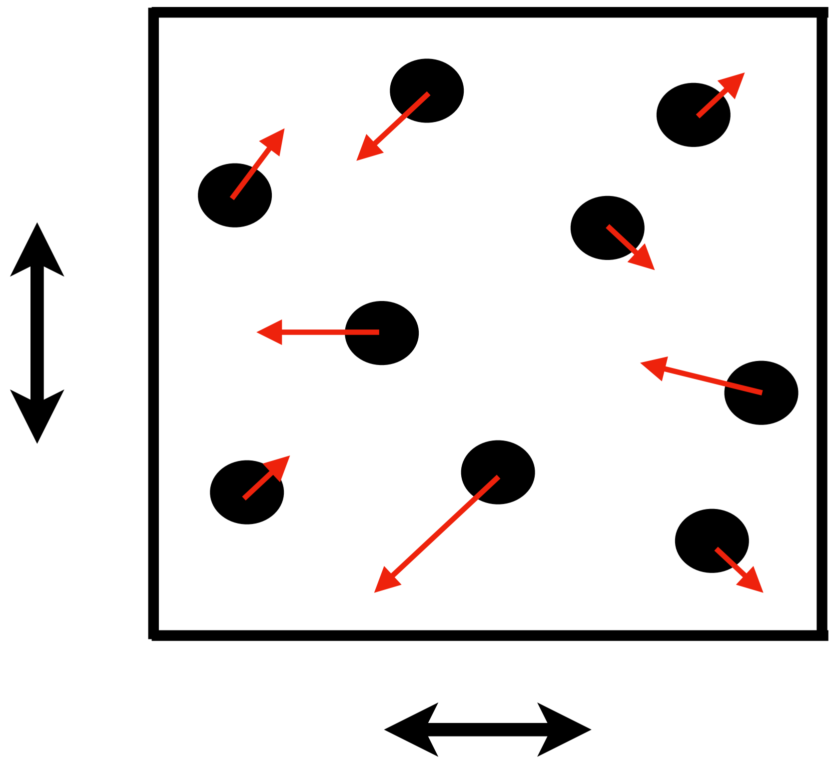

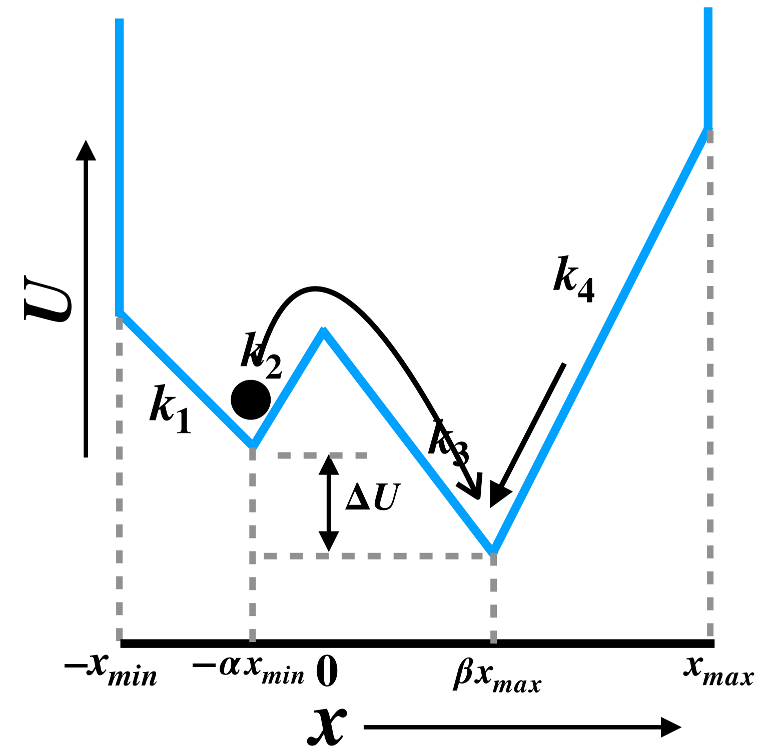

Mpemba effect: An anomalous relaxation phenomenon

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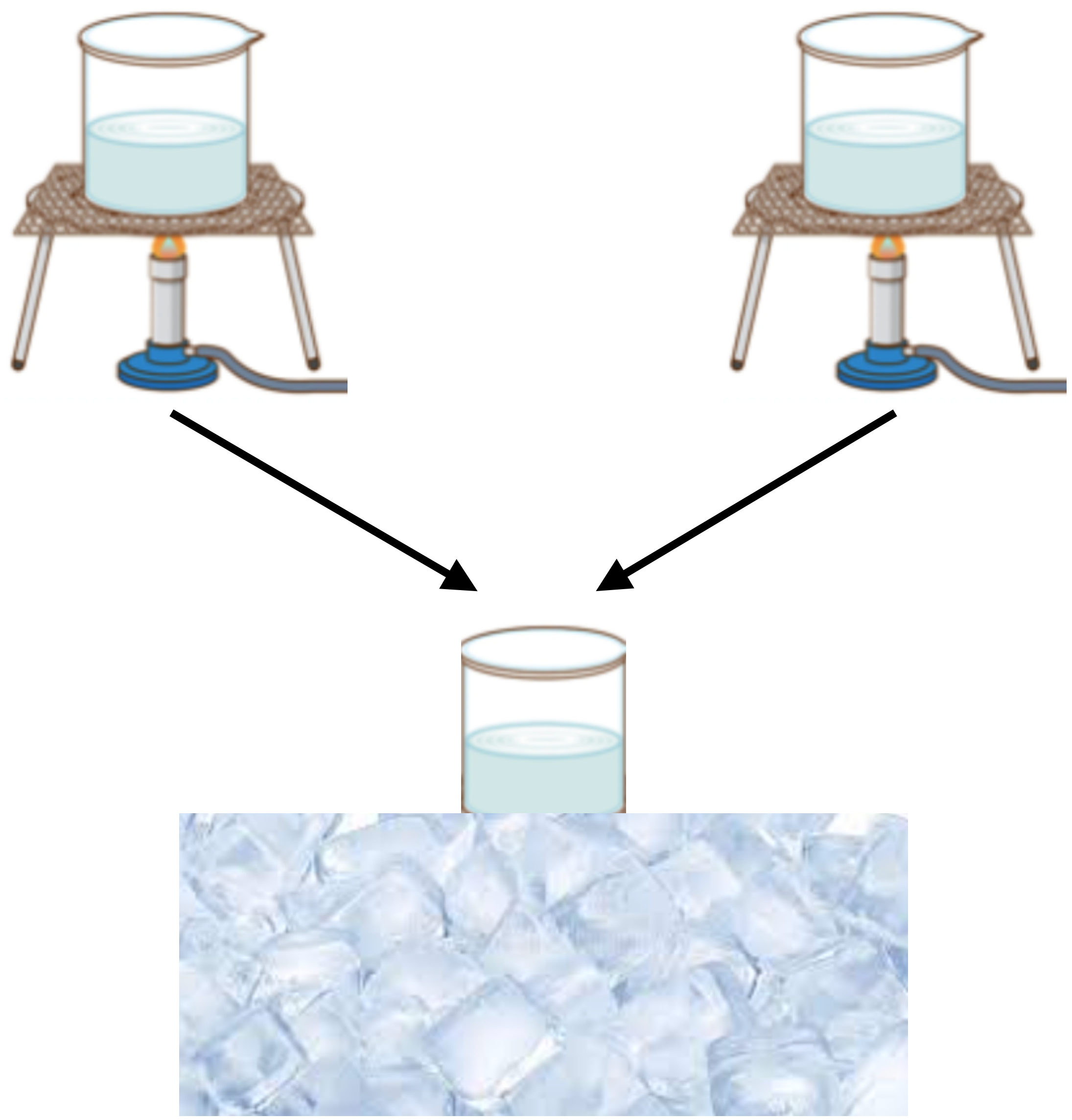
Apurba Biswas (IMSc, Bordeaux)

