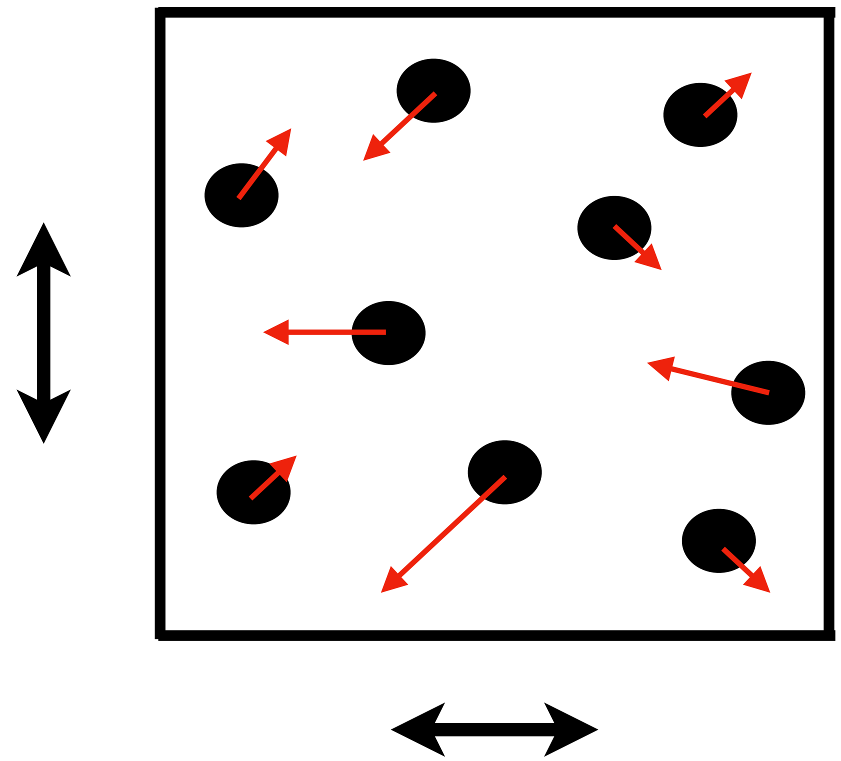
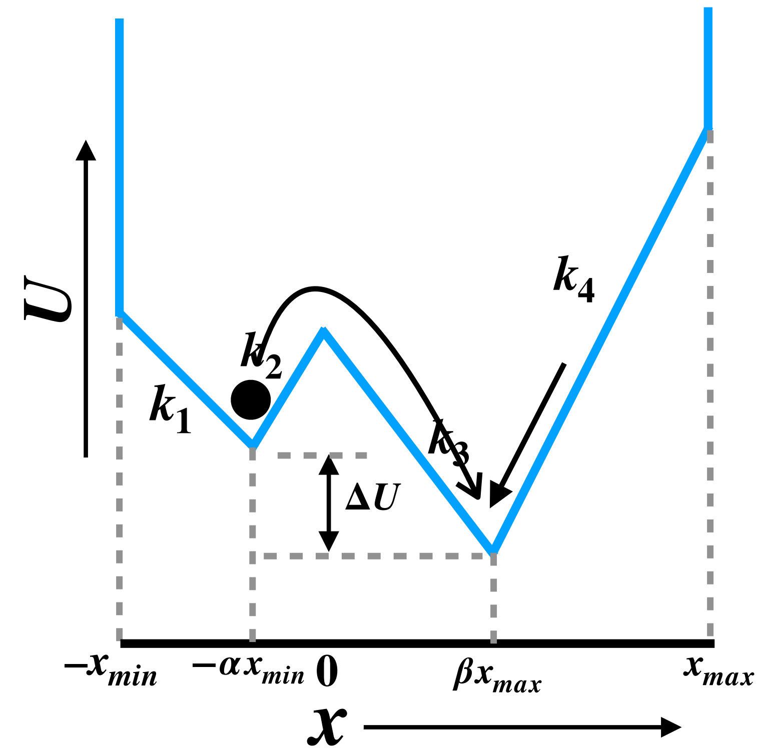




Mpemba effect: An anomalous relaxation phenomenon

R. Rajesh
The Institute of Mathematical Sciences (IMSc), Chennai
Homi Bhaba National Institute (HBNI), Mumbai

Apurba Biswas (Bordeaux)

V. V. Prasad (Cochin University)

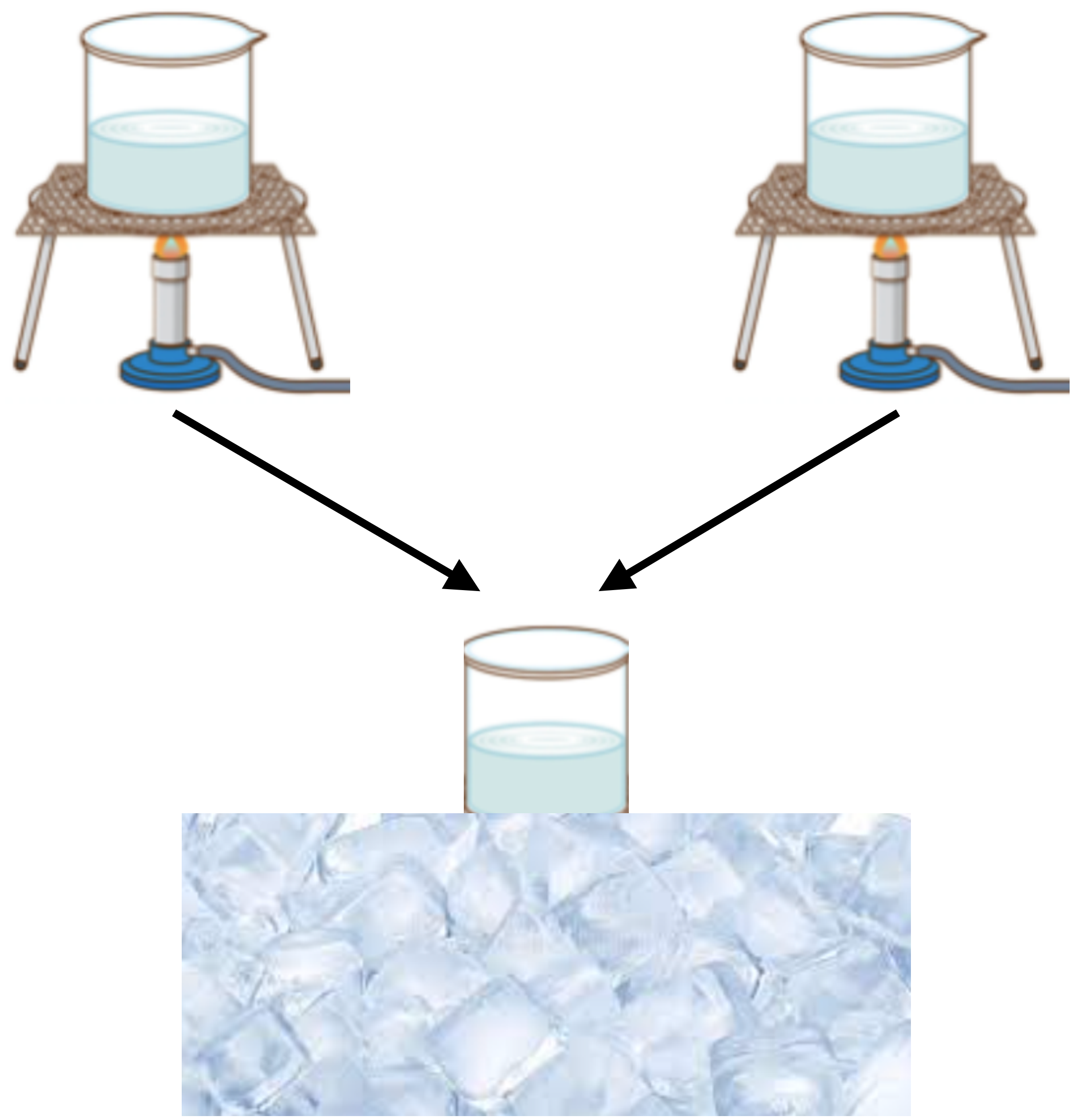
Oren Raz (Weizmann)

Arnab Pal (IMSc)

A. Biswas and RR, Physical Review E **108**, 024131 (2023)
A. Biswas and RR, ArXiv:2411.02652

Cooling two samples

T_c (say 30°) T_h (say 50°)

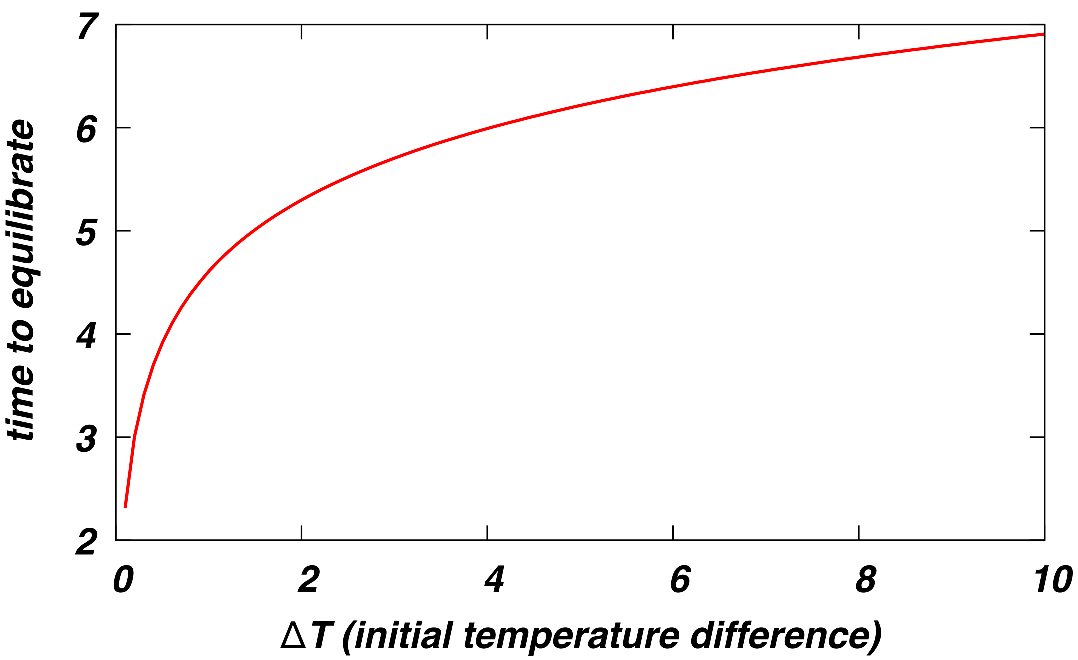


T_f (say 0°)

- Which system cools (or freezes) faster?

Conventional answer

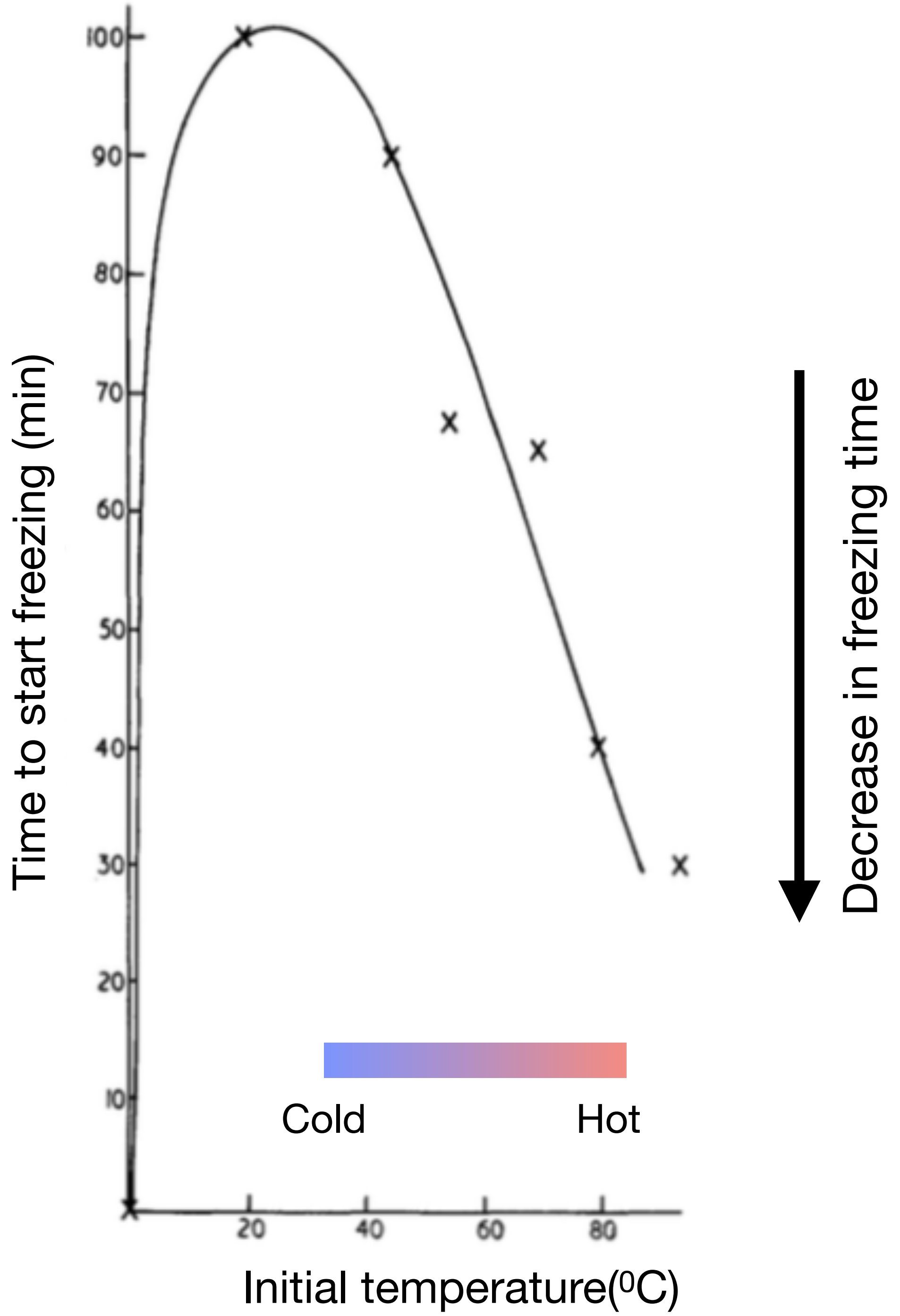
- $\Delta T = T(t) - T_b$
- Newton's law of cooling (for small ΔT)
  - $\dfrac{d\Delta T(t)}{dt} = -k\Delta T(t)$
  - $\Delta T(t) = \Delta T(0)e^{-kt}$
- Quasi-static relaxation



- Hotter system takes more time to equilibrate (as expected)

Mpemba effect

- Experiment
  - Take water at different temperatures
  - Put in freezer
  - Measure freezing time
- Hot water freezes faster!



