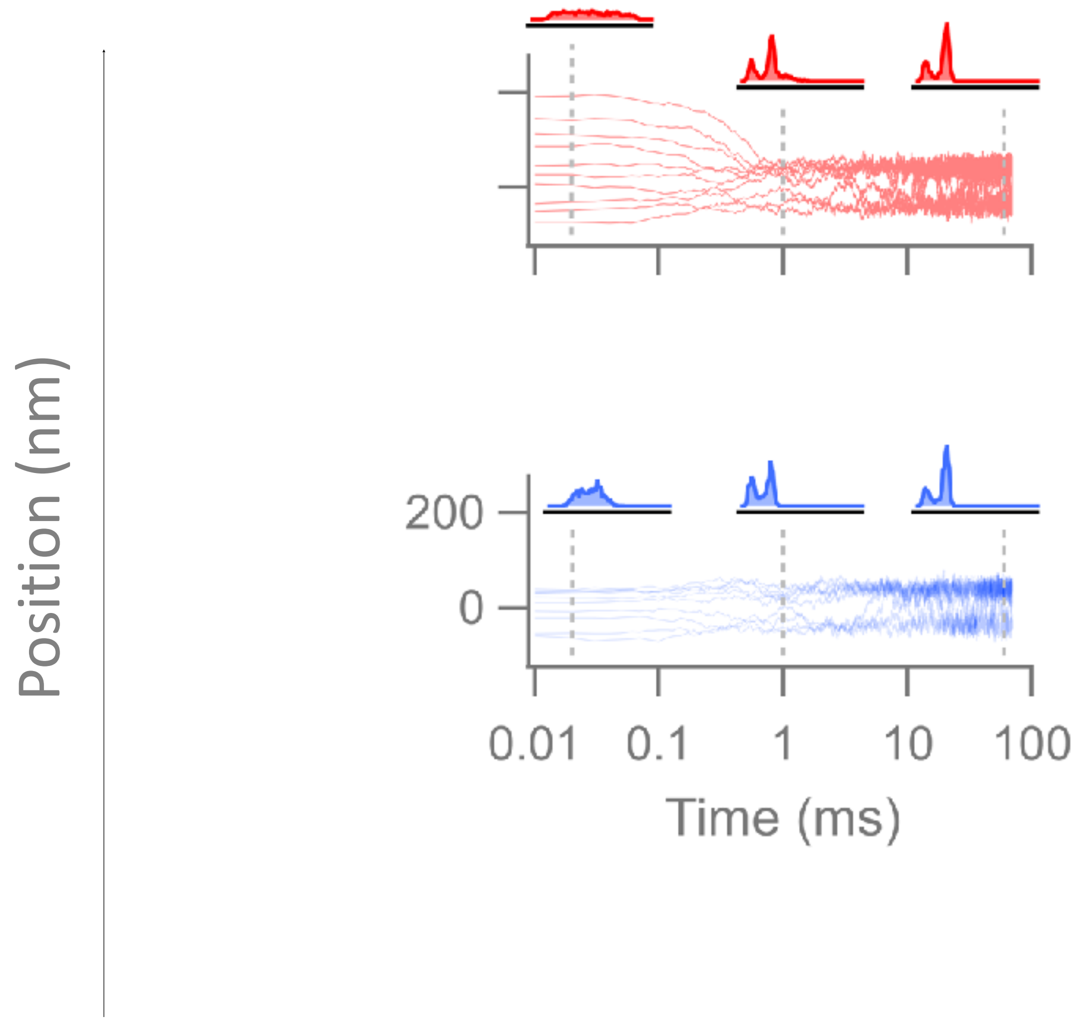
noise: 1000-trial ensemble

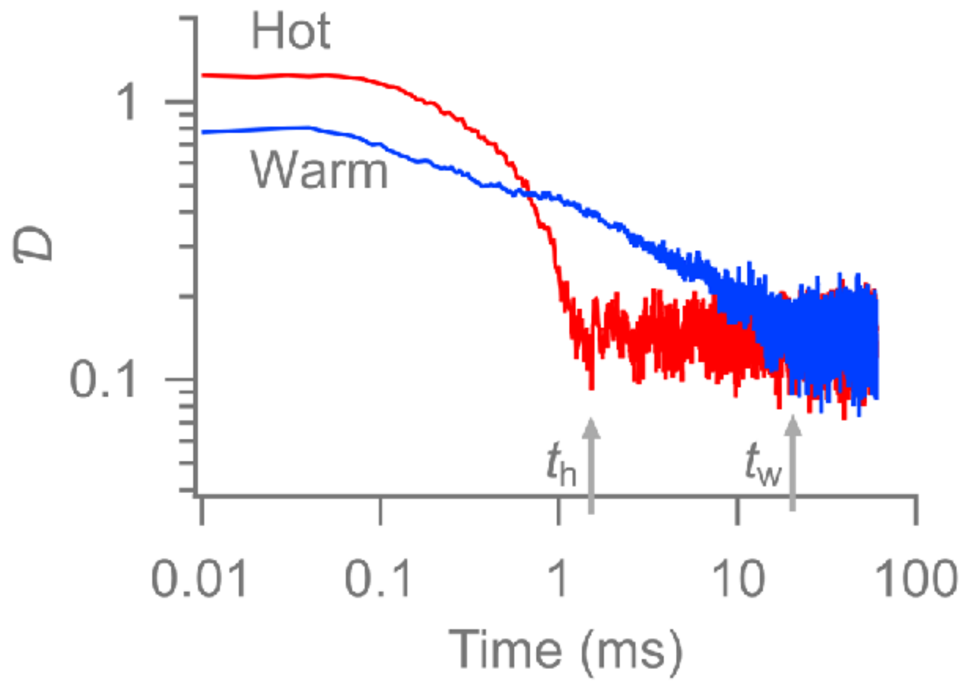
→ finite equilibration time

Mpemba effect



Measurement process





noise: 1000-trial ensemble
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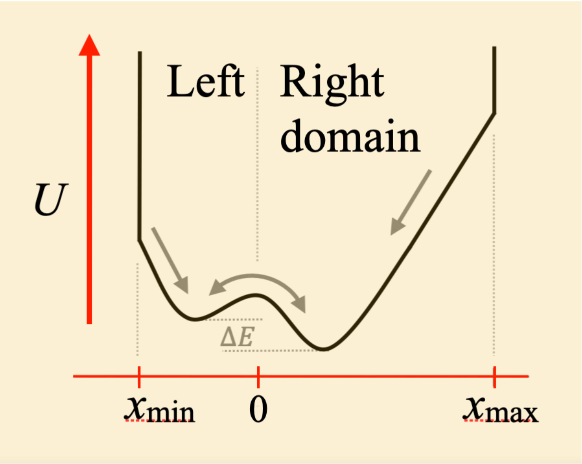
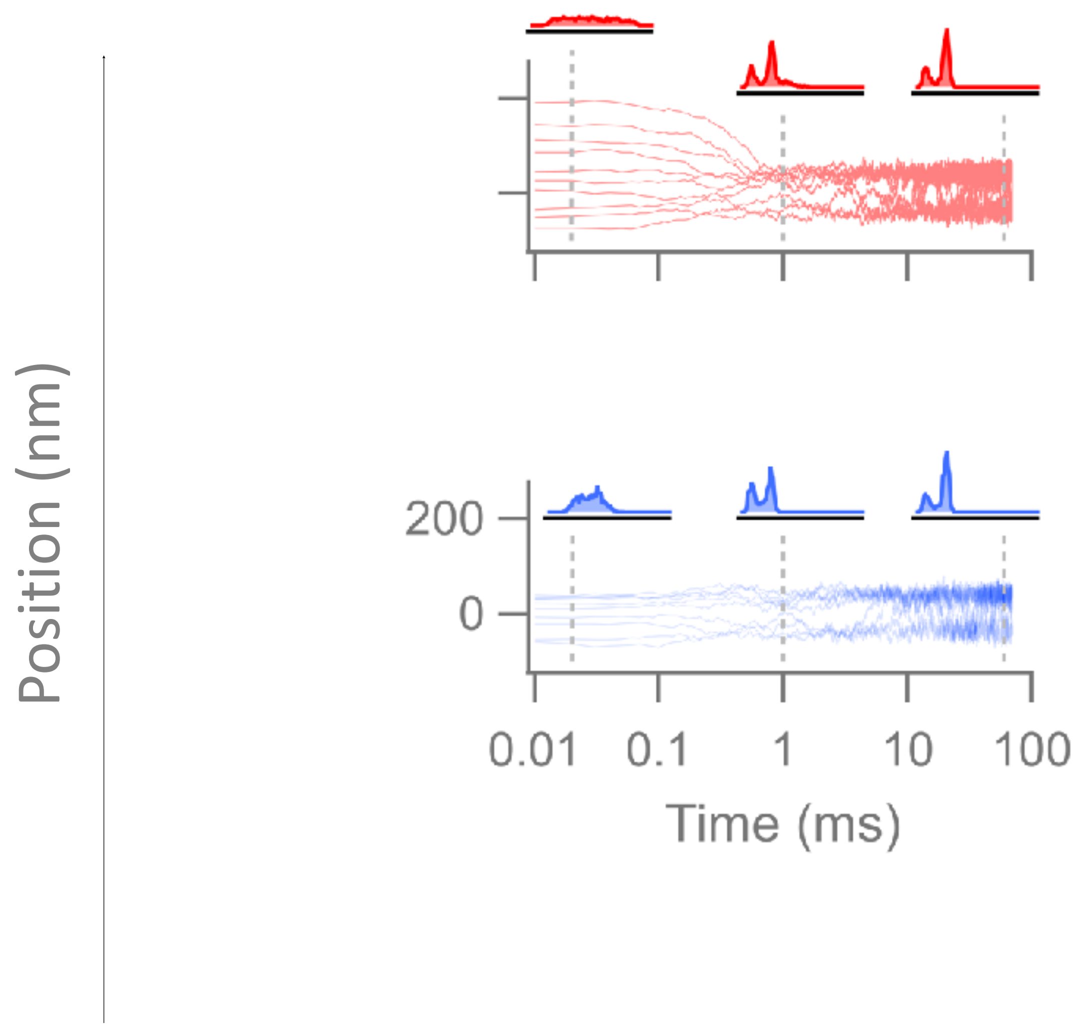
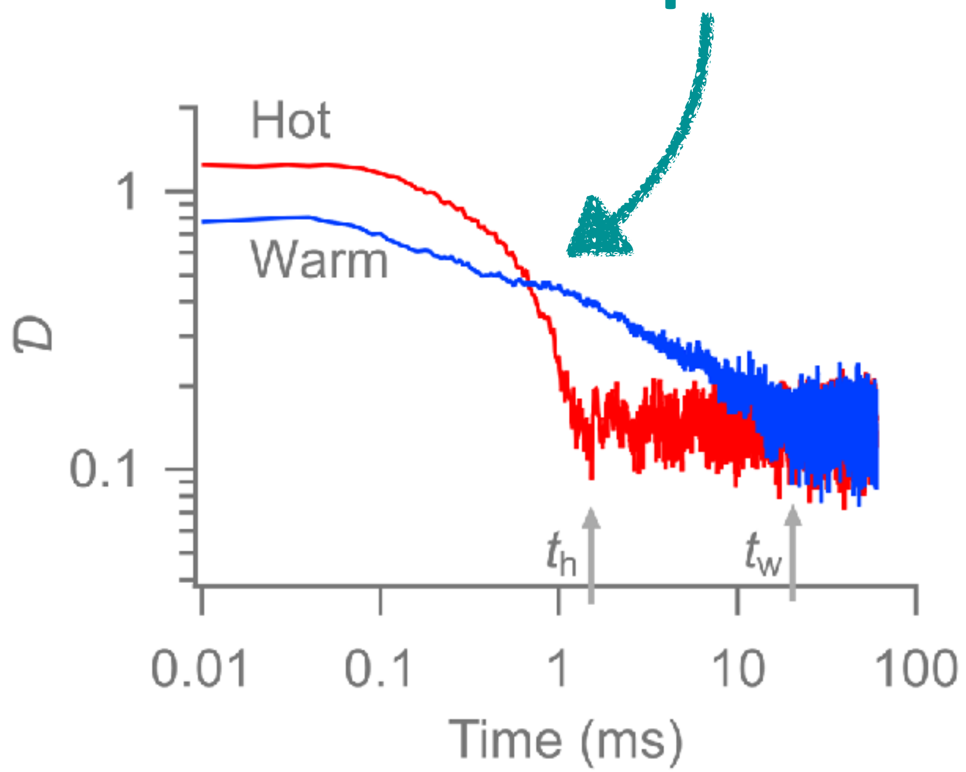
Mpemba effect



Measurement process

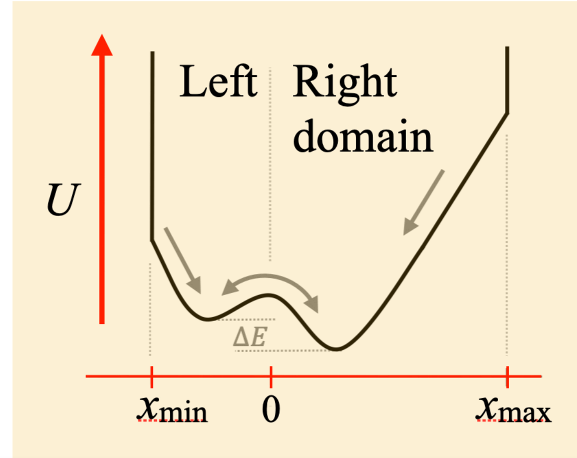


Mpemba!

