Anomalous thermal relaxation
in a colloidal system

NSERC CRSNG

Frontiers in Nonequilibrium Physics 2024
July 23, 2024

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SFU

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Outline

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

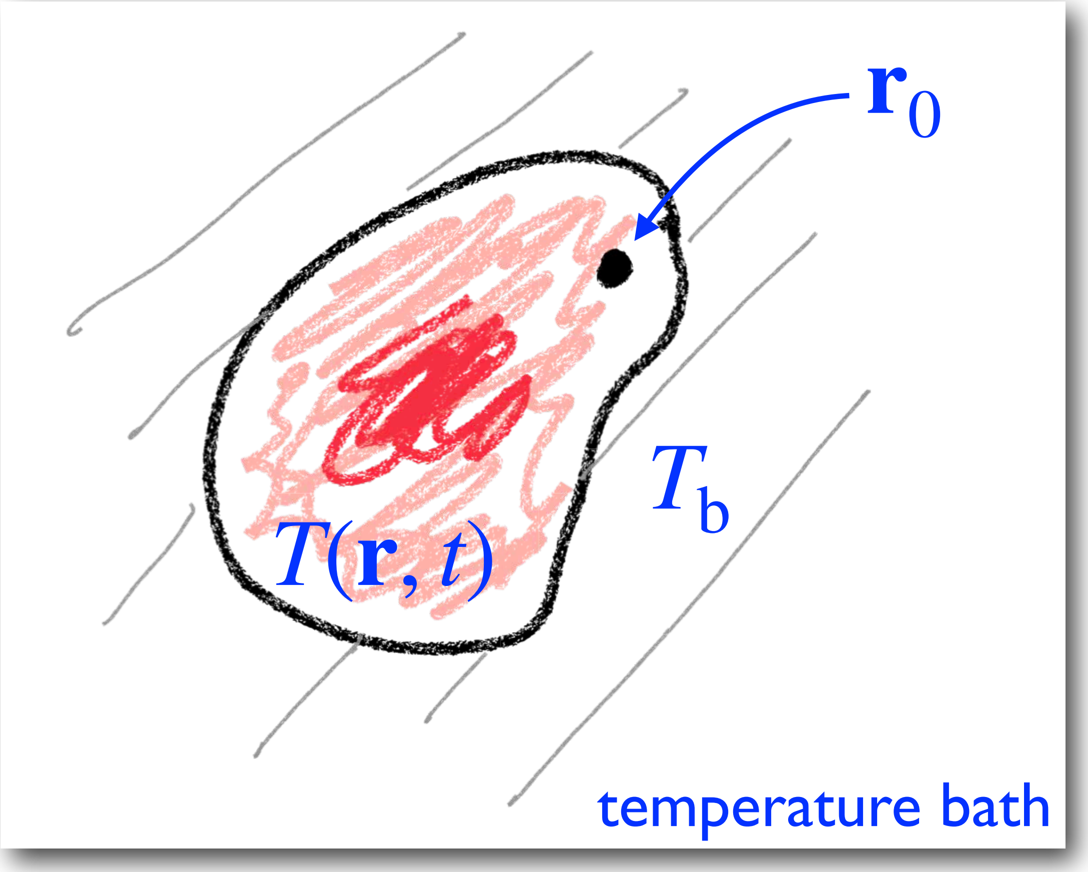
II. **Feedback traps & virtual potentials**

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

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

V. **Current project: Finite-rate quenches**

Exponential relaxation at long times



Thermal relaxation of an extended body

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

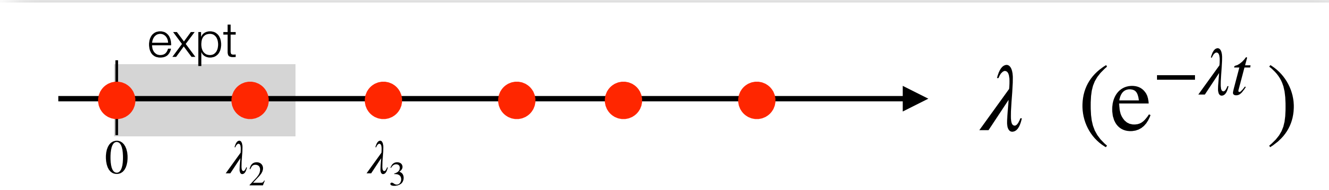
$$T(\mathbf{r}, t) = T_\mathrm{b} + \sum_{m=2}^{\infty} a_m\, v_m(\mathbf{r})\, \mathrm{e}^{-\lambda_m t}$$

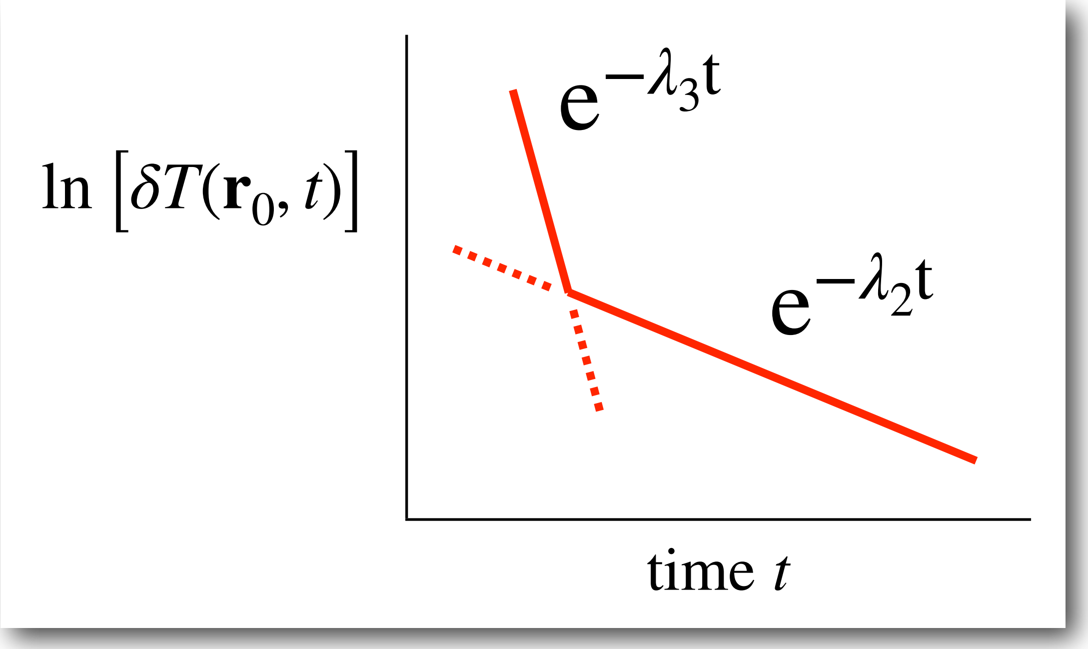
At long times $t \gg \lambda_3^{-1}$

temperature at one point relaxes exponentially

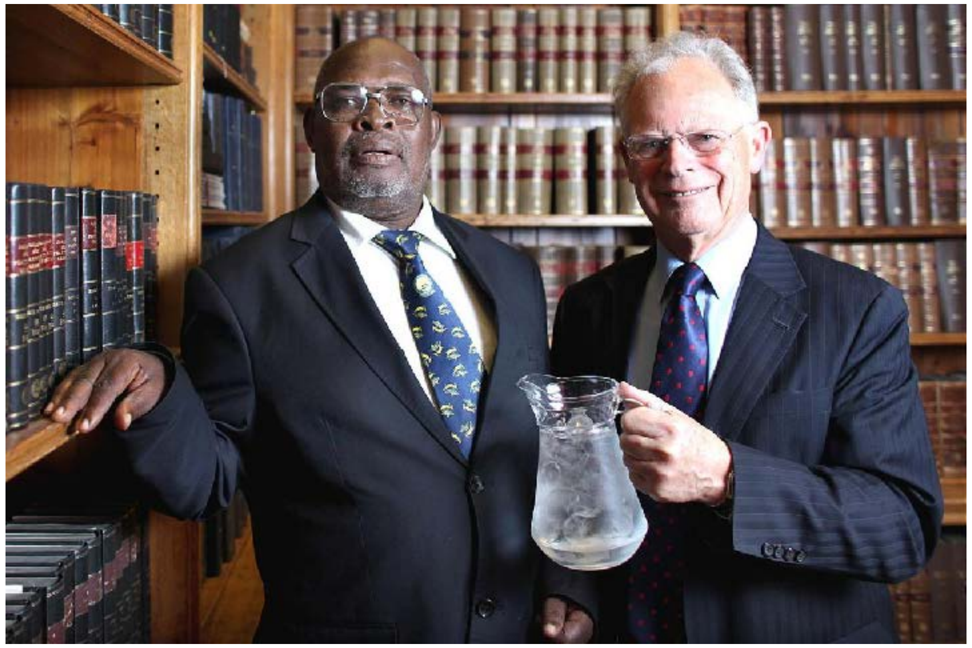
$$T(\mathbf{r}, t) \approx T_\mathrm{b} + a_2\, v_2(\mathbf{r})\, \mathrm{e}^{-\lambda_2 t}$$

$$\delta T(\mathbf{r}_0, t) \sim \mathrm{e}^{-\lambda_2 t}$$ ~ "Newton's law of cooling"



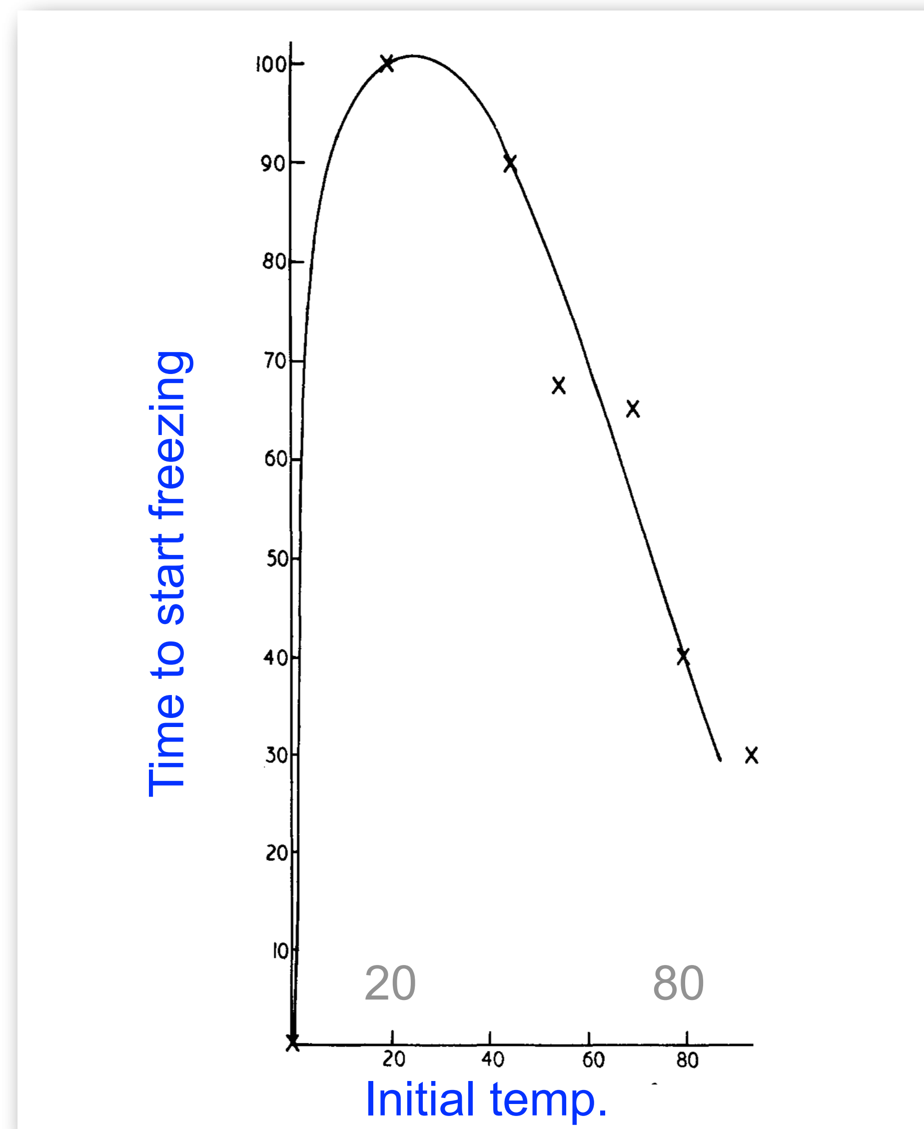


Mpemba effect



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?'

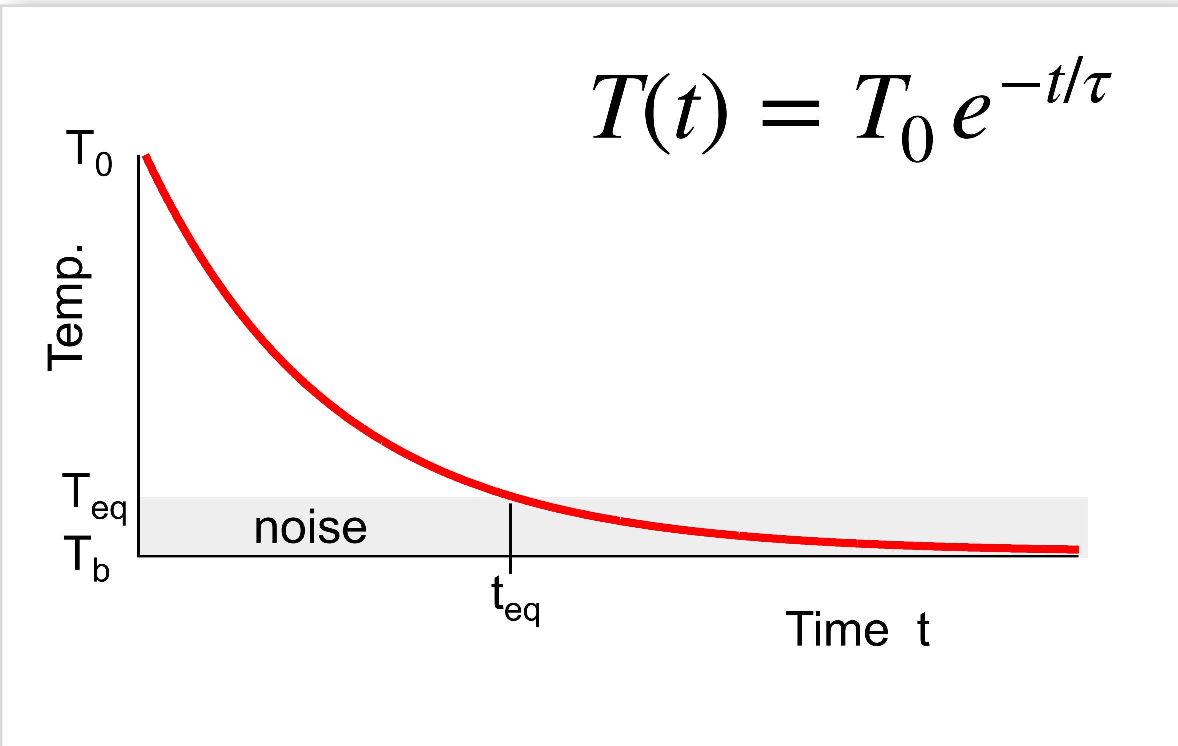


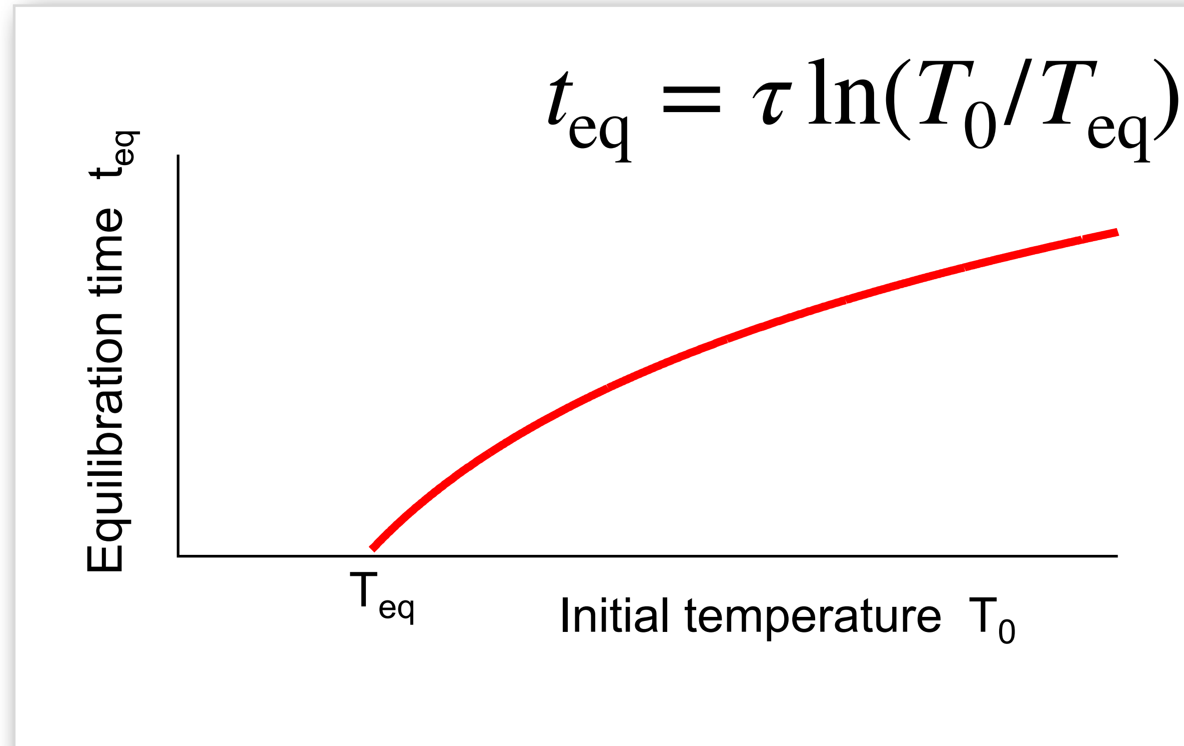
Hot water can freeze faster than warm water.
when quenched in the same (supercooled) bath.

Mpemba effect

Why a paradox?

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
- frost on bottom

Mpemba effect

Is there a universal / general / illuminating explanation?

Philip Ball, *Physics World*, 2006

(Too Many) Explanations for Water → Ice

- Evaporation
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Mpemba effect

Explanations?

Is there a universal / general / illuminating explanation?