Mpemba et al, Phys. Edu. (1969)

Mpemba effect in water (searching for reason)

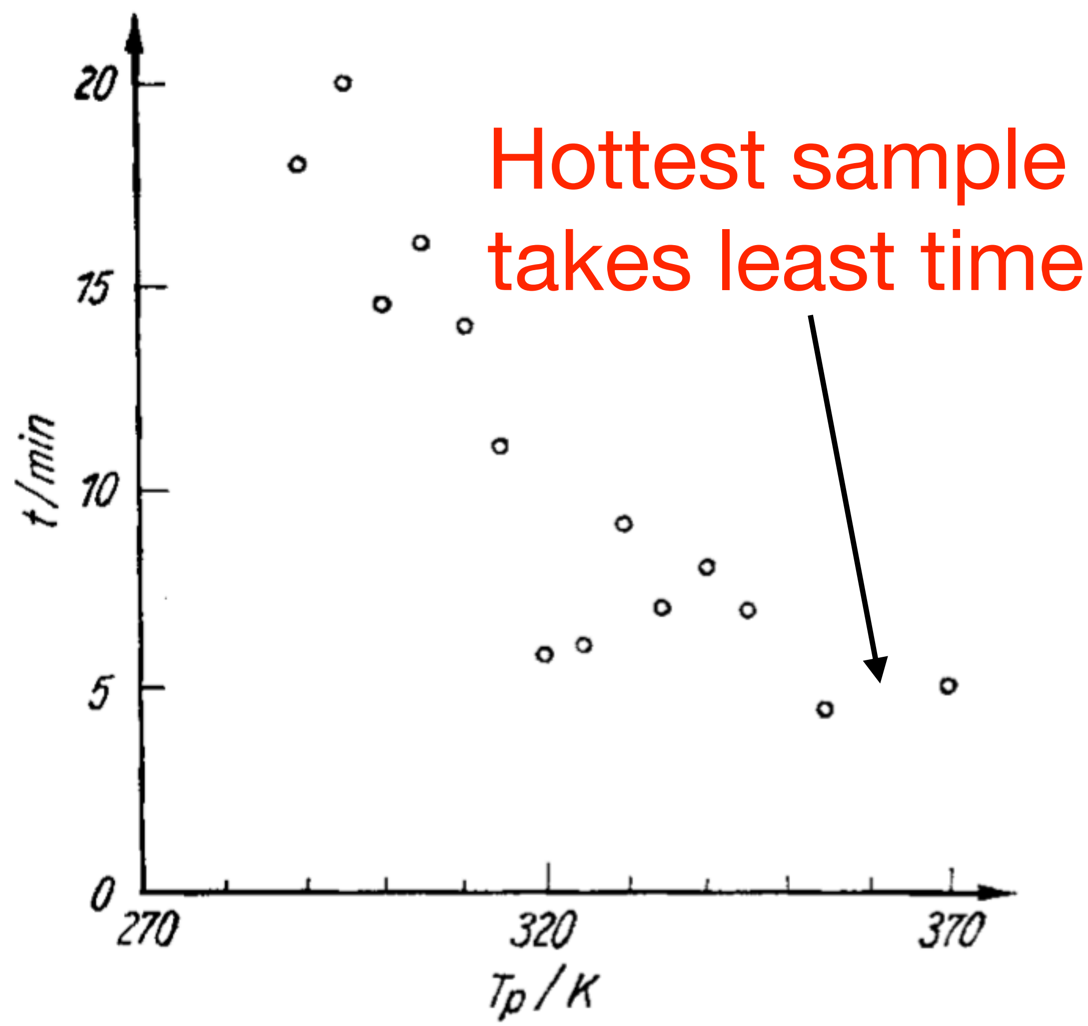
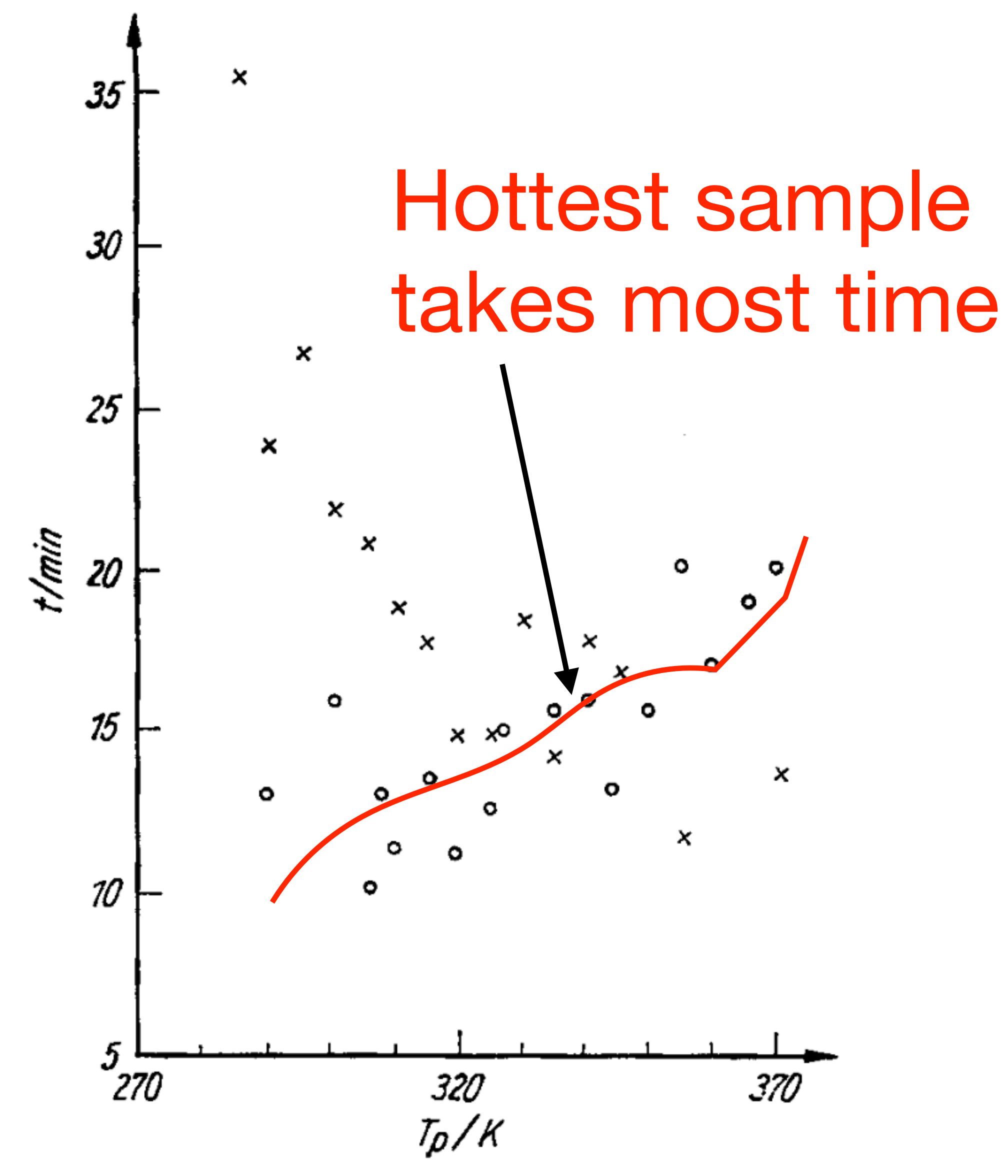


Fig. 4. Time of freezing of non-degased water as a function of start temperature for one of the sets of measurements

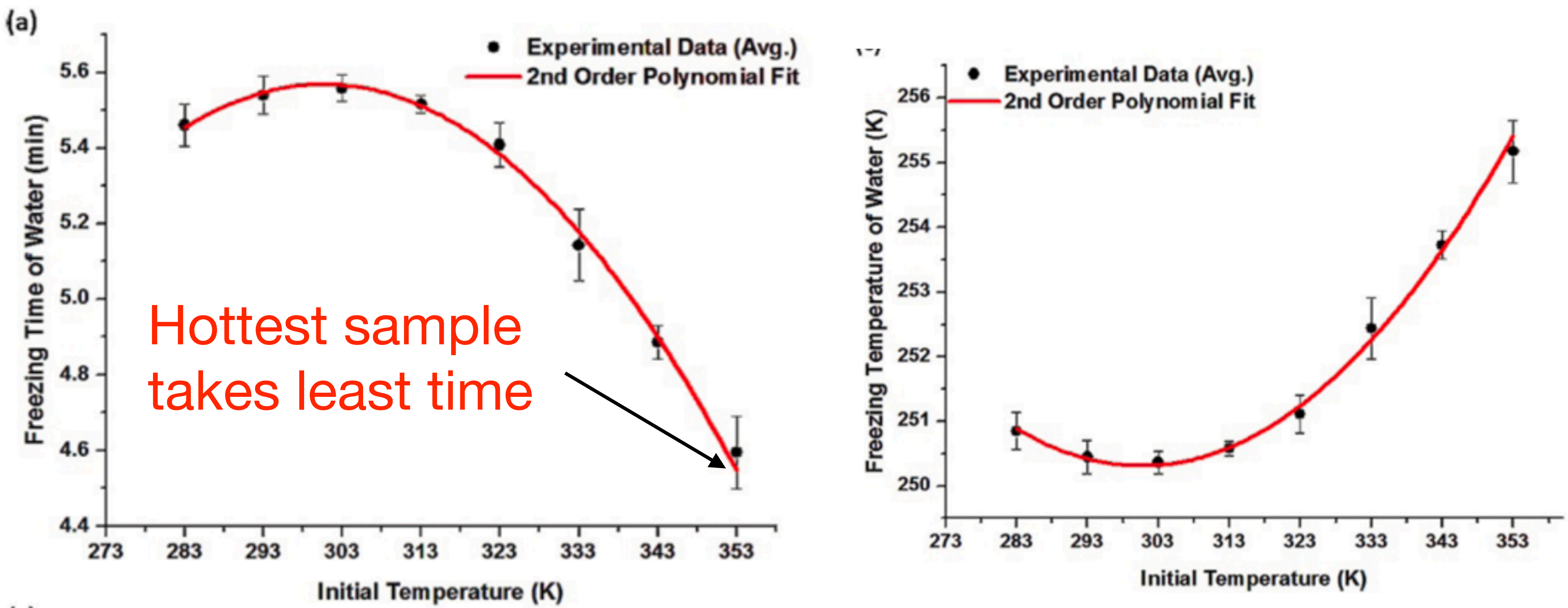
Non-degassed



Degassed

Wojciechowski et al, Cryst. Res. Technol. (1988)
(Dissolved gases being proposed)

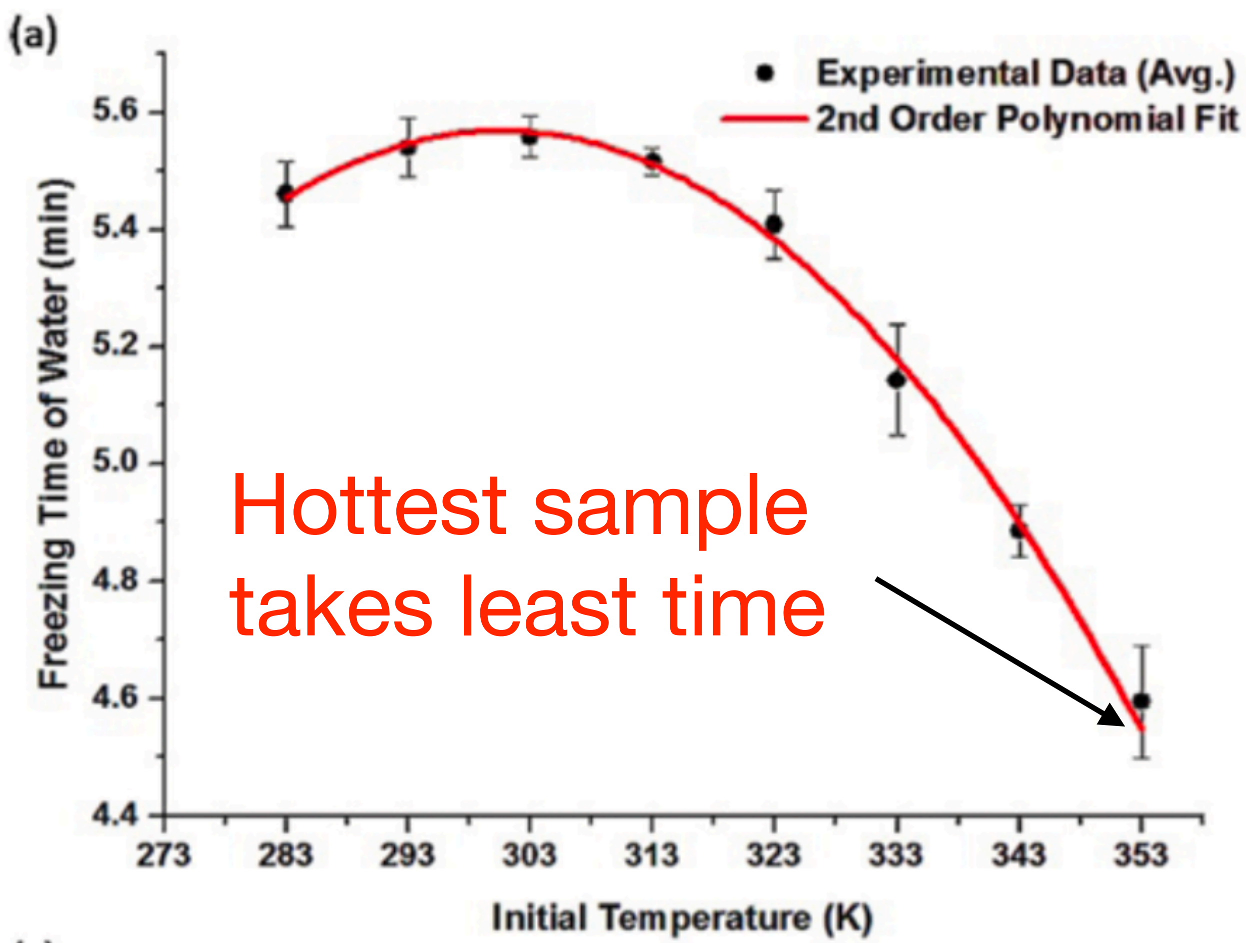
Mpemba effect in water (more reasons)

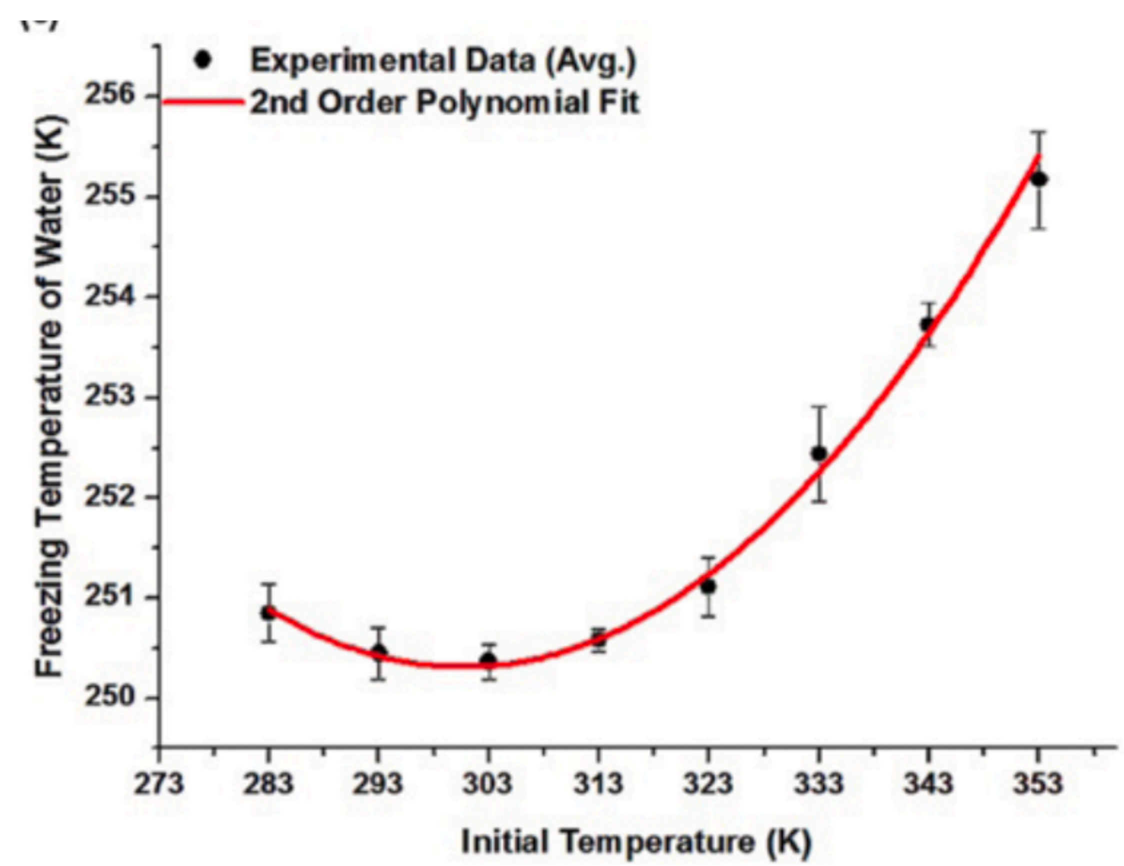


- Different freezing temperatures

Ahn et al, Korean J. Chem. Eng.(2016)
(Freezing temperature different for different initial temperatures)

Mpemba effect in water (more reasons)



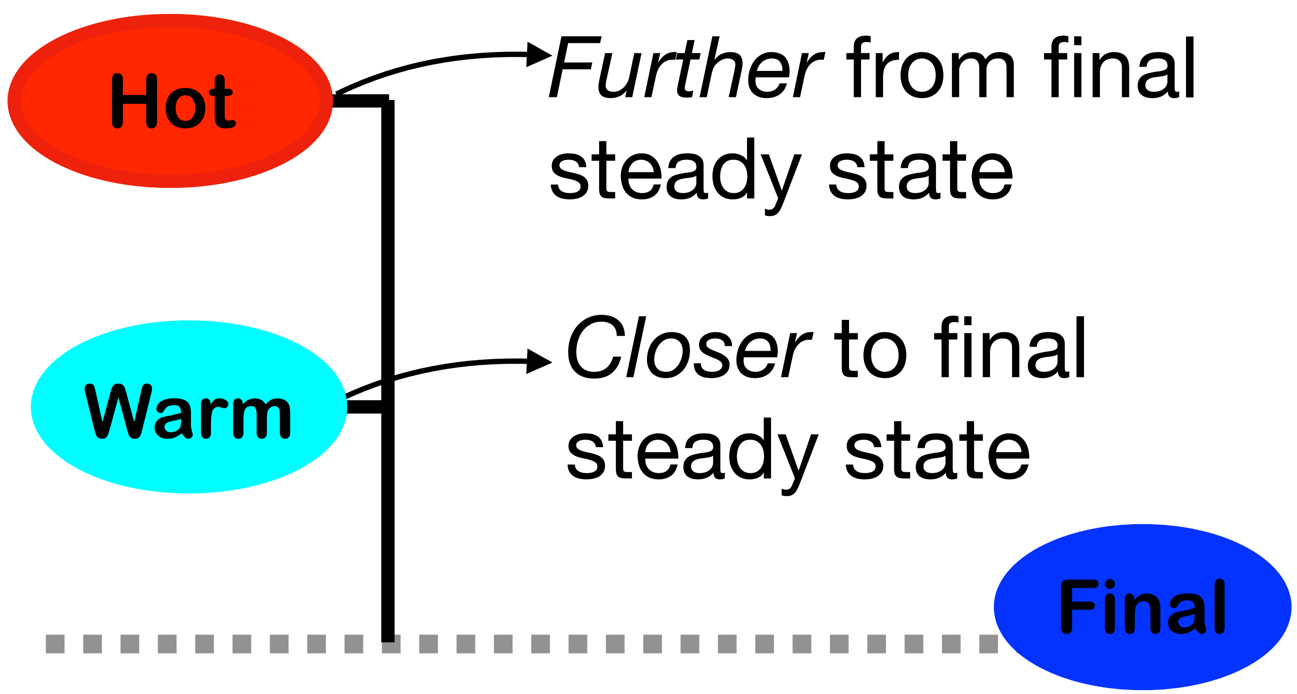


- Different freezing temperatures

- But enough of water

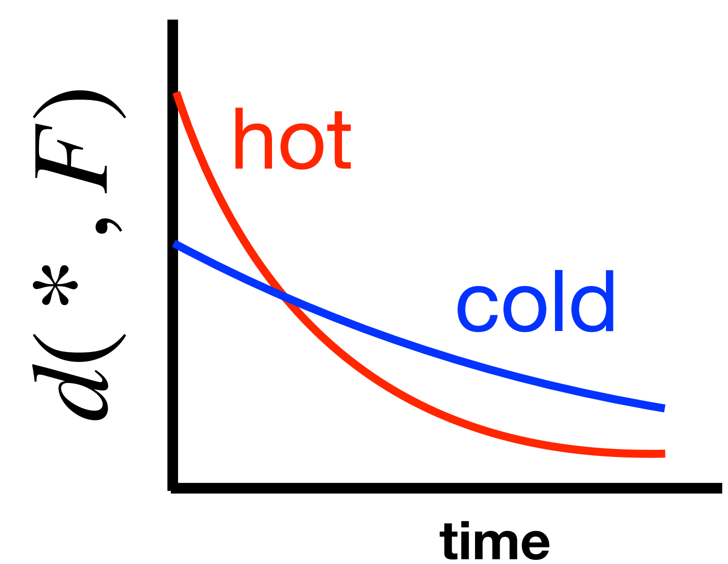
Ahn et al, Korean J. Chem. Eng.(2016) (Freezing temperature different for different initial temperatures)