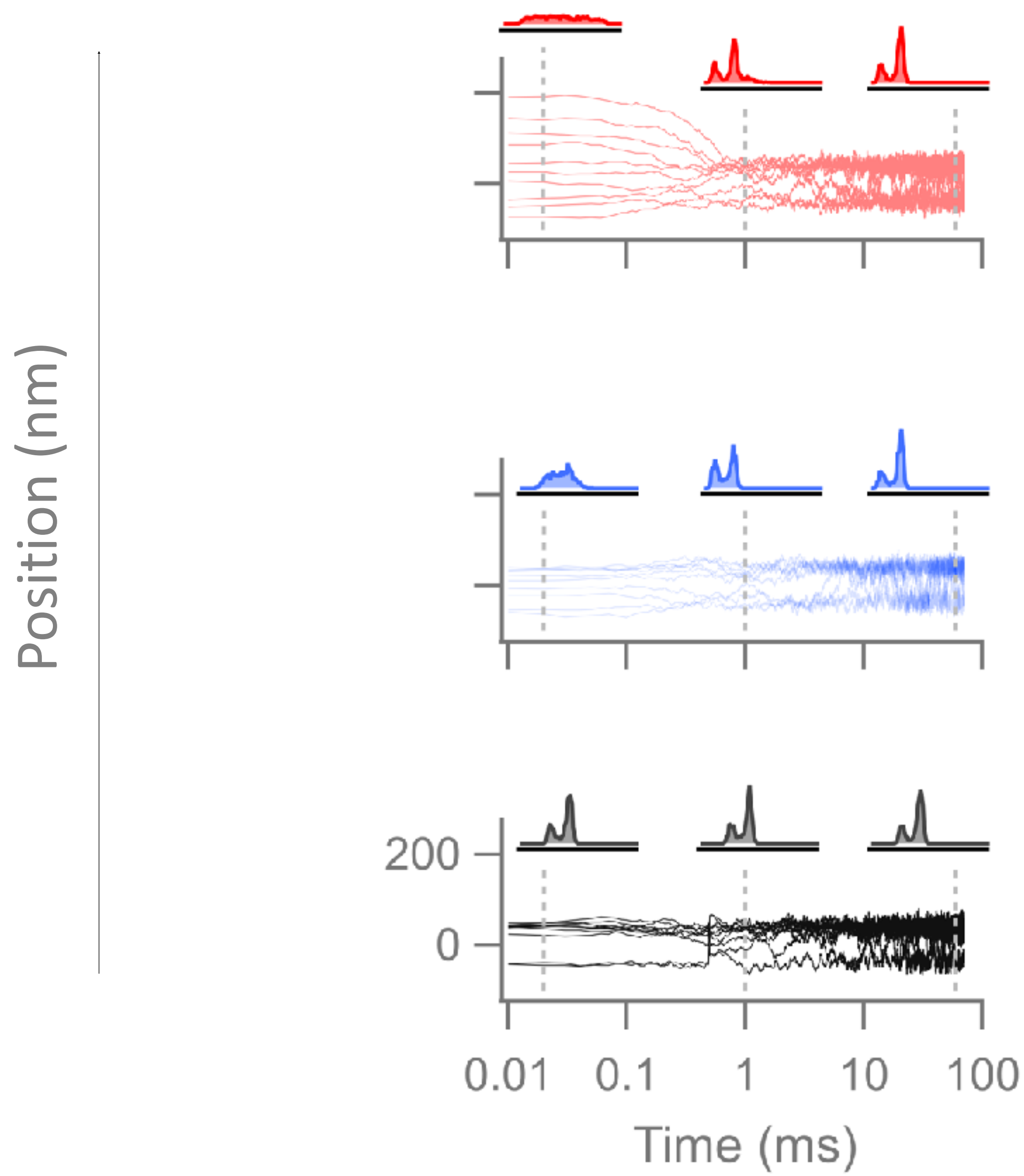


noise: 1000-trial ensemble
→ finite equilibration time

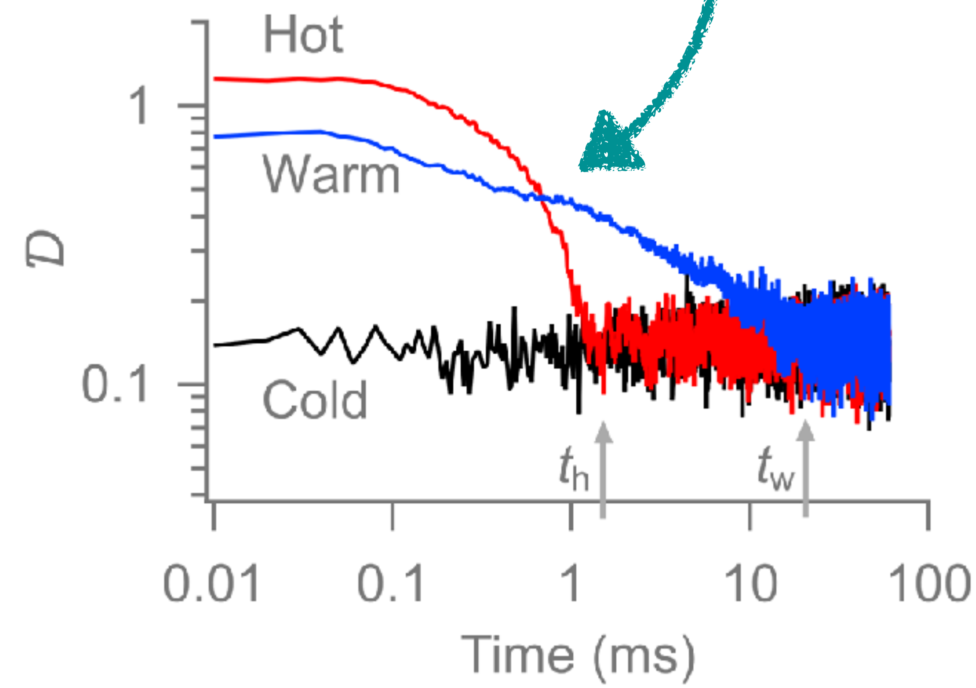
Mpemba effect



Measurement process

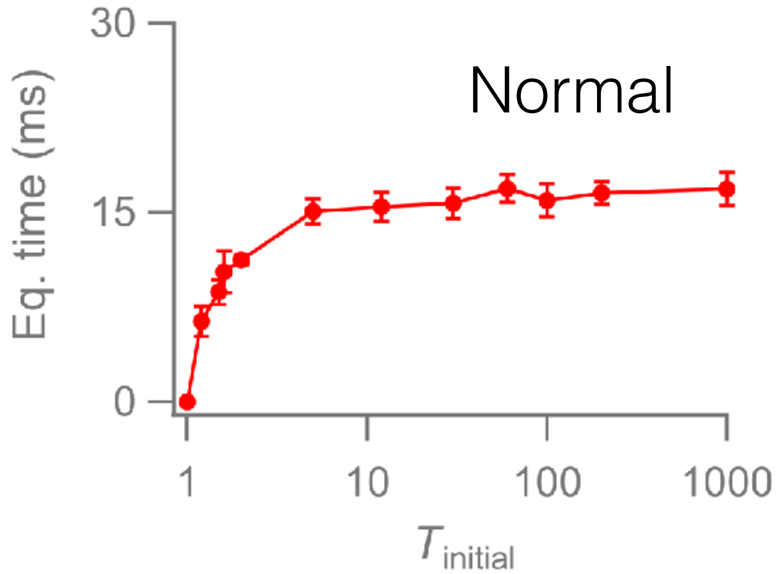


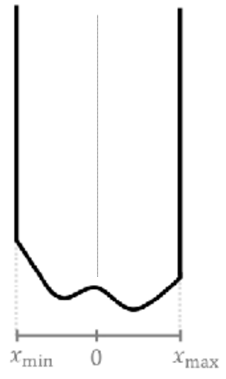
Mpemba!



noise: 1000-trial ensemble
→ finite equilibration time

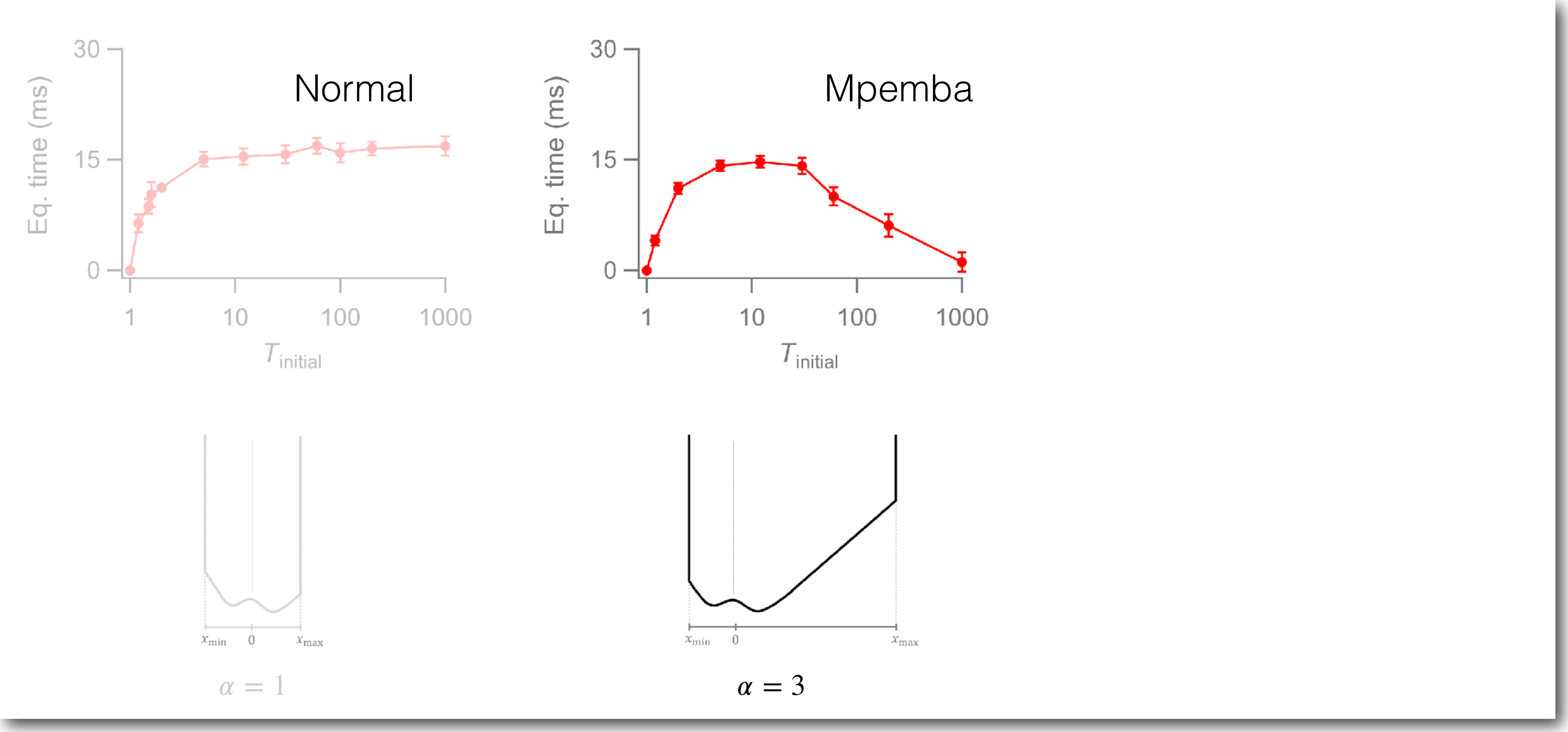
Equilibration time vs. initial temperature