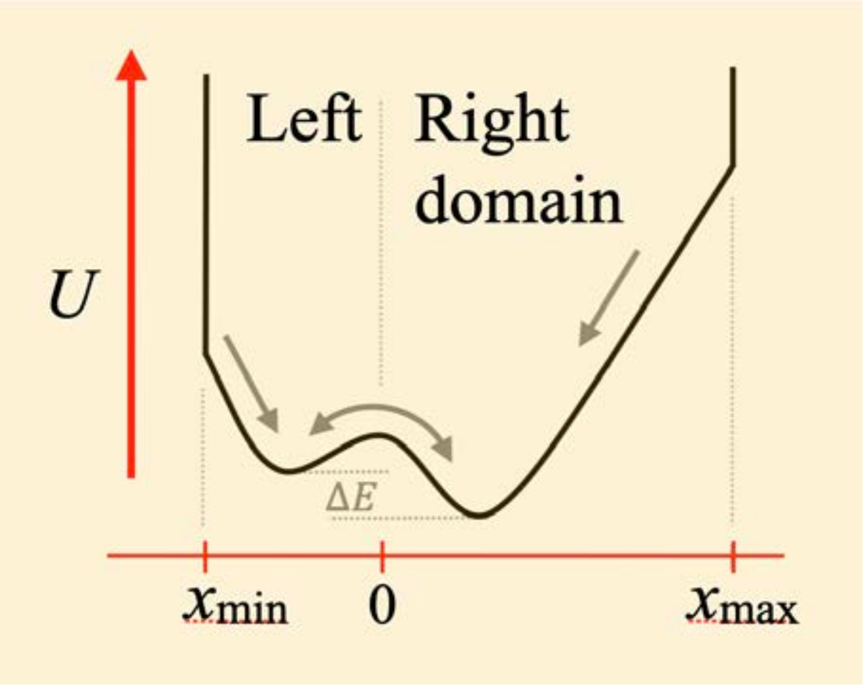
Philip Ball, *Physics World*, 2006

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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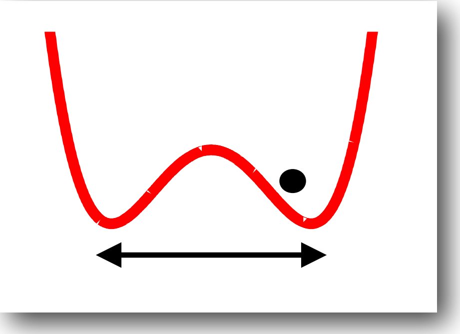
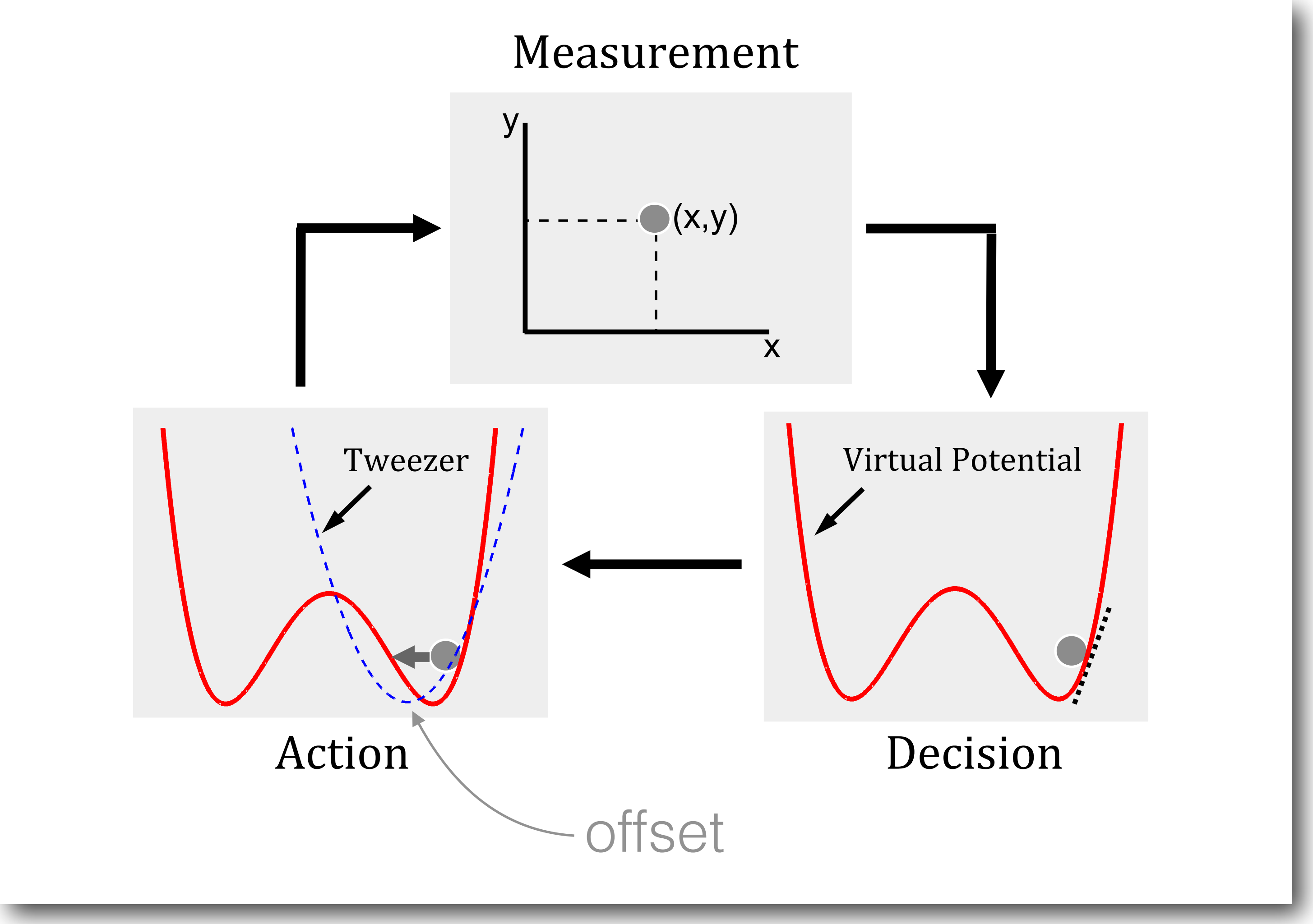
Feedback trap

ABEL = AntiBrownian ELectrokinetic

Put a diffusing particle in a virtual potential

micron-scale silica bead, in water

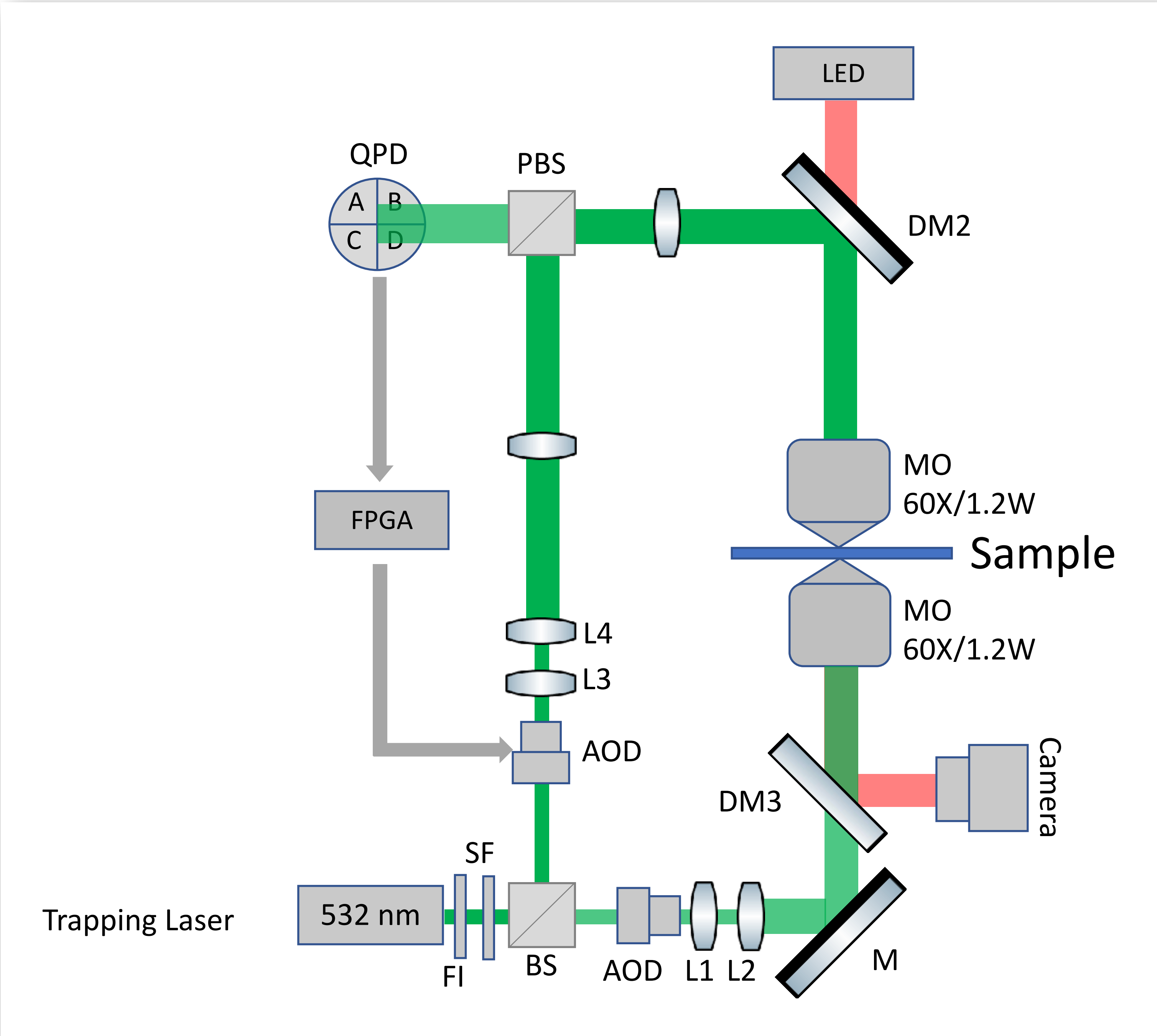




Here: offset optical tweezers
"source the force"

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

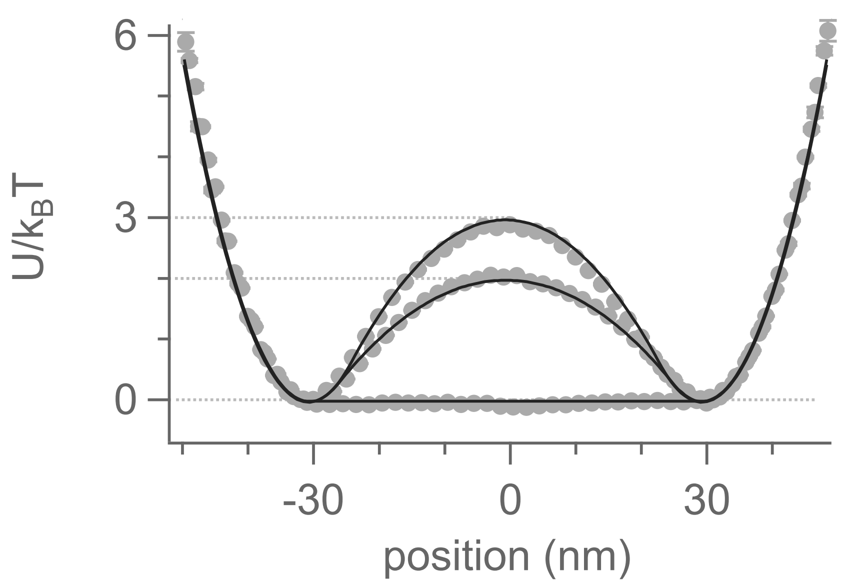
Feedback trap

The right tool for these experiments

- ~ arbitrary potential shapes

Change barrier height

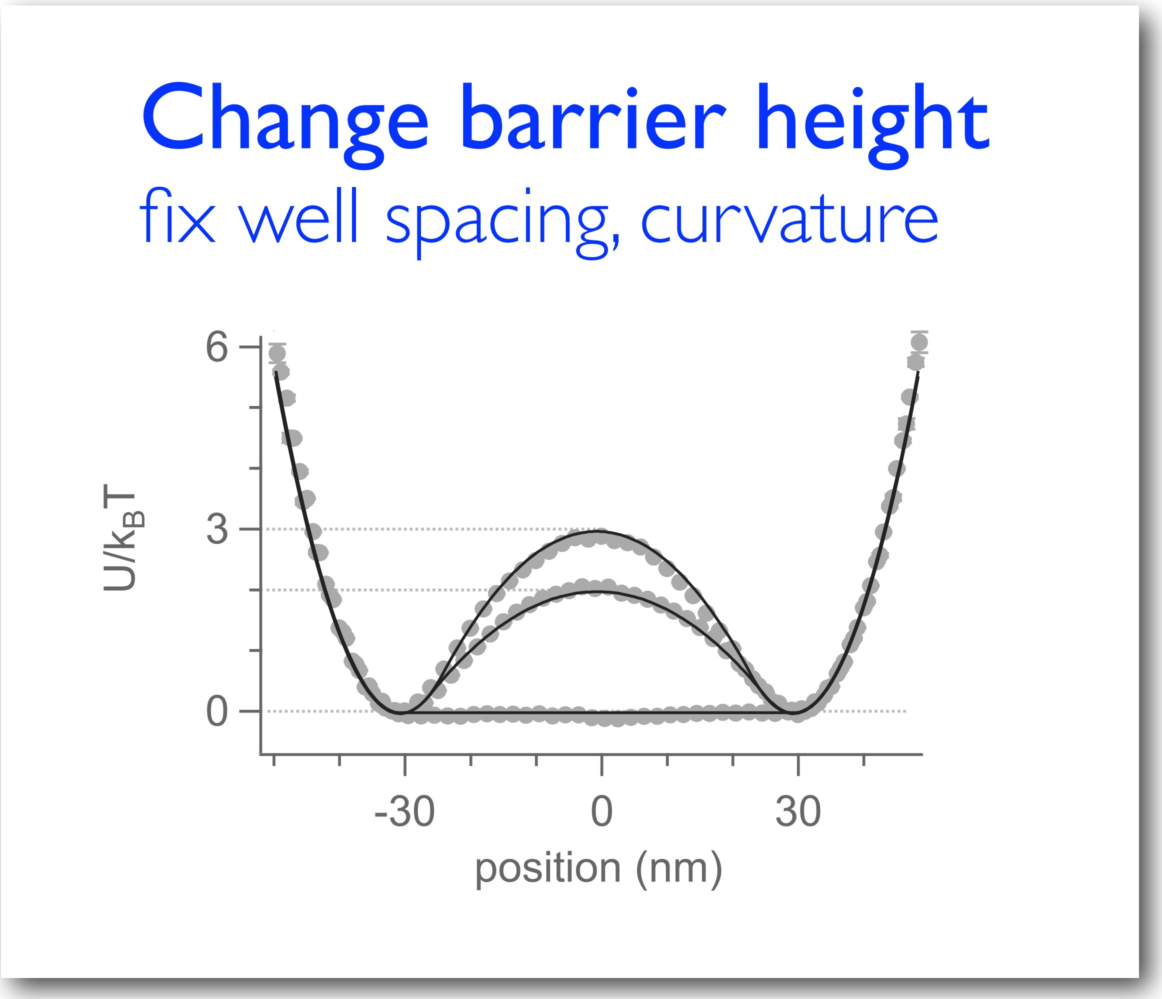
fix well spacing, curvature

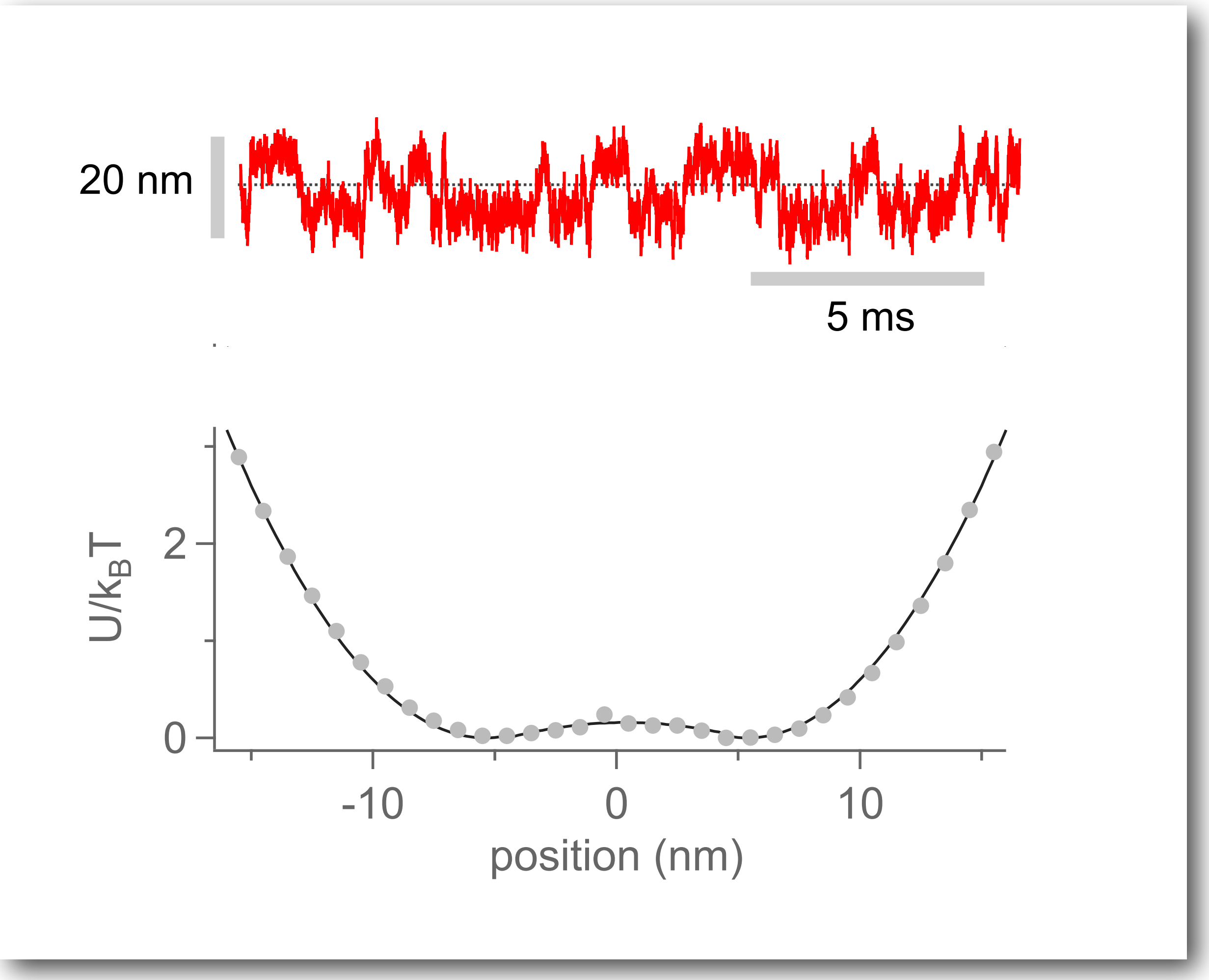


Feedback trap

The right tool for these experiments

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





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Mpemba effect

Careful definition

Zhiyue Lu and Oren Raz, *PNAS*, 2017

Traditional definition: initially hotter system cools and freezes more quickly

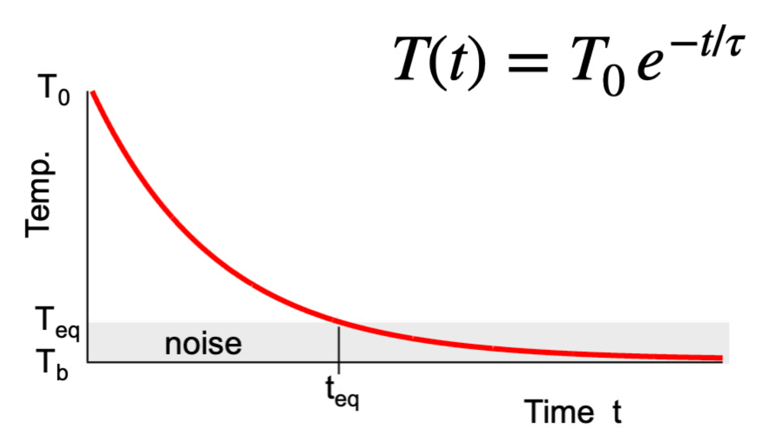
Ambiguities: nucleation (to initiate freezing) a sensitive stochastic process

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.