Mpemba effect in a more general scenario



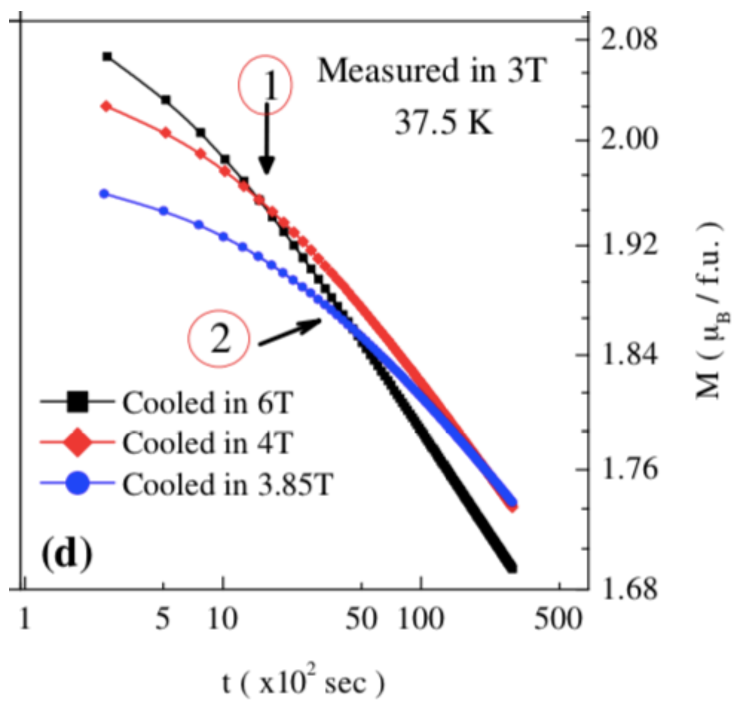
- Quench from initial state to final state
- What cools faster?

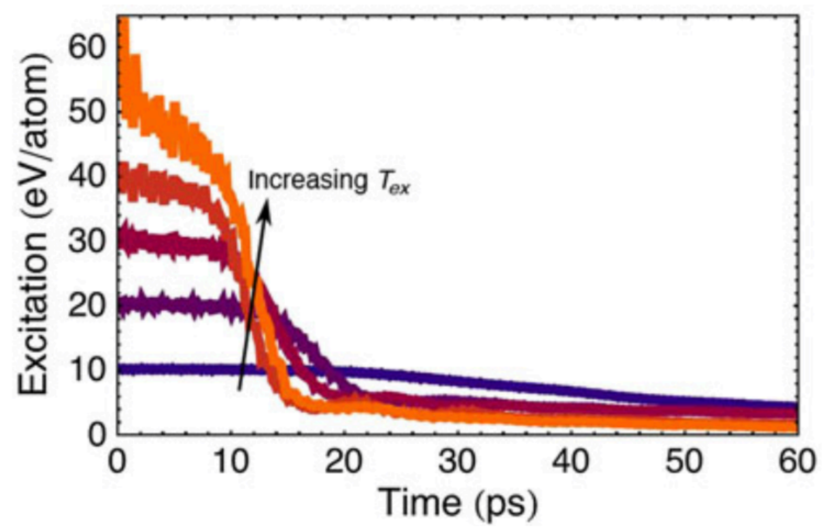
- A distance measure $d(*,F)$ between steady states
- Crossing of trajectories

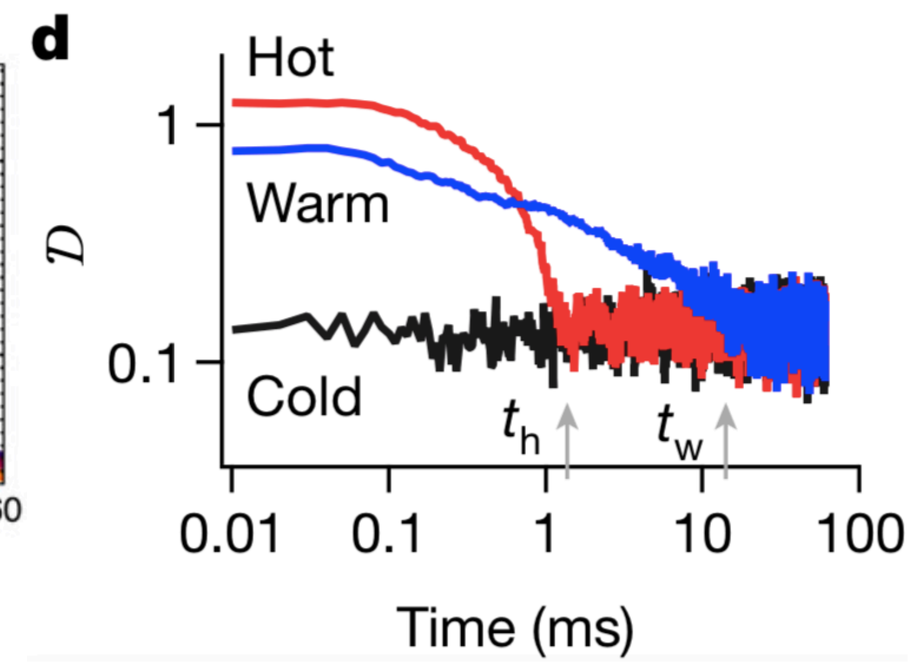


Mpemba effect (other systems)

M







Magneto resistance alloys ($La_{0.5}Ca_{0.5}MnO_3$)

Chaddah et al, arXiv (2010)

Carbon nanotubes

Greaney et al, Metallurgy Mater. Trans. A (2011)

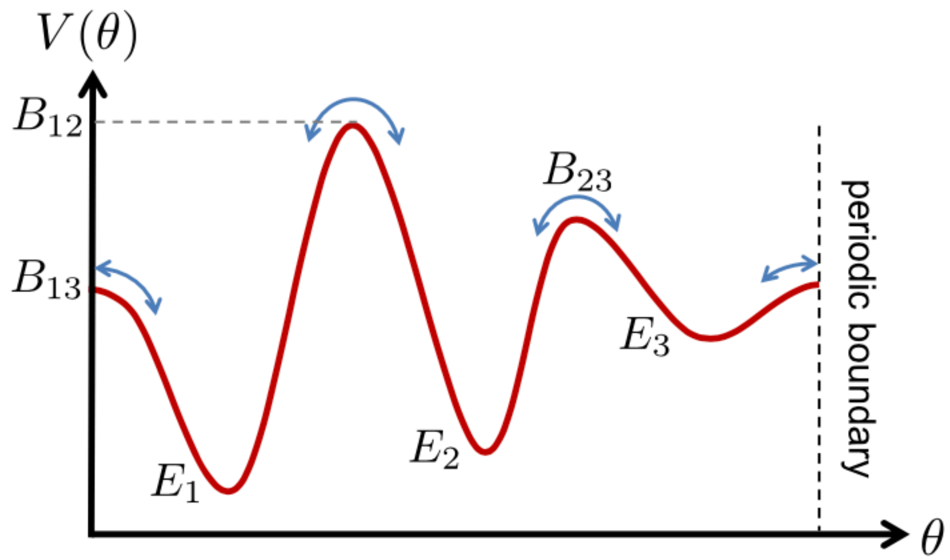
Colloidal systems

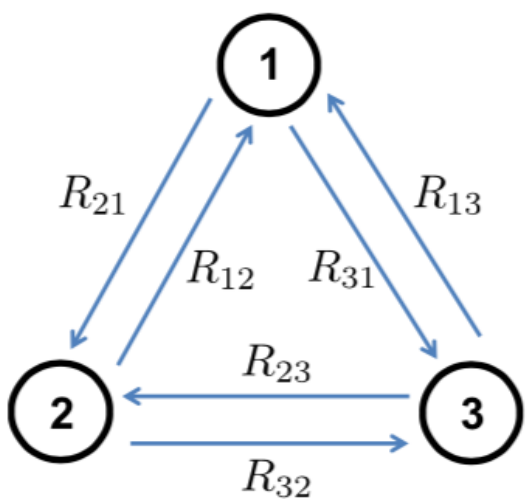
Kumar et al, Nature (2020)

Summary till now

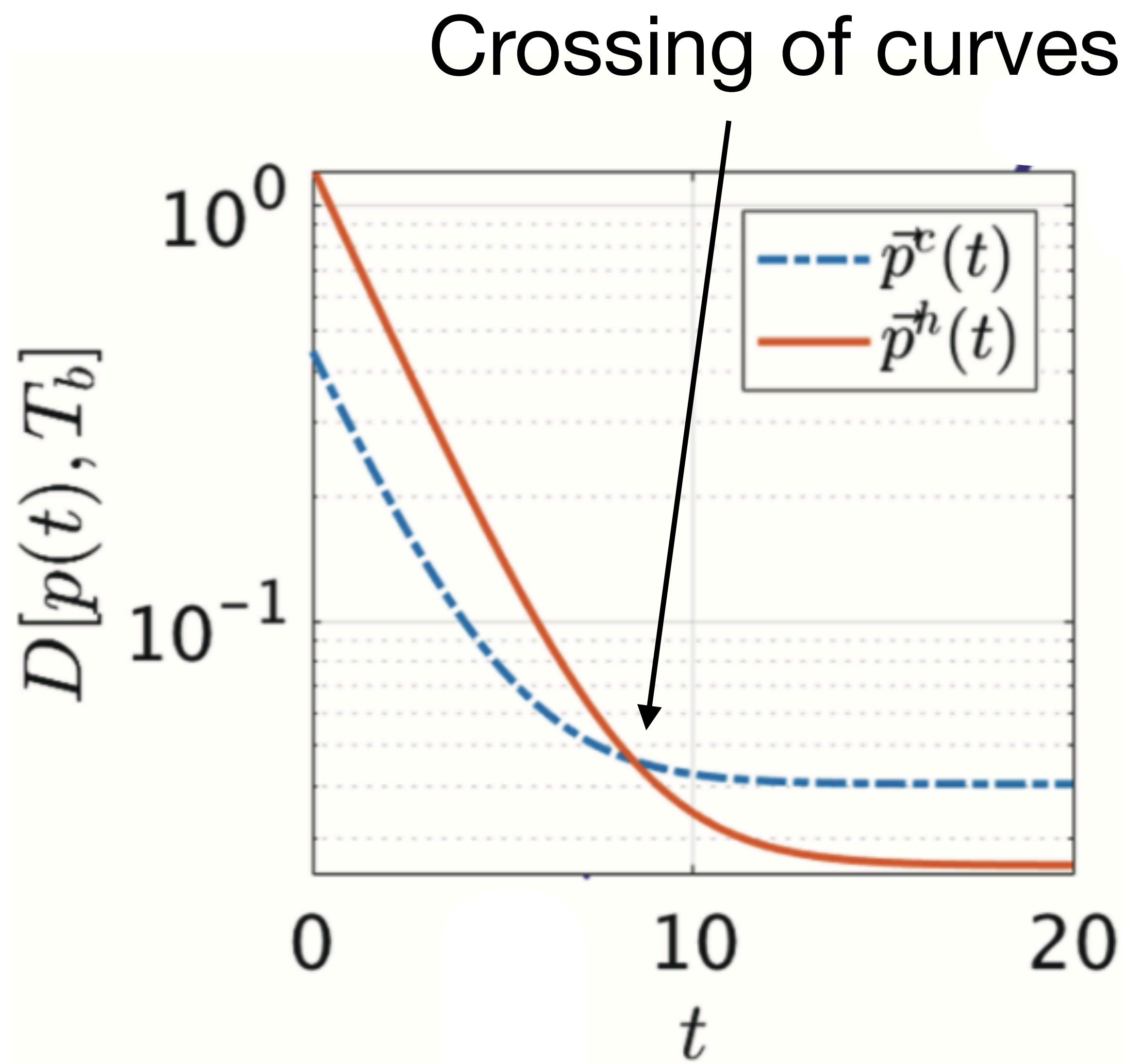
- Mpemba effect is generic
  - Seen in many physical systems
  - Not restricted to water alone
- How does one understand?
  - look at very simple systems/models

Simple models





$$R_{ij}(T_b) = \begin{cases} \Gamma e^{-\frac{B_{ij}-E_j}{k_B T_b}} & i \neq j \\ -\sum_{k\neq i} R_{ki} & i = j \end{cases},$$

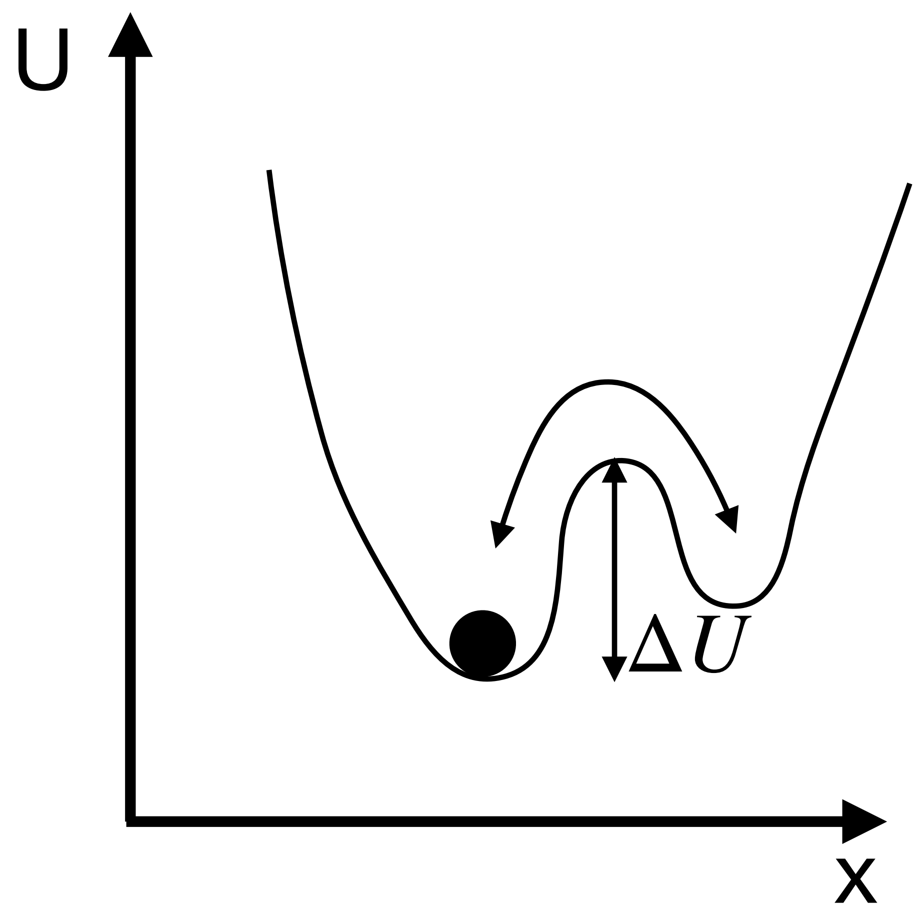


Lu et al, PNAS (2017)

Explanation: metastable states

- Mpemba effect: Metastable states in energy landscape
  - Intermediate energies get trapped
  - High energies have no barrier to cross

Lu et al, PNAS (2017)