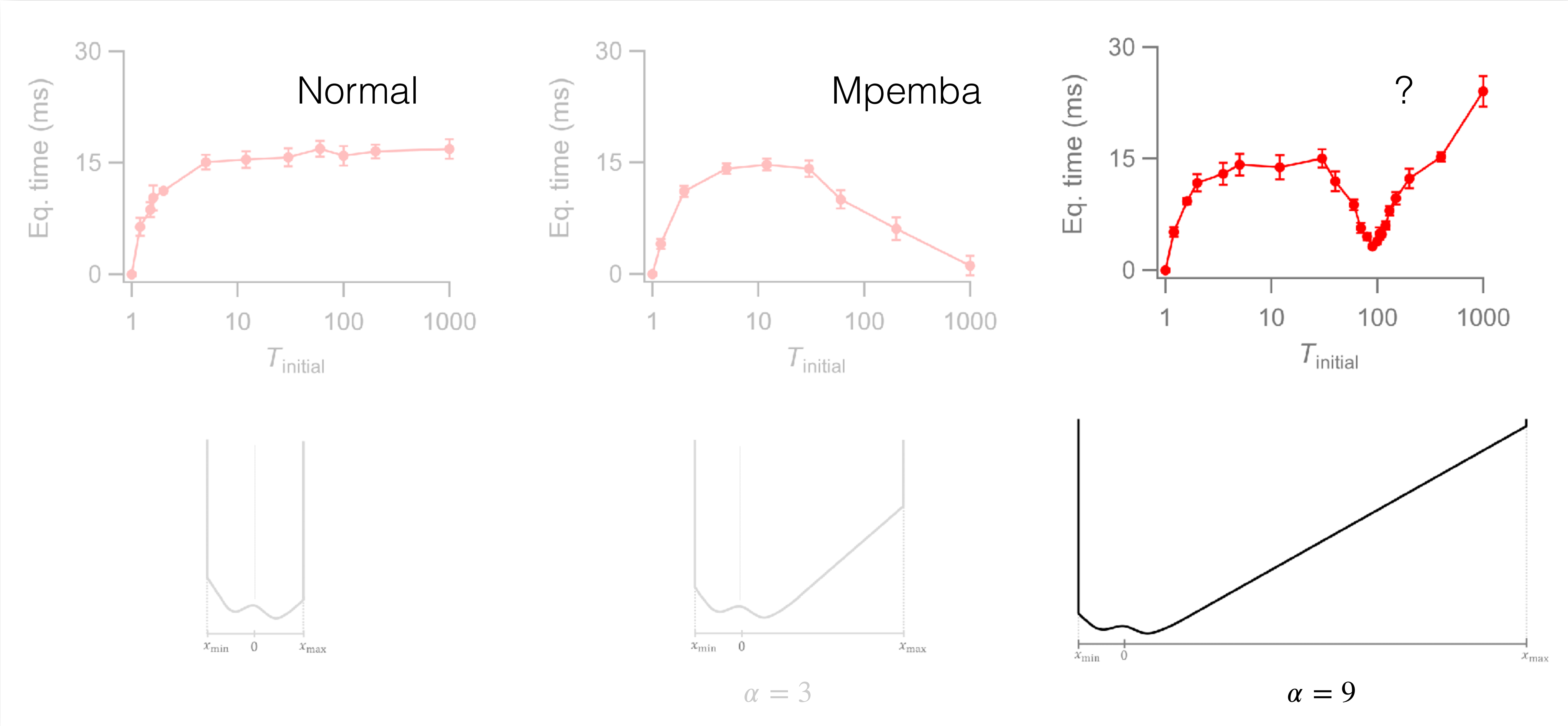


$\alpha = 1$

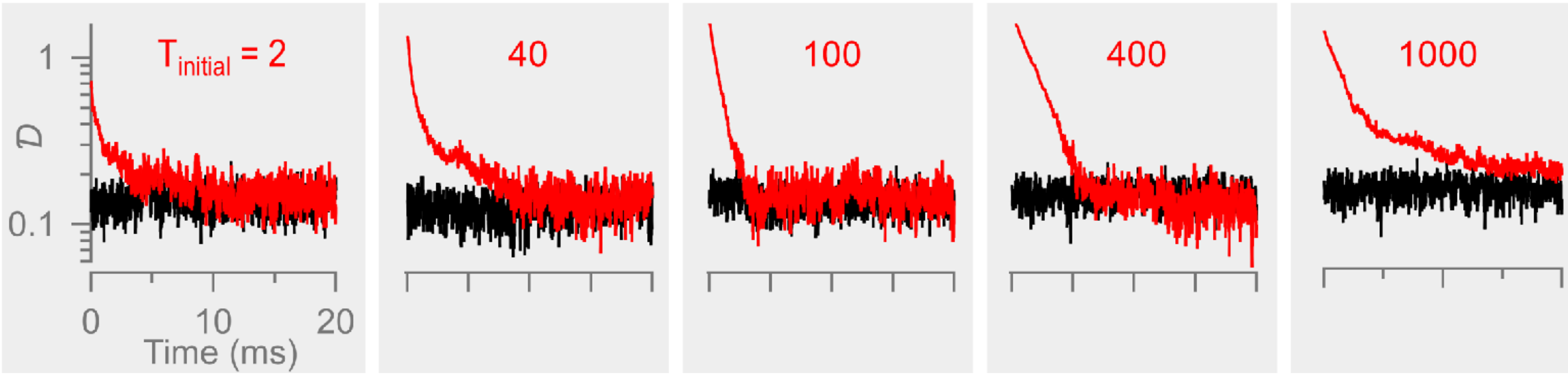
Equilibration time vs. initial temperature



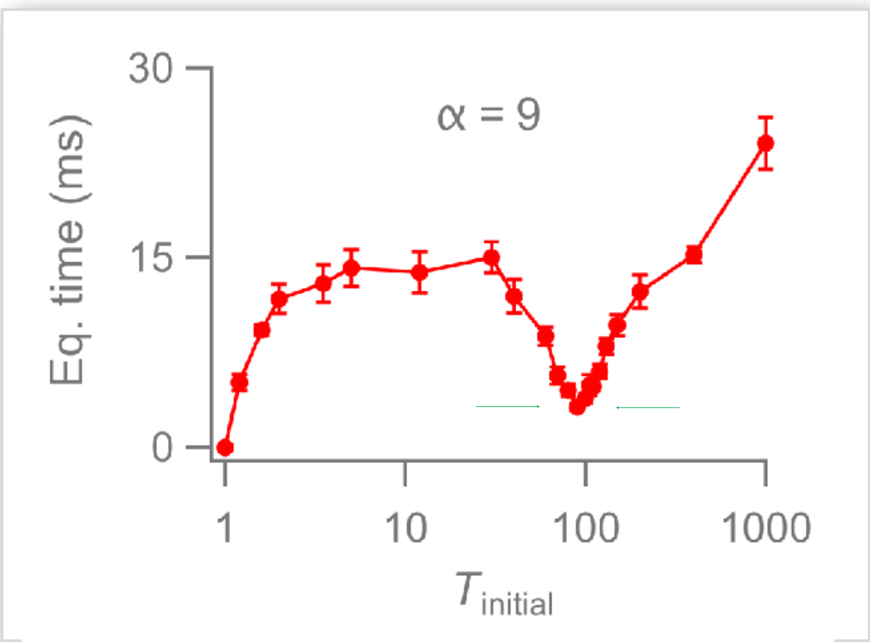
Equilibration time vs. initial temperature



Equilibration time vs. initial temperature



1000 trials



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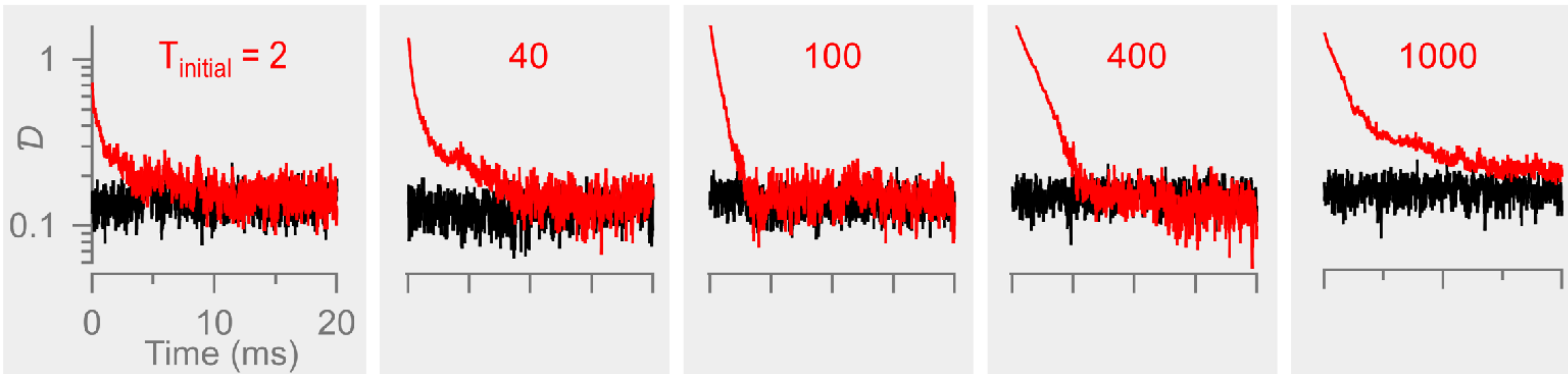
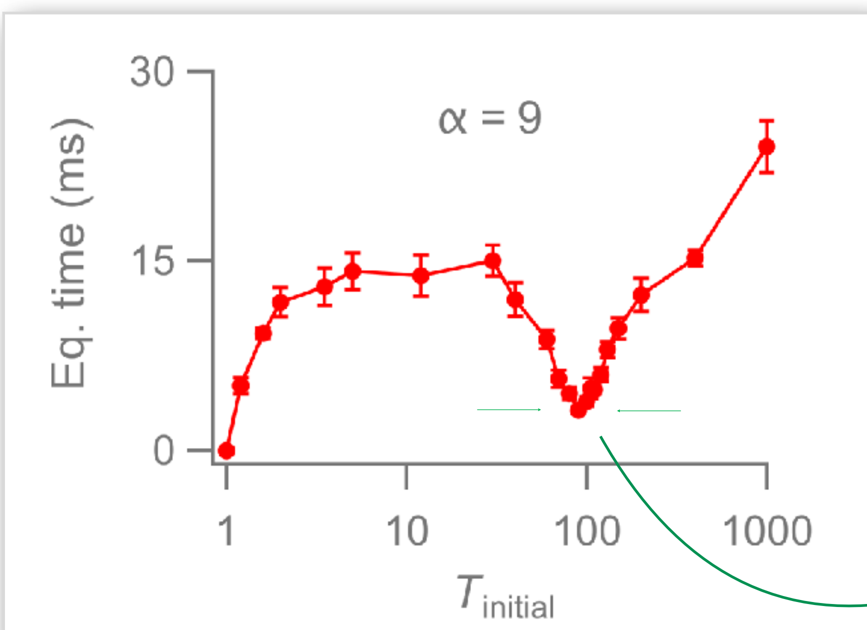


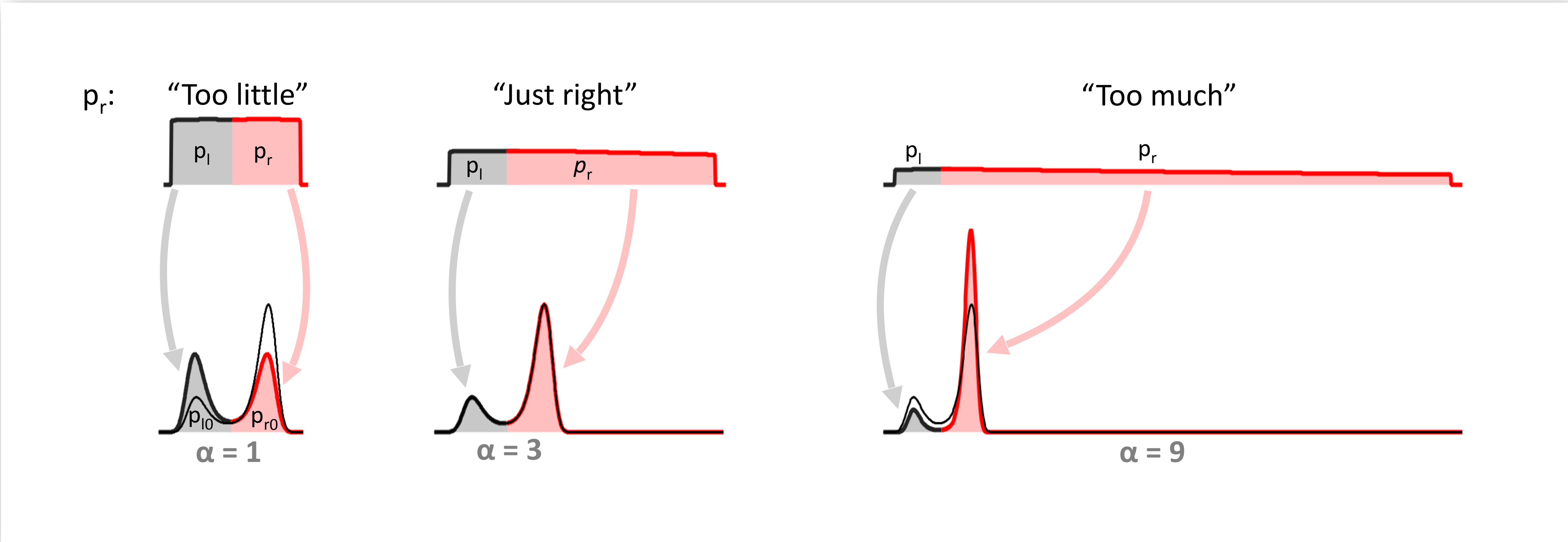
1000 trials

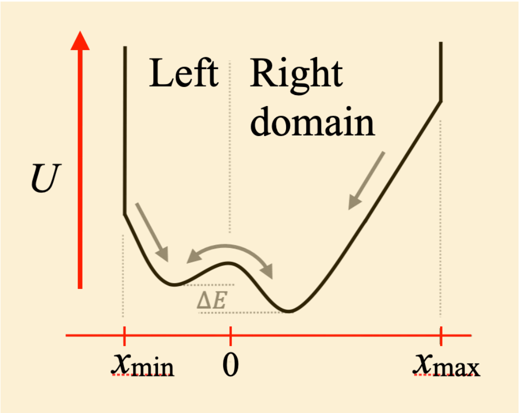


Exponentially
Faster cooling !