Cooling two samples

T_c (say 30°) T_h (say 50°)

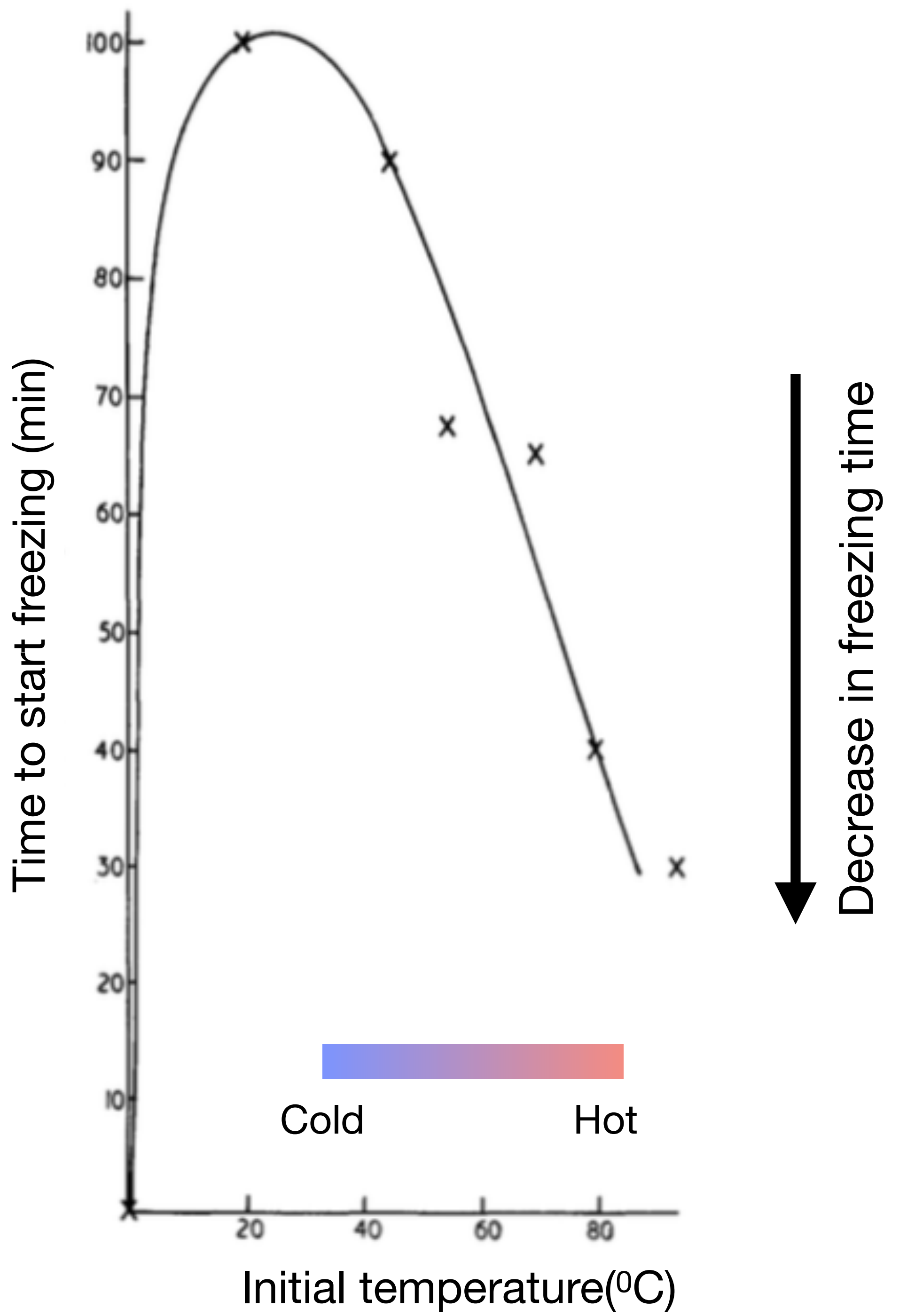


T_f (say 0°)

- Which system cools (or freezes) faster?