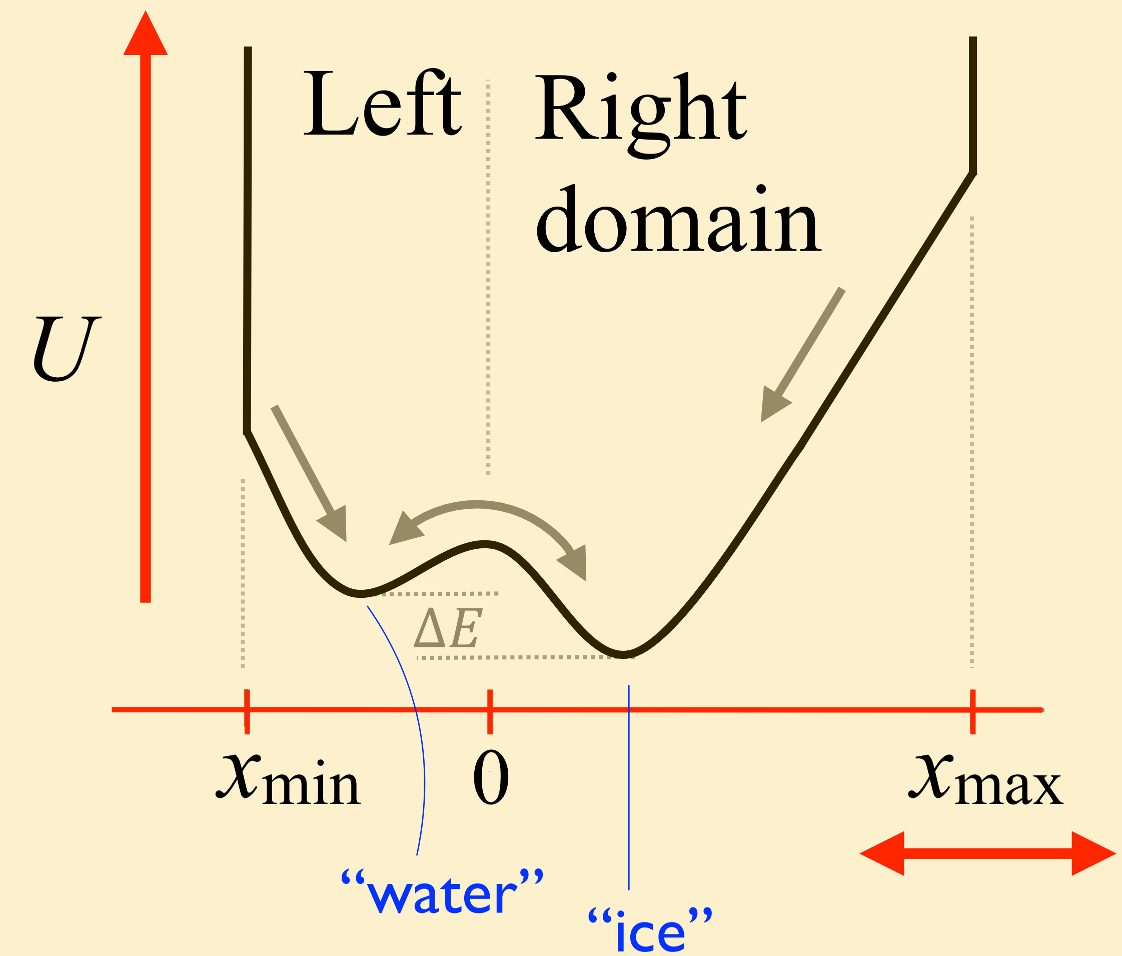


Equilibrium states are well defined.

Phase transition not a part of def.

Mpemba effect

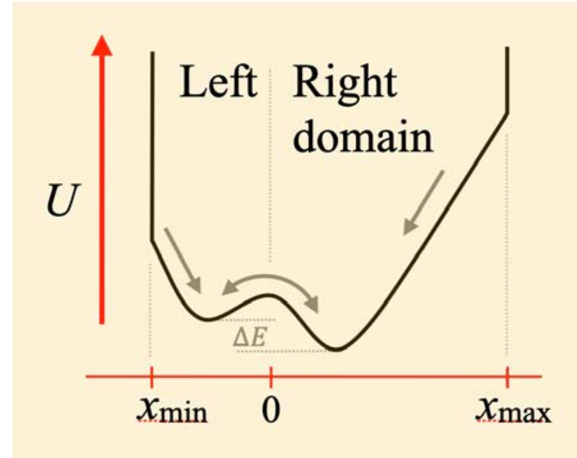
- **Colloidal particle in a potential**
  - in water at bath temperature
- **A tilted double-well potential**
  - metastable & stable macrostates
    "water" "ice"
  - Asymmetric domain
  - Small spatial dimension 200–800 nm
  - Fast equilibration time ≈ 0.1 s
  - 1,000–10,000 trials vs. ~10



"inspired by a true story"

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

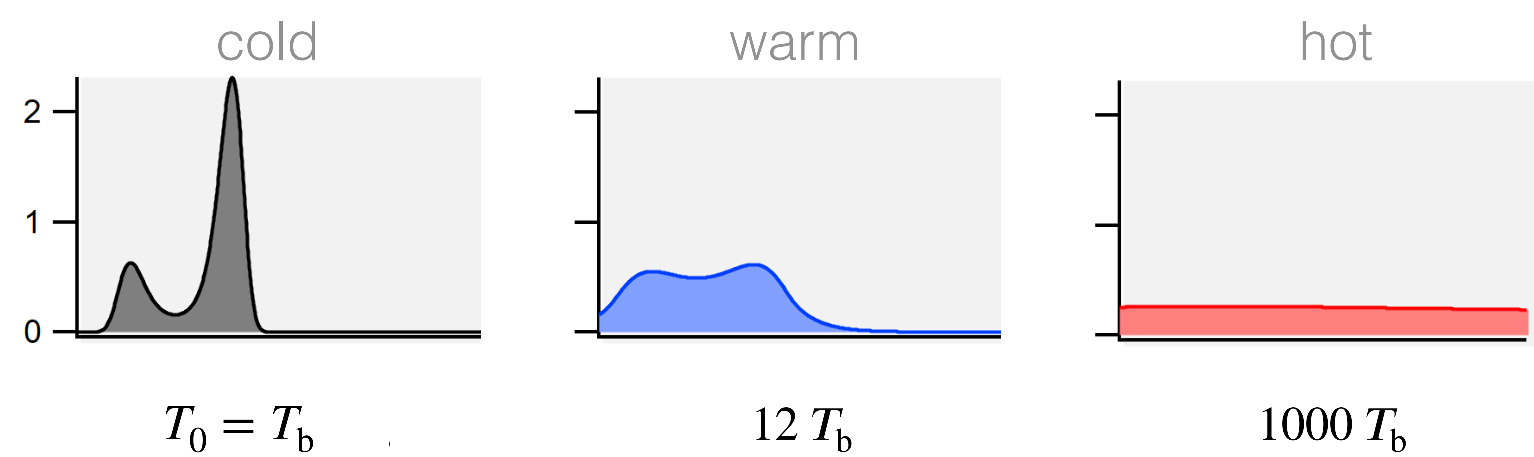
Mpemba effect



Quenching protocol

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

Boltzmann PDF

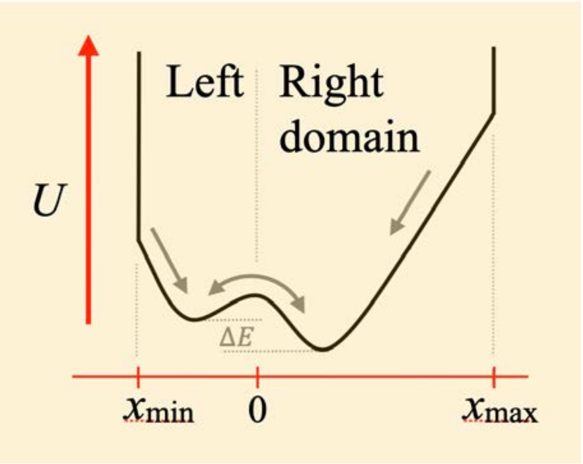


- Instantaneous quench in bath

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



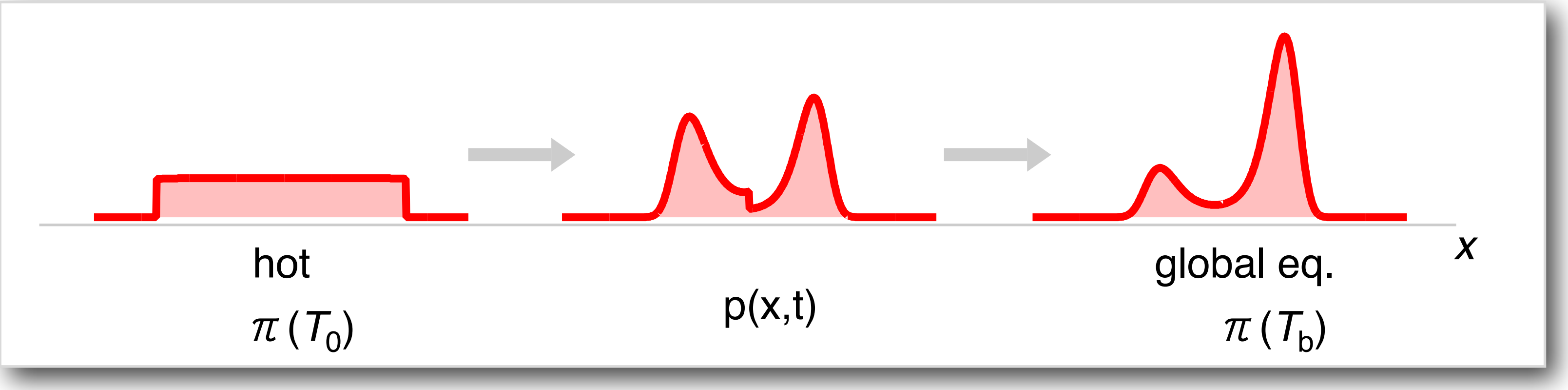
Measurement process

$p(x, t)$ Boltzmann, T_b

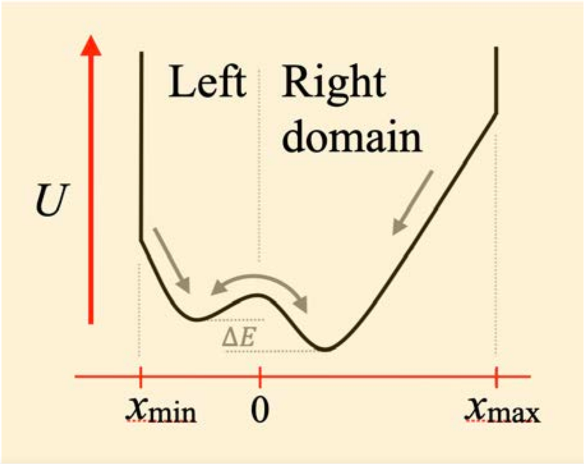
$$\mathscr{D} \approx \sum_{i=1}^{N_b} |p_i - \pi_i|$$

L_1 distance

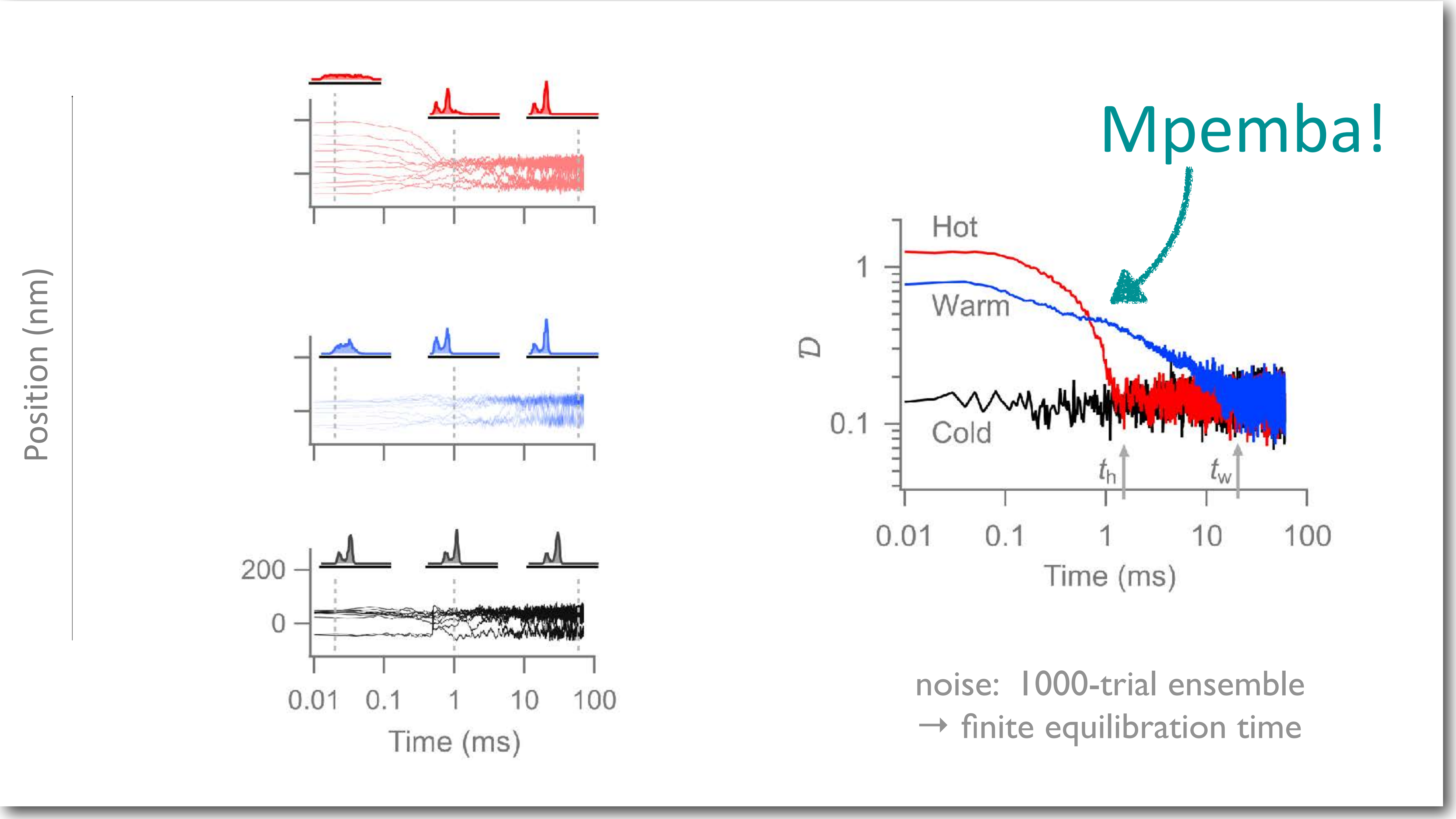
- System temperature well defined at beginning (T_0) and end (T_b)
- At intermediate times, $p(x,t)$ is not a Boltzmann dist. for any effective temperature
- Use metric / divergence between pdf's
  L_1, L_2, Kullback-Leibler, …
- see Mpemba in one, see in all*



Mpemba effect

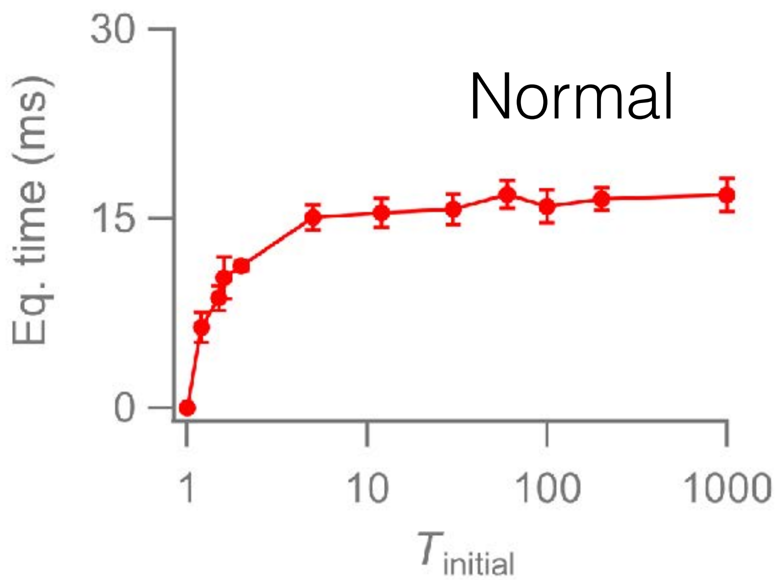


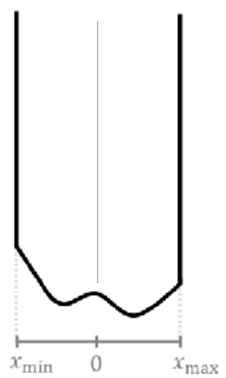
Measurement process



noise: 1000-trial ensemble
→ finite equilibration time

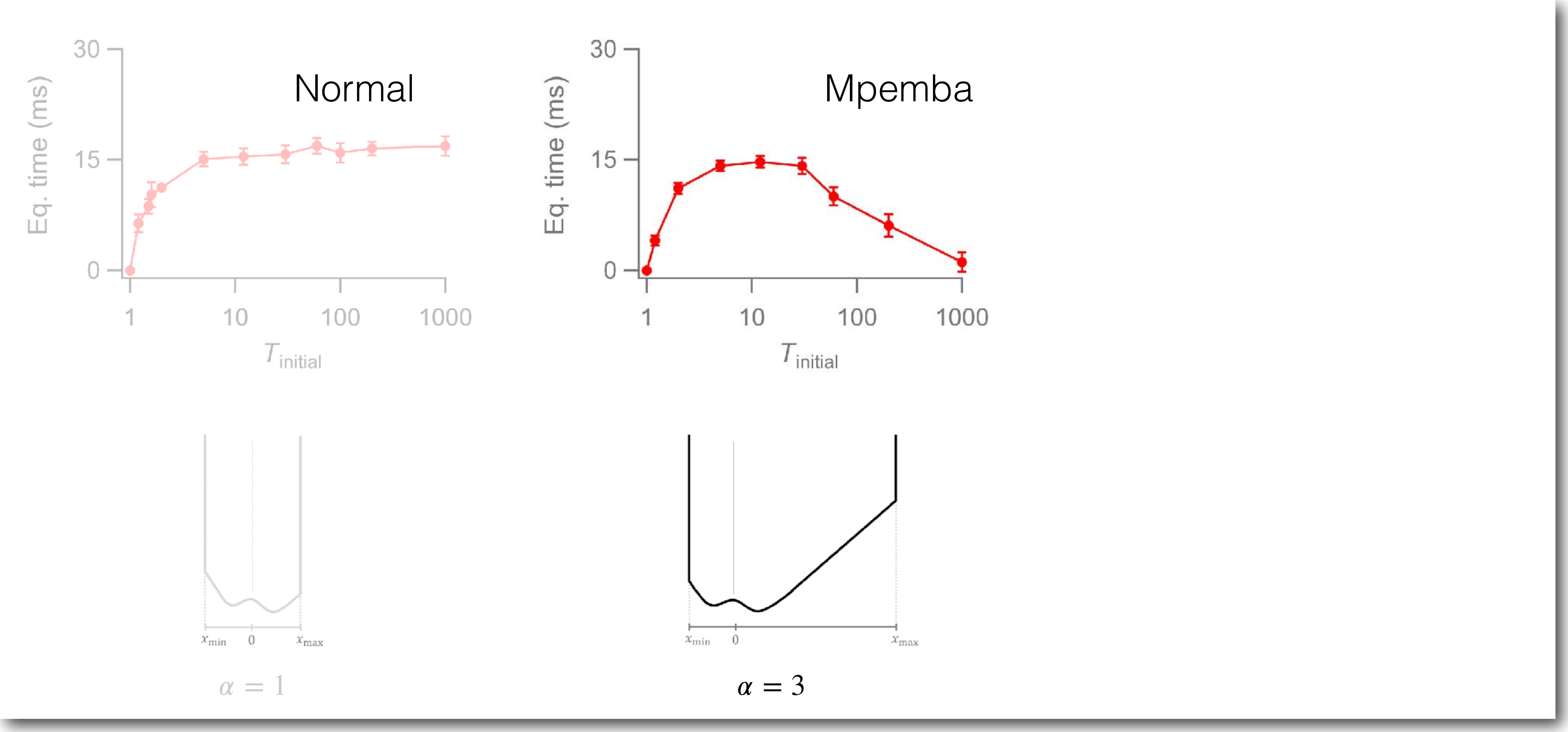
Equilibration time vs. initial temperature