A. Kumar & J. Bechhoefer, *Nature* 2020

Mpemba explanation

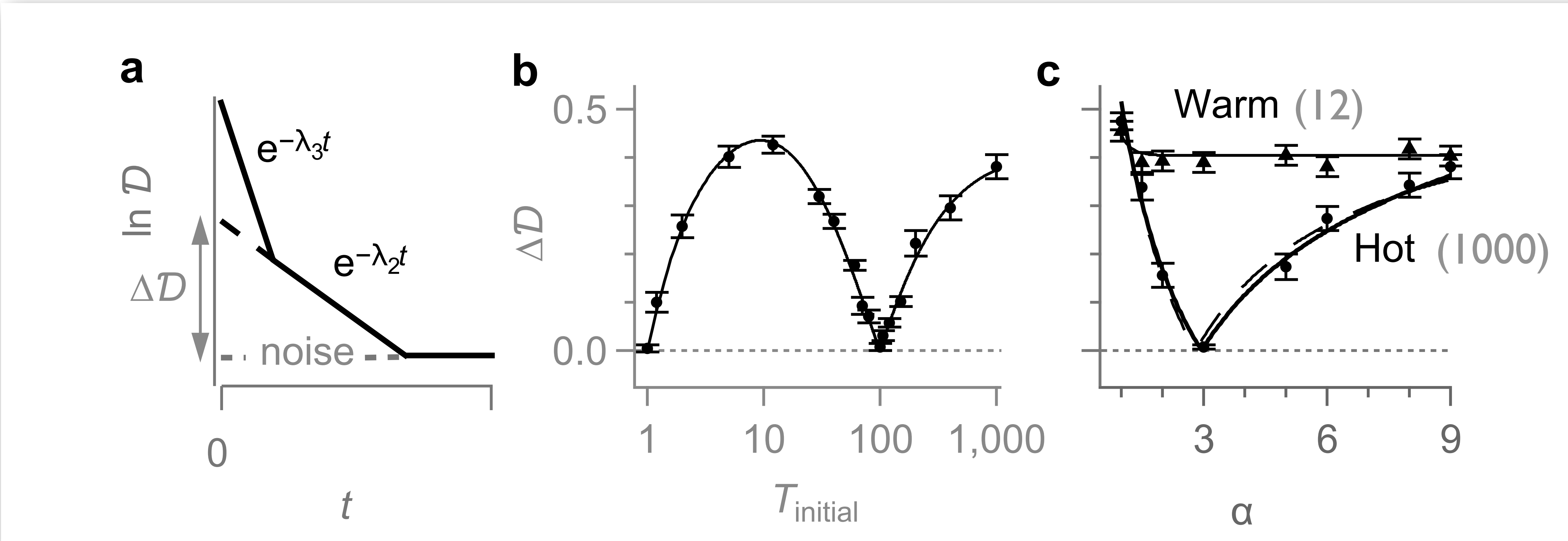




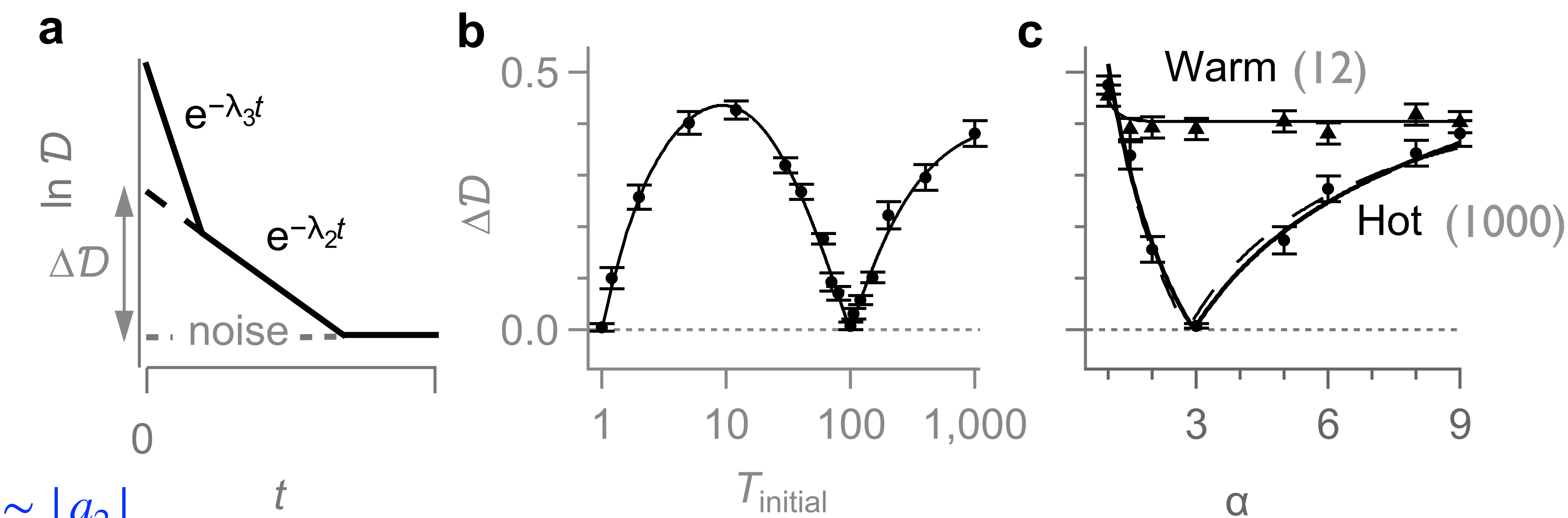
argument can be made rigorous
and generalized to finite temperatures

— Walker & Vucelja, arXiv 2022.07496

Mpemba explanation



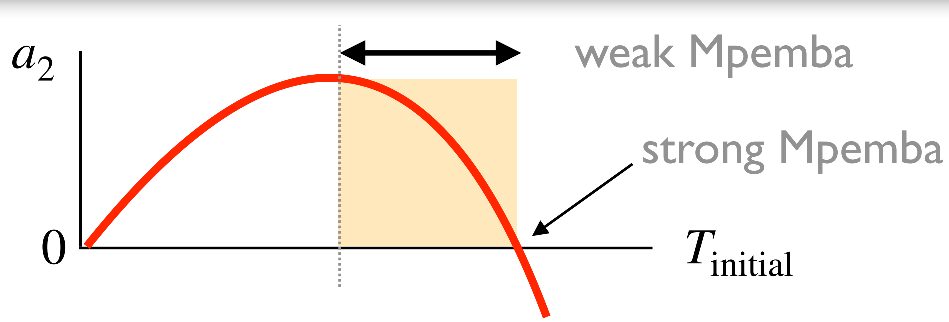
Mpemba explanation



$\Delta D \sim |a_2|$

Fokker-Planck ⇒ $$p(x,t) = \pi(x;T_\mathrm{b}) + \sum_{m=2}^{\infty} a_m(\alpha, T_0)\,\mathrm{e}^{-\lambda_m t}\, v_m(x;\alpha,T_\mathrm{b})$$

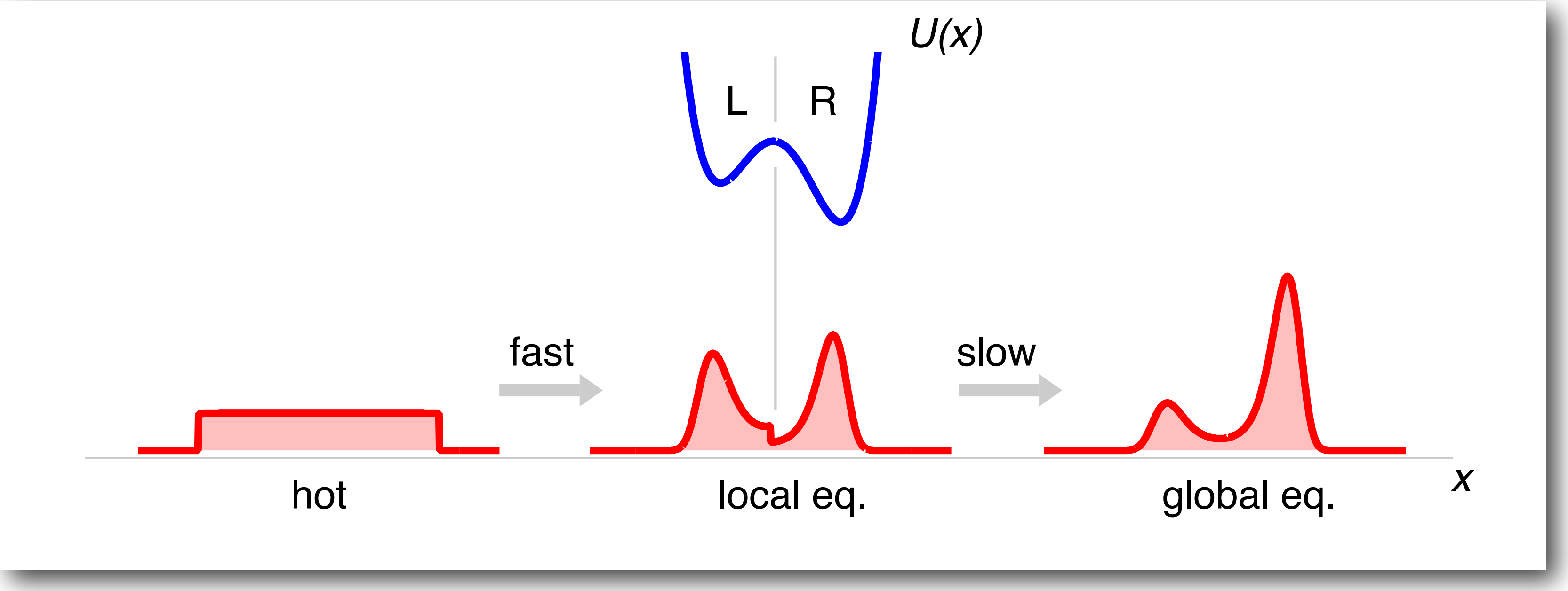
$$\approx \pi(x;T_\mathrm{b}) + a_2(\alpha,T_0)\,\mathrm{e}^{-\lambda_2 t}\, v_2(x;\alpha,T_\mathrm{b})$$