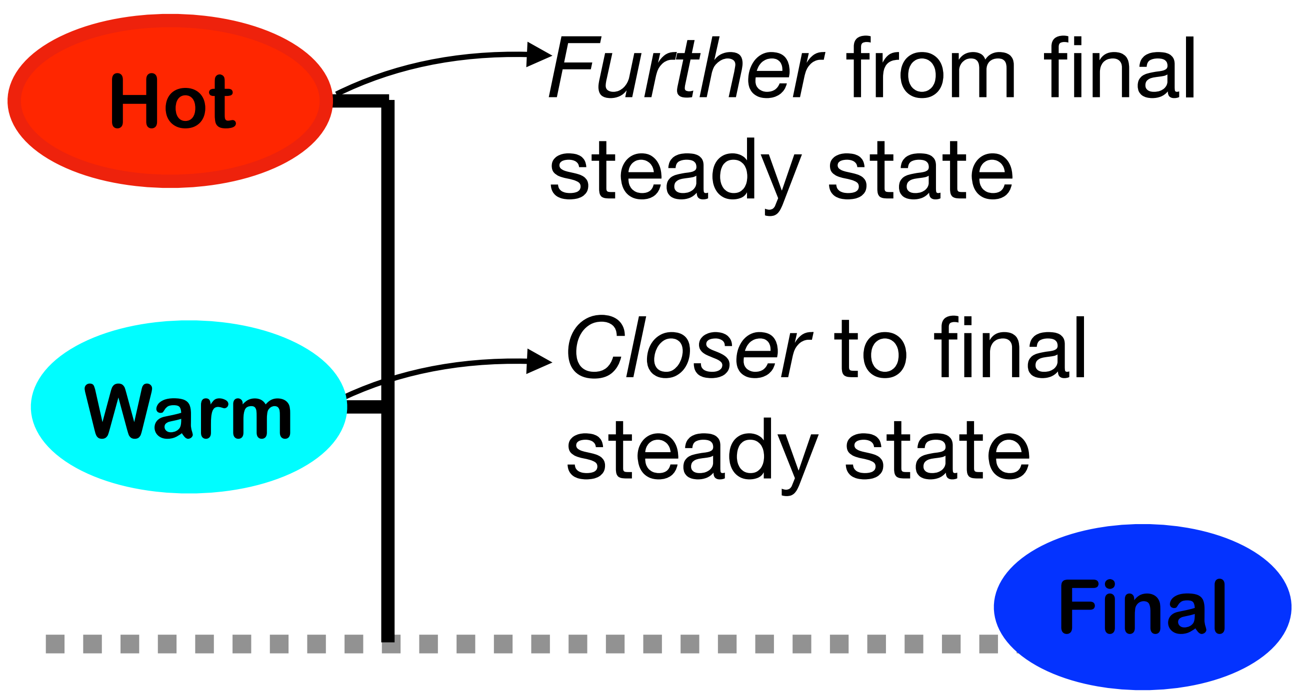
Mpemba effect

- Experiment
  - Take water at different temperatures
  - Put in freezer
  - Measure freezing time
- Hot water freezes faster!
- Multiple reasons proposed
  - Dissolved gases
  - Hydrogen bonding …
- But enough of water



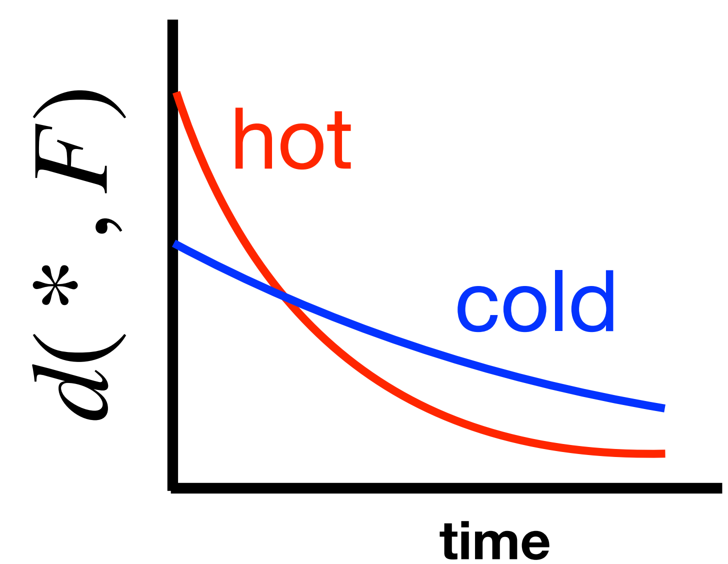
Mpemba et al, Phys. Edu. (1969)

Mpemba effect in a more general scenario

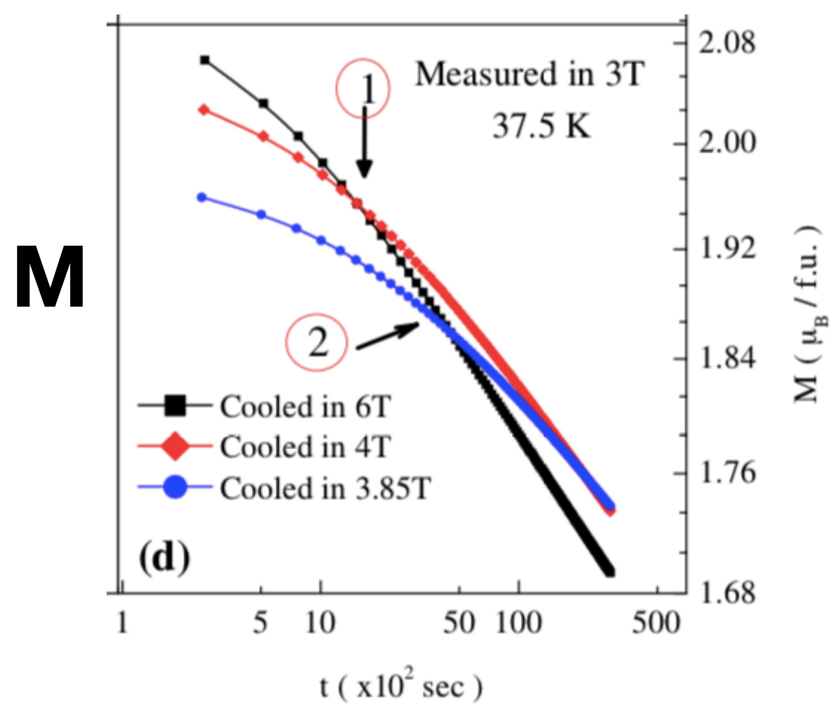


- Quench from initial state to final state
- What cools faster?

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

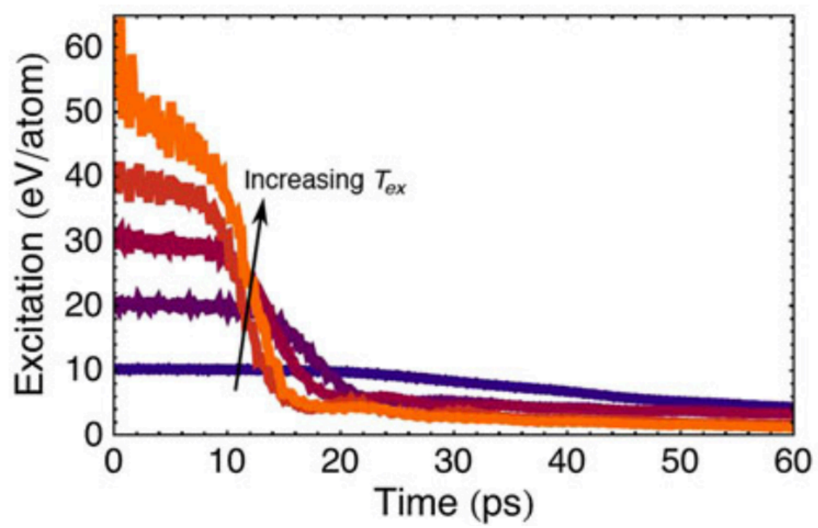


Mpemba effect is generic



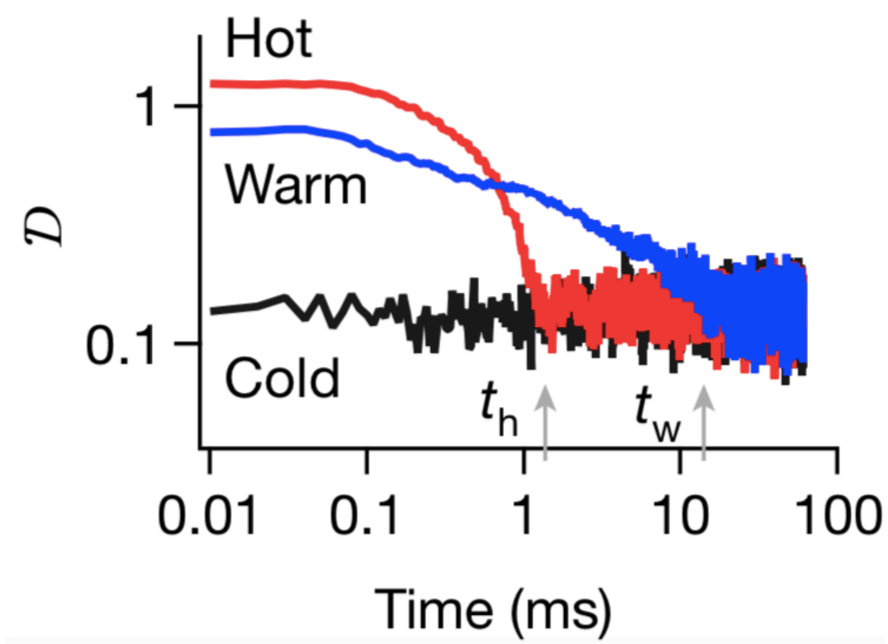
Magneto resistance alloys ($La_{0.5}Ca_{0.5}MnO_3$)