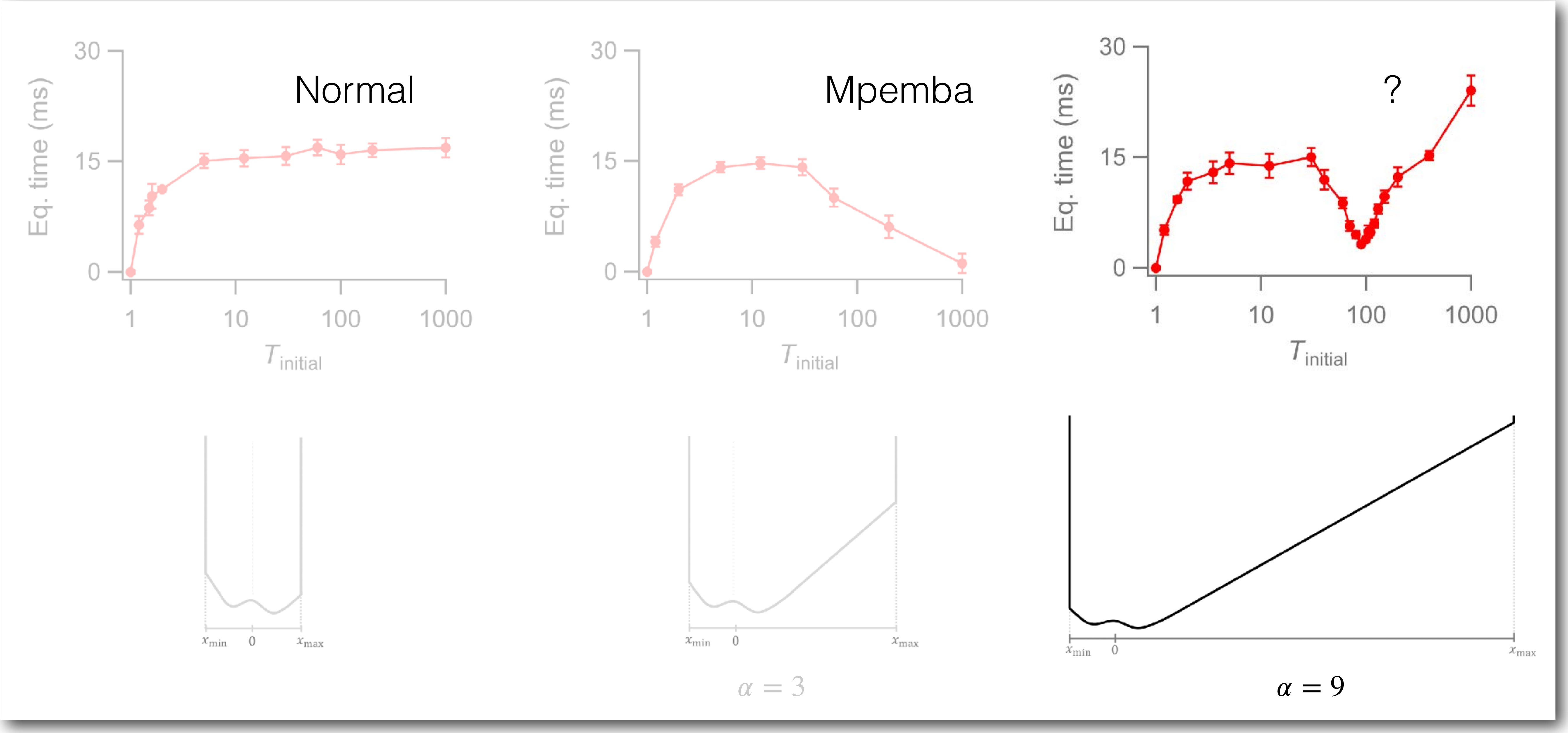


$\alpha = 1$

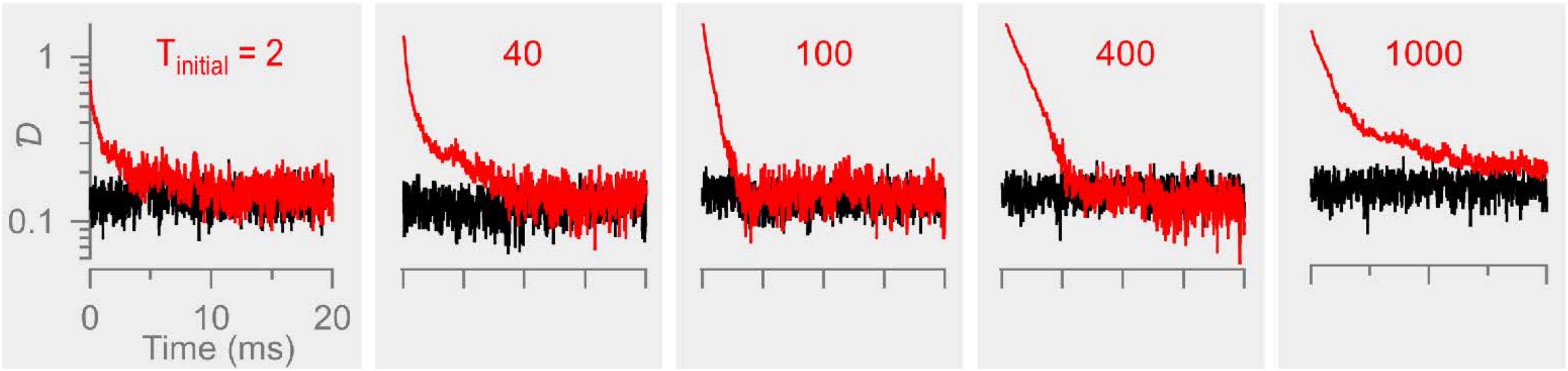
Equilibration time vs. initial temperature



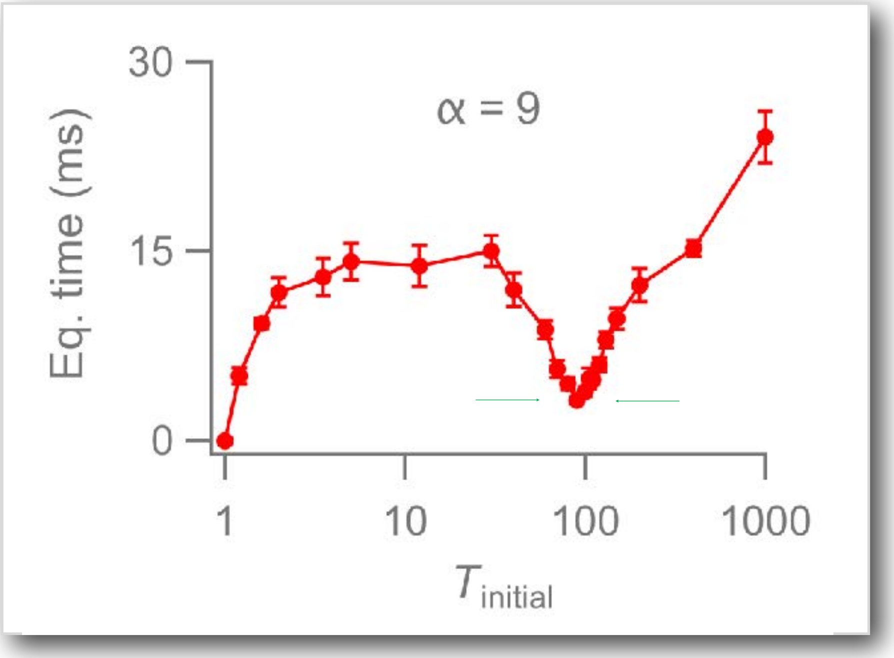
Equilibration time vs. initial temperature



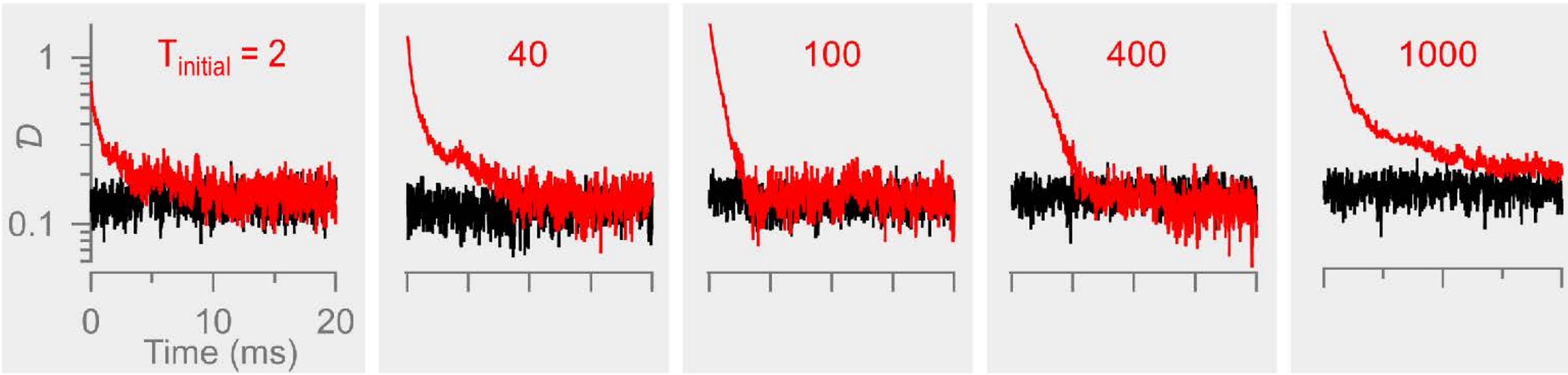
Equilibration time vs. initial temperature



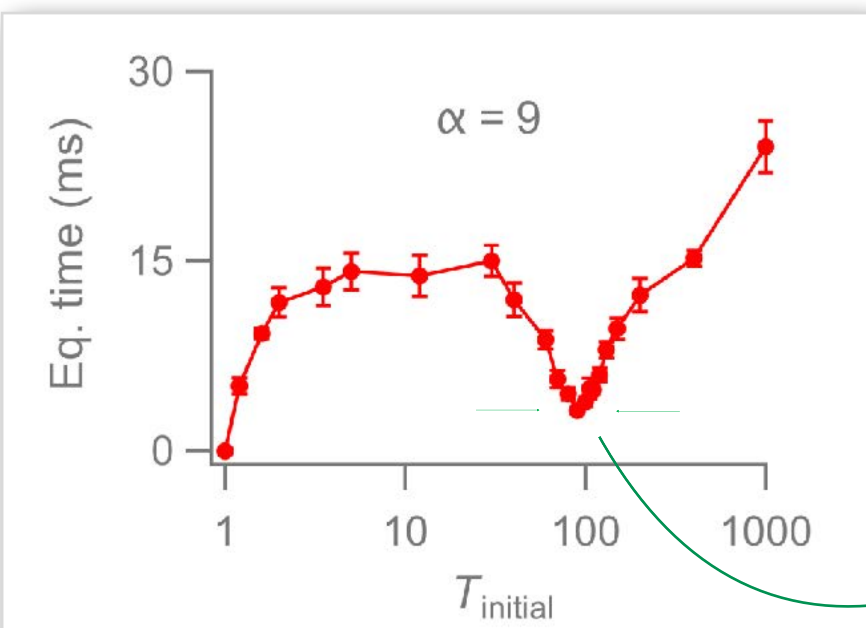
1000 trials



Equilibration time vs. initial temperature



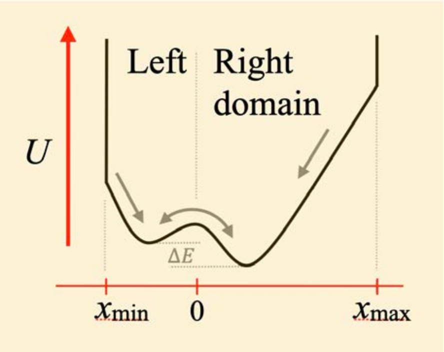
1000 trials



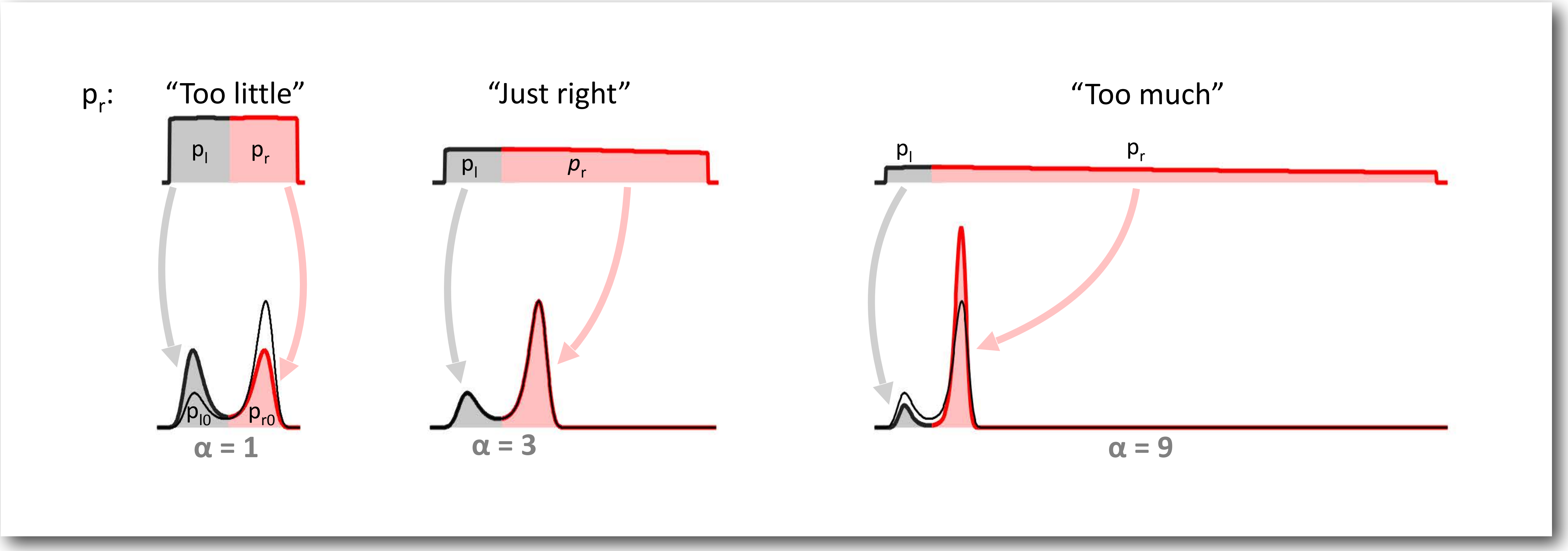
Exponentially
Faster cooling !

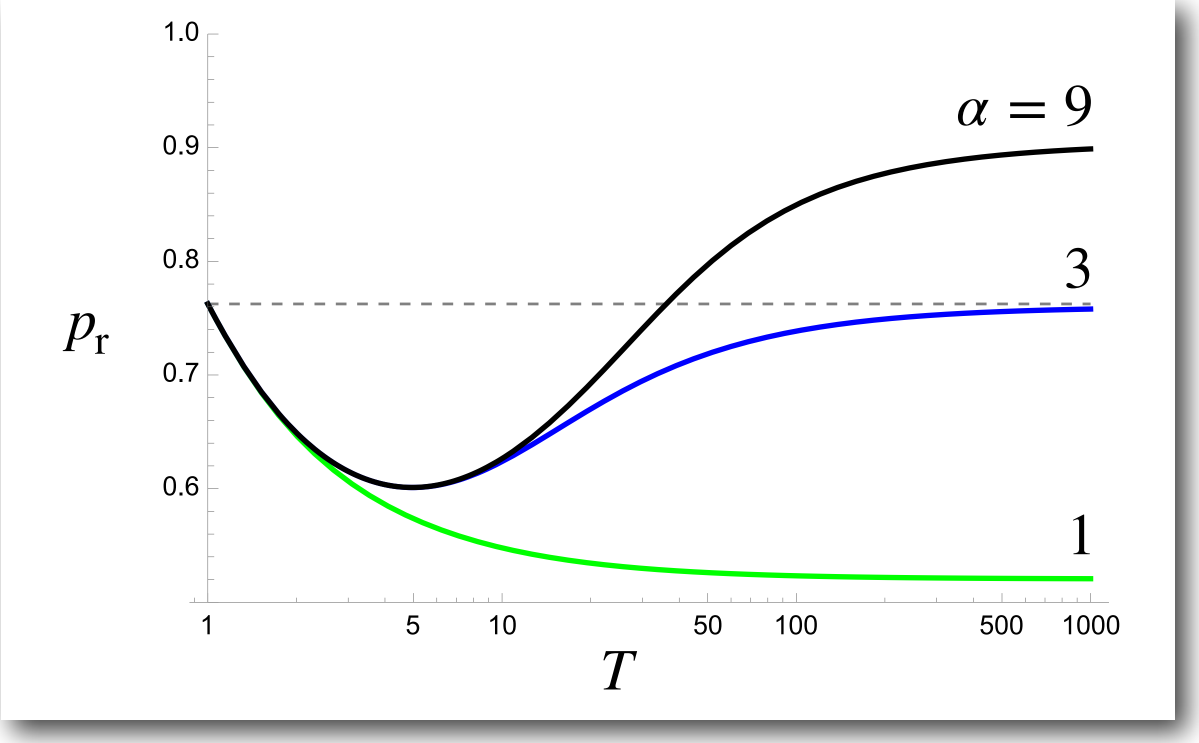
A. Kumar & J. Bechhoefer, *Nature* 2020

Mpemba explanation



1. Intuitive

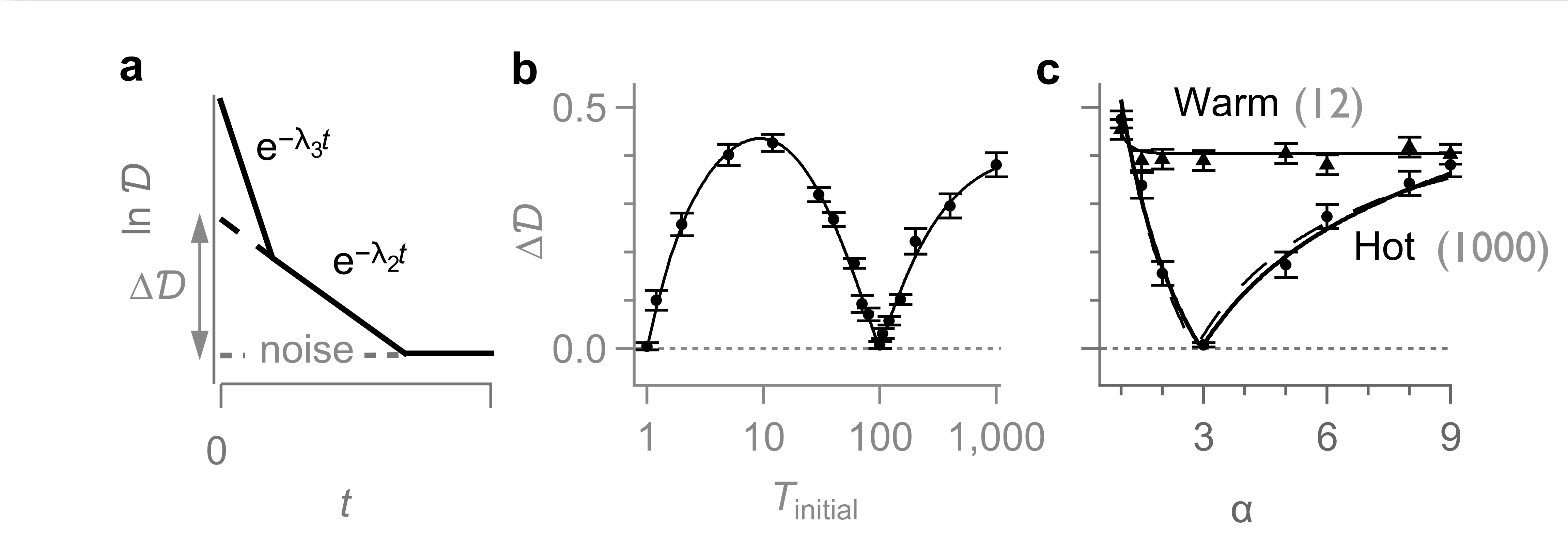




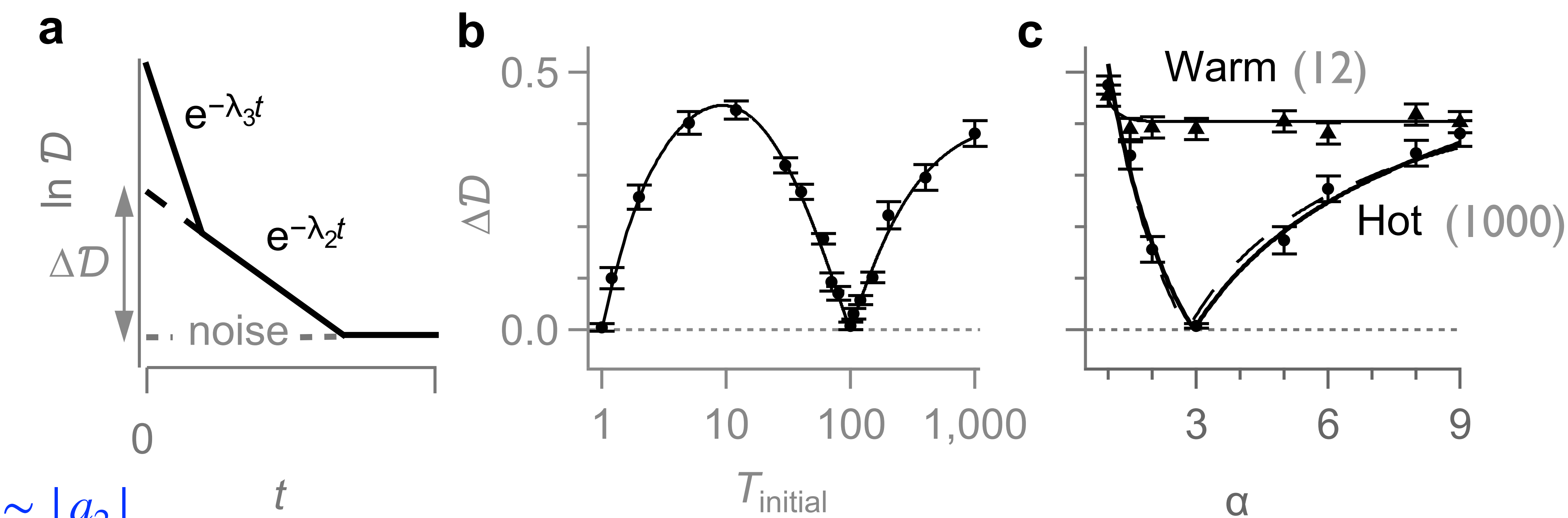
argument can be made rigorous
and generalized to higher order in $\tau_{MFP} / \lambda_2^{-1}$