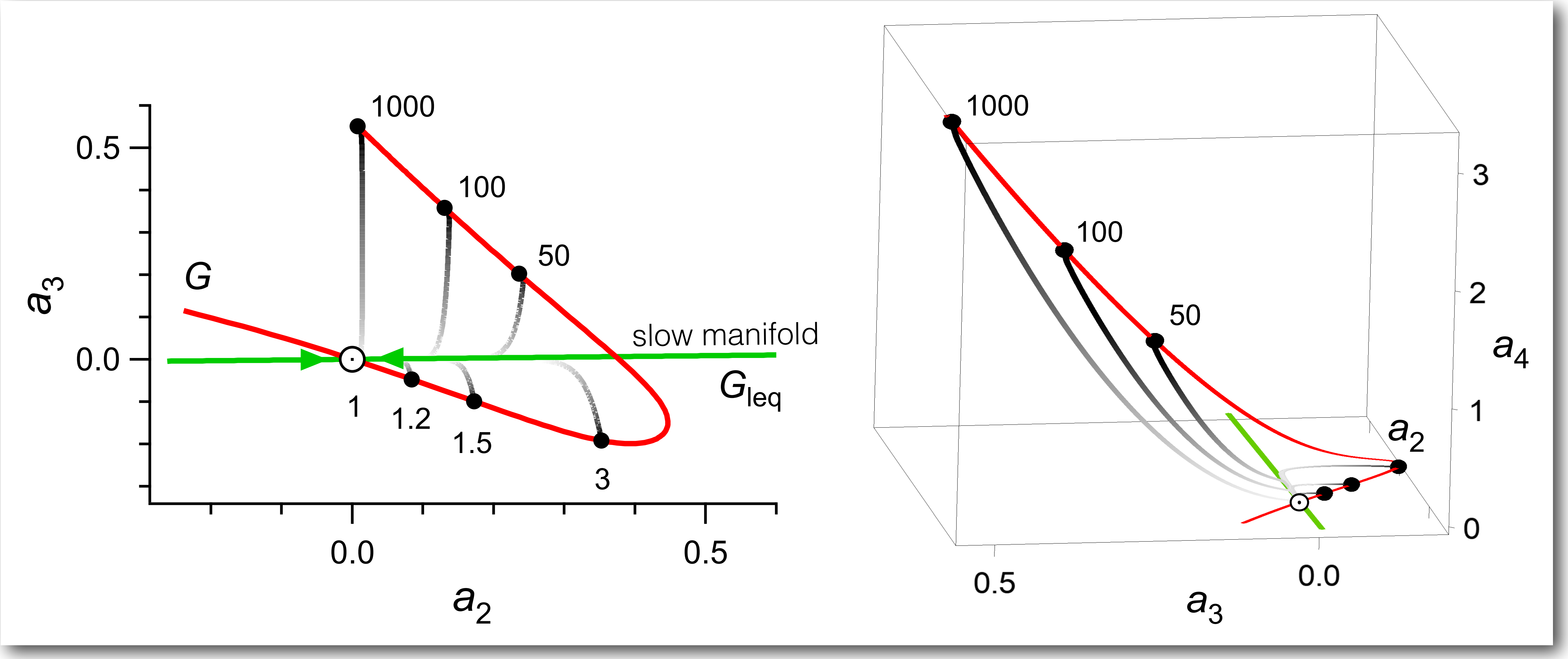


Z. Lu and O. Raz, *PNAS* 2017

Klich et al., *PRX* 2019

Mpemba explanation





R. Chétrite, A. Kumar, & J. Bechhoefer, *Frontiers in Physics* 2021

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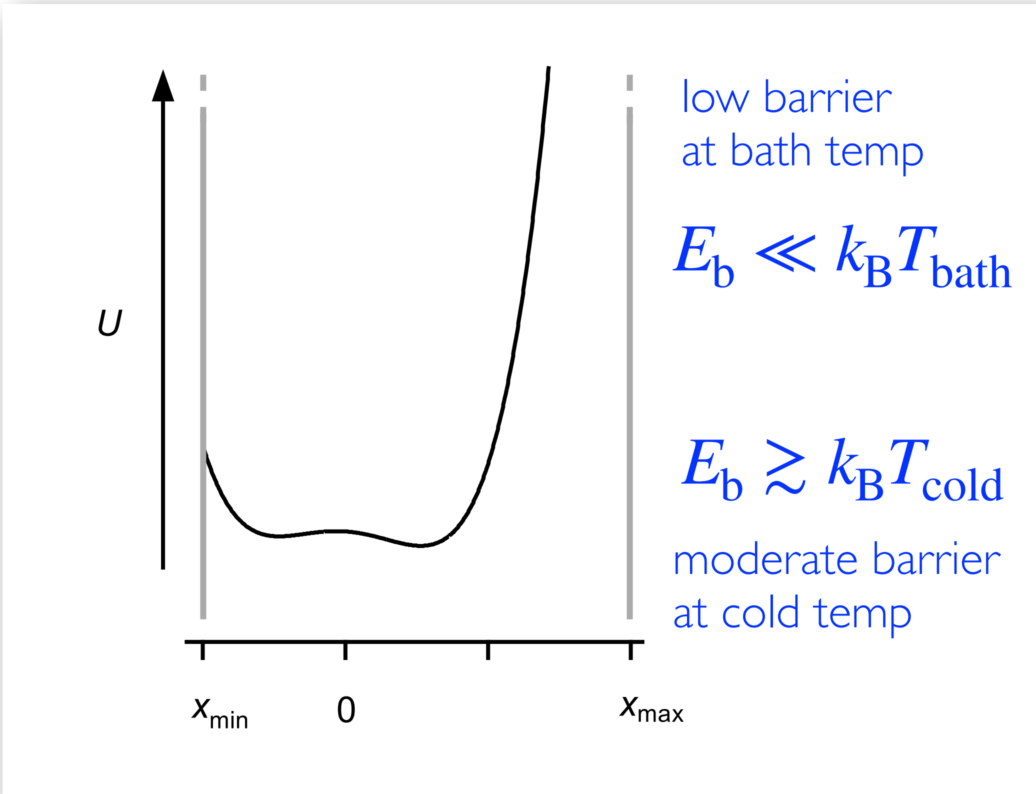
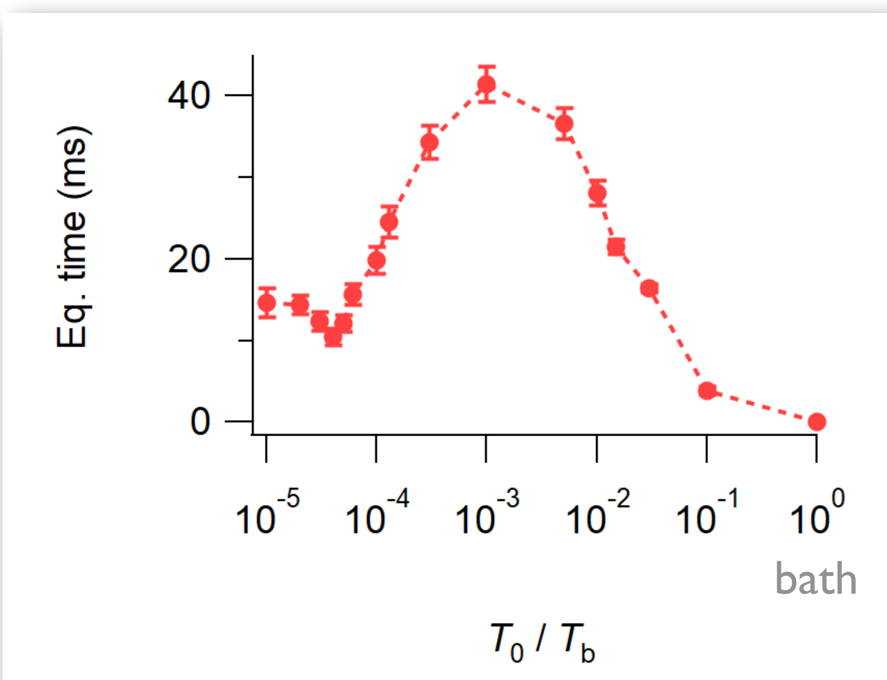
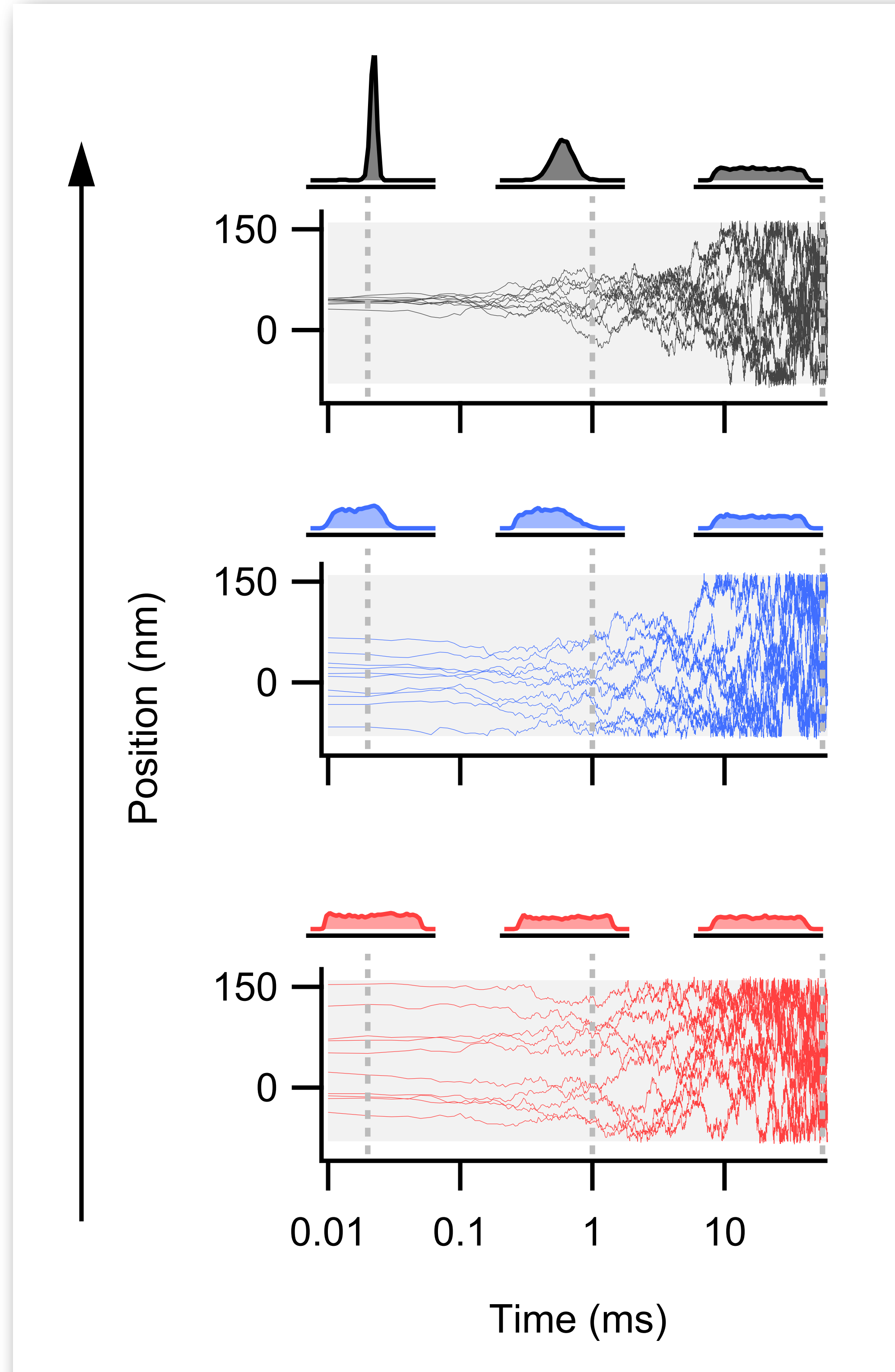
Inverse Mpemba effect

First observation in any system!







A. Kumar, R. Chétrite, JB, *PNAS* 2022

Inverse Mpemba effect

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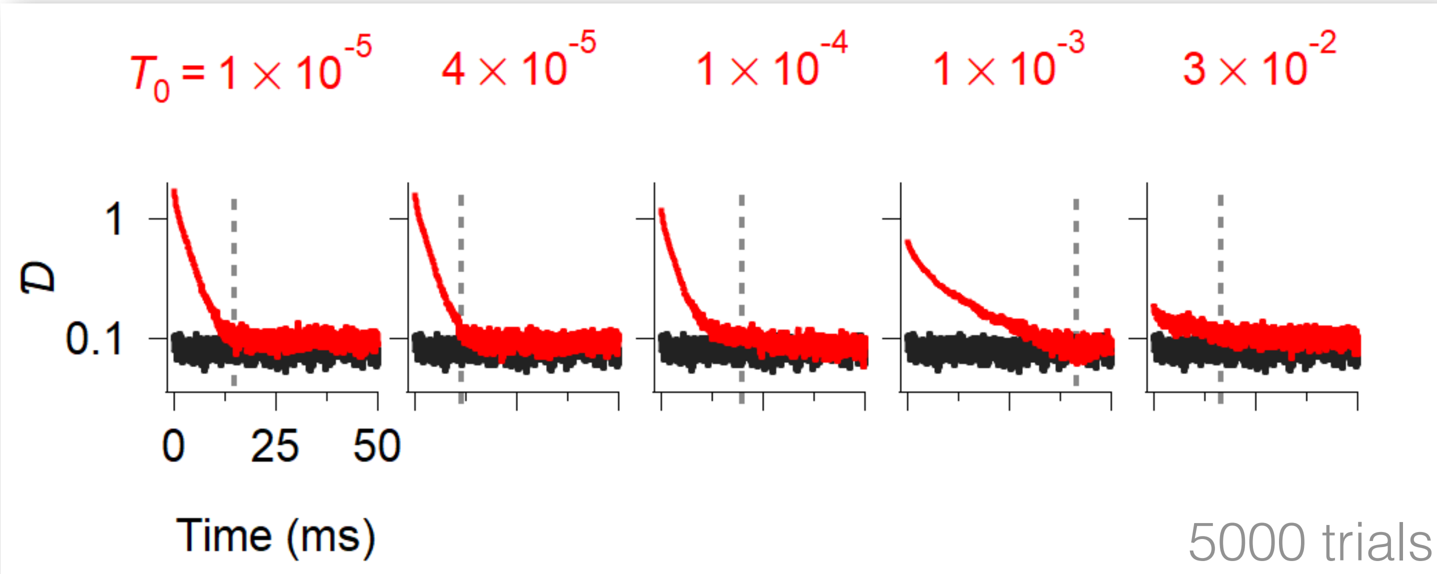
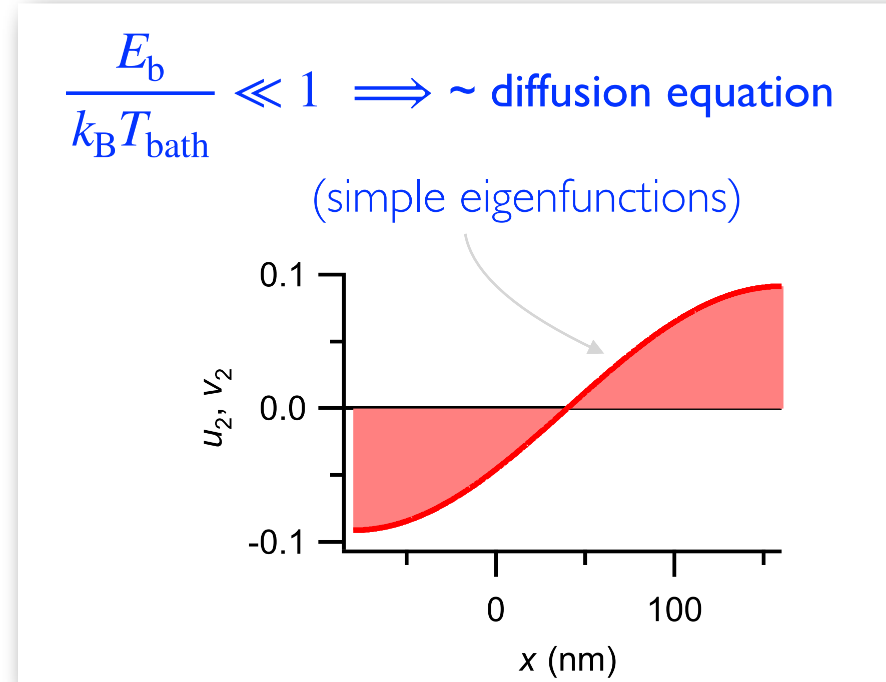
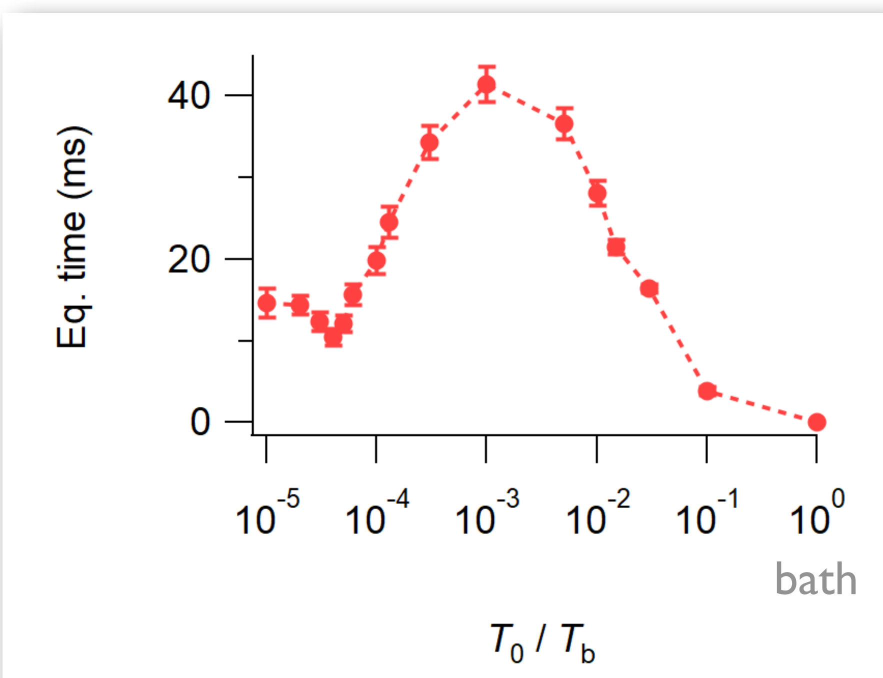
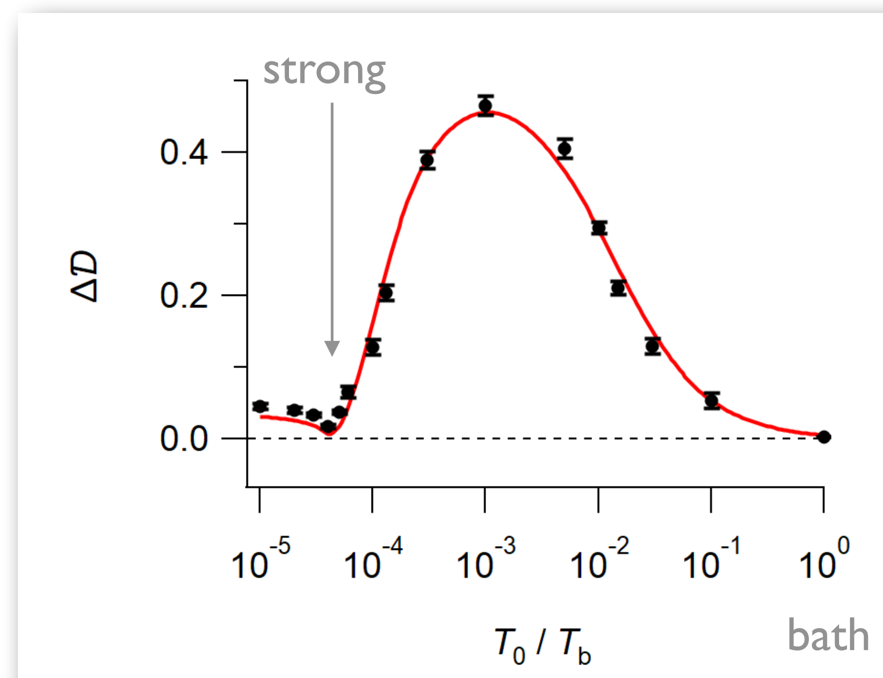