Chaddah et al, arXiv (2010)



Carbon nanotubes

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



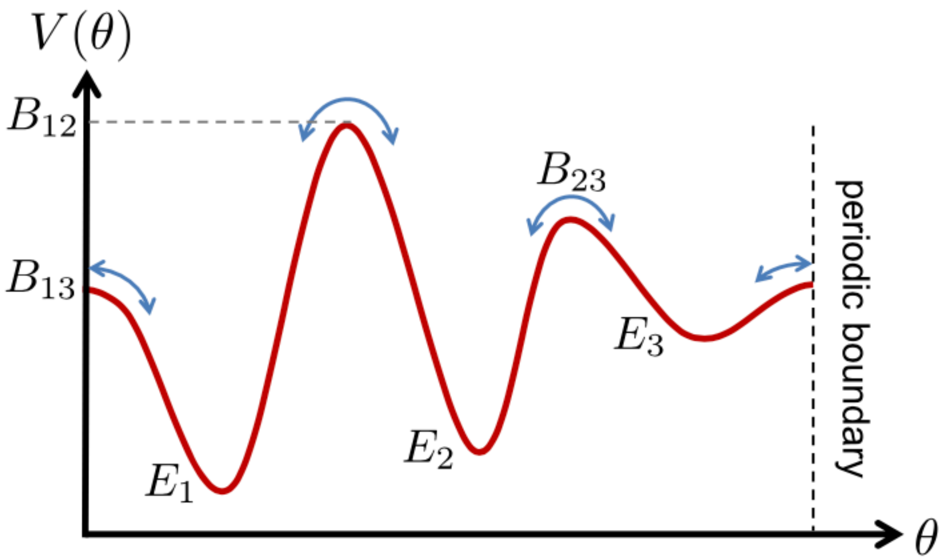
Colloidal systems

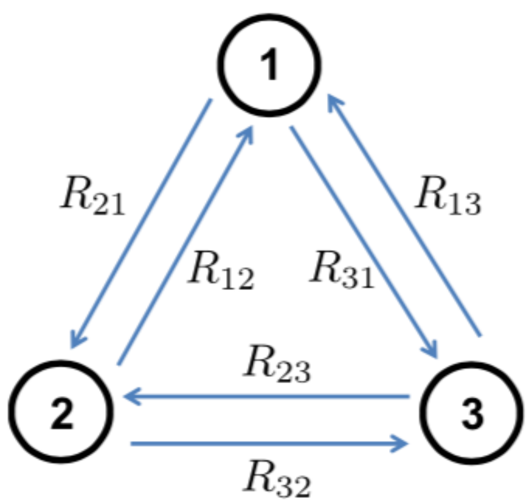
Kumar et al, Nature (2020)

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
  - Analyse them
  - Once understood, increase difficulty bit by bit

