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Mechanism of Mpemba Effect in overdamped system

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2026.03.18
Mini workshop

Mpemba effect

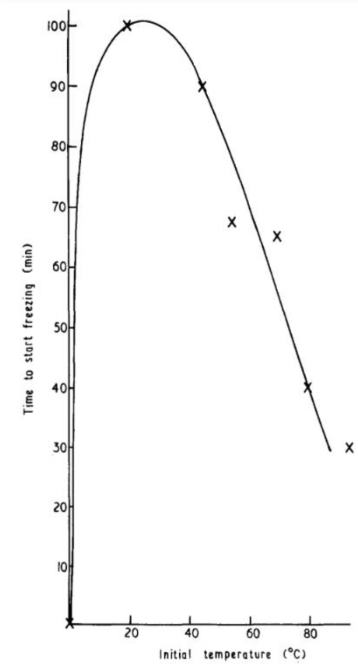
Erasto Mpemba (1950-2023)

Cool?

E B Mpemba† and D G Osborne‡
† College of African Wildlife Management
Moshi Tanzania
‡ University College Dar es Salaam
Tanzania

Phys. educ. **4**, 172

I asked: "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?" He first

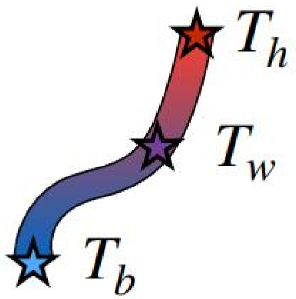


Hot water can freeze faster than warm water, when quenched in the same cooler bath

Why a paradox?

Cooling: Identical systems prepared at T_h and T_w, and coupled to a bath with T_b

$$T_\mathrm{h} > T_\mathrm{w} > T_\mathrm{b}$$

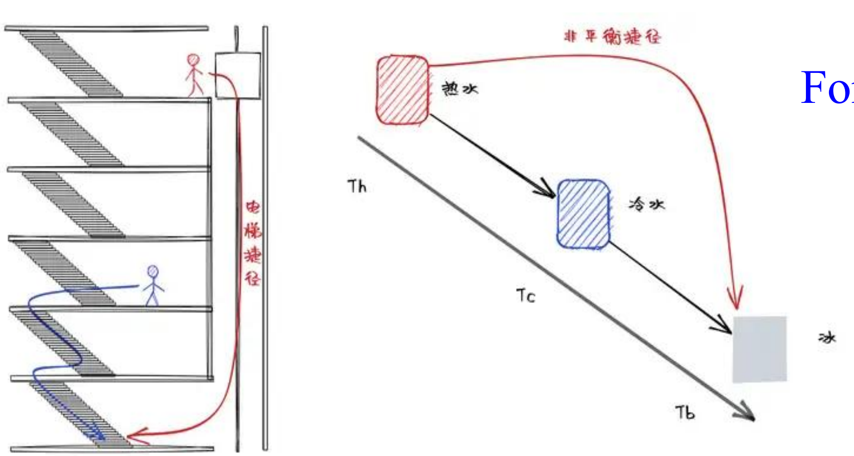


Newton cooling law

$$T(t) = T(0)e^{-t/\tau}$$

the timescale τ is proportional to the heat capacity

Slow cooling: temperature decreases through all intermediate values



Zhihu, Shiling Liang

For quench process, there are nonequilirium shortcuts

like elevator

what mechanism induce the shortcut?

Mpemba effect

Too many explanations for
Water→Ice

- Evaporation
- Supercooling
- Convection
- Heat exchange
- Frost on bottom
- Hydrogen bond

....

Observation in other system

- Granular fluids
- Polymers
- Spin glasses
- Cold gassed
- Nanotube resonators
- Magnetic system

......

Is there a universal / general / illuminating explanation?