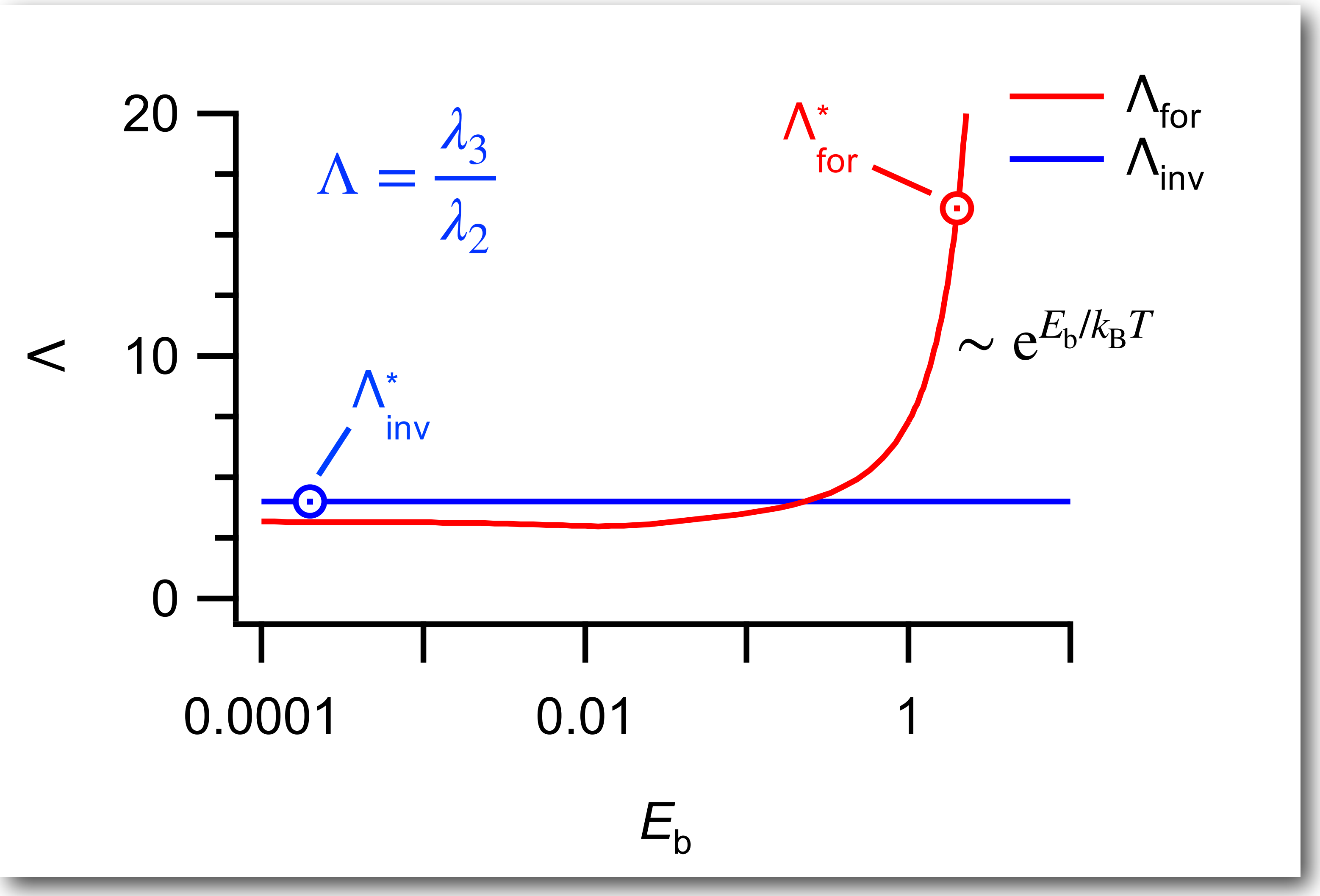
A. Kumar, R. Chétrite, JB, *PNAS* 2022

Inverse Mpemba effect

First observation in any system!

Forward Mpemba is easier to observe

barriers → bigger spectral gap



Forward: 1000 trials
"driven by energy"

Reverse: 5000 trials
"driven by entropy"

A. Kumar, R. Chétrite, JB, *PNAS* 2022

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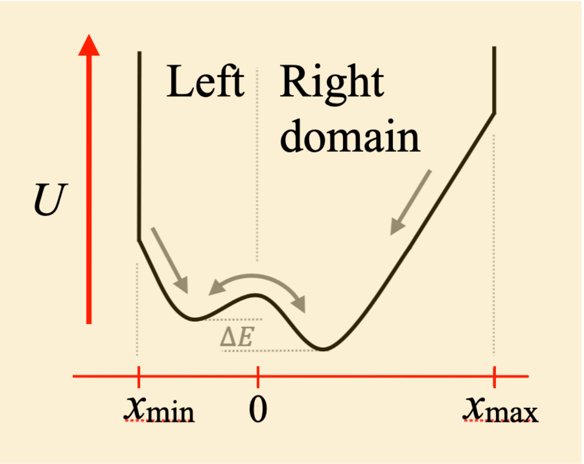
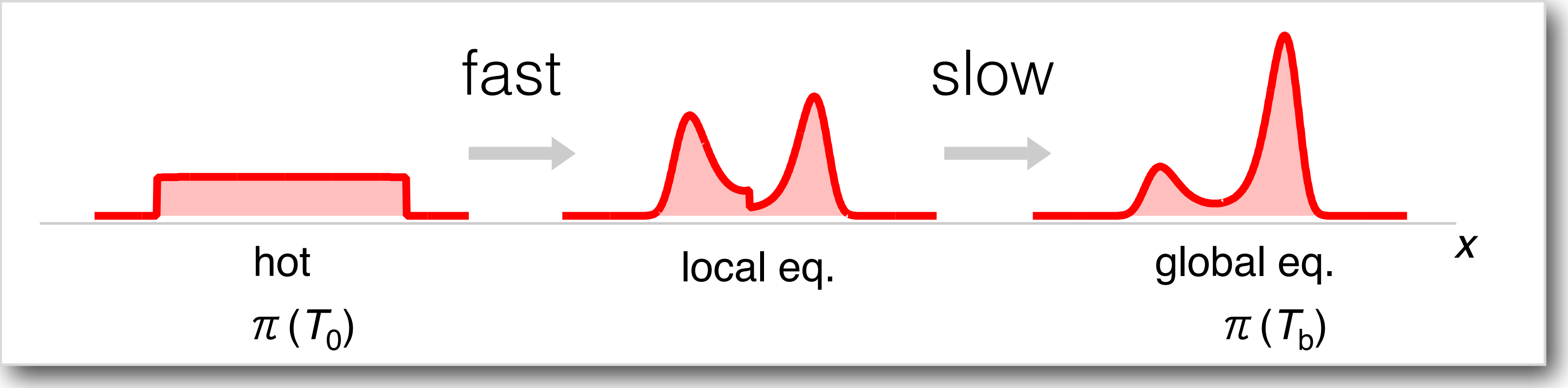
IV. Inverse Mpemba: Can a cold system heat faster?

V. What potentials lead to a Mpemba effect?

What potentials lead to Mpemba?



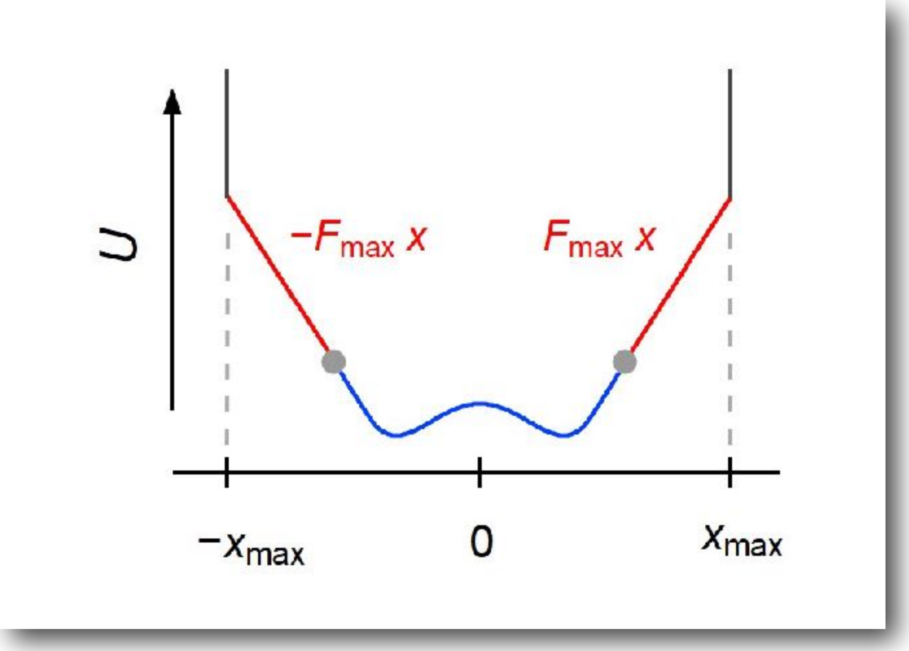
metastability mechanism

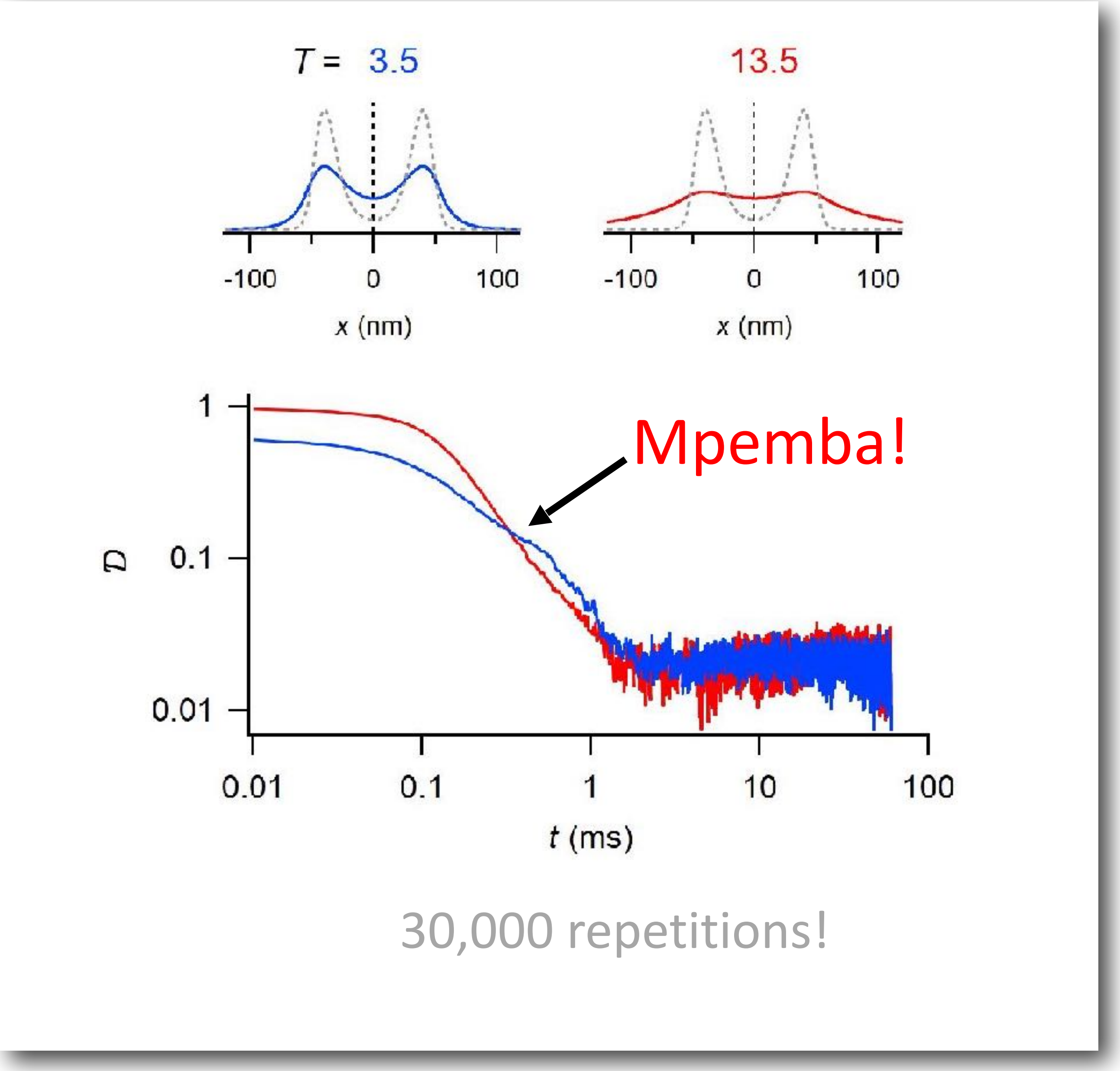


- Is metastability necessary?
- Other physical scenarios?