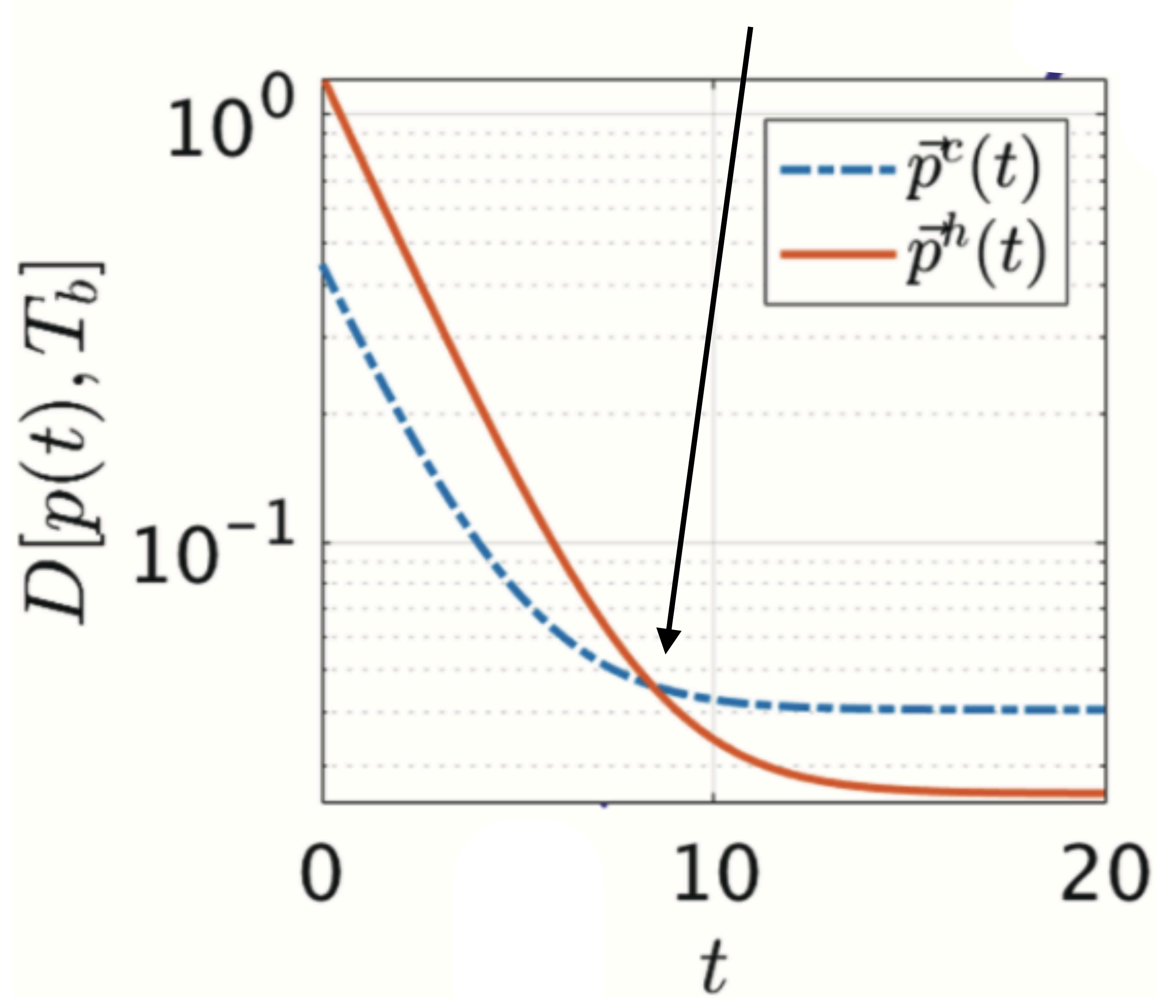
Simple models





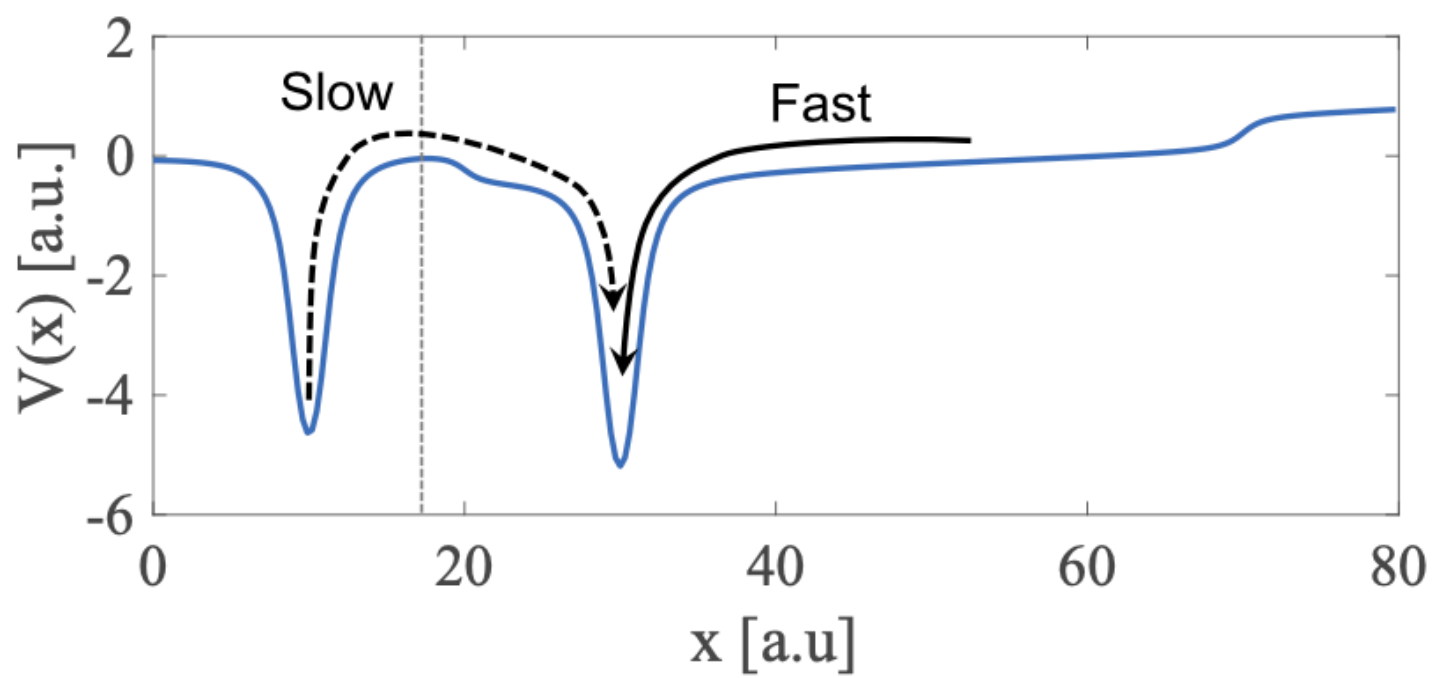
$$R_{ij}(T_b) = \begin{cases} \Gamma e^{-\frac{B_{ij}-E_j}{k_B T_b}} & i \neq j \\ -\sum_{k\neq i} R_{ki} & i = j \end{cases},$$

Crossing of curves



Lu et al, PNAS (2017)

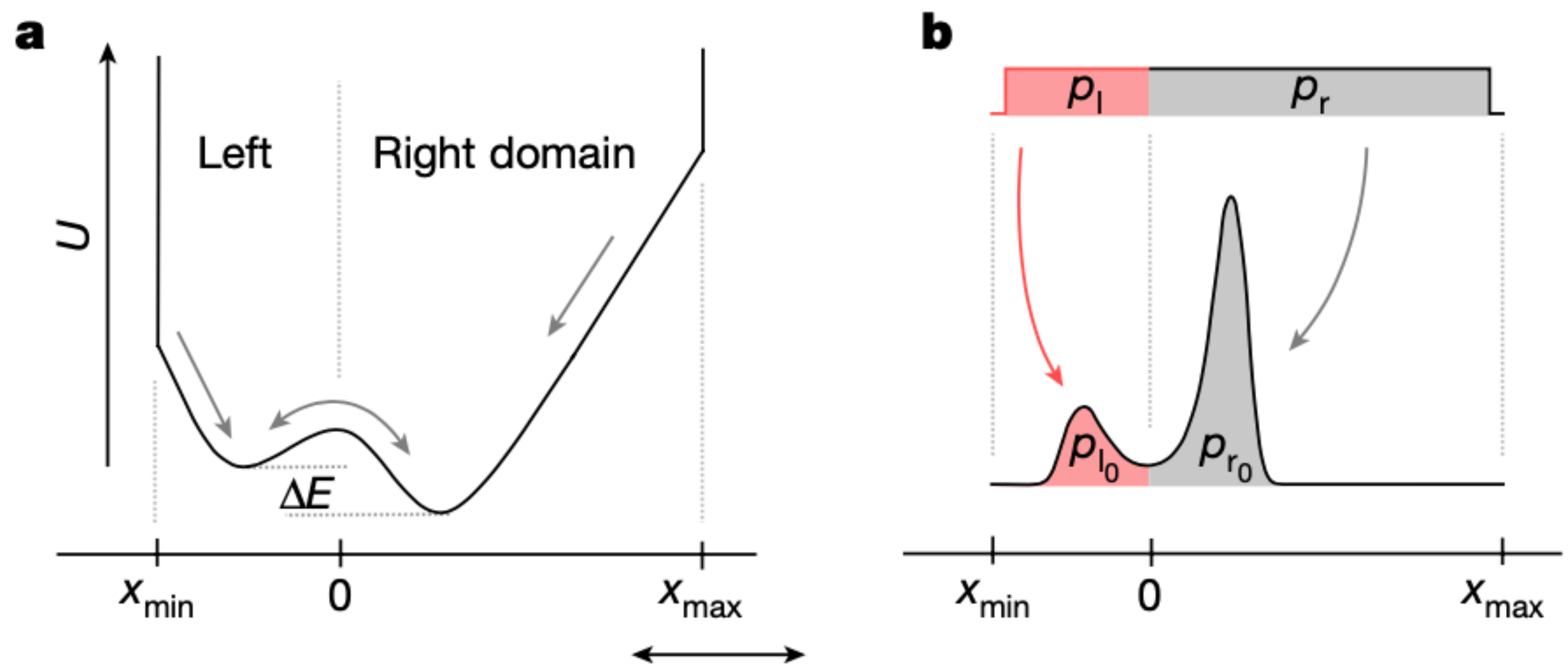
Explanation: metastable states



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

Lu et al, PNAS (2017)