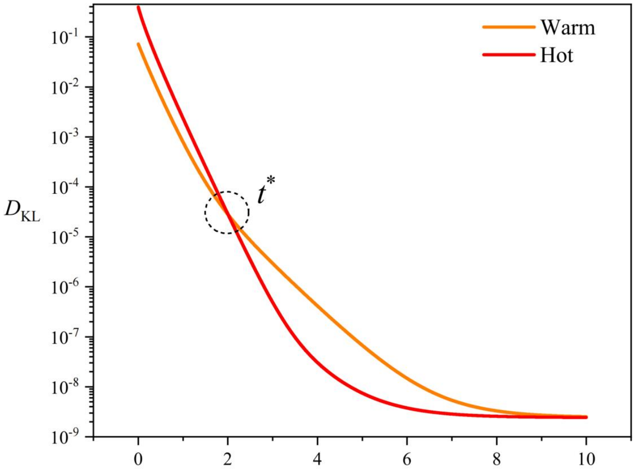
Philip Ball, Physics World, 2006

From the perspective of stochastic thermodynamics

Z. Lu and O. Raz, PNAS **144**, 5803 (2017)

Markov master equation

$$\partial_t p = \mathcal{W} p$$



distance function with final state

$$D[p(t), \pi(T_{\rm b})]$$

such as Kullback-Leibler divergence

$$D_{\rm KL} = \int p(x,t) \ln[p(x,t)/\pi(x,T_{\rm b})] dx$$

Definition of Mpemba effect

$$\text{for } D[p_{\rm h}(0), \pi(T_{\rm b})] > D[p_{\rm w}(0), \pi(T_{\rm b})]$$

$$\exists t^* \text{ such that for all } t > t^*\text{: } D[p_{\rm h}(t), \pi(T_{\rm b})] < D[p_{\rm w}(t), \pi(T_{\rm b})]$$

From the perspective of stochastic thermodynamics

Z. Lu and O. Raz, PNAS **144**, 5803 (2017)

$$\partial_t p = \mathcal{W} p$$

$$\mathcal{W} r_n(x) = \lambda_n r_n(x)$$

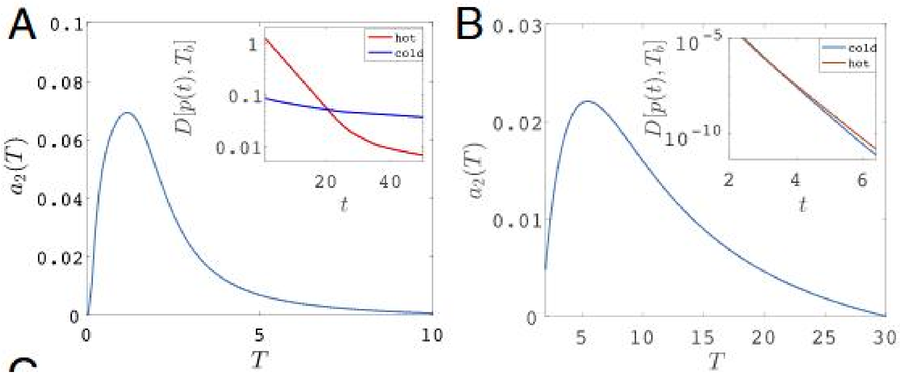
$$\mathcal{W}^\dagger l_n(x) = \lambda_n l_n(x)$$

$$p(x,t) \approx \pi(T_\mathrm{b}, x) + a_2 r_2 e^{-\lambda_2 t}$$

$$a_n = \int dx\, l_n(x) p(x,0)$$

Sufficient Condition for Mpemba effect

for $T_\mathrm{i}^\mathrm{h} > T_\mathrm{i}^\mathrm{w} > T_\mathrm{b}$ we have $|a_2^\mathrm{h}| < |a_2^\mathrm{w}|$ $\quad \exists T_i \; s.t. \; \frac{da_2}{dT_i} = 0$



Quantum Mpemba effect

VIEWPOINT

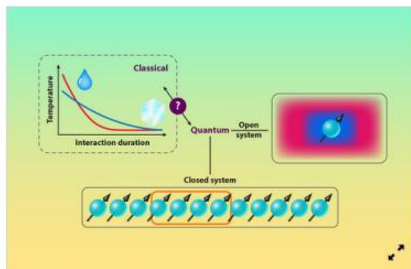
PDF Version

Exploring Quantum Mpemba Effects

Ulrich Warring
Institute of Physics, University of Freiburg, Freiburg, Germany

July 1, 2024 • *Physics* 17, 105

In the Mpemba effect, a warm liquid freezes faster than a cold one. Three studies investigate quantum versions of this effect, challenging our understanding of quantum thermodynamics.