What potentials lead to Mpemba?

Higher-order Mpemba effect in a symmetric double well

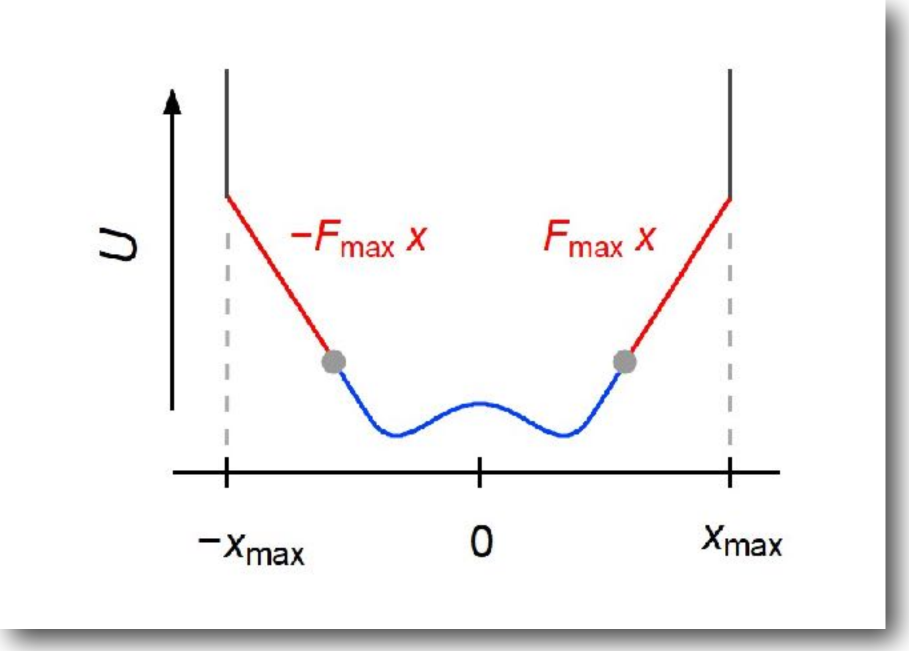


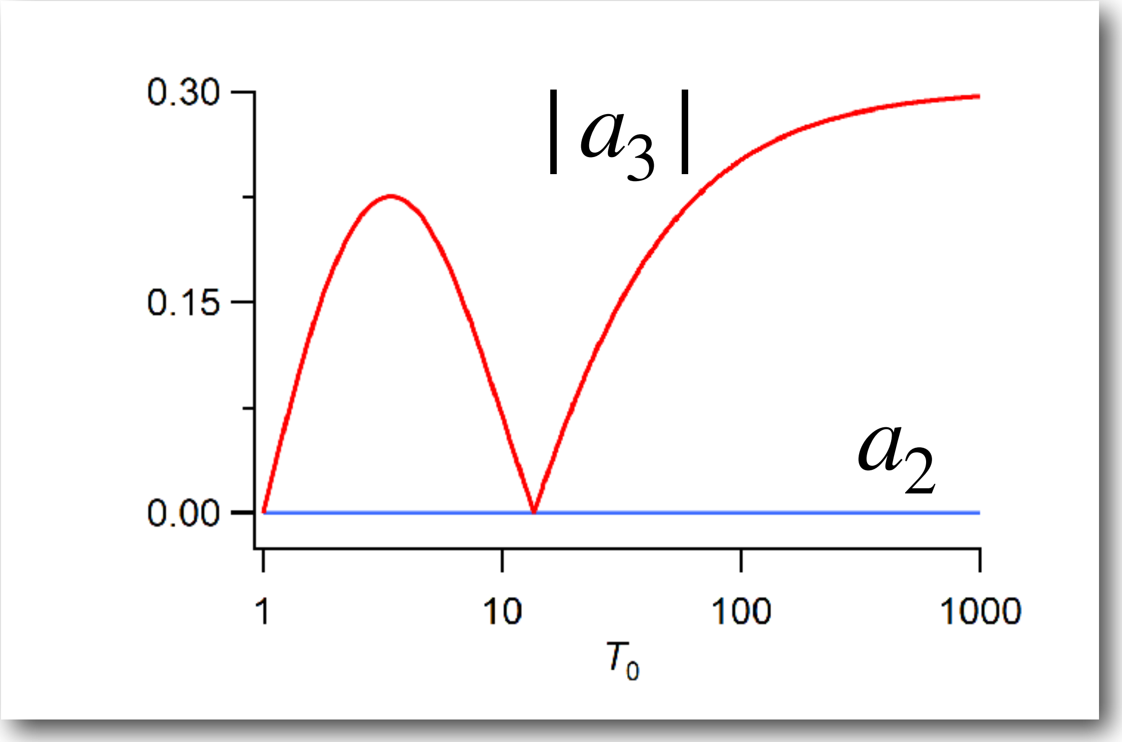


A. Kumar, PhD thesis, 2021

What potentials lead to Mpemba?

Mpemba if a_3 non-monotonic in T_0





$$p(x,t) = \pi(x;T_b) + a_2(\alpha,T_0)\, e^{-\lambda_2 t} v_2(x;\alpha,T_b) + a_3(\alpha,T_0)\, e^{-\lambda_3 t} v_3(x;\alpha,T_b)$$

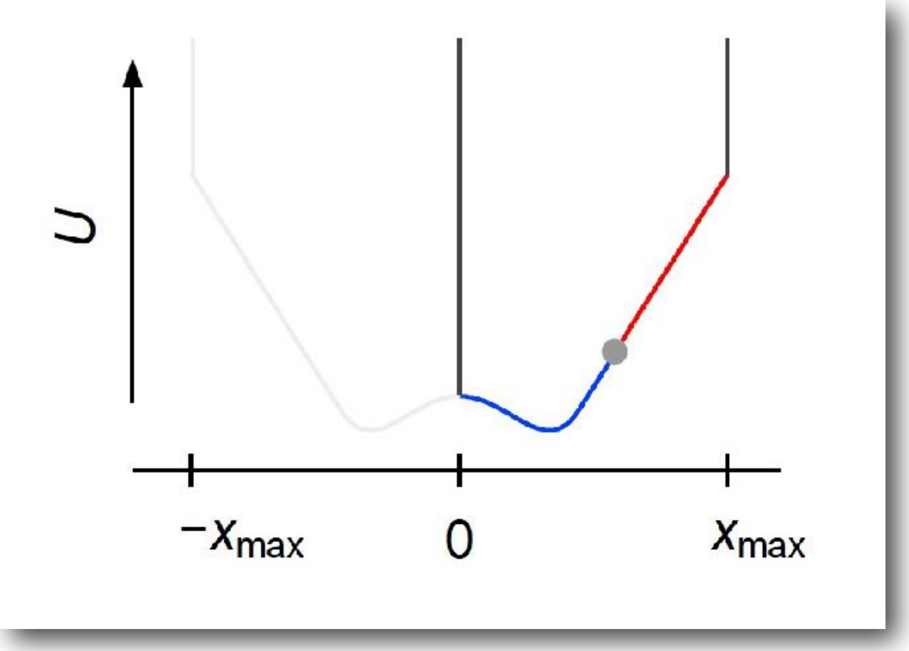
even even odd even

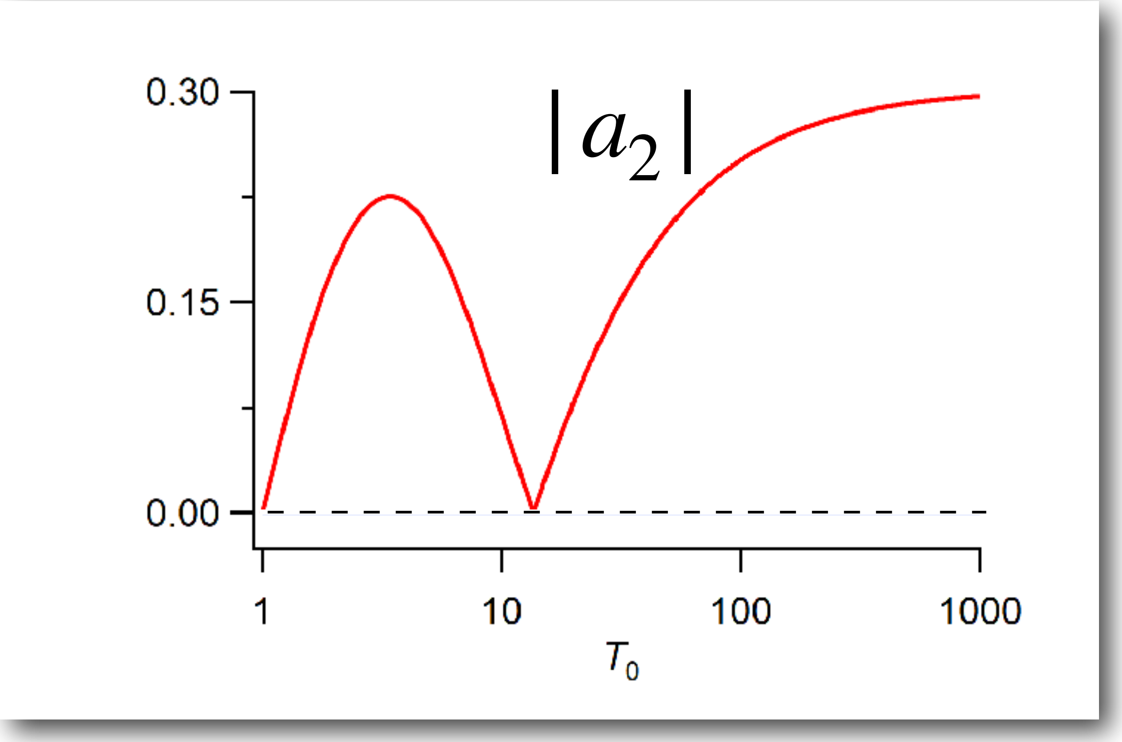
A. Kumar, PhD thesis, 2021

What potentials lead to Mpemba?

Double well not necessary!

No reflection symmetry $\Rightarrow a_2 \neq 0!$





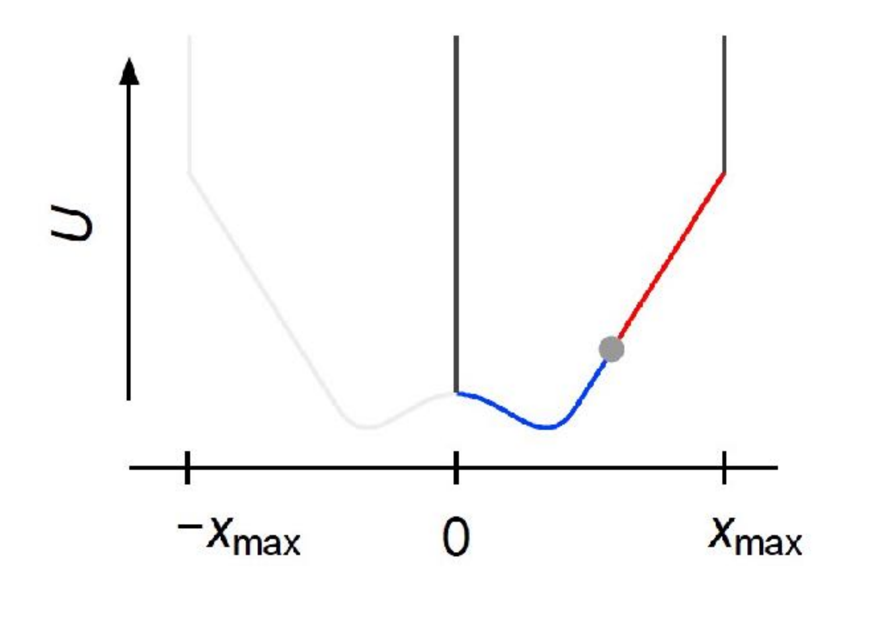
can't make vertical wall and result is very sensitive to slope at $x = 0$....

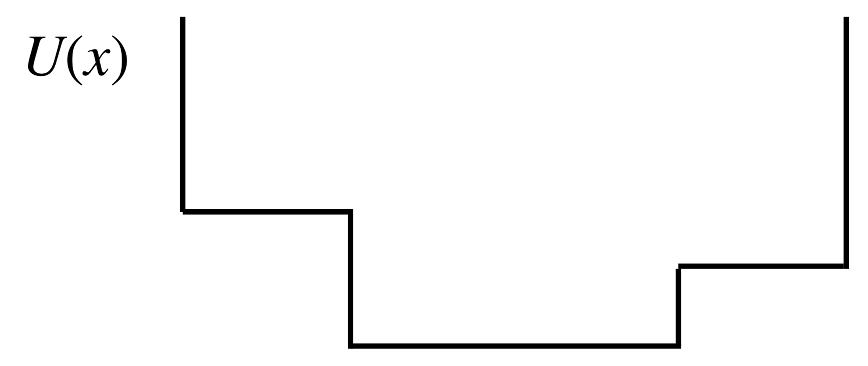
A. Kumar, PhD thesis, 2021

What potentials lead to Mpemba?