— Walker & Vucelja, arXiv 2212.07496

Mpemba explanation



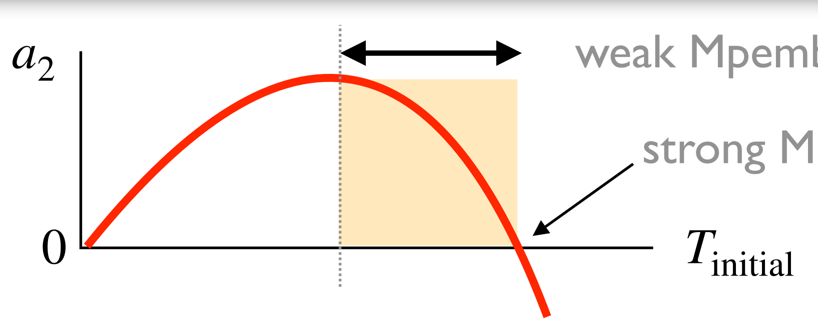
Mpemba explanation



$\Delta D \sim |a_2|$

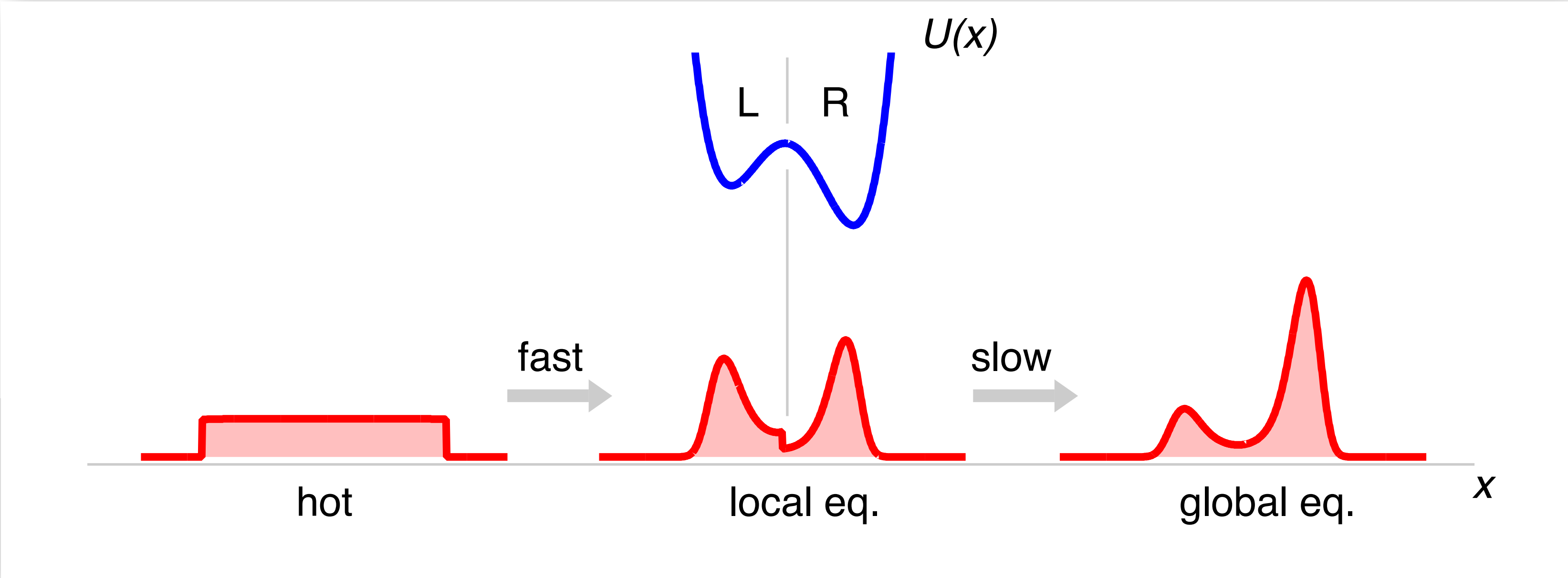
Fokker-Planck ⇒ $p(x,t) = \pi(x; T_b) + \sum_{m=2}^{\infty} a_m(\alpha, T_0)\, e^{-\lambda_m t}\, v_m(x; \alpha, T_b)$

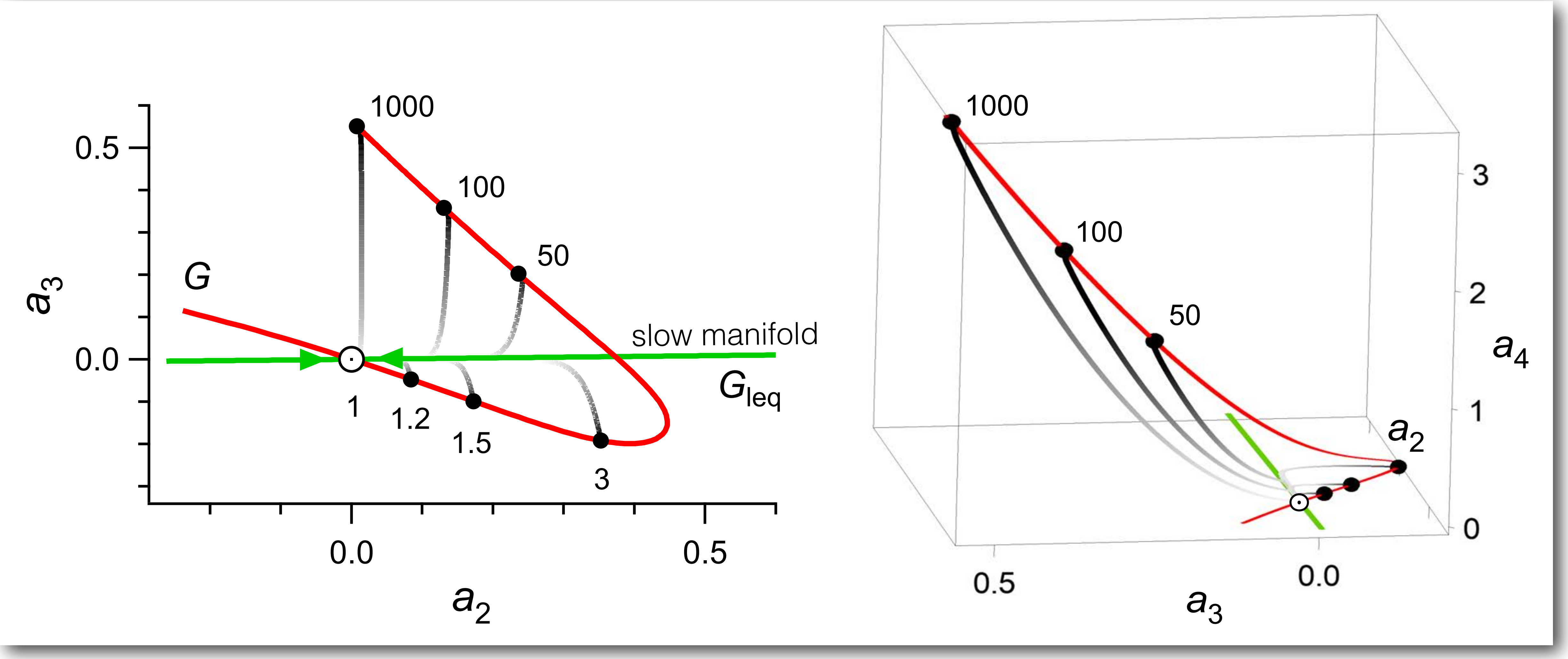
$$\approx \pi(x; T_b) + a_2(\alpha, T_0)\, e^{-\lambda_2 t}\, v_2(x; \alpha, T_b)$$



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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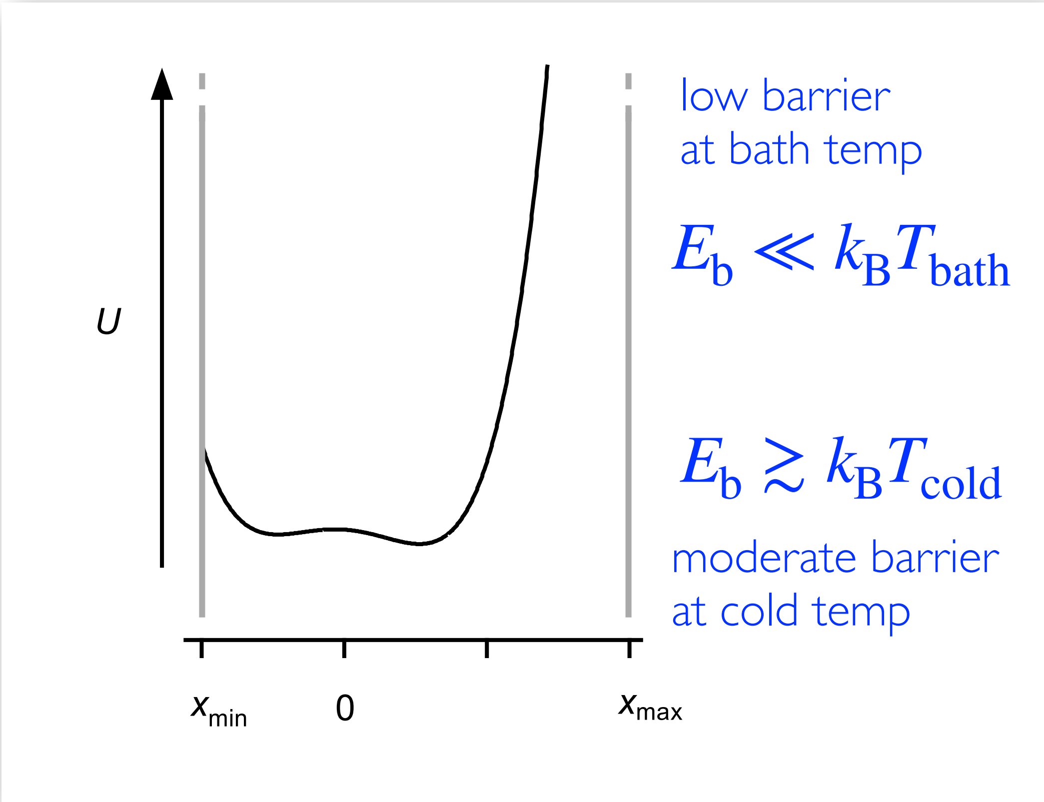
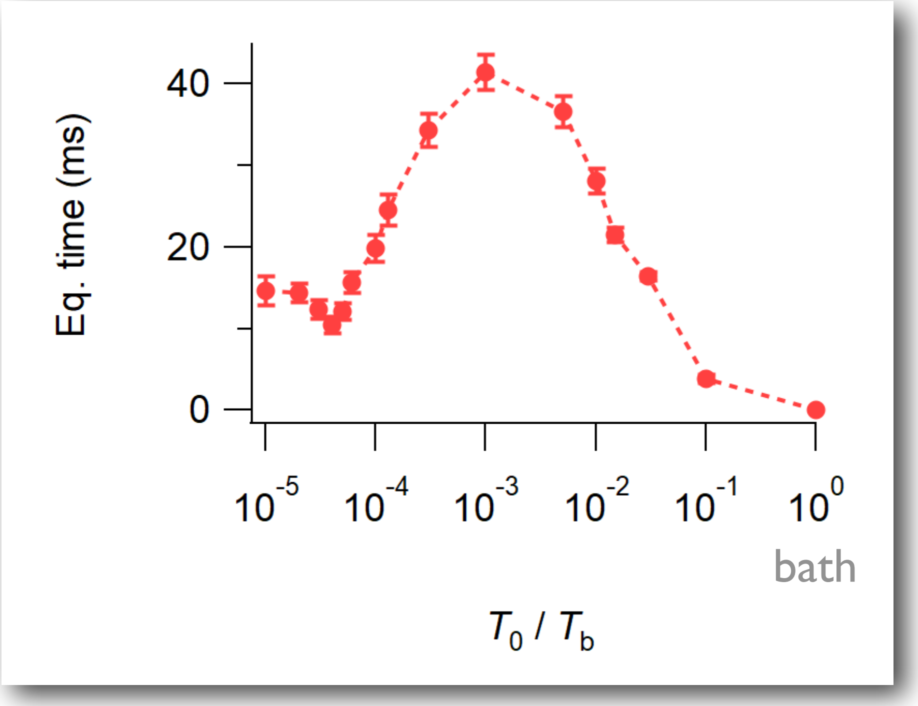
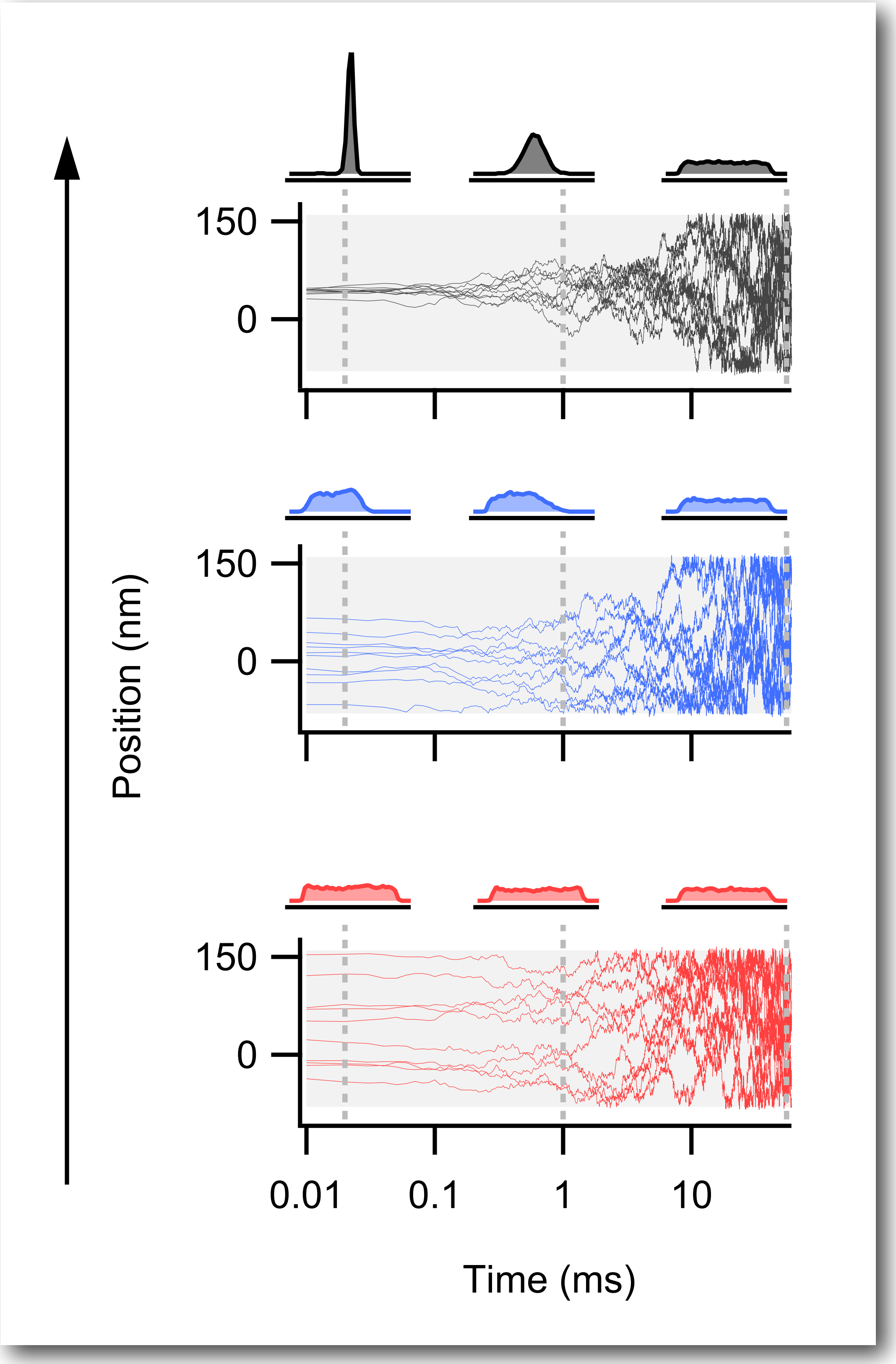
Inverse Mpemba effect

First observation in any system!