- Rate $\propto \exp \frac{-\Delta U}{k_B T}$

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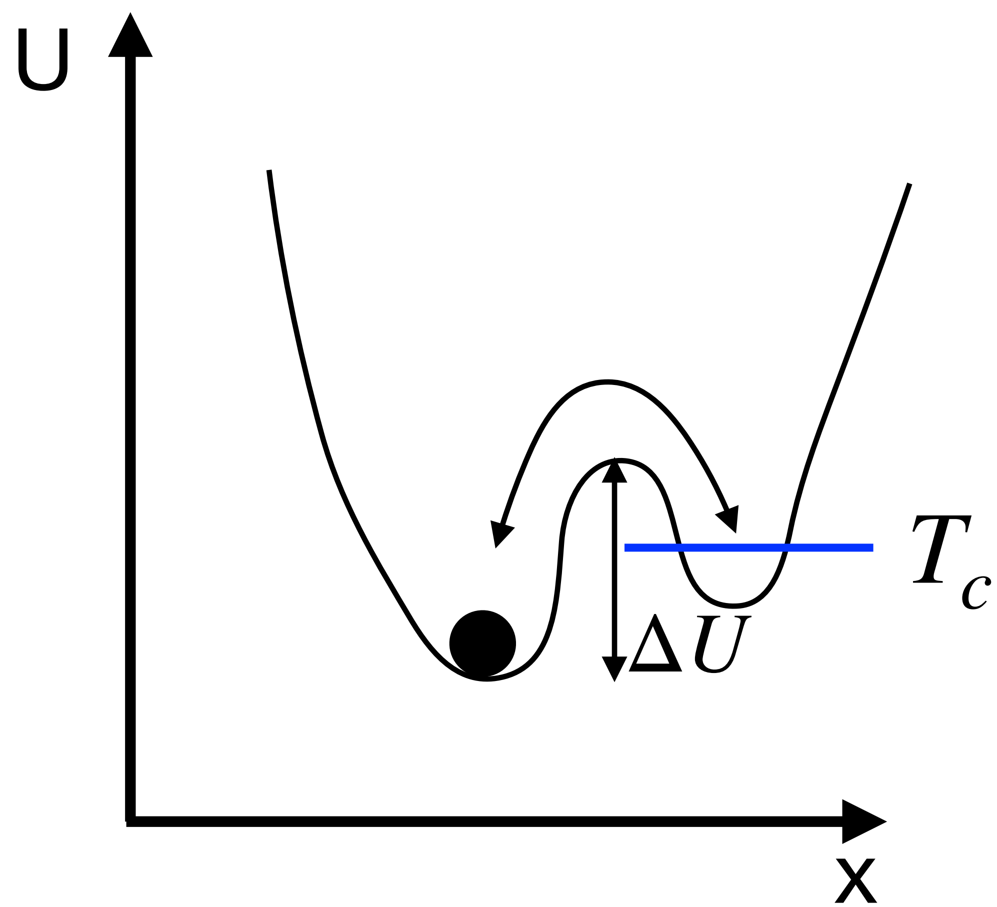
Lu et al, PNAS (2017)



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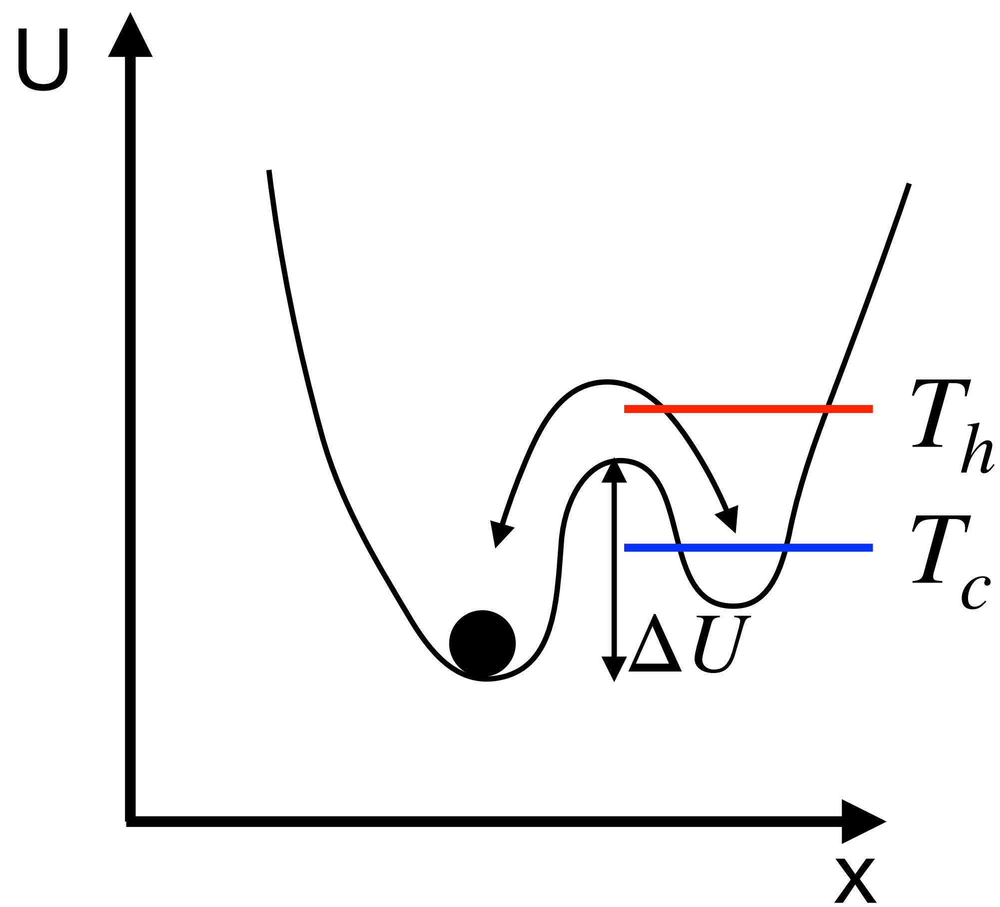
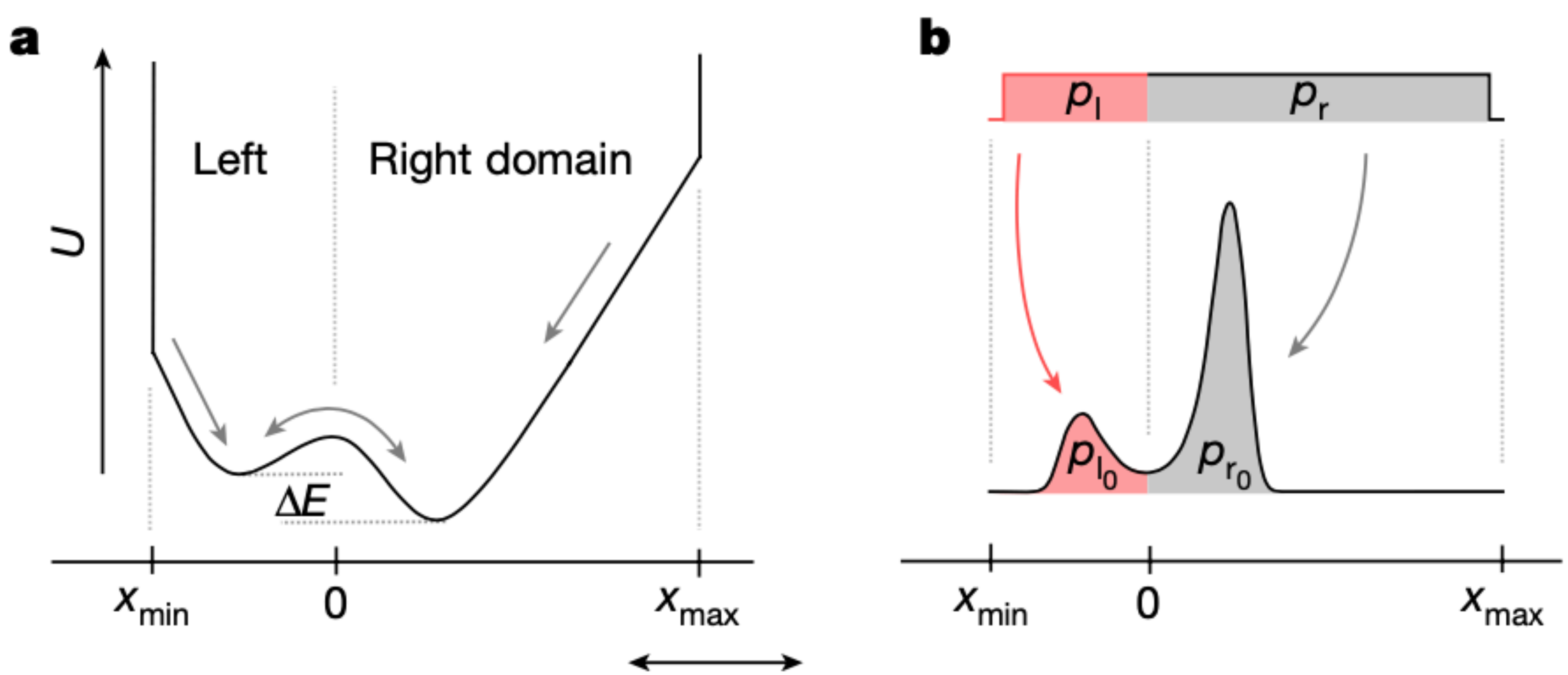


- Rate $\propto \exp \frac{-\Delta U}{k_B T}$

Experiment using metastability: colloidal system

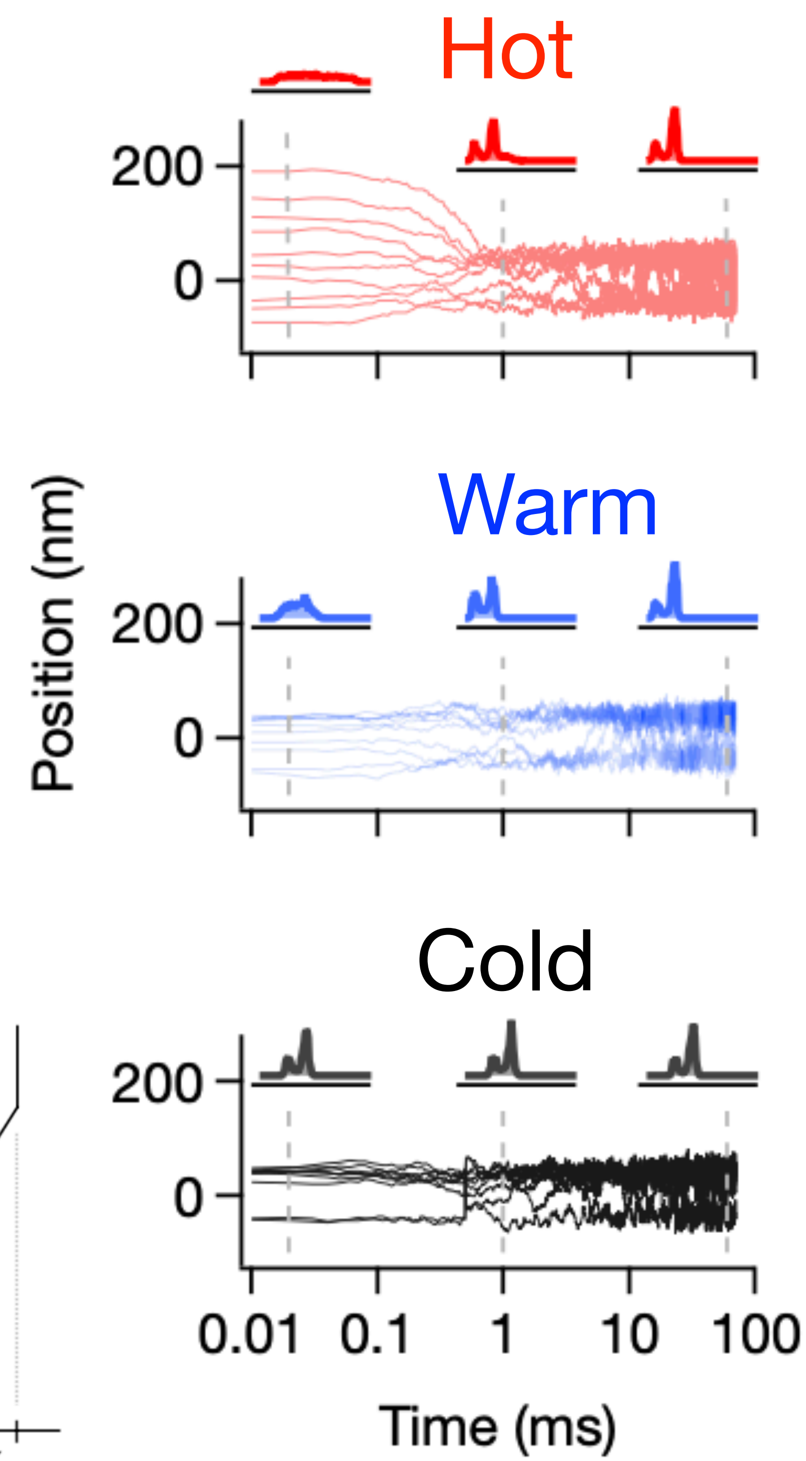


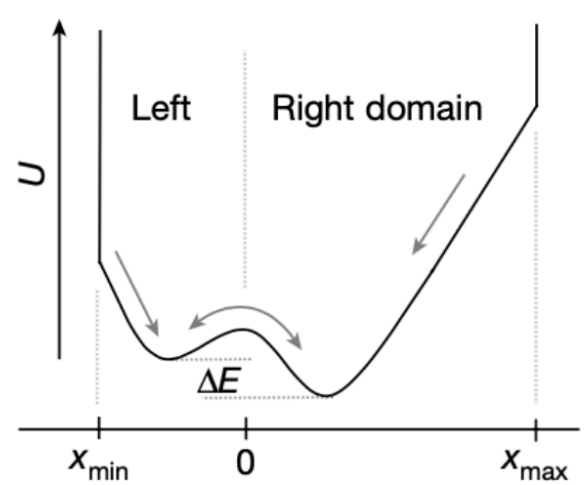
- A brownian particles
- Asymmetric double well
- Quadratic and linear
- Infinite at boundary

Kumar and Bechhoefer, Nature 584 (2020)

Different quenches

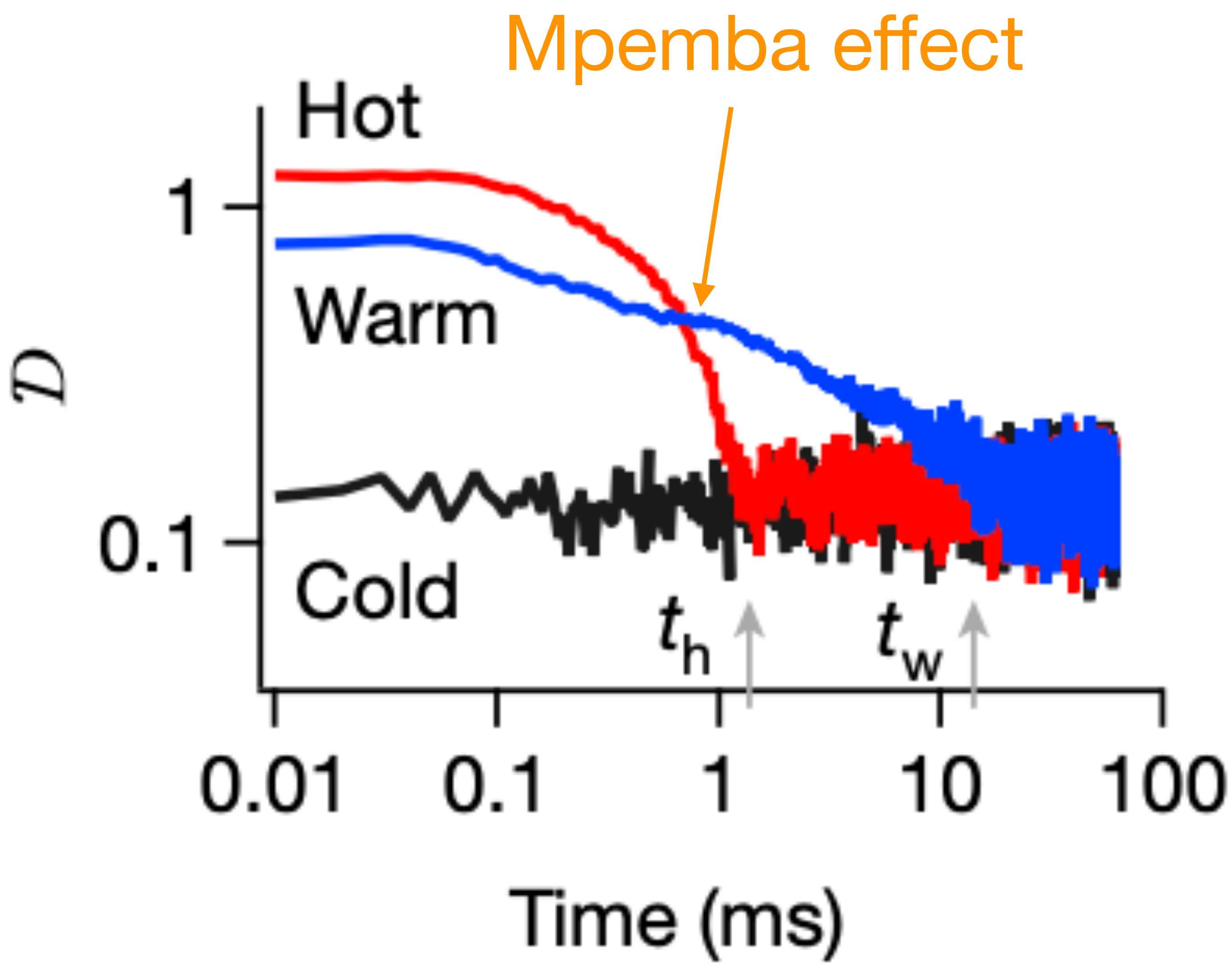
- Equilibrate at different temperatures (initial condition)
- Quench to bath temperature (explain)
- Study evolution of position
- Construct probability distributions from several trials