Experiment using metastability: colloidal system

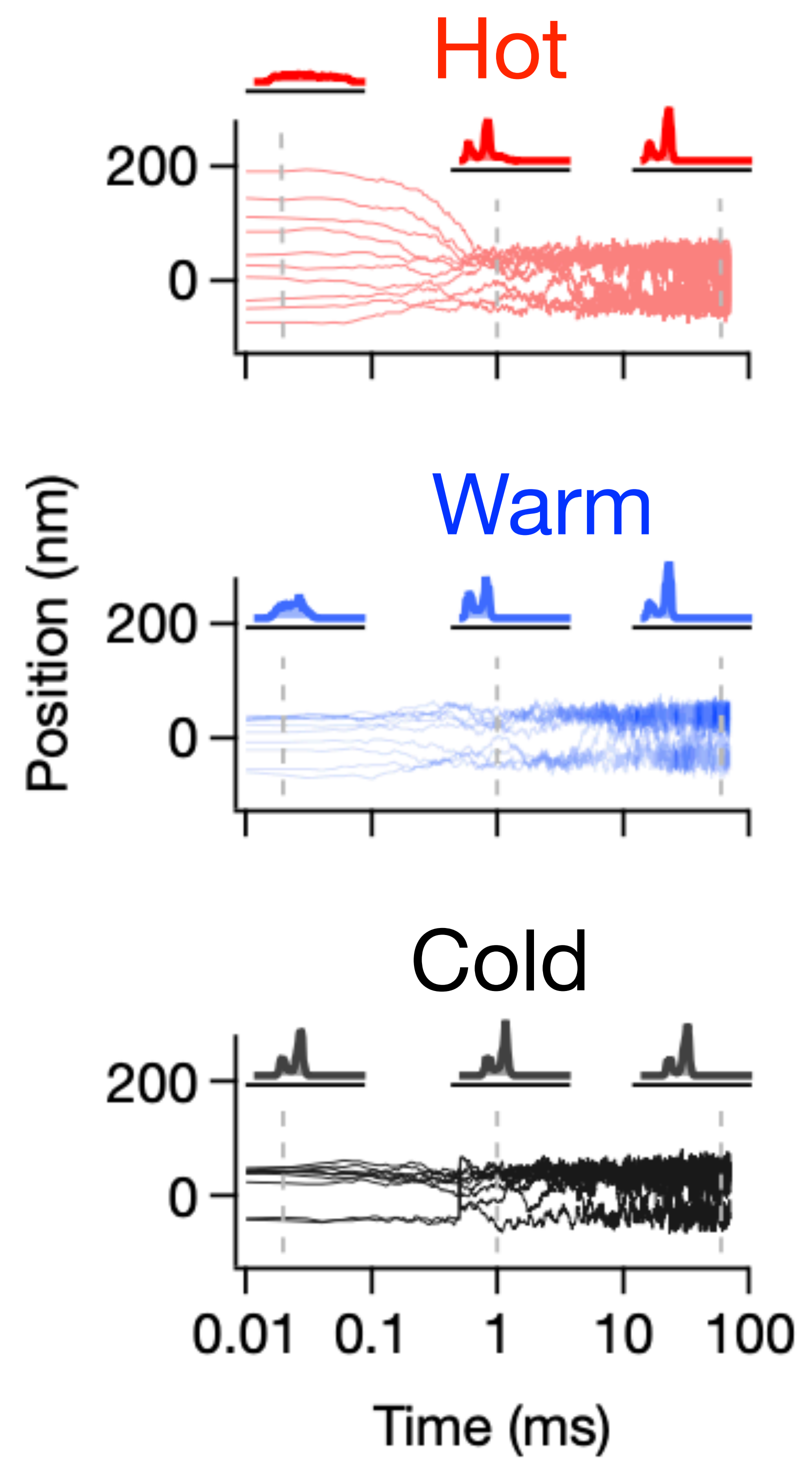


- A brownian particles
- Asymmetric double well
- Quadratic and linear
- Infinite at boundary

Kumar and Bechhoefer, Nature 584 (2020)