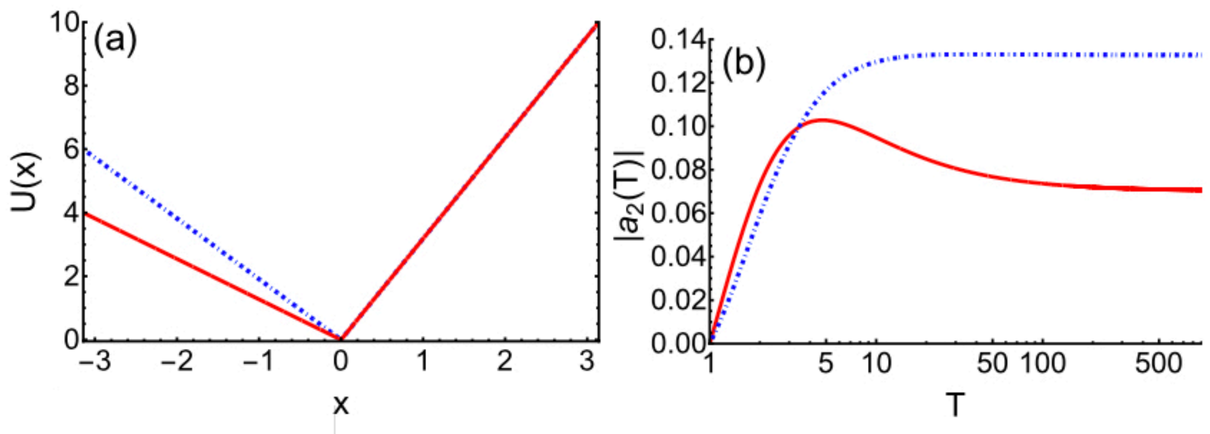
Double well not necessary!

Many other similar shapes





M. Walker and M. Vucelja, J Stat Mech 2021



A. Biswas and R. Rajesh, arXiv 2305.06613

Physical intuition?

strong Mpemba ↔ match probs

Theory status

- using the Fokker-Planck / Master eq. & eigenfunction approach, Mpemba effects have been predicted in
  – Ising systems
  – polymers
  – granular fluids
  – quantum dots [NEXT TALK!] …
  – NESS to NESS

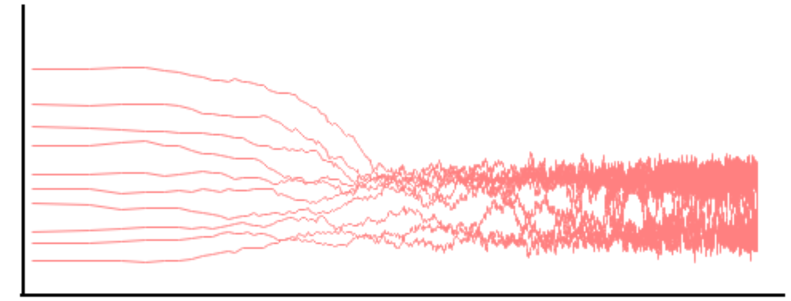
- these many-body systems have mostly been studied by "brute force", e.g., by simulation for *N* not too big.

- phenomenological approach: project onto observables x_1 , x_2
  – in mean-field Ising antiferromagnet, leads to picture similar to discrete spectrum
  – Klich et al., *PRX* 2019

- Is there a more general many-body condensed-matter-style approach?

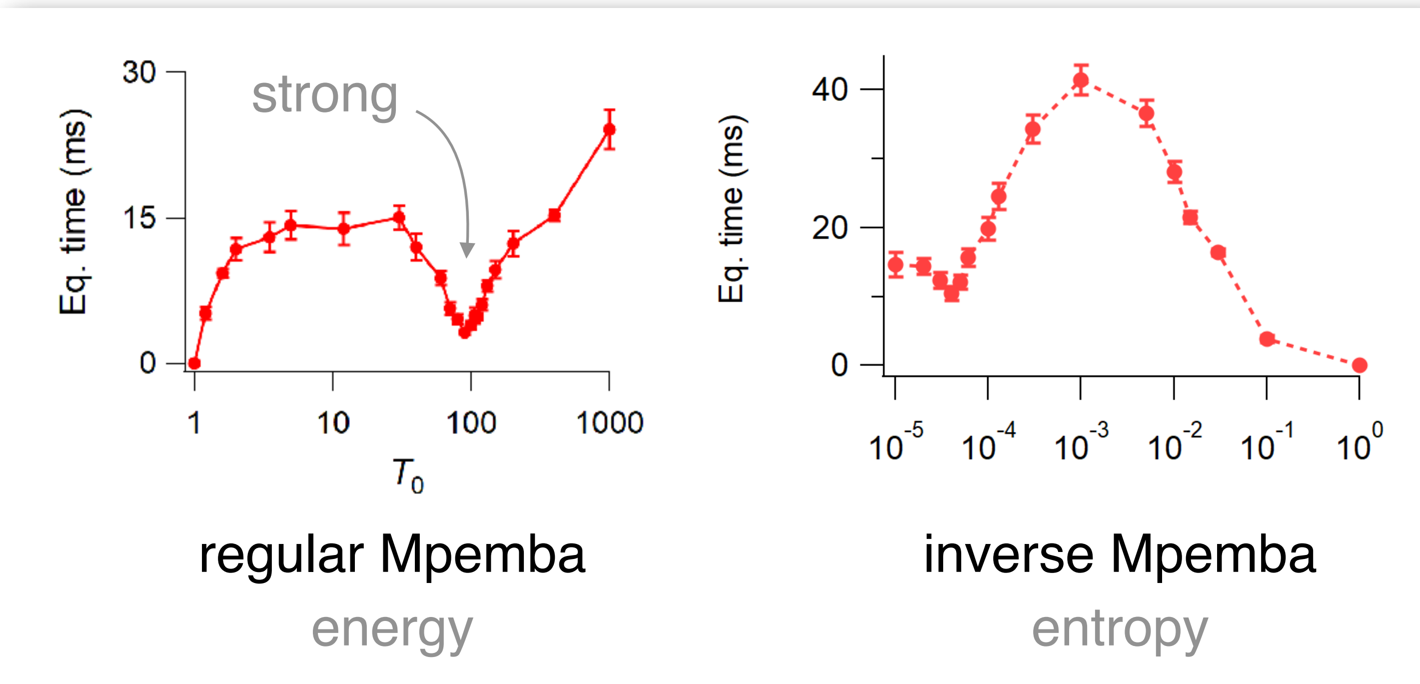
Summary

- Mpemba: prototype of "new" class of relaxation effects for strong quenches

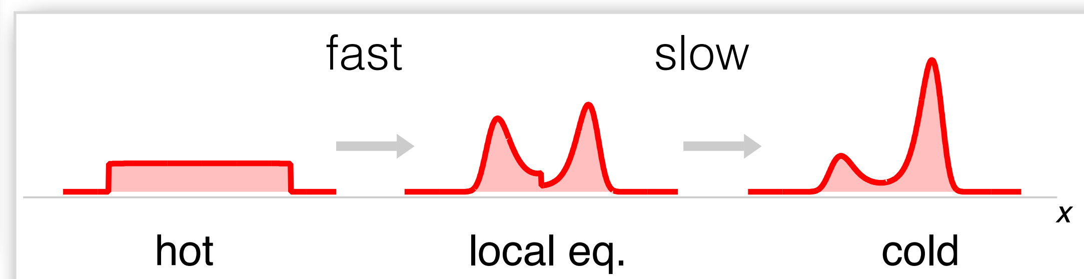


- Quenching: a strongly nonequilibrium process

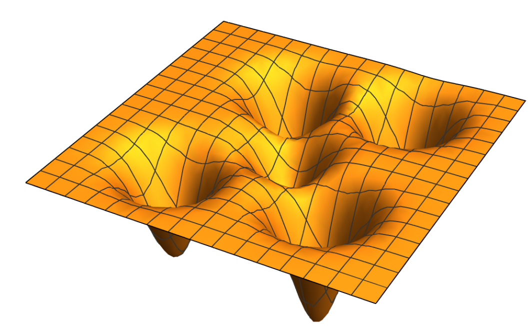
- Regular / Inverse Mpemba: cooling / heating



1) Is the effect real? ✓
2) Would an explanation be ~~trivial~~ or illuminating ✓ ?



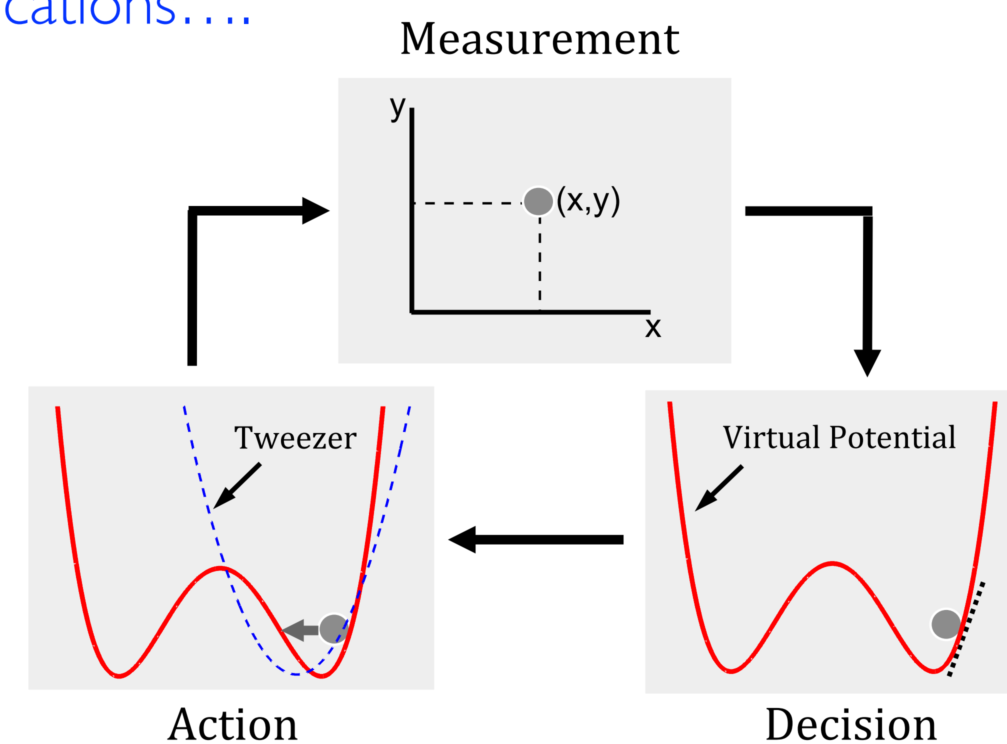
- Strong effects: exponential speedup

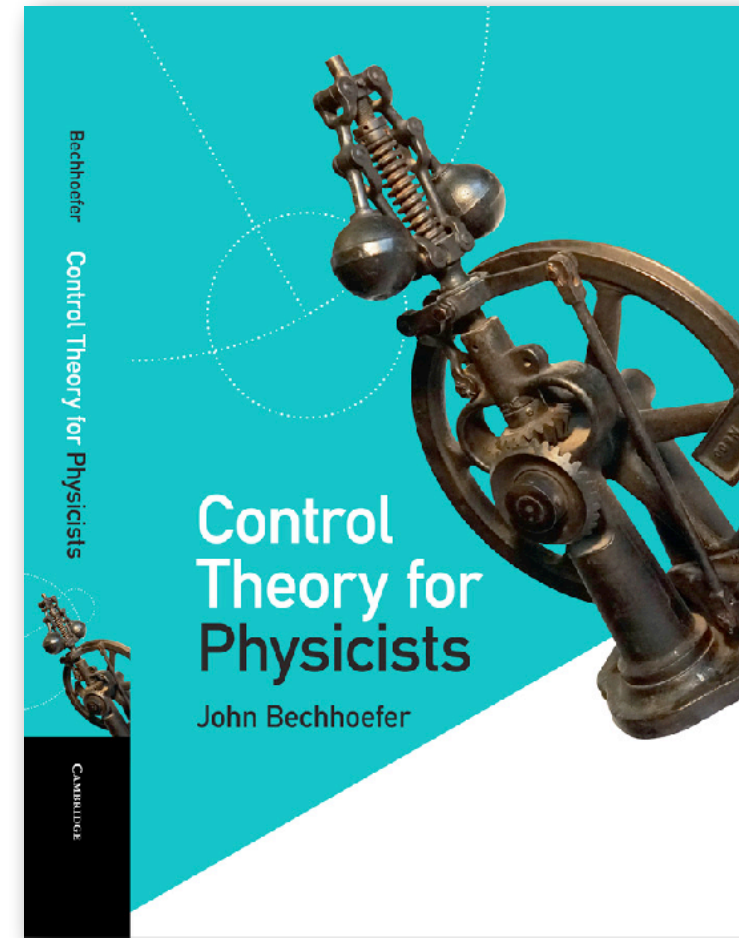


- Metastability mechanism: what often leads to slow dynamics here leads to a speed-up

Outlook

- Feedback trap dynamics in arbitrary, time-dependent potentials: cyberphysics many applications….
- creative use of feedback





Cambridge Univ. Press, 2021

- Other systems: predicted in Ising systems, polymers, granular fluids, qbit relaxation, …
- Water / ice ?
- Other protocols: Kovacs, precooling, …
- For many-body systems: Need a more systematic understanding?