Kumar and Bechhoefer, Nature 584 (2020)

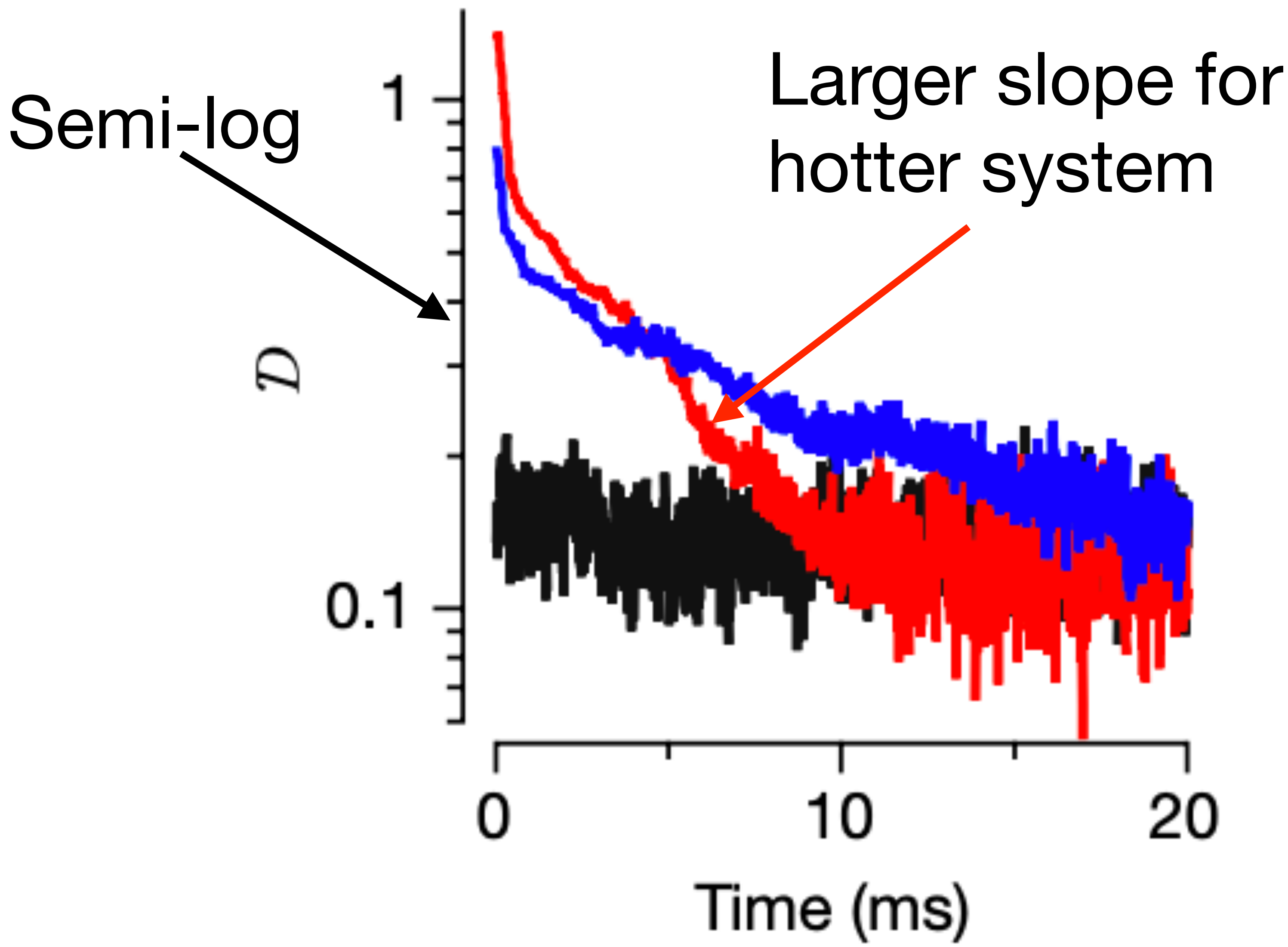
Existence of Mpemba effect



$$\mathscr{D} = \int dx \, | \, p(x, t) - \pi(x, T_b) \, |$$

Kumar and Bechhoefer, Nature 584 (2020)

Strong Mpemba effect



- Hotter system cools exponentially faster

Kumar and Bechhoefer, Nature 584 (2020)

How to define Mpemba effect

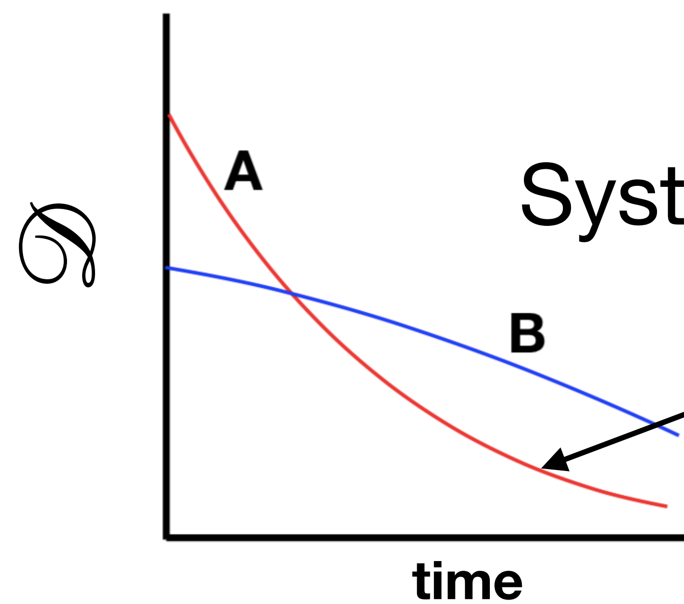
- Markov process: dynamics defined by transition rates between configurations: $\dfrac{dP}{dt} = WP$
- $P(\{C\}, t) = P_1(\{C\}) + a_2 e^{-\lambda_2 t} P_2(\{C\}) + \dots$
- $\lambda_2 > 0$ is determined only by the rates (not dependent on initial probability distribution)
- $a_2 = \langle P_2^{left} | P(t=0) \rangle$ is a function of initial state
- Now quench two systems, one at high temperature (T_h) and other at cool temperature (T_c) to T_b

How to define Mpemba effect

Only quantity to depend on initial condition

$$P(\{C\},t) = P_1(\{C\}) + a_2 e^{-\lambda_2 t} P_2(\{C\}) + \ldots$$

$$\mathscr{D} = \sum_C |P(C,t) - P_1(C)| = |a_2| e^{-\lambda_2 t} \sum_C |P_2(\{C\})|$$



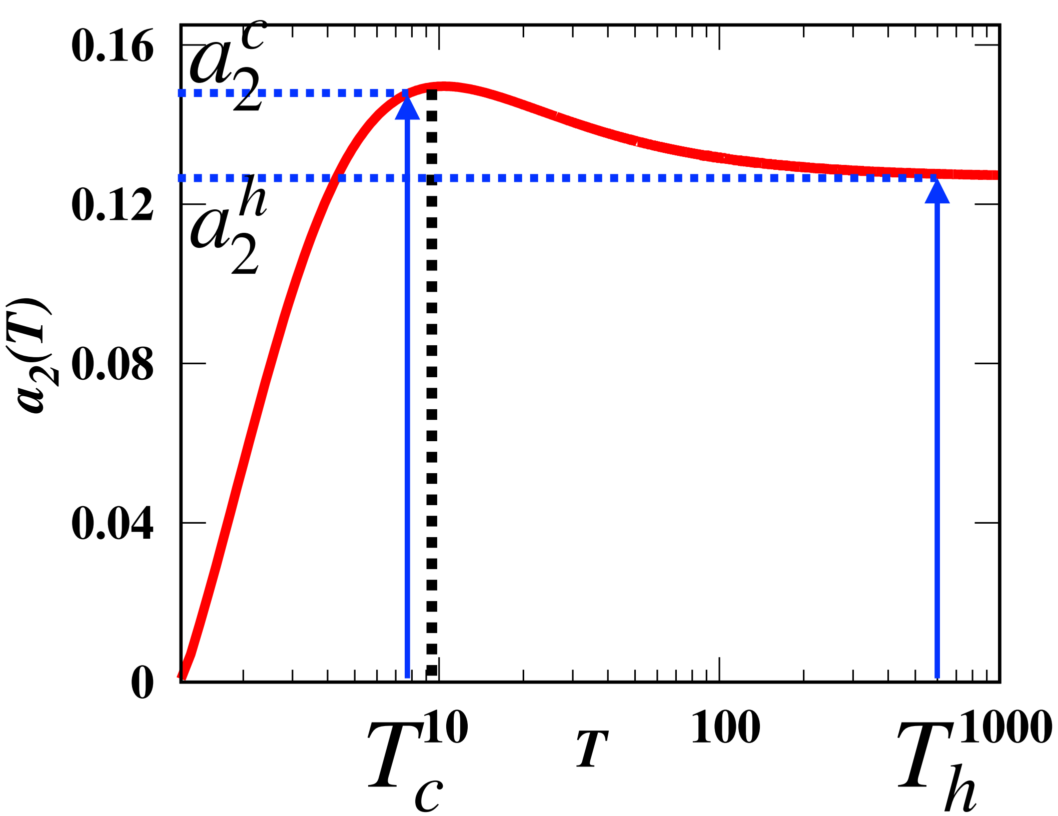
System with smaller $|a_2|$

- Equilibrium systems, initially $\mathscr{D}_h(0) > \mathscr{D}_c(0)$ (can be shown)
- If $|a_2^h| < |a_2^c|$, then $\mathscr{D}_h(t) < \mathscr{D}_c(t)$ and hotter system equilibrates faster $\implies$ Mpemba effect

Protocol with a_2

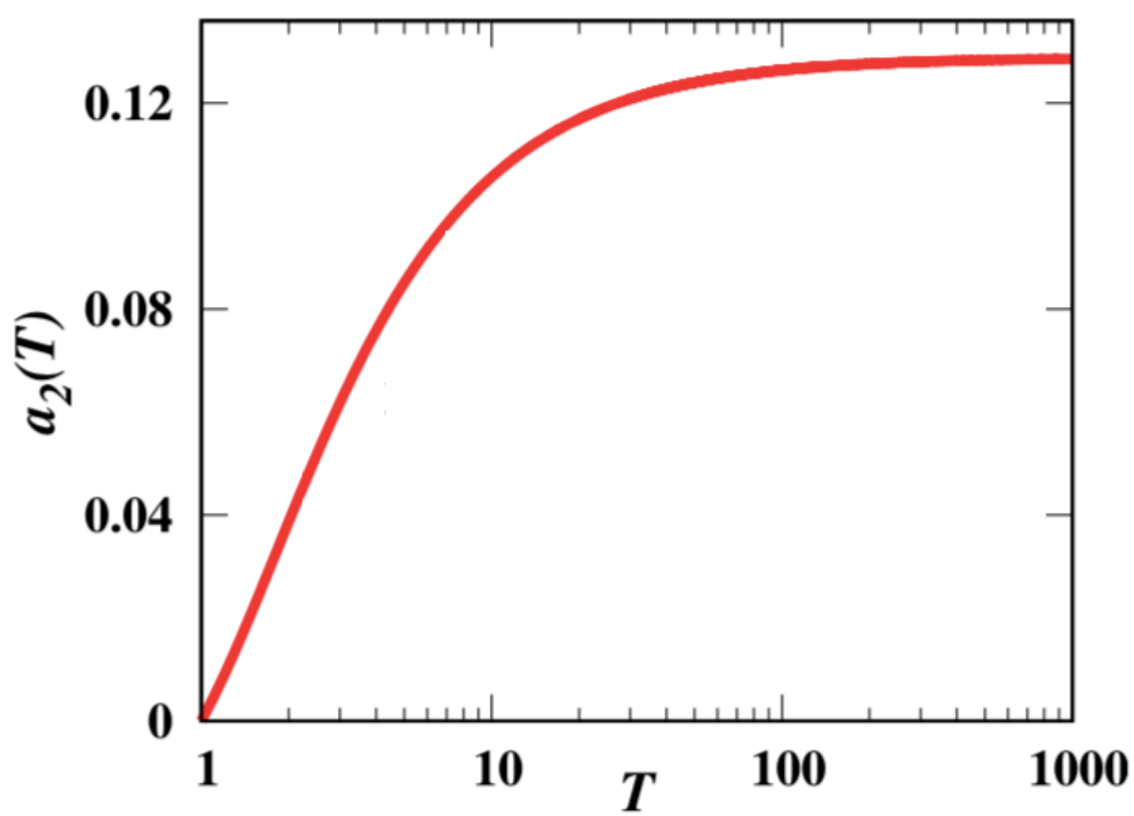
- Remember a_2 is only a function of initial temperature
- Calculate $a_2(T)$ given T_b (look for non-monotonicity)

Mpemba present



$|a_2^h| < |a_2^c|$

Mpemba absent



Strong Mpemba effect

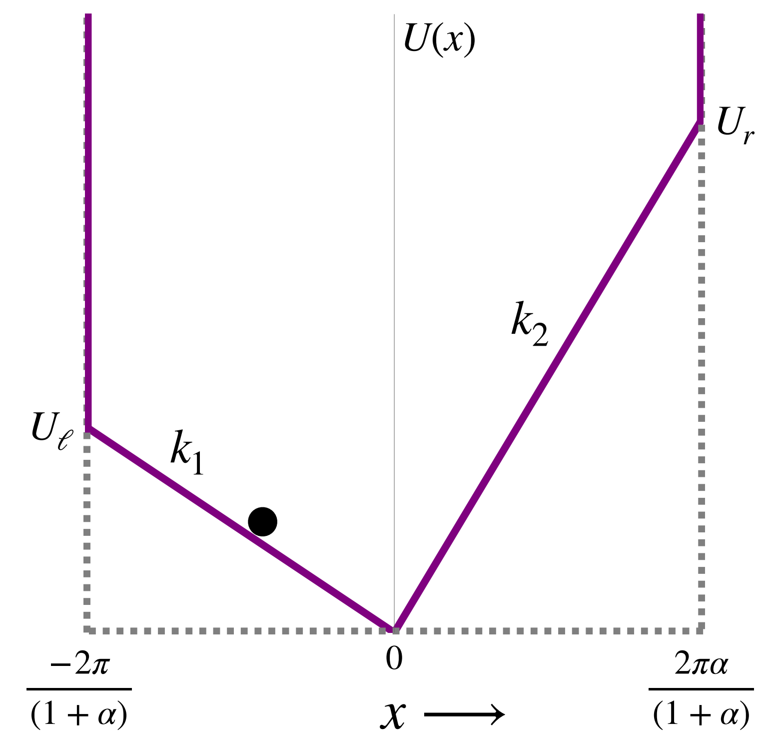
- $P(\{C\}, t) = P_1(\{C\}) + a_2 e^{-\lambda_2 t} P_2(\{C\}) + a_3 e^{-\lambda_3 t} P_3(\{C\}) + \dots$
- Suppose $a_2^h = 0$
- $P(\{C\}, t) = P_1(\{C\}) + a_3 e^{-\lambda_3 t} P_3(\{C\}) + \dots$
- Then hotter system cools exponentially faster
- $\implies$ strong Mpemba effect
- Summary
  - Look for non-monotonicity of $a_2(T)$ [Mpemba]
  - Look for zeros of $a_2(T)$ [Strong Mpemba]

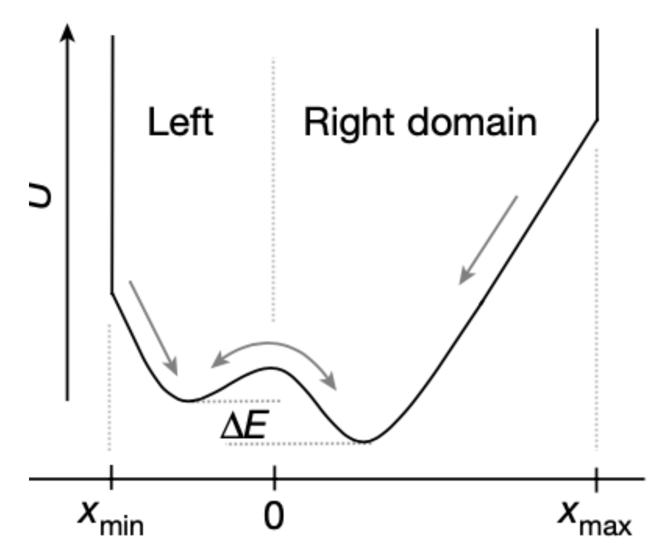
Questions

- What is the explanation of Mpemba effect?
  - Metastability?
  - Hidden variables?
  - System specific reasons?
- How sensitive is Mpemba effect to the choice of charactering parameter and distance function? (a_2 versus temperature (say))
- What is the role of activity?
- What is the role of rate of cooling?