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

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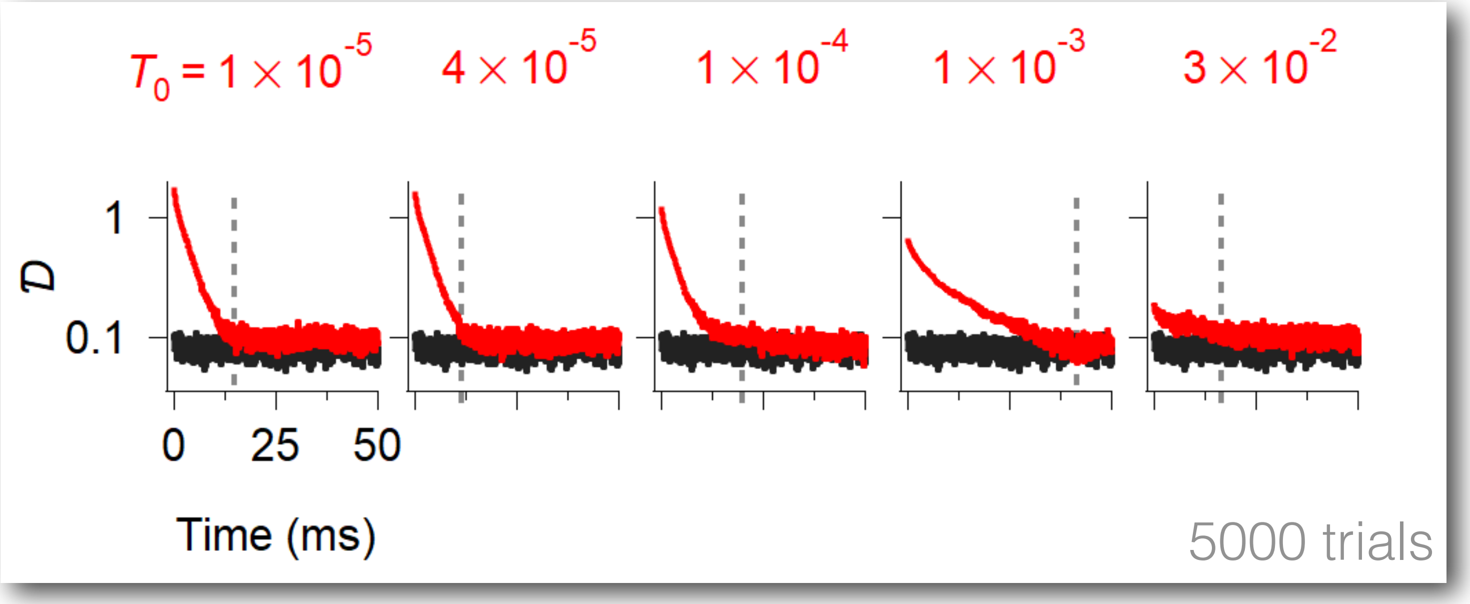
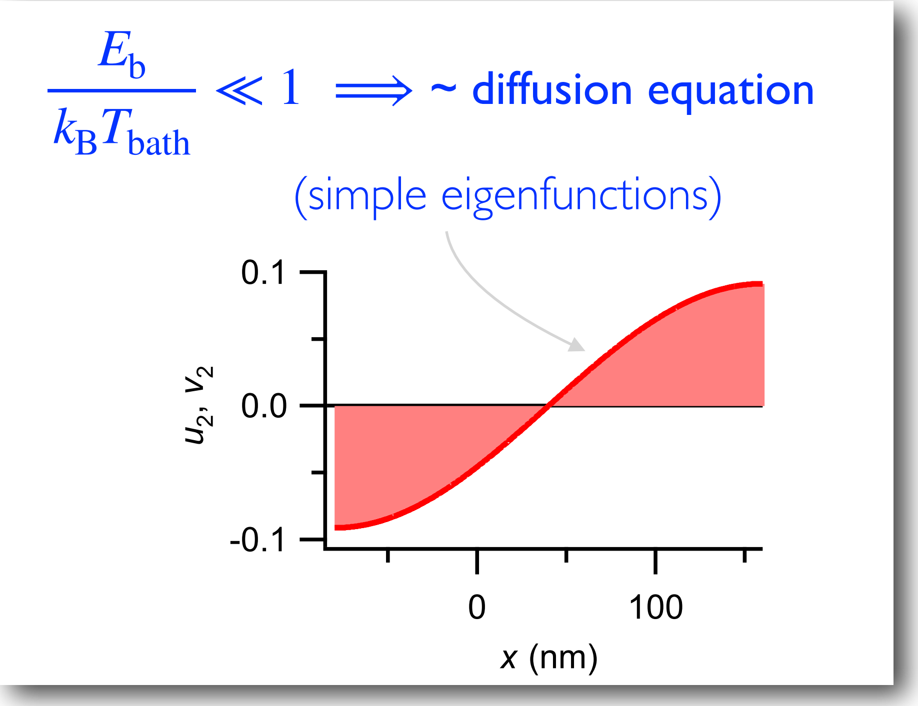
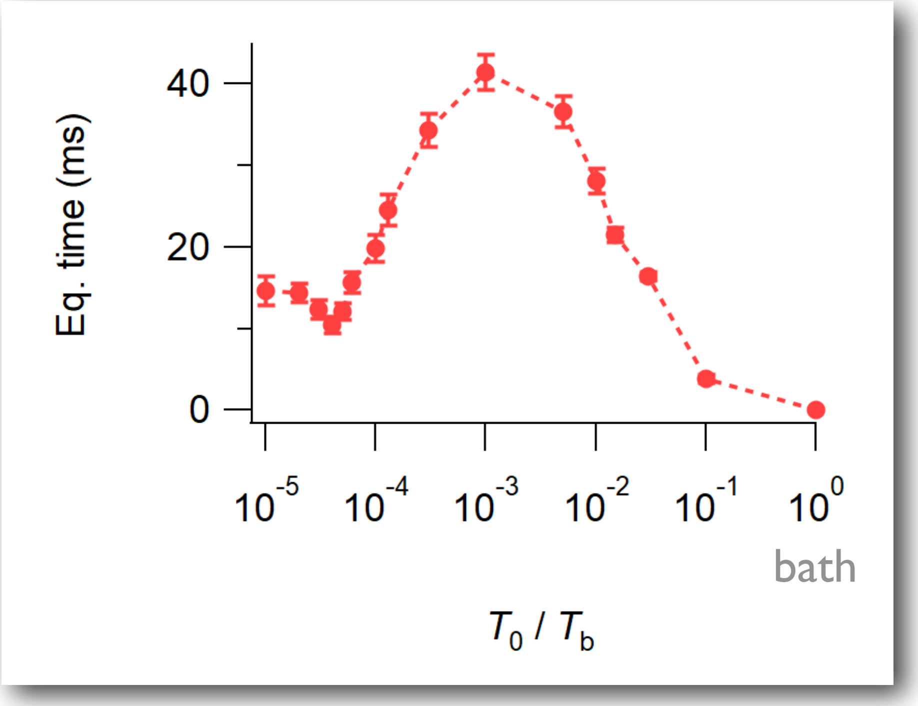
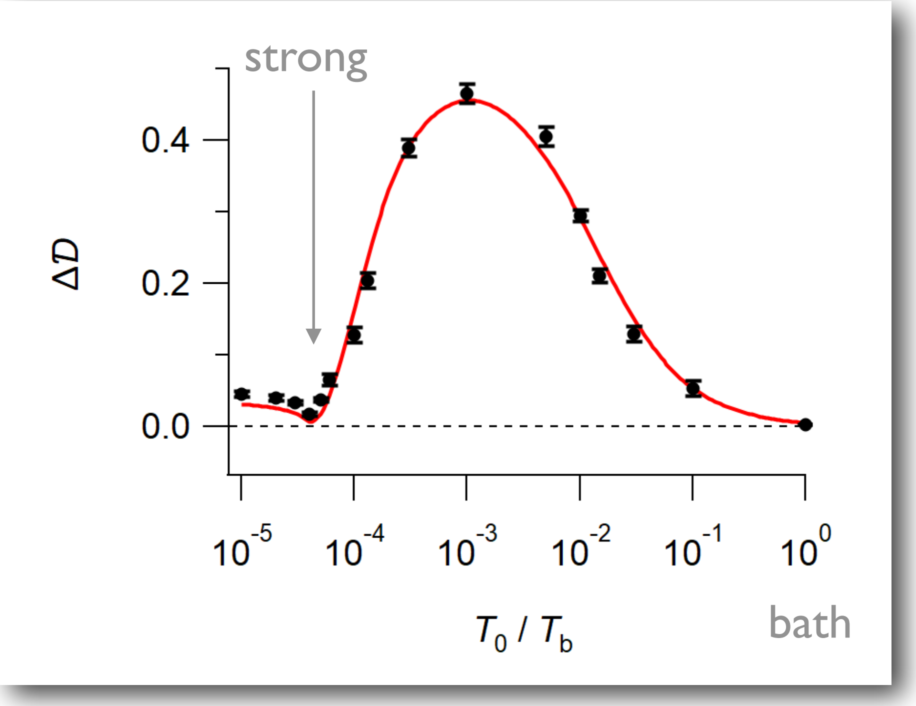








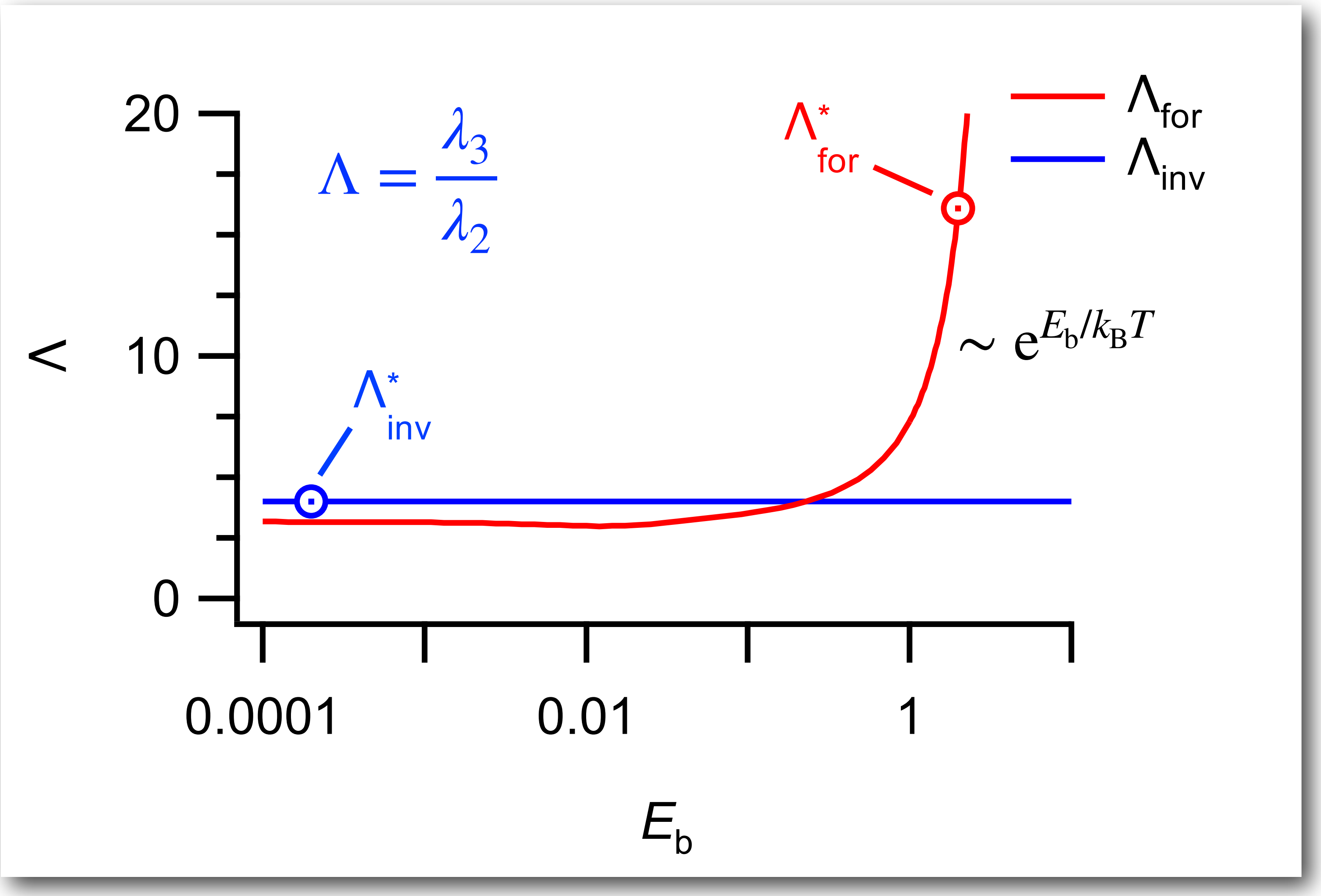
A. Kumar, R. Chétrite, JB, *PNAS* 2022

Inverse Mpemba effect

First observation in any system!

Forward Mpemba is easier to observe

barriers → bigger spectral gap

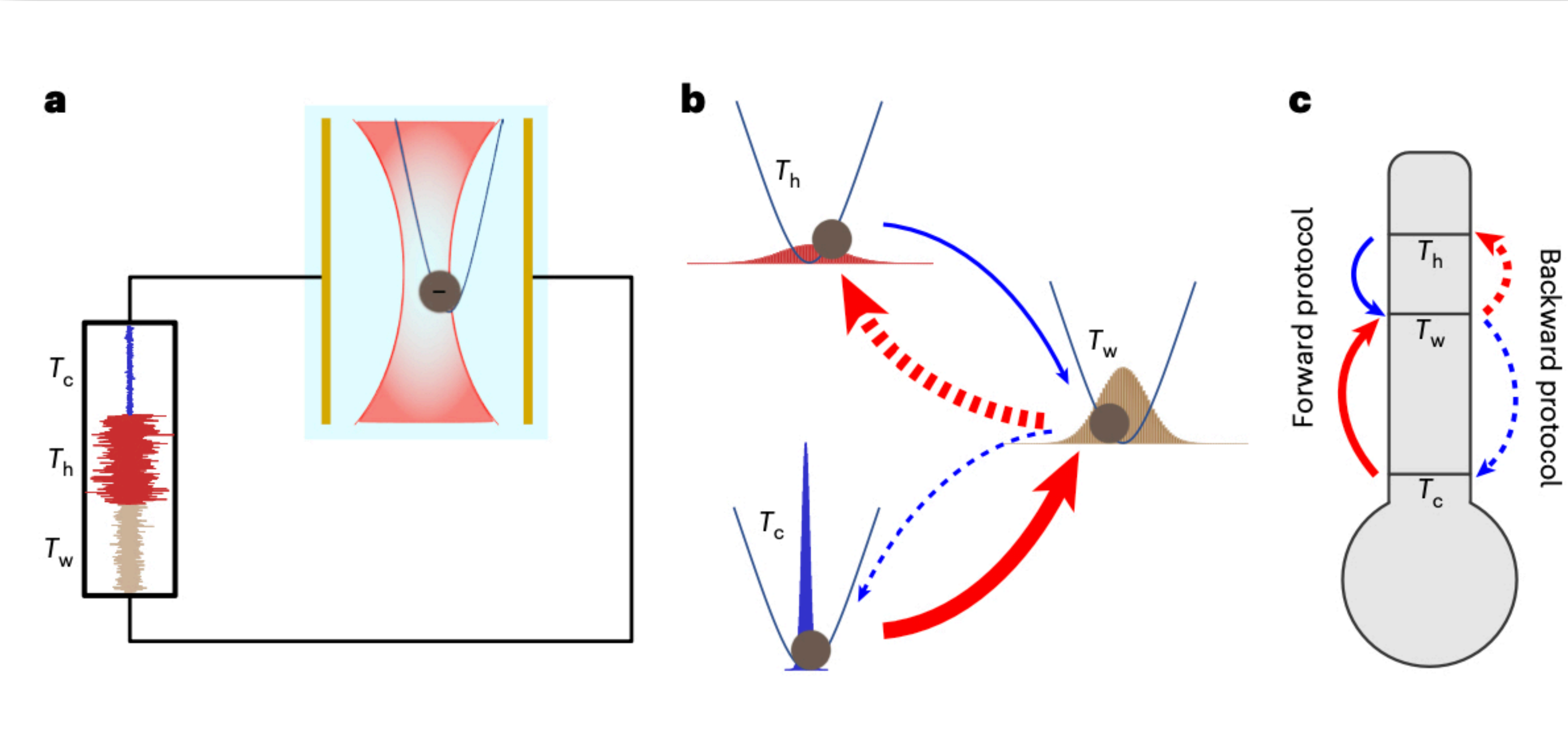


Forward: 1000 trials
"driven by energy"

Reverse: 5000 trials
"driven by entropy"

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

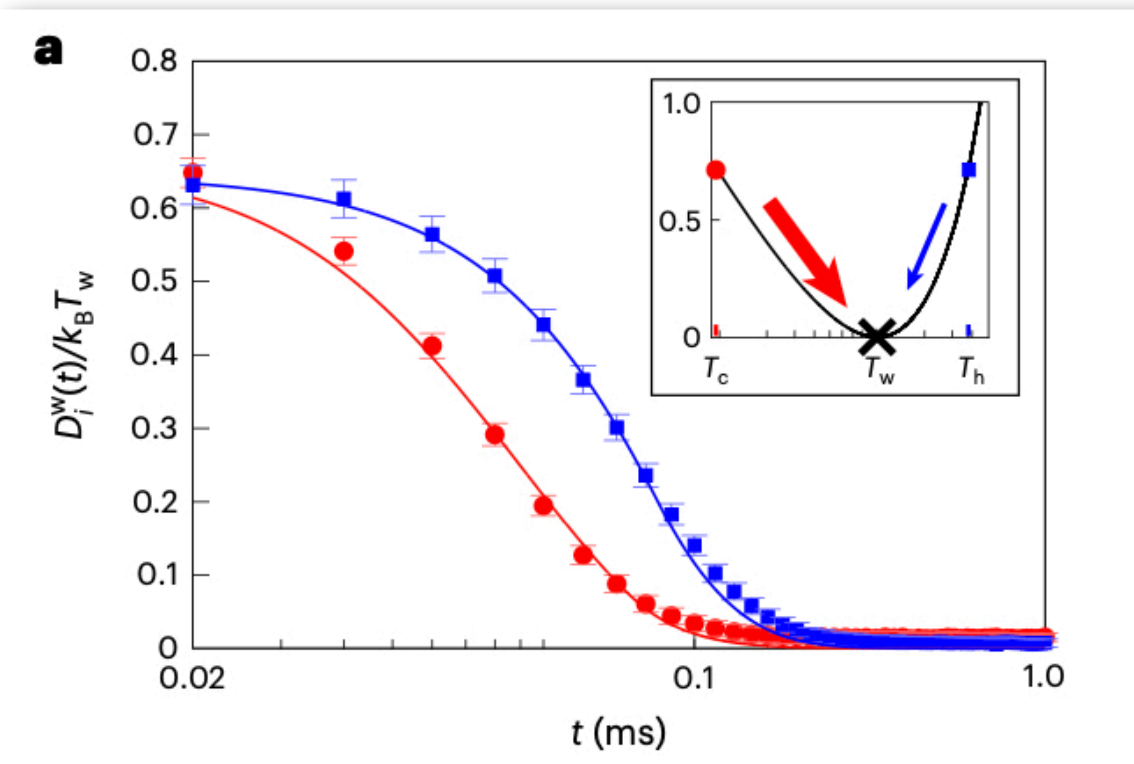
Contrast with Asymmetric Heat / Cool

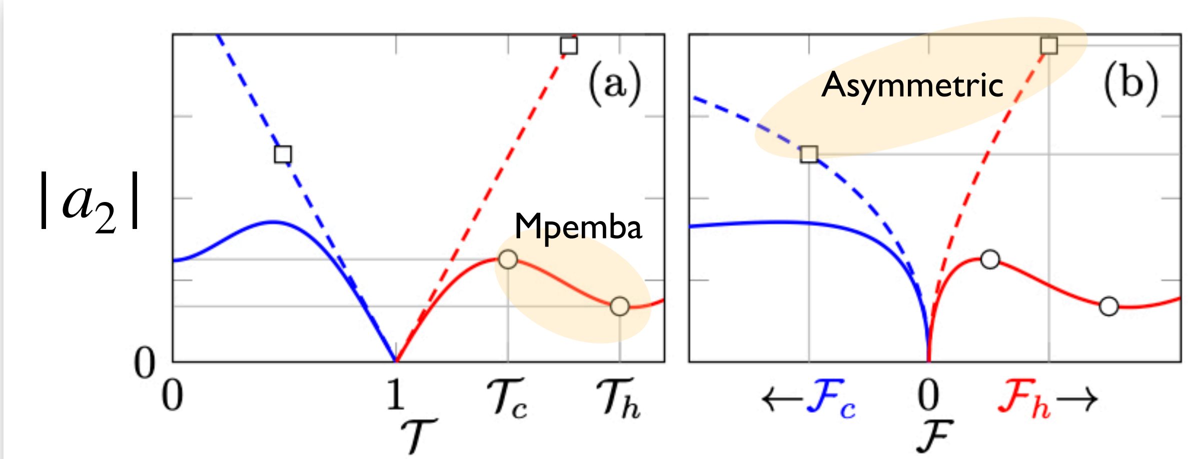


For "equidistant" quenches (in noneq. free energy)

heating is faster than cooling

(for ~harmonic potentials)