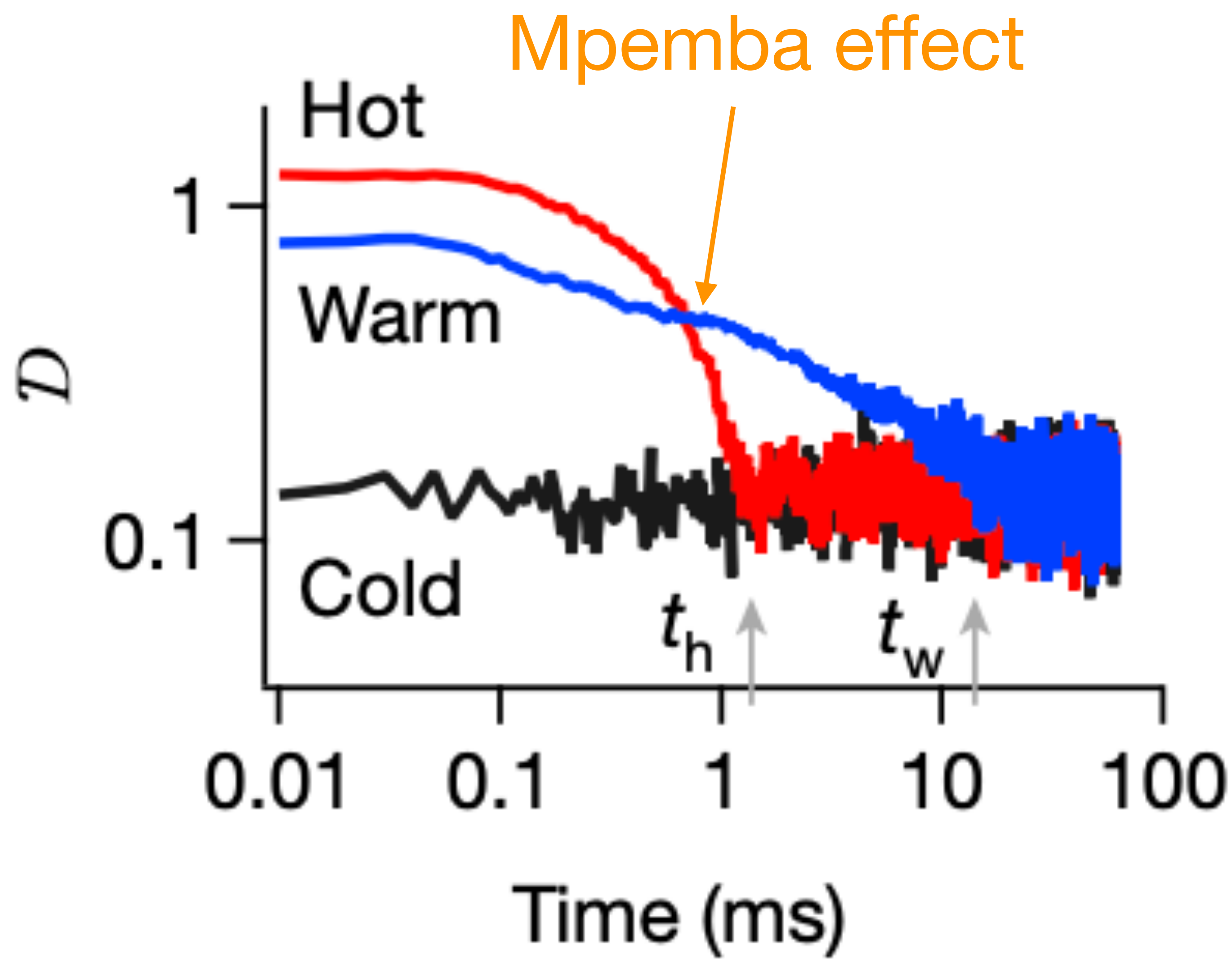
Different quenches

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



Kumar and Bechhoefer, Nature 584 (2020)

Existence of Mpemba effect



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

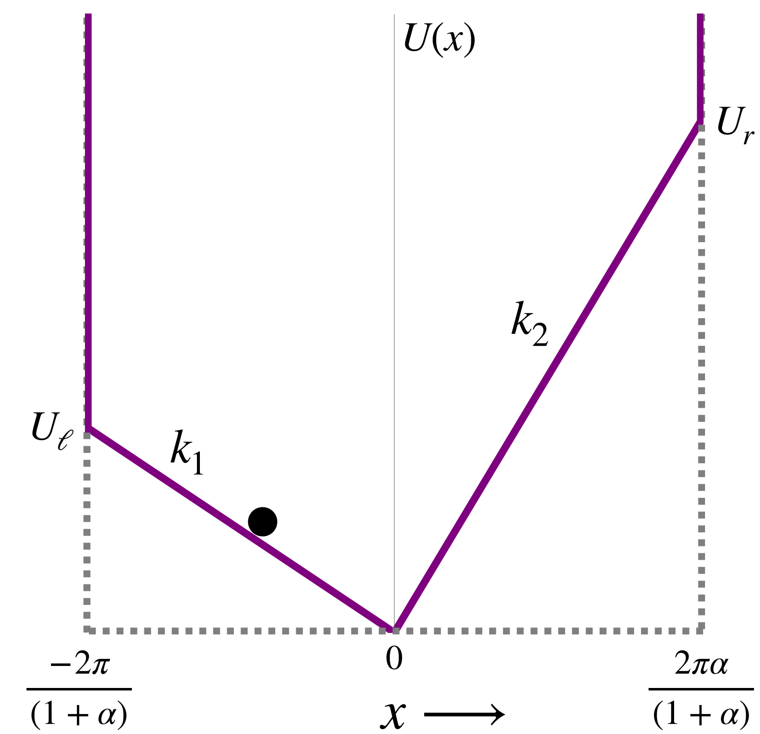
Kumar and Bechhoefer,
Nature 584 (2020)

Questions

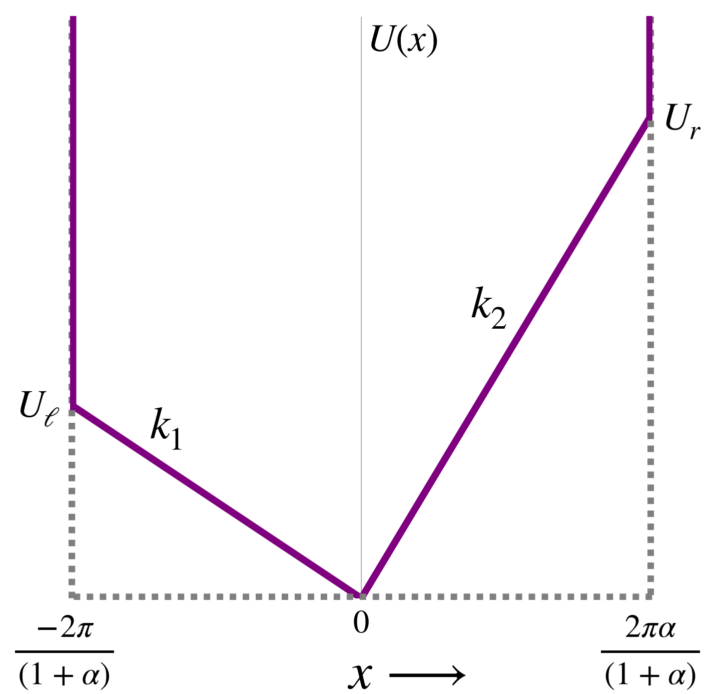
- What is the explanation of Mpemba effect?
  - Metastability?
  - Hidden variables?
  - System specific reasons?
- How sensitive is Mpemba effect to the choice of charactering parameter and distance function? (a_2 versus temperature (say))
- What is the role of activity?
- Given a system, can we predict if Mpemba effect is present without solving/simulating?

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?