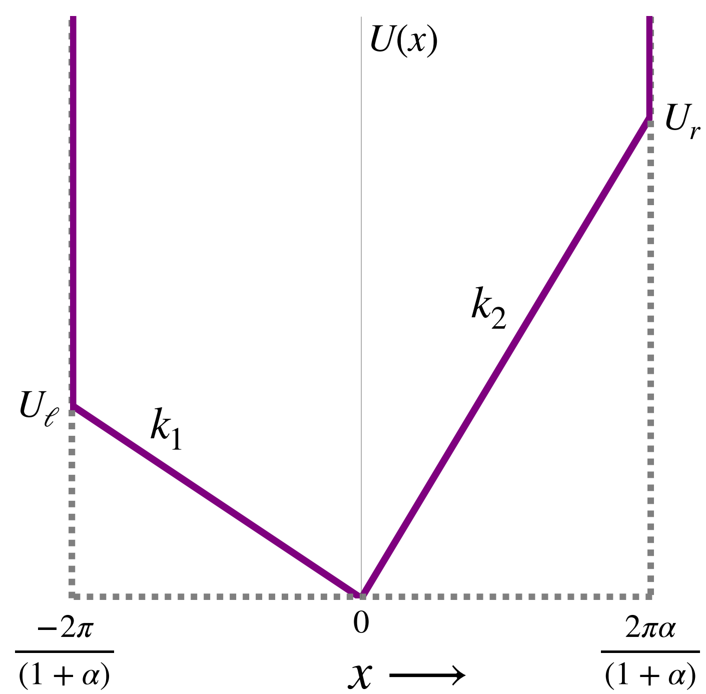
Colloidal particle in a single-well potential

- Why this example?
  - Experimentally realisable
  - An explicit solution can be constructed
- Single well potential has no metastable minimum
  - Is a metastable state a necessary condition for Mpemba effect?
  - If no, what is the phase diagram?





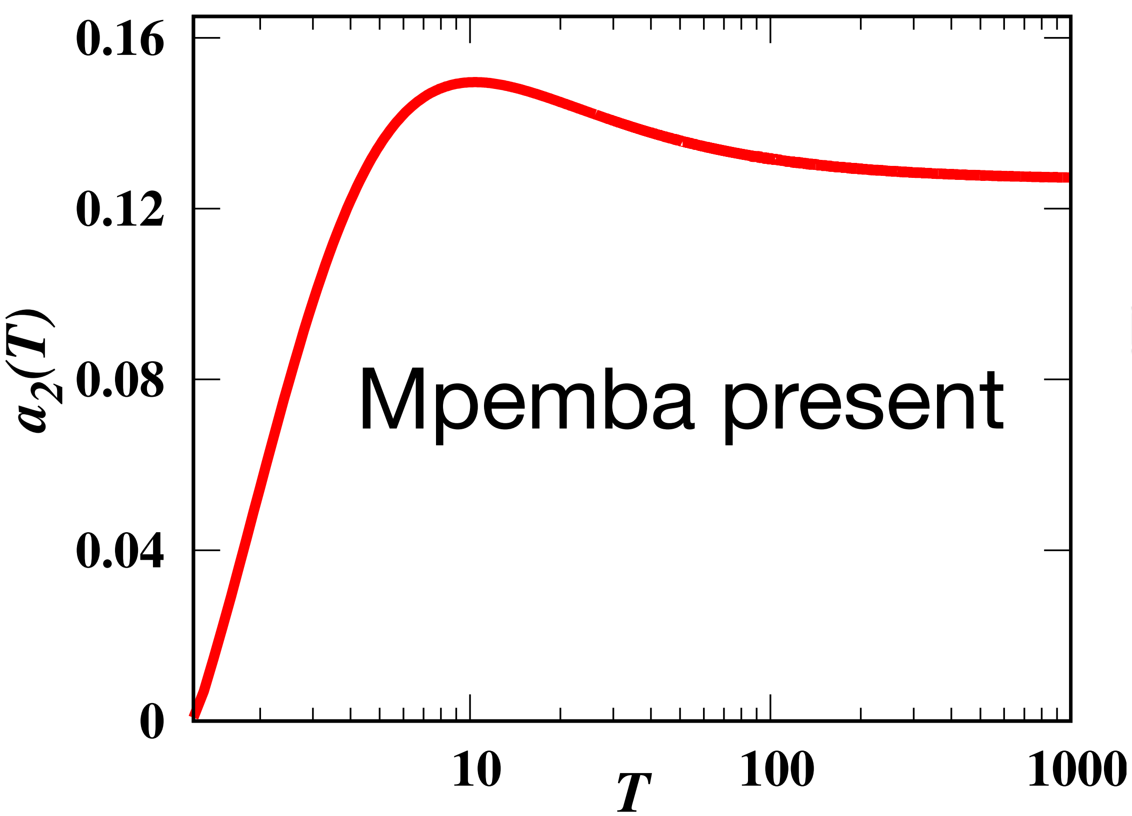
Single particle problem

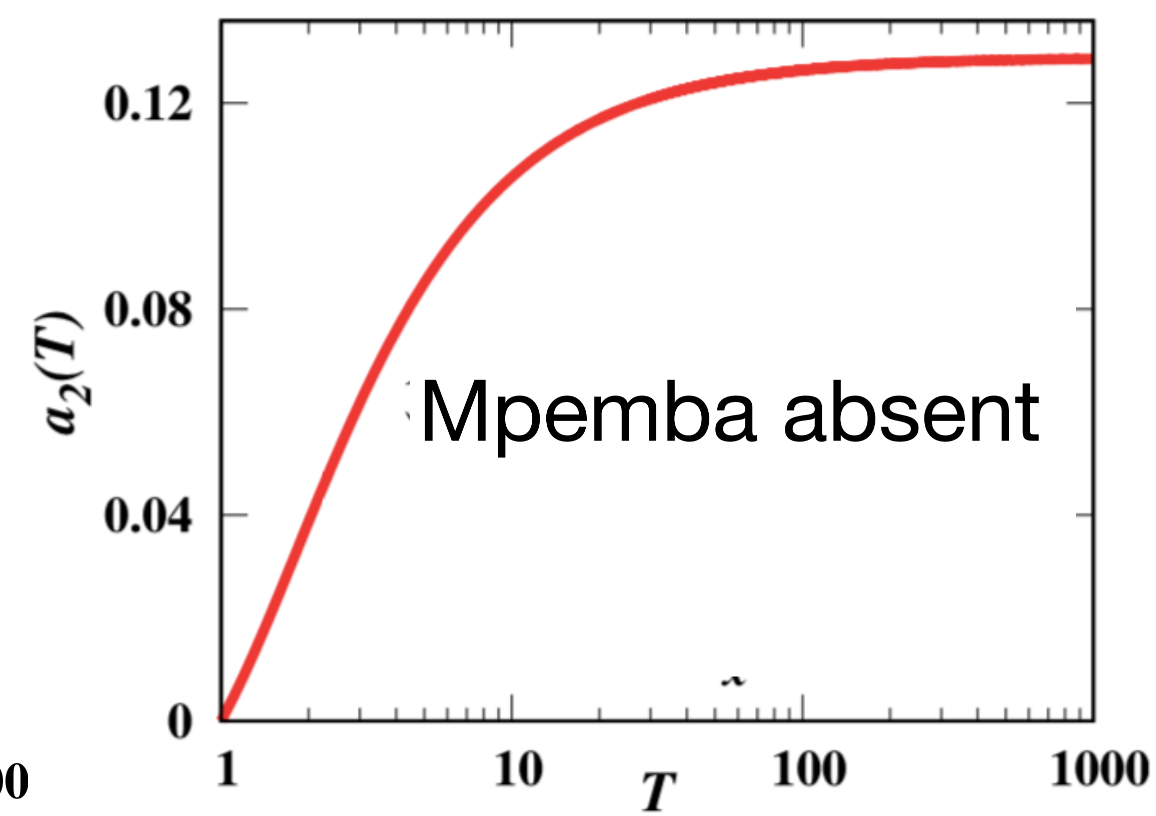


- Over-damped Langevin equation:
$$\gamma \frac{dx}{dt} = -\frac{dU}{dx} + \eta(t)$$
- Corresponding Fokker-Planck description: $\dfrac{\partial p}{\partial t} = \dfrac{\partial}{\partial x}\left[\dfrac{dU}{dx}p\right] + \dfrac{\partial^2 p}{\partial x^2}$
- Solution using eigenspectrum decomposition:
$$p(x,t) \simeq \frac{e^{-U(x)}}{\mathcal{Z}(1)} + a_2 e^{\frac{-U(x)}{2}} \psi_2(x) e^{-|\lambda_2| t}$$

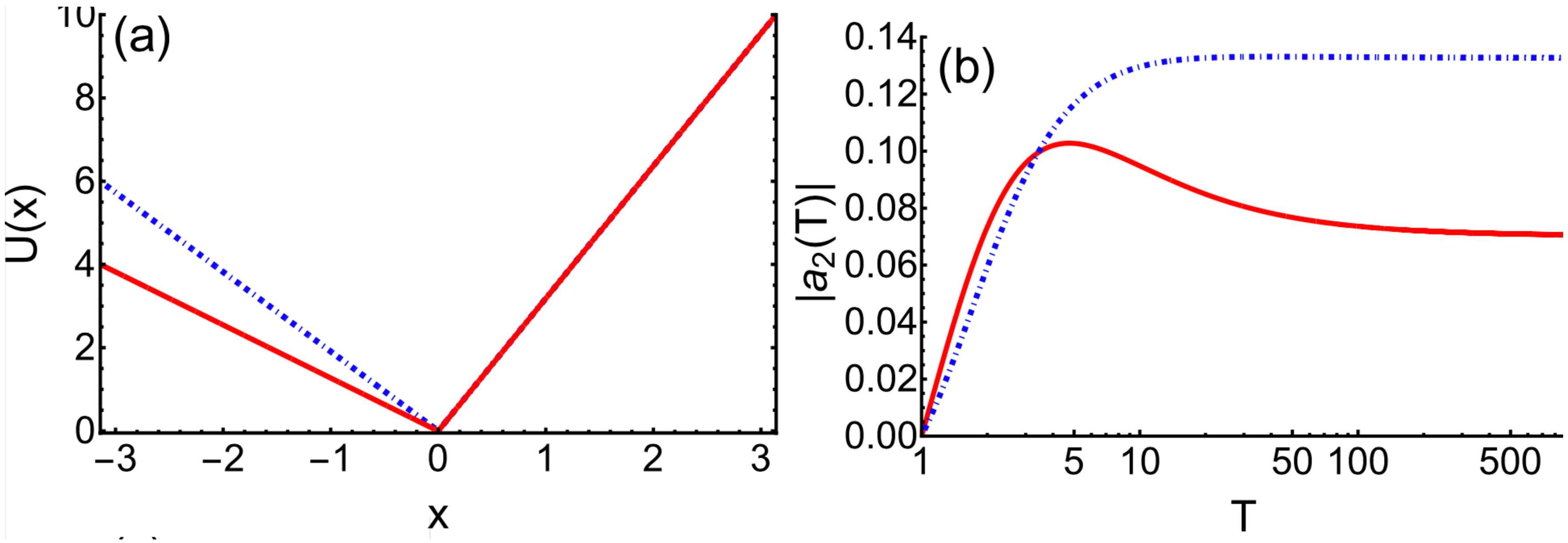
Recall: criterion for Mpemba effect

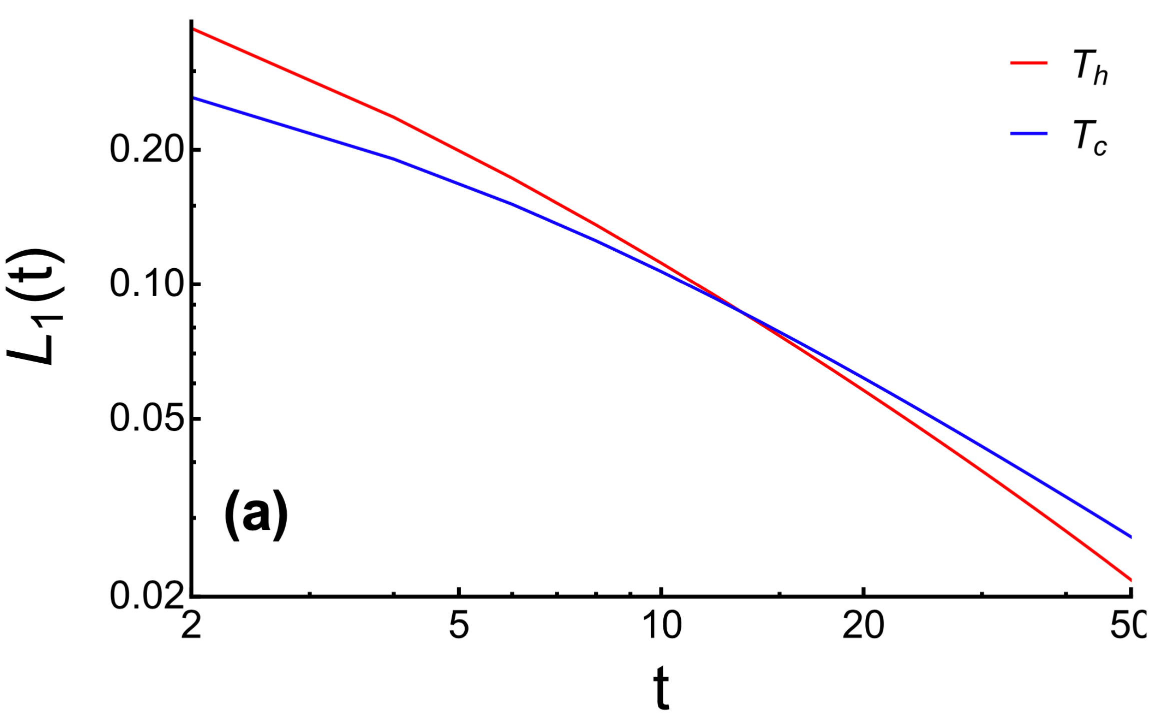
- $a_2 = \int dx\ \pi(x, T) e^{\frac{U(x)}{2}} \psi_2(x)$
- $|a_2^{hot}| < |a_2^{cold}|$