J. Meibohm, D. Forestiere, T. Adeleke-Larodo, K. Proesmans, *PRE* 2021

M. Ibáñez, C. Dieball, A. Lasanta, A. Godec, R. M. Rica, *Nat. Physics* 2024

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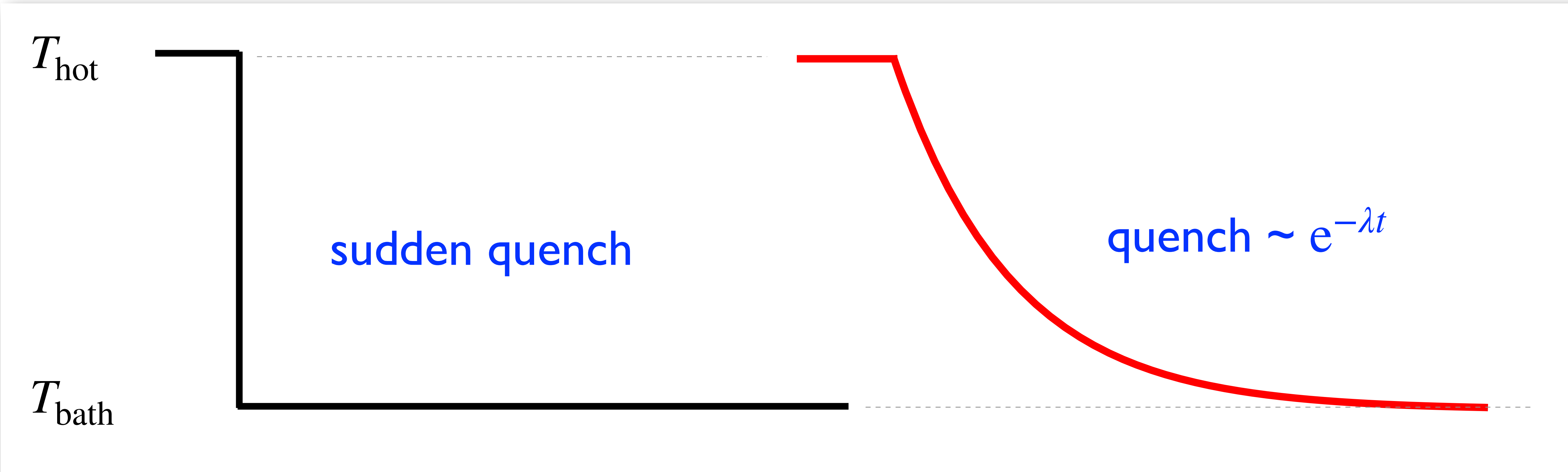
Finite-rate quenches



can find Mpemba effect

no Mpemba for quasistatic

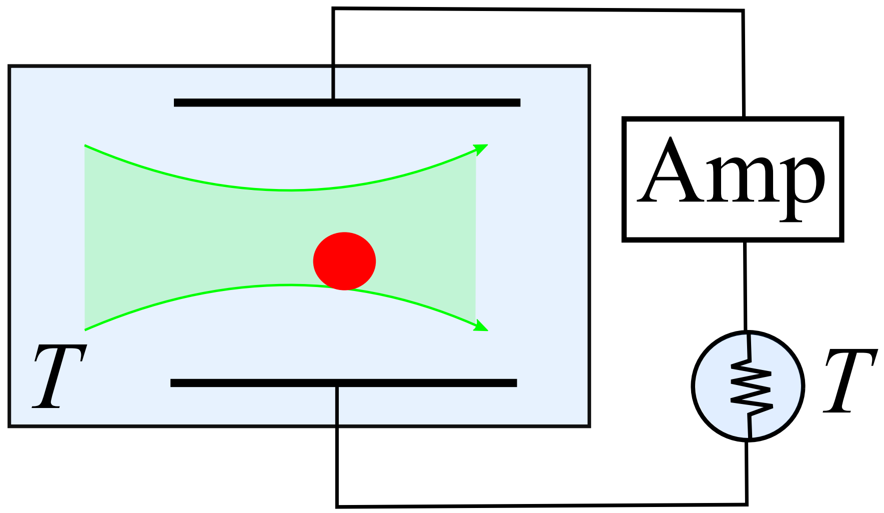
($\lambda \ll \lambda_2$)

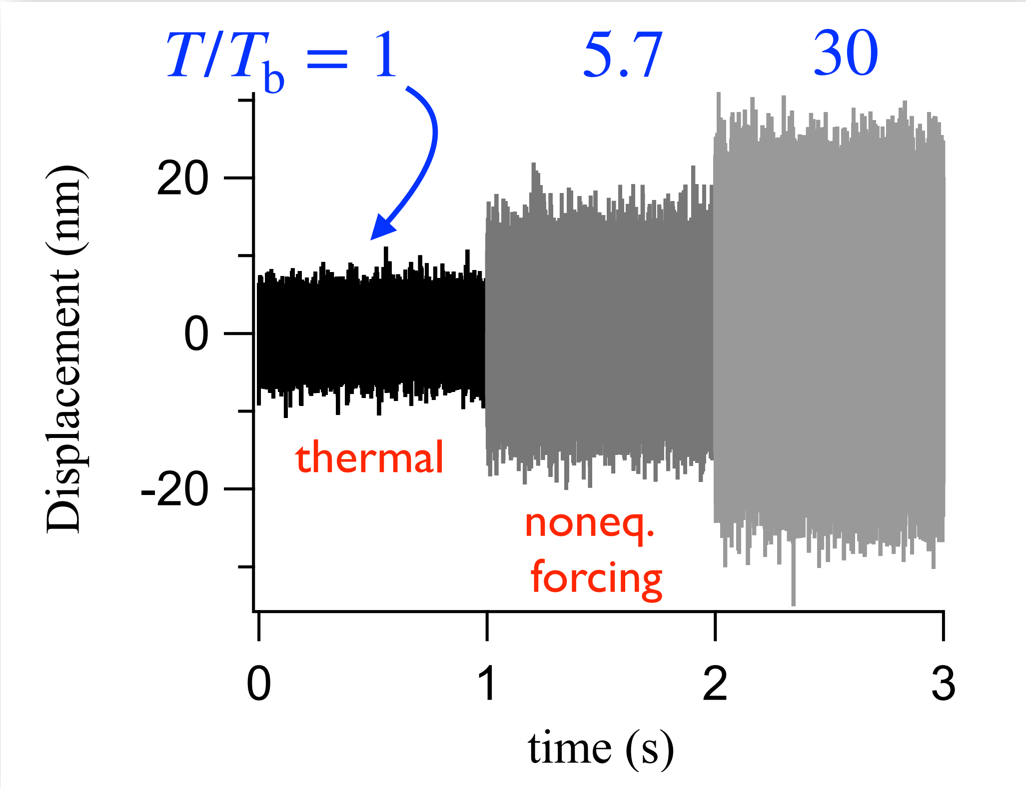
critical value of λ for the transition?

$$\lambda^* \approx \lambda_3 ?$$

Finite-rate quenches

harmonic potential



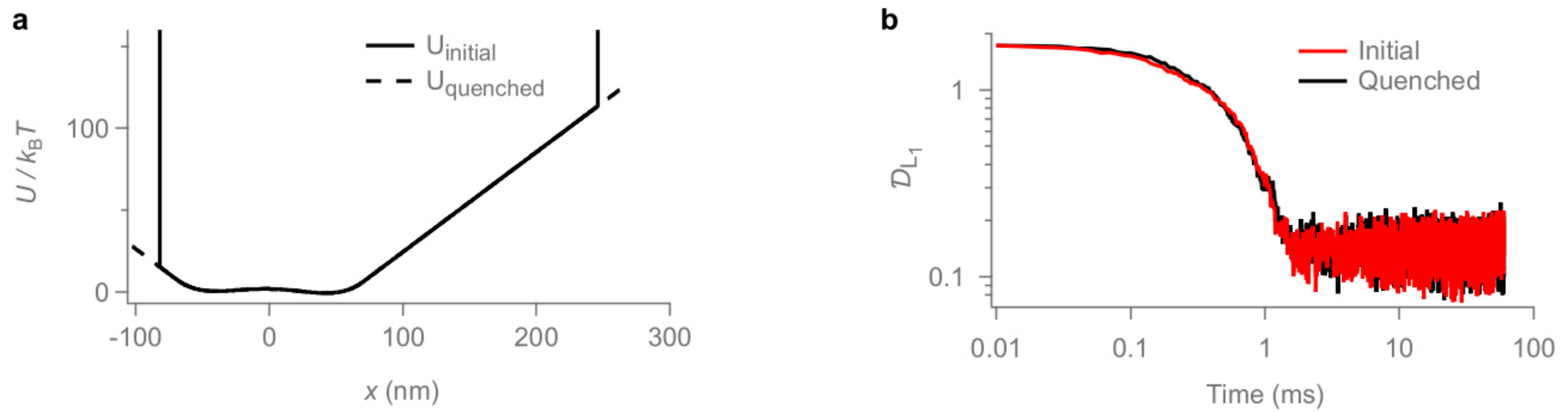


- add fluctuating electrical forces
- applied noise white, up to bandwidth $\gg$ trap cutoff frequency
- adjust gain → time-dependent protocols $T(t)$
- easier alternative: add forces by shaking laser beam (lower T_{eff})

- I.Martinez, E. Roldan, JMR Parrondo, DM Petrov, *PRE* 2013
- T Saha, J Ehrich, M Gavrilov, S Still, DA Sivak, JB, *PRL* 2023
- M Ibanez, C Dieball, A Lasanta, A Godec, RM Rica, Nat. Phys. 2024

Finite-rate quenches

Just one problem…



Extended Data Fig. 5 | Finite maximum slope of the potential does not affect particle dynamics substantially. a, The energy landscape for the Mpemba effect. Solid line depicts the initial energy landscape with infinite potential walls at the domain boundaries. The equilibrium distribution of the particle is calculated based on this potential (U_{initial}). Dashed line shows the potential (U_{quenched}) in which the particle is quenched. **b**, Langevin simulations of the Mpemba effect using both potentials show no notable differences between the two cases.

A. Kumar and JB, *Nature* 2020

towards the back of the supplementary material….

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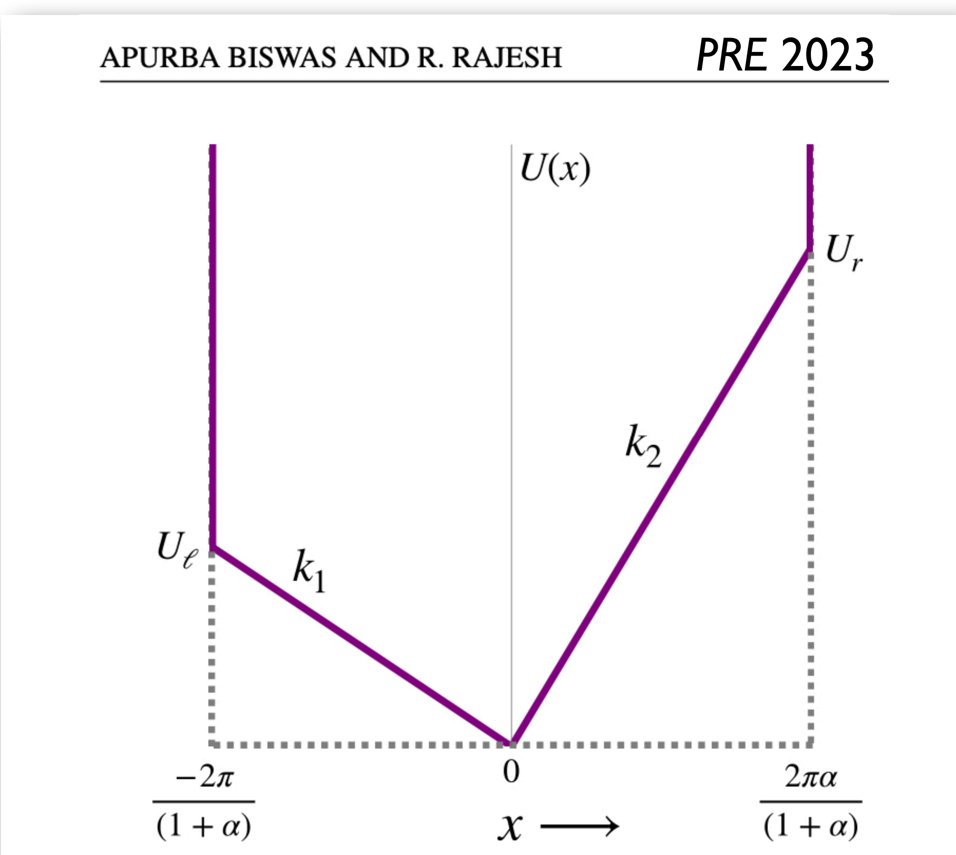
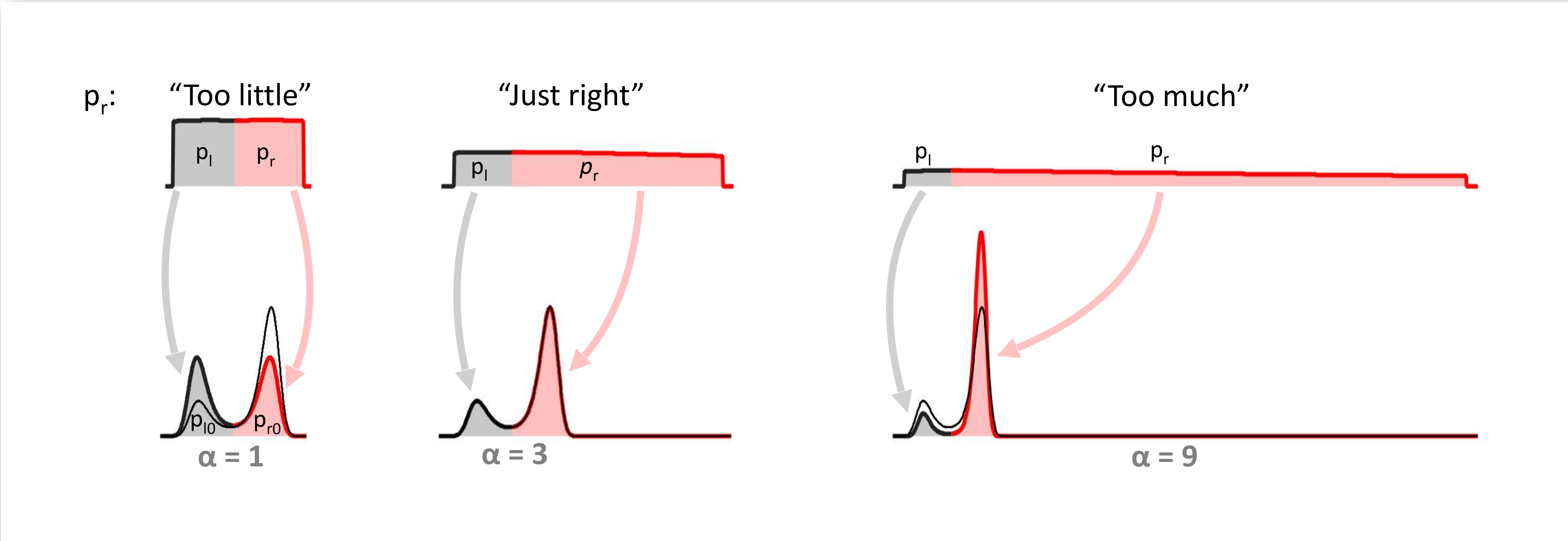


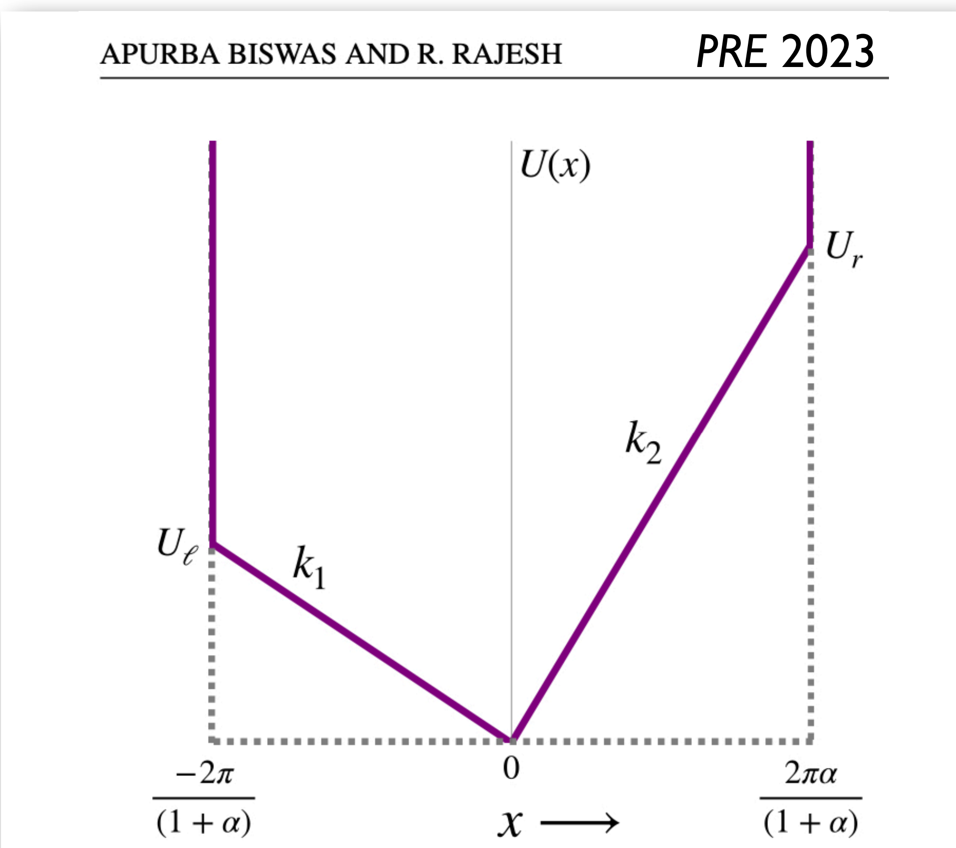
not just us — a lot of studies use

(and <u>need</u>) the infinite potential "box"

- convenient to keep domain small (and fixed) at high temp.
- plays an underappreciated role in Mpemba mechanism