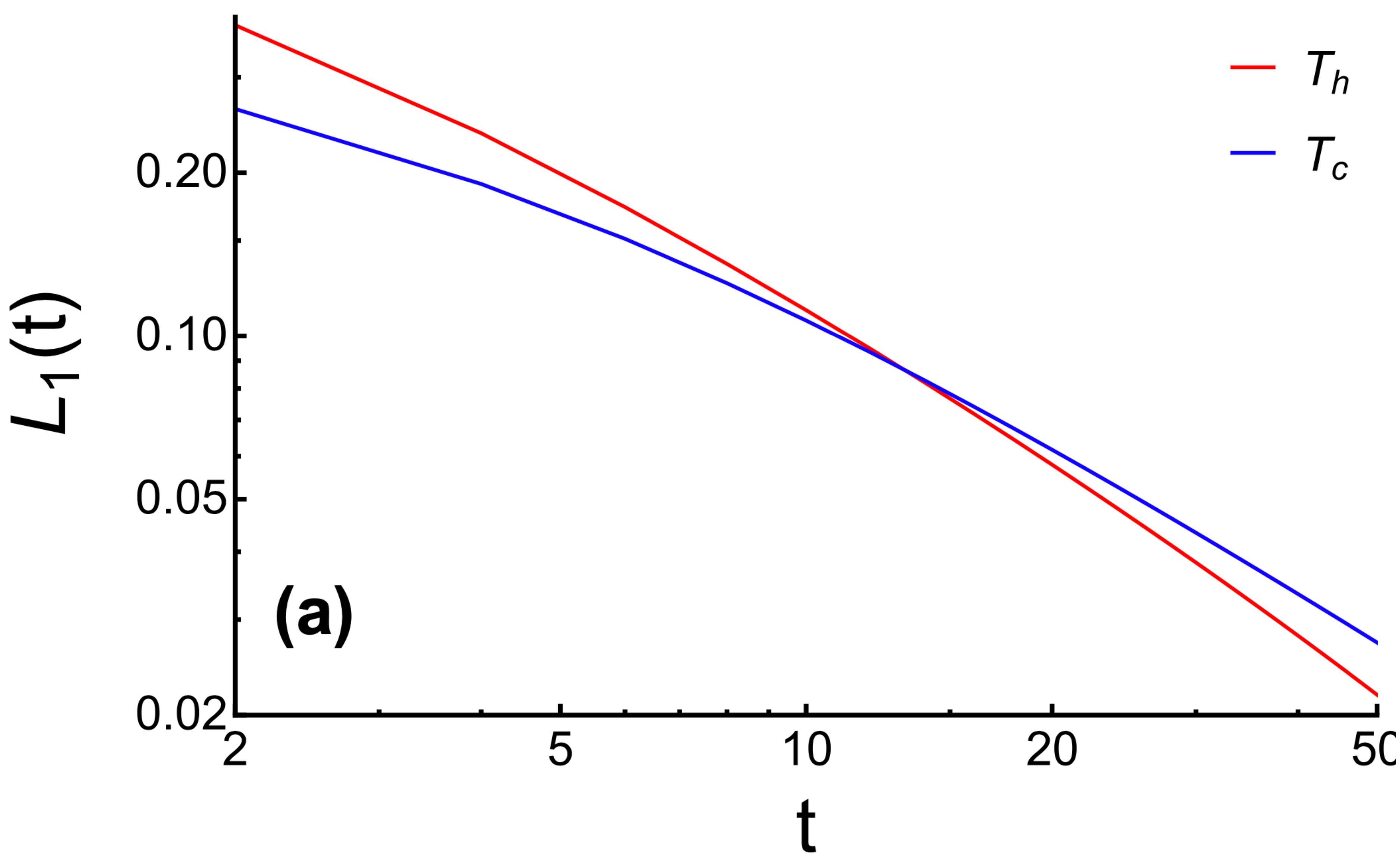


Single particle problem



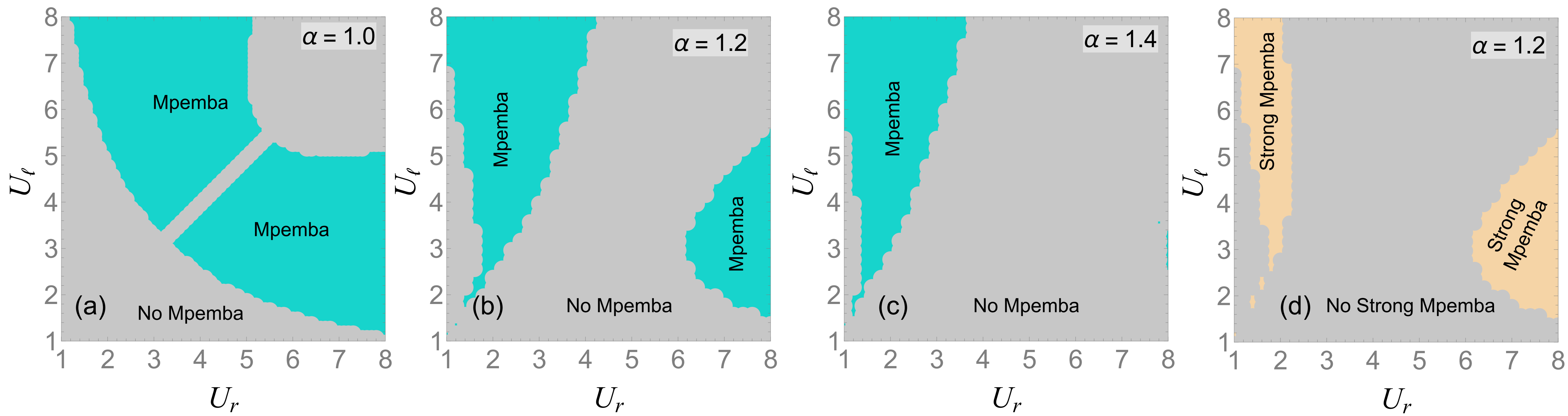
- Over-damped Langevin equation:
$$\gamma \frac{dx}{dt} = -\frac{dU}{dx} + \eta(t)$$
- Corresponding Fokker-Planck description: $$\frac{\partial p}{\partial t} = \frac{\partial}{\partial x}\left[\frac{dU}{dx} p\right] + \frac{\partial^2 p}{\partial x^2}$$
- Solution using eigenspectrum decomposition: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

Crossing of trajectories

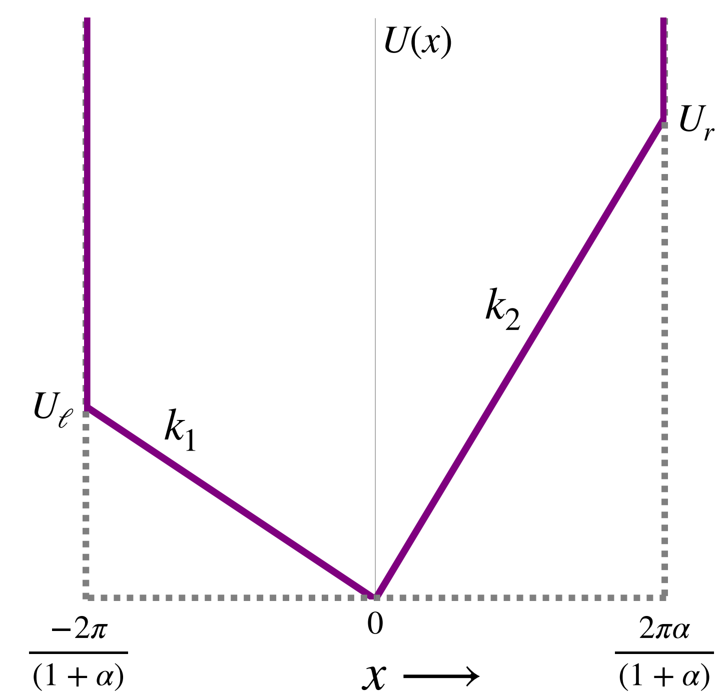


- Showed one example of existence of Mpemba effect without metastable minima
- Is the Mpemba effect generic or does it require fine tuning of potential parameters?

Phase diagrams



- Mpemba effect is generic
- Asymmetry in U_ℓ, U_r necessary
- More asymmetry leads to less Mpemba effect!



Summary

- Mpemba effect a counterintuitive phenomena in systems relaxing to steady states (or equilibrium)
- Metastability has been an appealing and plausible explanation
- But metastability is not necessary requirement
    - In fact Mpemba effect is generic in single well

Outlook

- Single well result unsatisfactory: it would seem that the effect is in some detail of the initial states
- Activity can increase/decrease the effect
- An explanation in terms of entropy production, work extracted, etc?
- 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)

People and References

Apurba Biswas (Bordeaux)

V. V. Prasad (Cochin University)

Oren Raz (Weizmann)

Arnab Pal (IMSc)

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