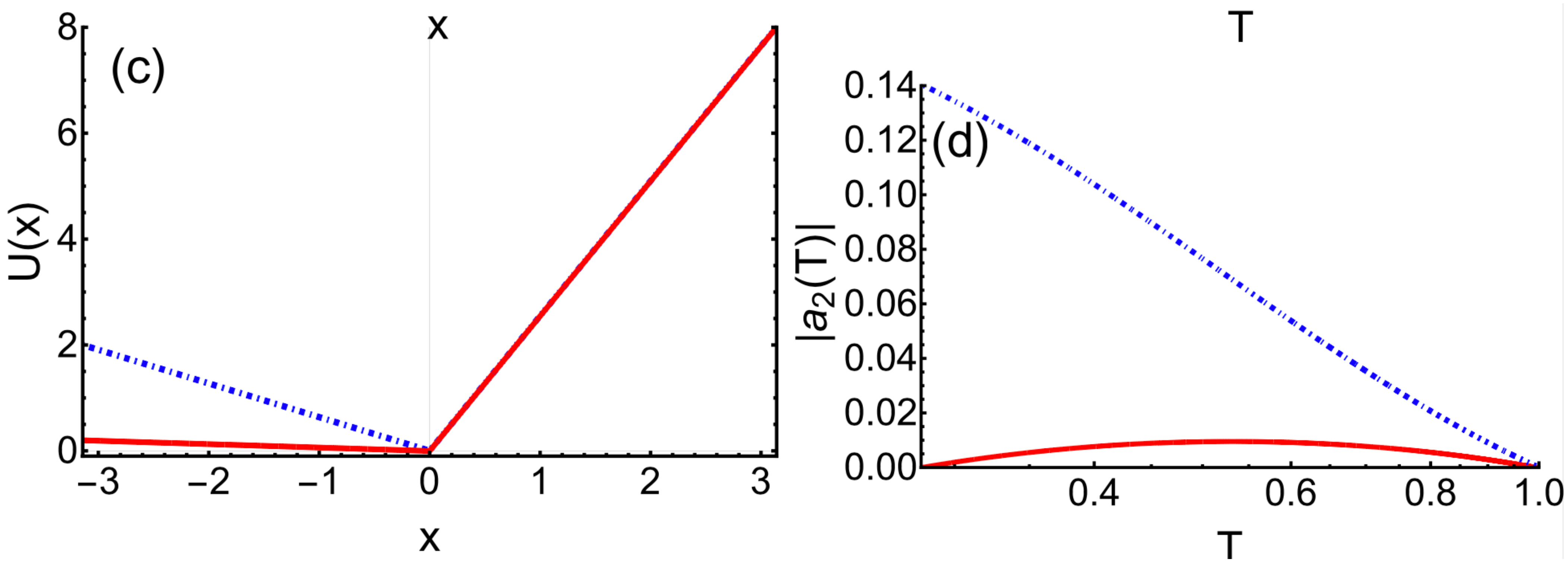


Metastability is not necessary



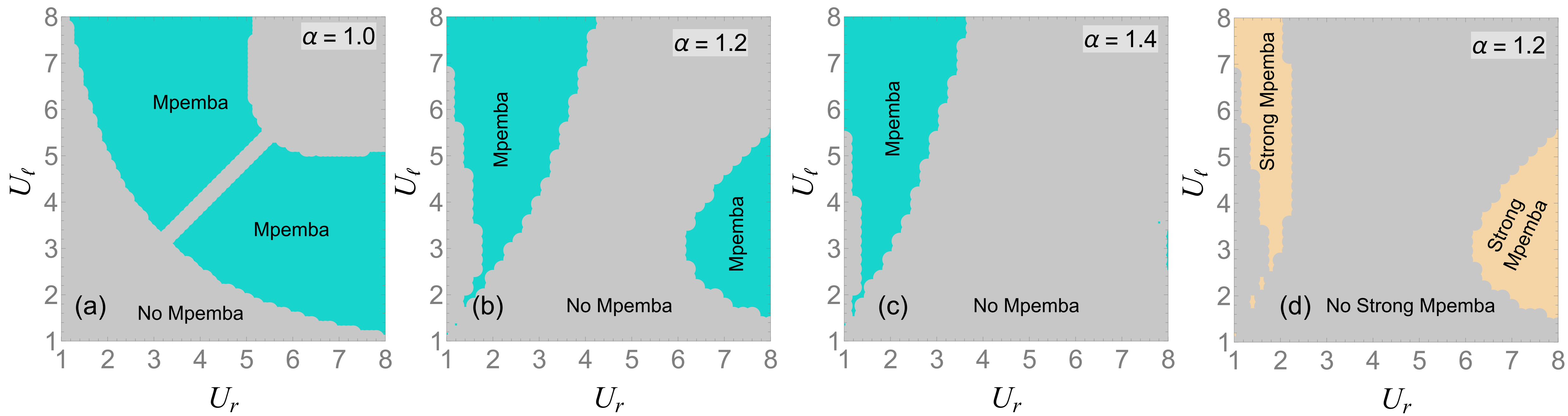


Inverse Mpemba effect

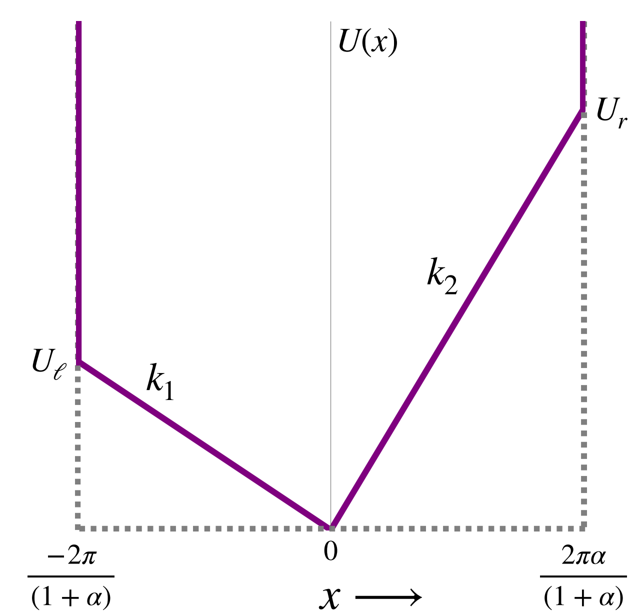


- Showed one example of existence of Mpemba effect without metastable minima
- Is the Mpemba effect generic or does it require fine tuning of potential parameters?

Phase diagrams



- Asymmetry in $U_\ell,\ U_r$ necessary
- More asymmetry leads to less Mpemba effect!
- Strong Mpemba effect is present generically



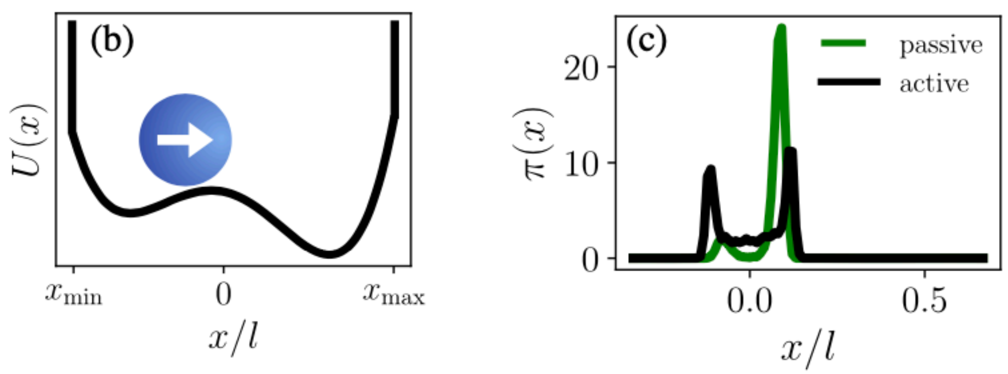
- Three parameters: $U_\ell,\ U_r, \alpha$

Active Brownian particle

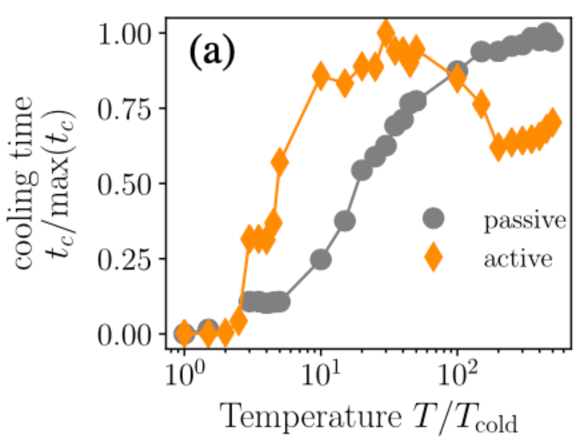
- Particles with an internal energy
- An inherent speed in addition to stochasticity
- Example: birds, bacteria, many biological systems
- A simple model: run and tumble particles (RTP)
- Particles move at constant speed. Direction of velocity orients randomly at constant rate

Role of activity

Studied for double well potential



Boundaries are more populated



Existence of Mpemba effect

Schwarzendahl and Lowen, PRL, 2022

Role of activity

$$\frac{d\tilde{x}}{d\tilde{t}} = \tilde{v}_0 n - \frac{1}{\gamma}\frac{d\tilde{U}}{d\tilde{x}} + \tilde{\eta}(\tilde{t})$$

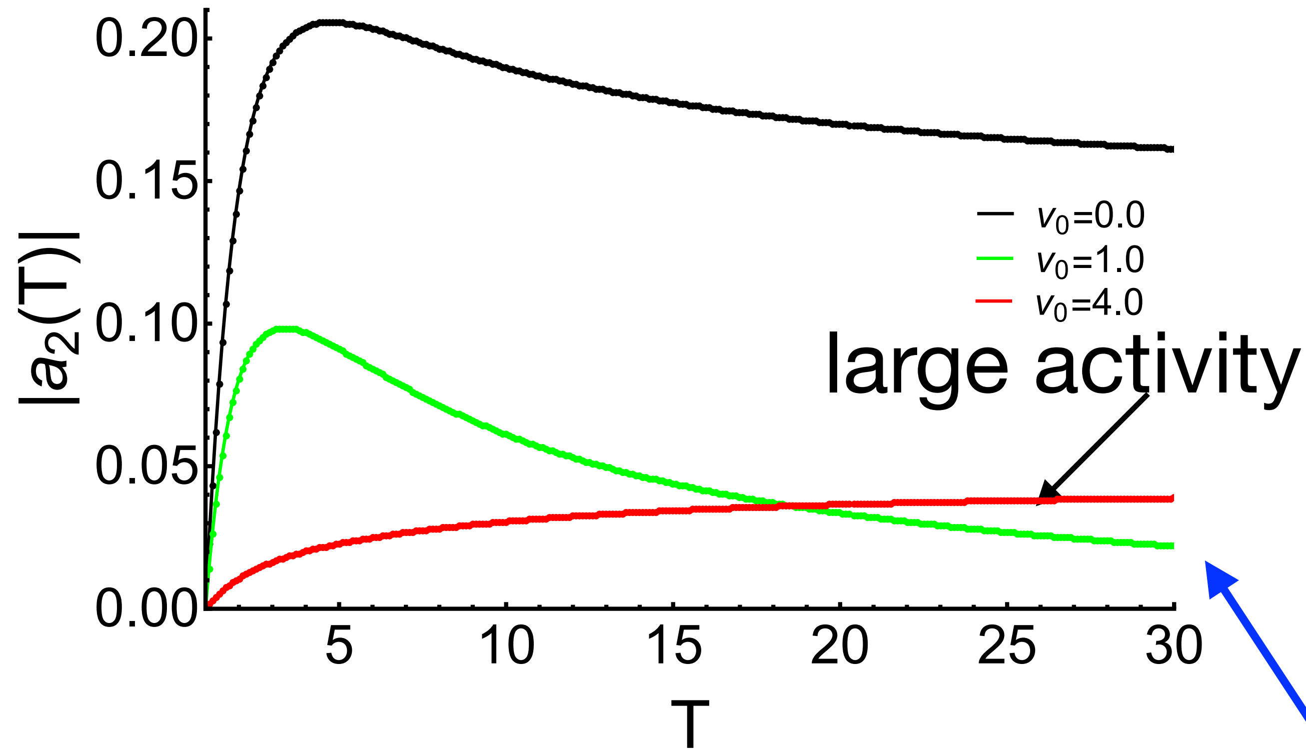
- Direction of velocity flips, introducing a time scale τ_p

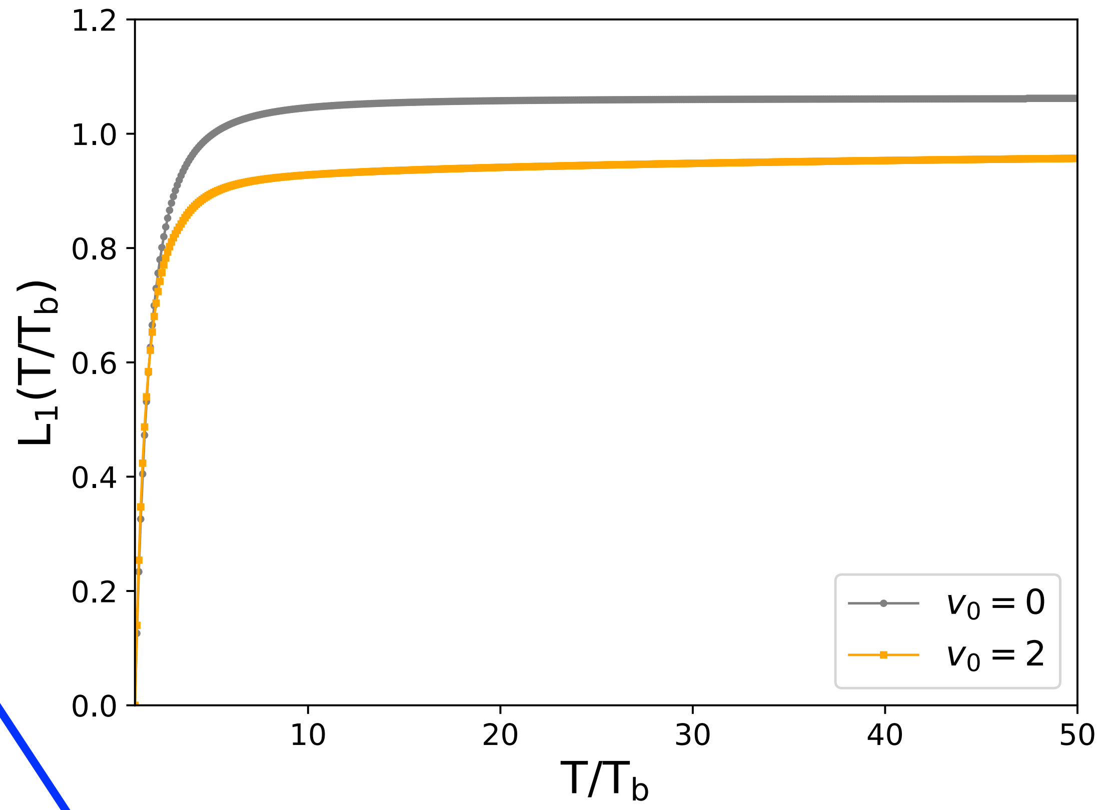
$$\frac{\partial P_l}{\partial t} = v_0 \frac{\partial P_l}{\partial x} + \tau_p \frac{\partial}{\partial x}\left[\frac{dU}{dx}P_l\right] + \tau_p \frac{\partial^2 P_l}{\partial x^2} - P_l + P_r,$$

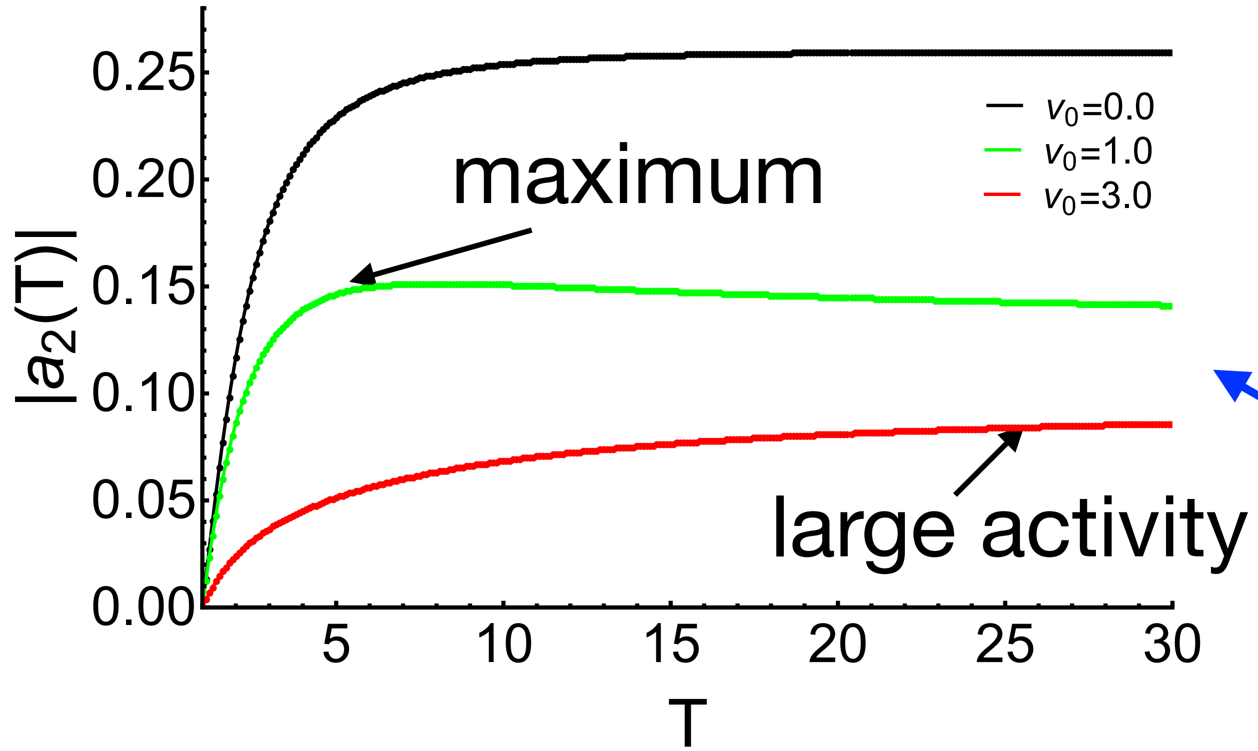
$$\frac{\partial P_r}{\partial t} = -v_0 \frac{\partial P_r}{\partial x} + \tau_p \frac{\partial}{\partial x}\left[\frac{dU}{dx}P_r\right] + \tau_p \frac{\partial^2 P_r}{\partial x^2} - P_r + P_l$$

- Solve numerically

Activity can go either way



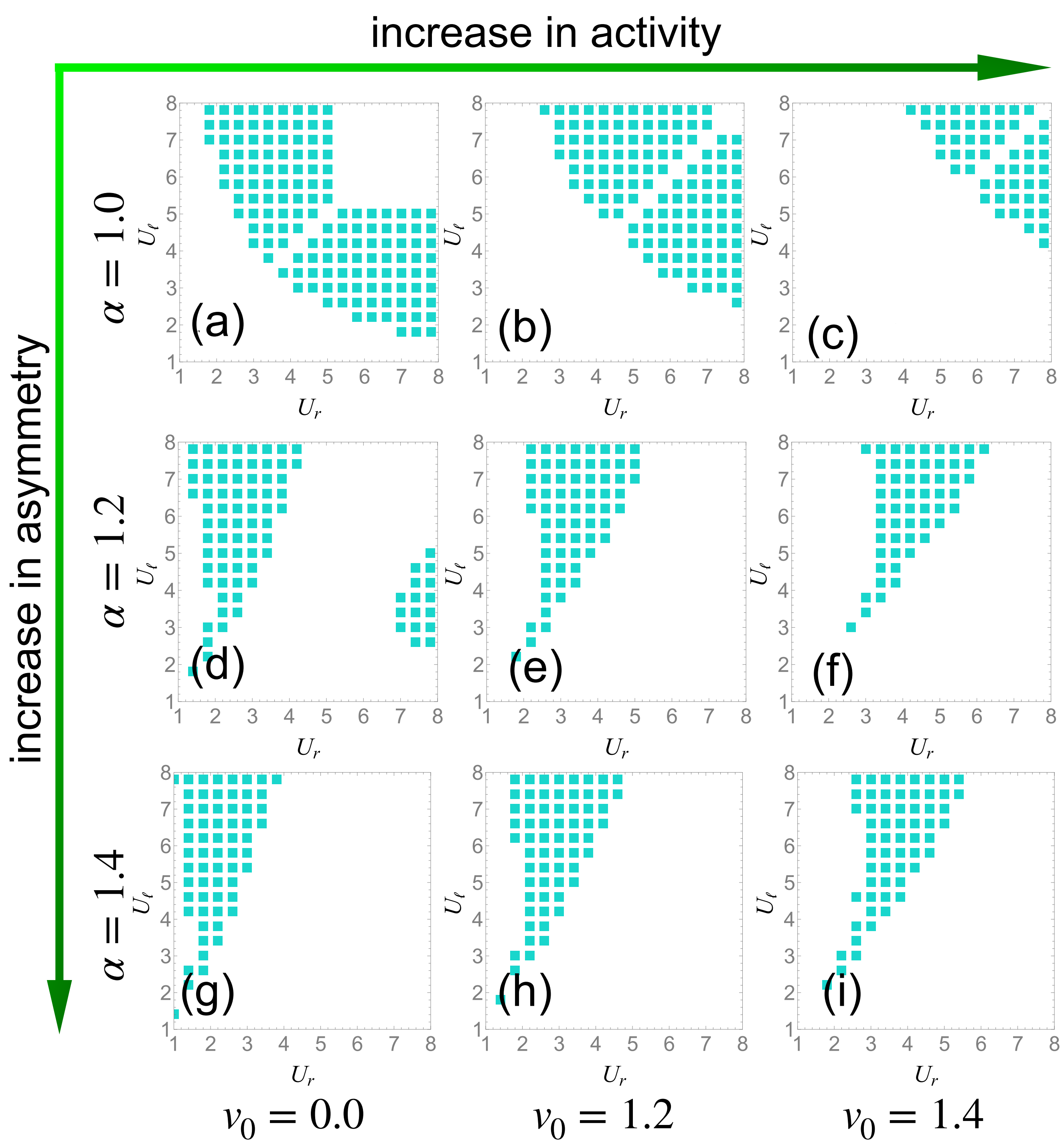




Activity can reduce Mpemba effect

Activity can increase Mpemba effect

Phase diagram: Activity



- Activity can increase or decrease Mpemba effect (see along first row)