Finite-rate quenches





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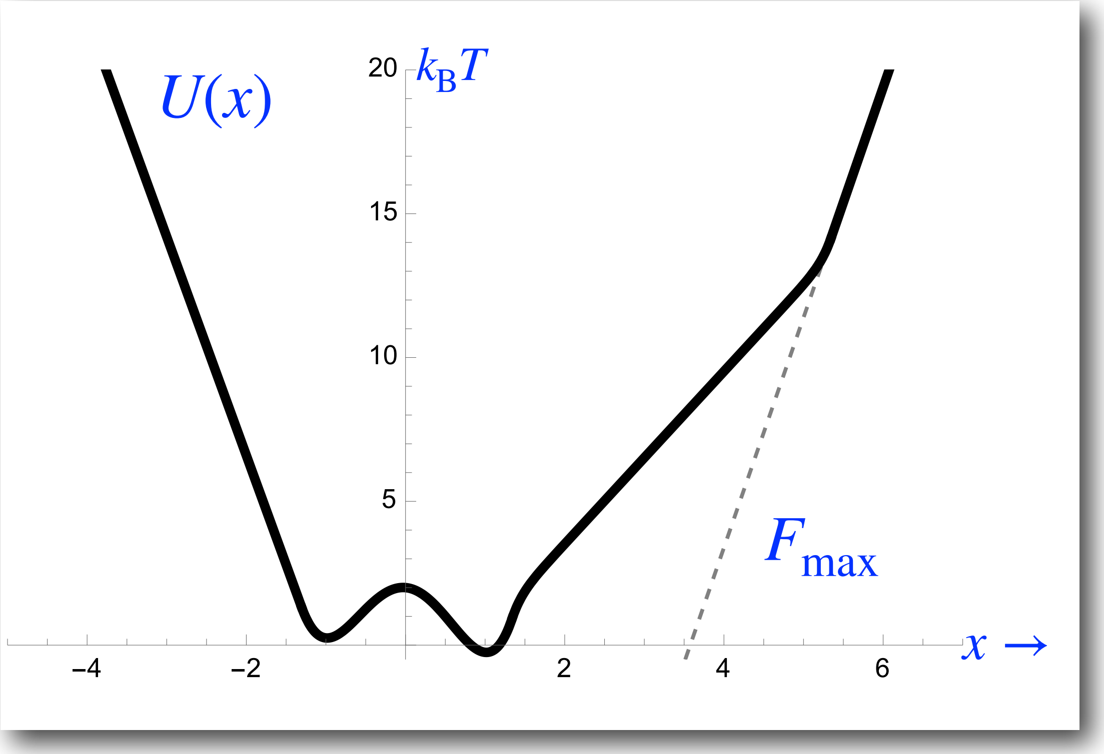
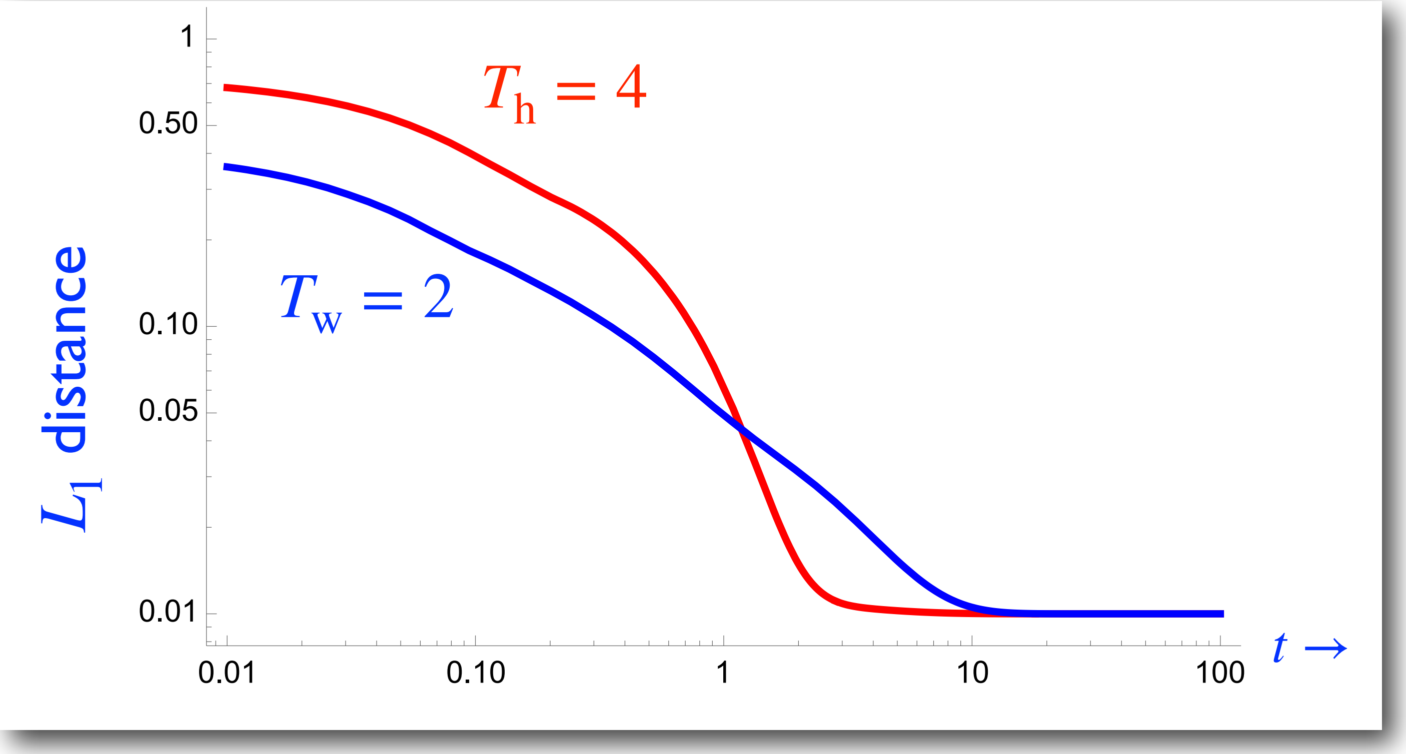
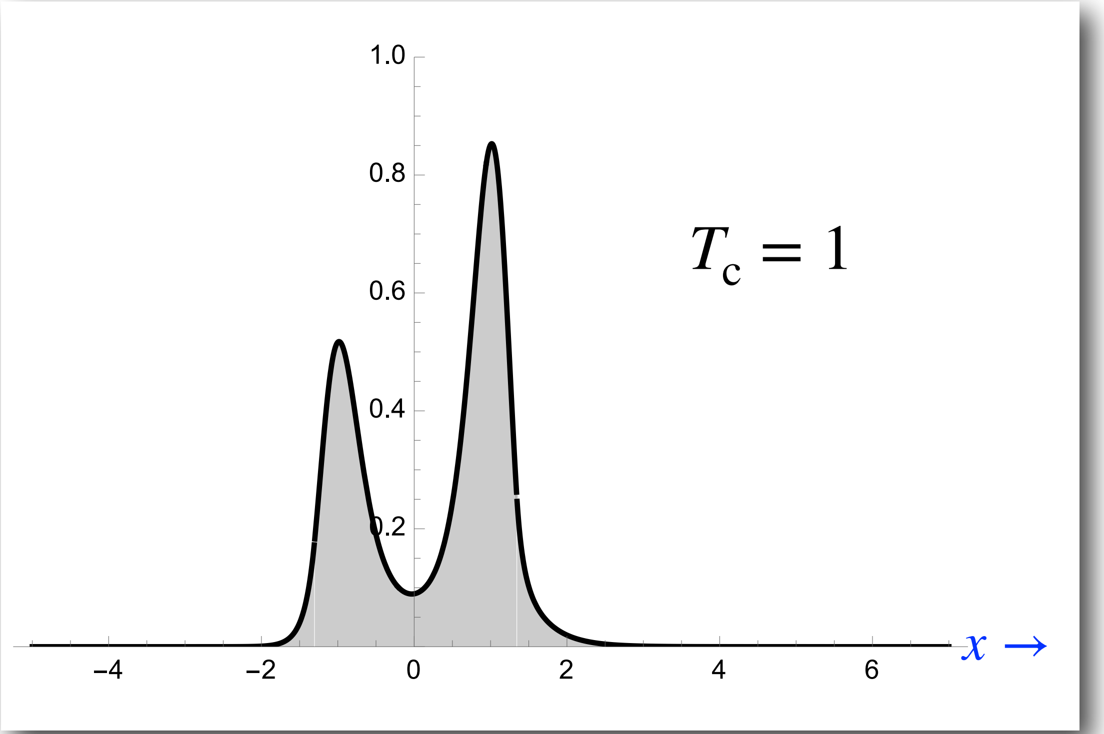
  $\longrightarrow$ enforces $p_\mathrm{r}(T_\mathrm{h}) = p_\mathrm{r}(T_\mathrm{b})$

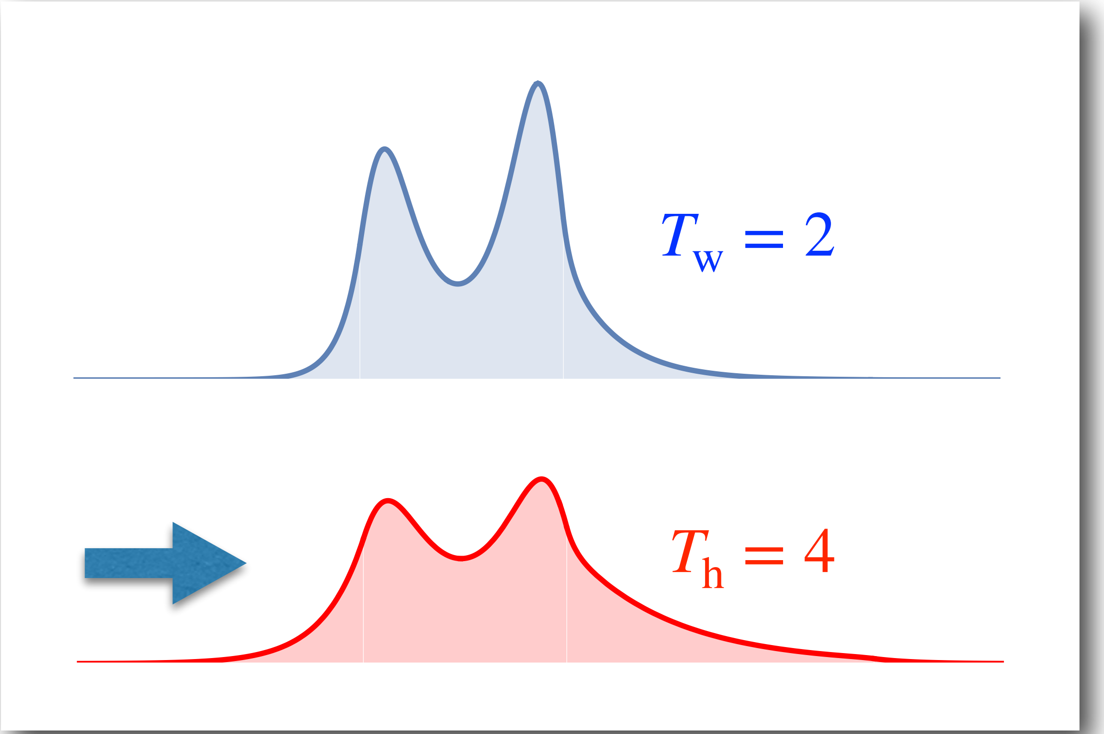
Finite-rate quenches

Can we find a potential showing Mpemba effect without a box?





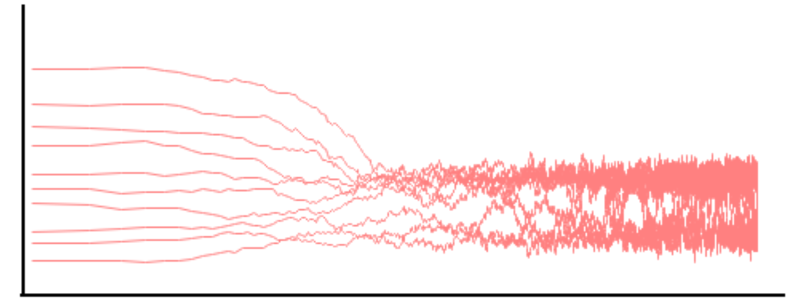




Yes, but it was hard, and we still need to find parameters that can be realized experimentally.

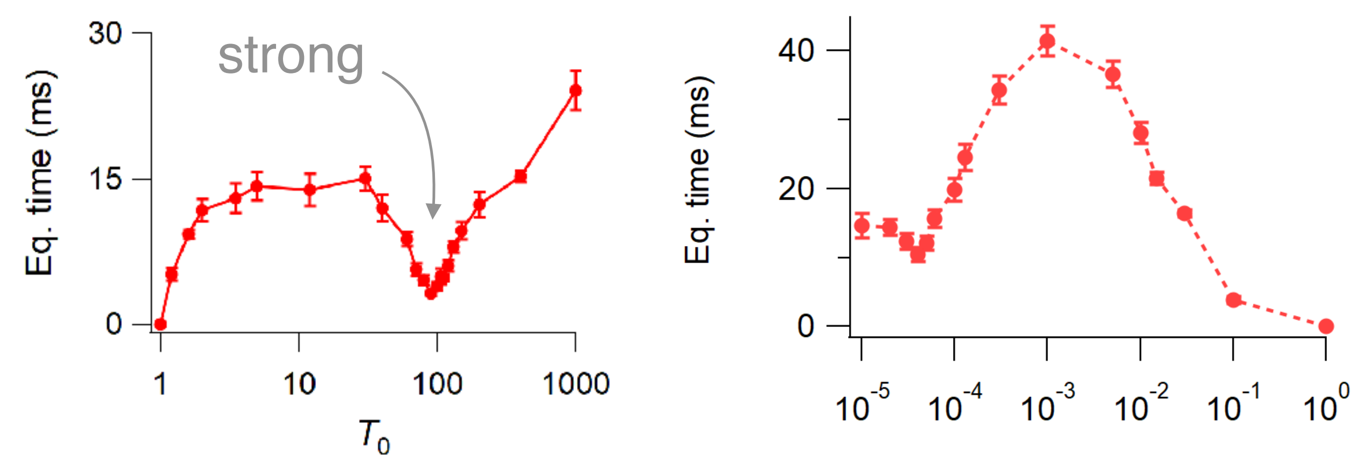
Summary

- **Mpemba:** prototype of anomalous relaxation effects for strong quenches



- **Quenching:** a strongly nonequilibrium process

- **Regular / Inverse Mpemba:** cooling / heating

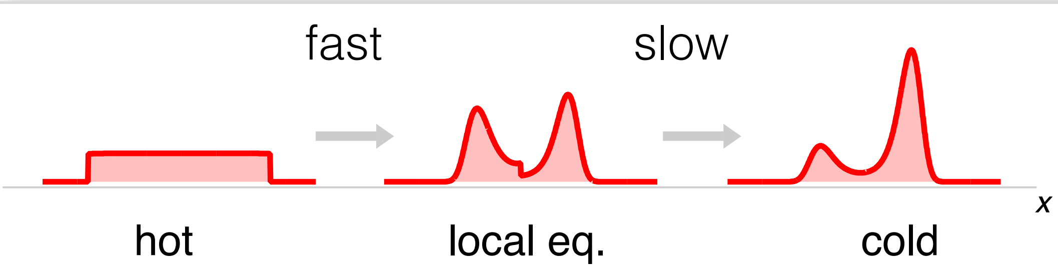


regular Mpemba
energy

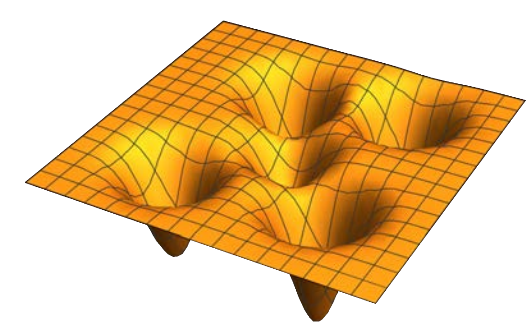
inverse Mpemba
entropy

1) Is the effect real? ✓

2) Would an explanation be ~~trivial~~ or <u>illuminating</u> ✓ ?



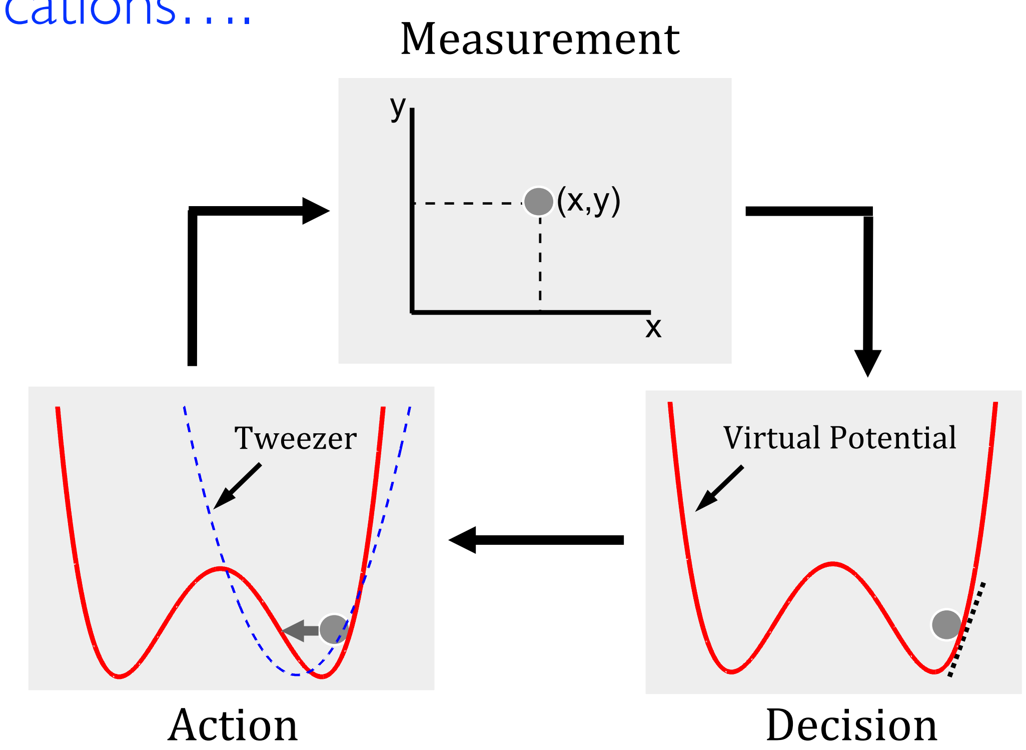
- **Strong effects:** exponential speedup

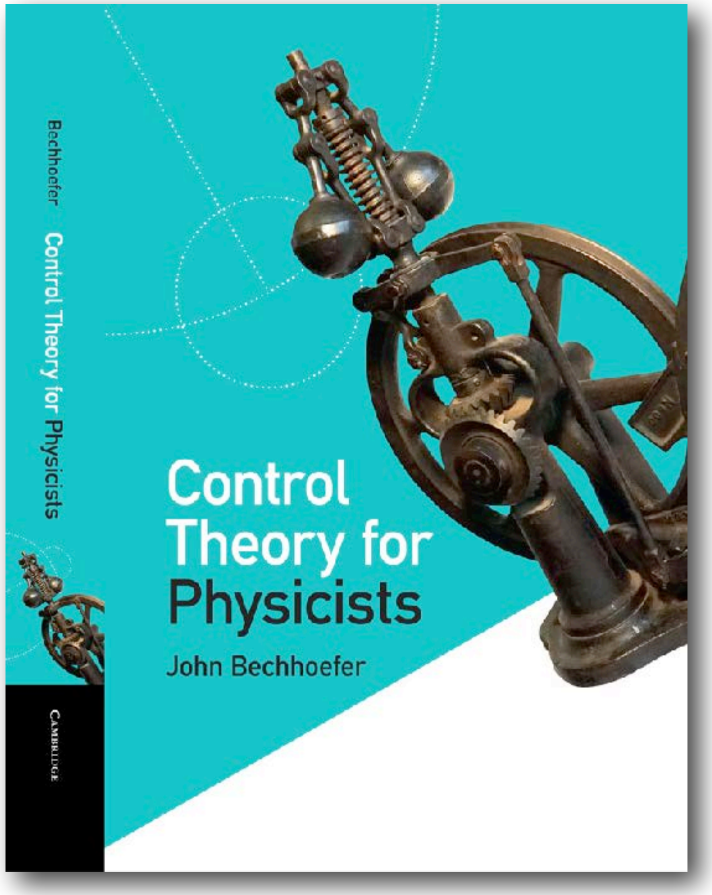


- **Metastability mechanism:** what often leads to slow dynamics here leads to a speed-up

Outlook

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





Cambridge Univ. Press, 2021

- A la mode: three back-to-back-to-back papers on quantum Mpemba in recent PRL! + other observations & predictions in polymers, granular fluids, Ising antiferromagnets, systems undergoing phase transitions, NESS to NESS relaxation, active matter, …
- Water / ice ?
- Other protocols: Kovacs, precooling, …
- Applications: improved piezoelectric materials, faster temp. changes for AFM cantilevers, ….