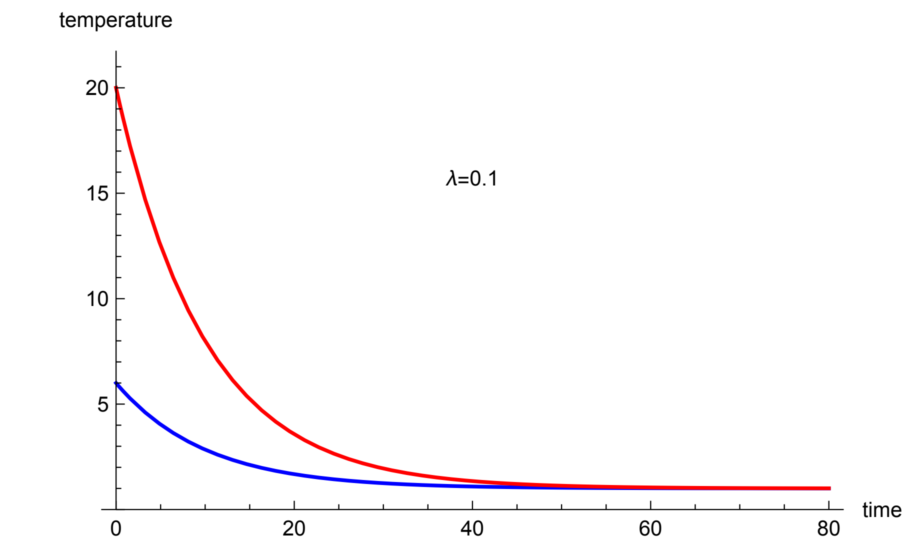
Summary

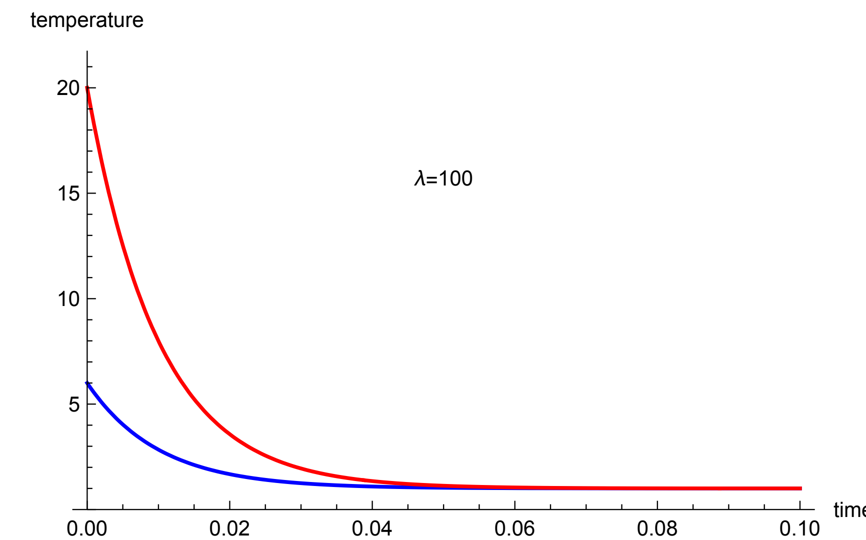
- Mpemba effect a counterintuitive phenomena in systems relaxing to steady states (or equilibrium)
- Brownian particle in a single well potential a minimal model for studying the effect
- Metastability has been an appealing and plausible explanation
- But metastability is not necessary requirement
    - In fact Mpemba effect is generic in single well
    - Also, does not work well for the inverse effect
- Activity can increase/decrease the effect

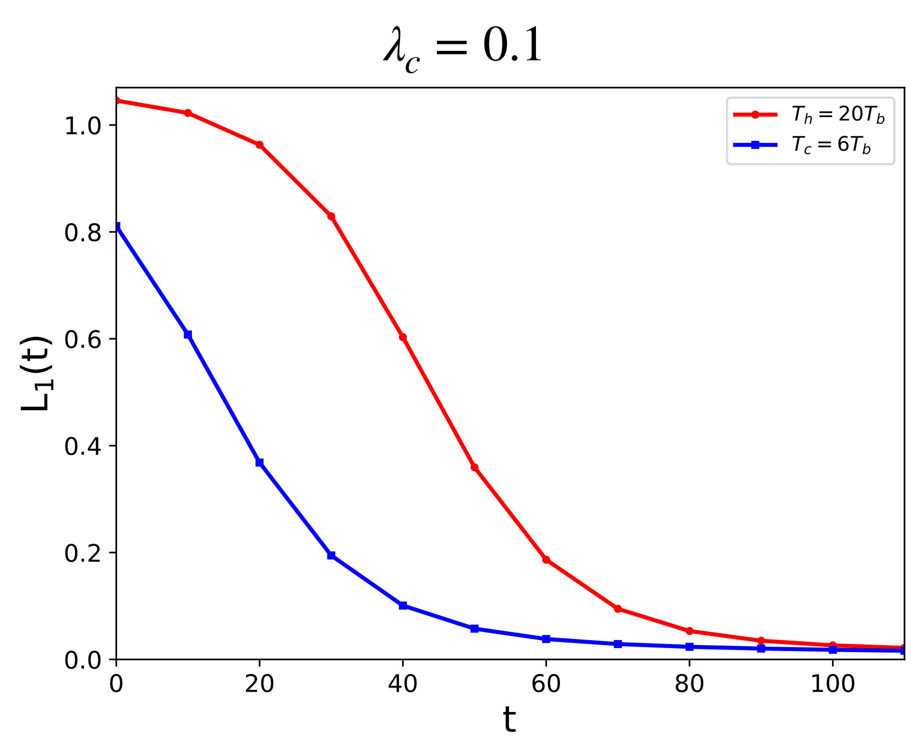
Outlook

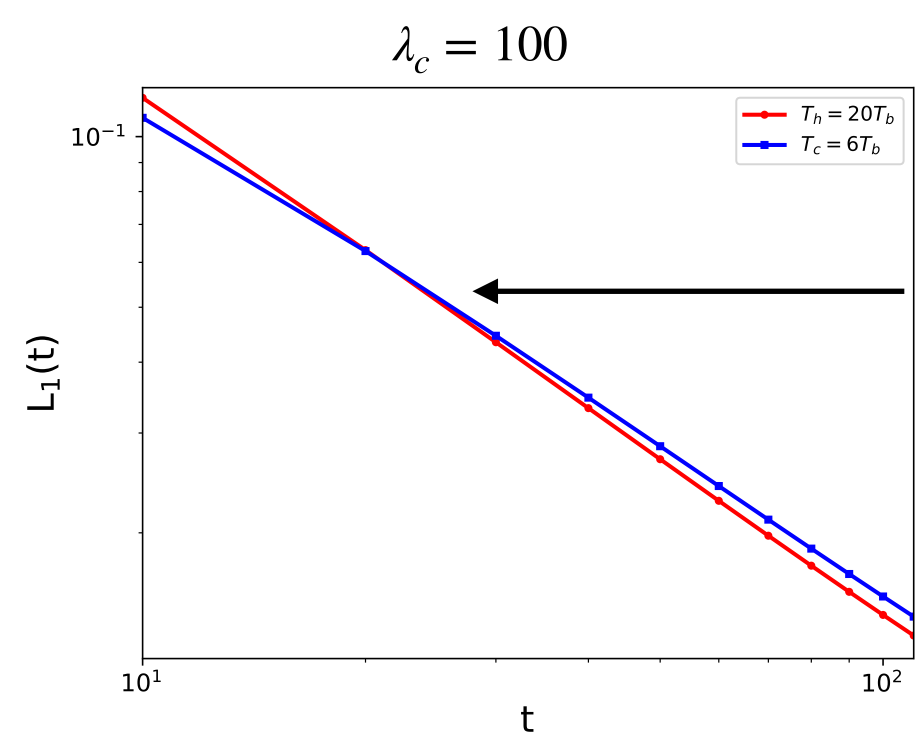
- Single well result unsatisfactory: it would seem that the effect is in some detail of the initial states
- An explanation in terms of entropy production, work extracted, etc?
- What is the role of rate of cooling?
  - Slow cooling $\Longrightarrow$ Newton's law
  - Fast cooling $\Longrightarrow$ Mpemba effect sometime
  - Crossover?

Newton to Mpemba





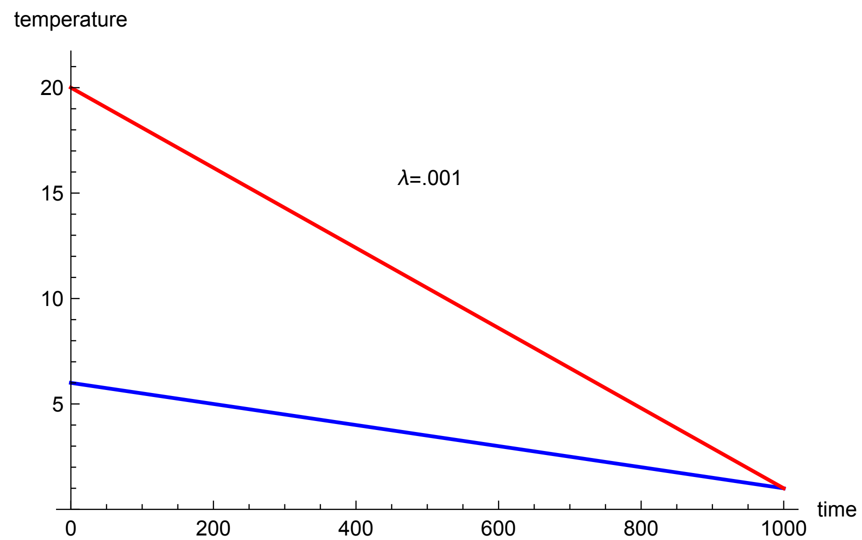


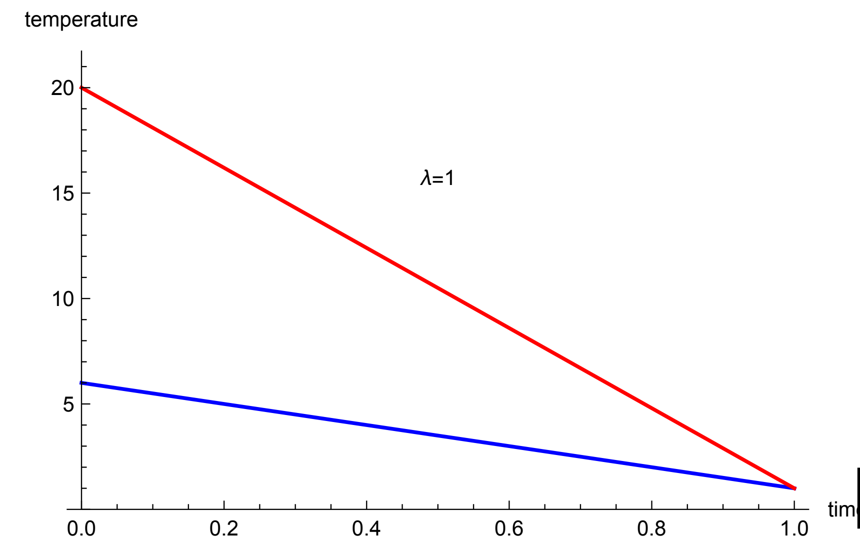


Mpemba present

$$T(t) = 1 + [T(0) - 1]e^{-\lambda_c t}$$

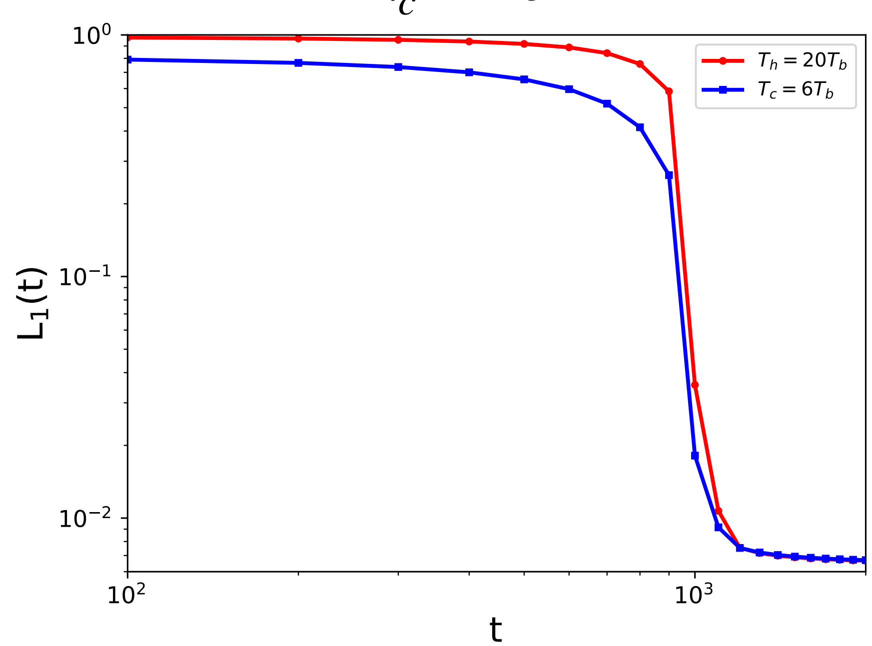
Newton to Mpemba



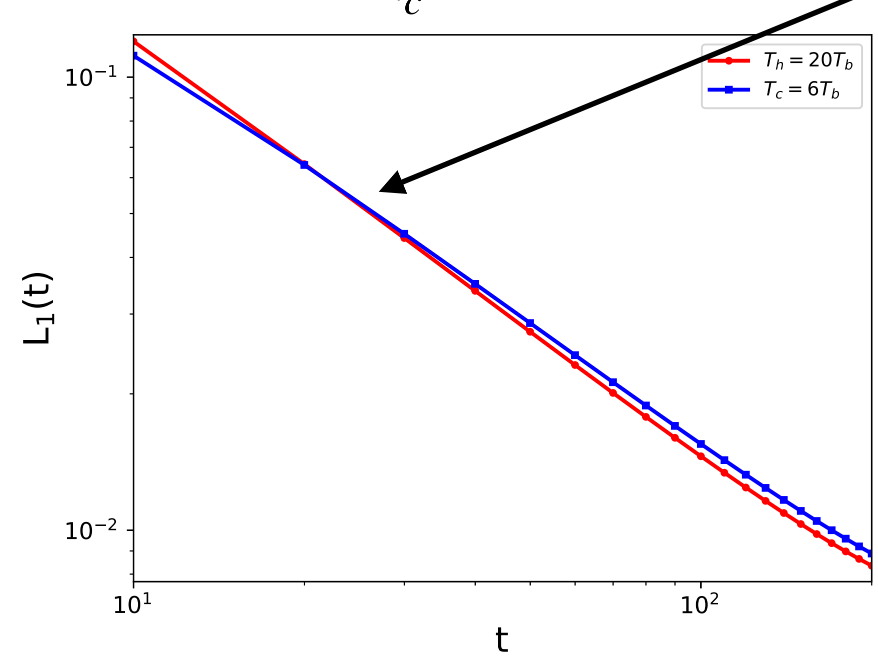


Mpemba present

$\lambda_c = 10^{-3}$



$\lambda_c = 1$



$$T(t) = T(0) - \lambda_c t \left[T(0) - 1\right]$$

Outlook

- Strong Mpemba effect gives a pathway for faster cooling. Heat first and then cool (Teza et al, PRL, 2023)
  - What is the thermodynamic cost?
- What is the particular reason for water? (Is it possible to do experiments in other fluids)