APS/Carin Cain

Figure 1: (Top left) Under specific conditions, hot water (red curve) can freeze faster than cold water (blue curve) when interacting with an external environment. This classical phenomenon is known as the Mpemba effect. (Right) Aharony Shapira and colleagues studied an inverse quantum Mpemba-like effect in an open quantum system, consisting of a single cold trapped ion, interacting with a warm external environment [3]. (Bottom) Joshi and colleagues studied a quantum Mpemba-like effect in subsystems of a closed quantum system, consisting of 12 interacting trapped ions [4]. Lastly, Rylands and colleagues theoretically studied the microscopic mechanisms driving quantum Mpemba-like effects in closed quantum systems [5]. A remaining question is how to establish a link between these classical and quantum phenomena.

Under certain conditions, warm water can freeze faster than cold water. This phenomenon was named the Mpemba effect after Erasto Mpemba, a Tanzanian high schooler who described the effect in the 1960s [1]. The phenomenon

Observing the Quantum Mpemba Effect in Quantum Simulations
Lata Kh. Joshi, Johannes Franke, Aniket Rath, Filiberto Ares, Sara Murciano, Florian Kranzl, Rainer Blatt, Peter Zoller, Benoît Vermersch, Pasquale Calabrese, Christian F. Roos, and Manoj K. Joshi
Phys. Rev. Lett. 133, 010402 (2024)
Published July 1, 2024
Read PDF

Inverse Mpemba Effect Demonstrated on a Single Trapped Ion Qubit
Shahaf Aharony Shapira, Yotam Shapira, Jovan Markov, Gianluca Teza, Nitzan Akerman, Oren Raz, and Roee Ozeri
Phys. Rev. Lett. 133, 010403 (2024)
Published July 1, 2024
Read PDF

Microscopic Origin of the Quantum Mpemba Effect in Integrable Systems
Colin Rylands, Katja Klobas, Filiberto Ares, Pasquale Calabrese, Sara Murciano, and Bruno Bertini
Phys. Rev. Lett. 133, 010401 (2024)
Published July 1, 2024
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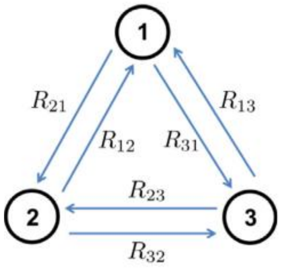
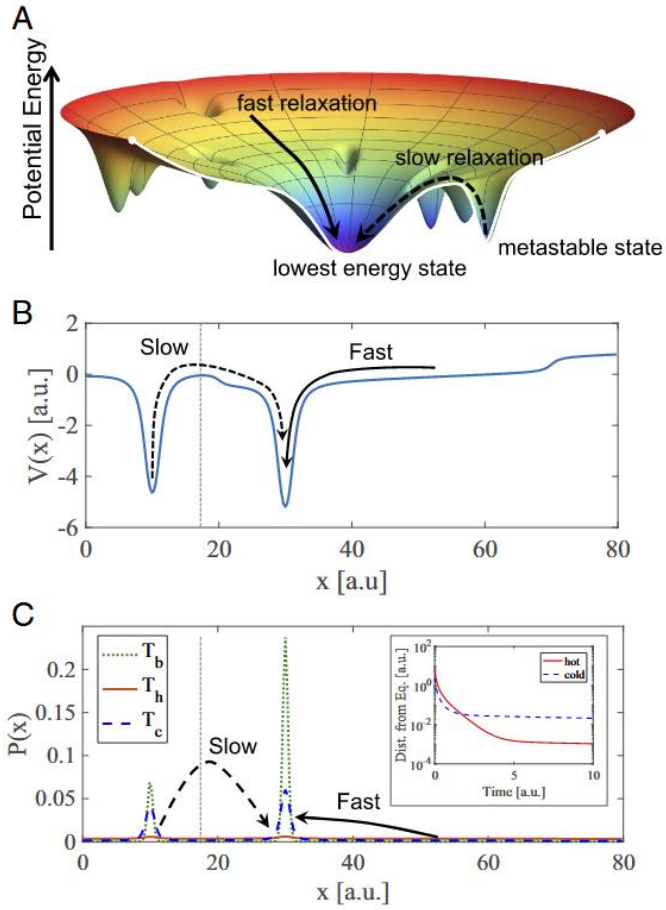
- Distance function
- Construct nonequilibrium initial state
- Strong Mpemba effect

……

From the perspective of stochastic thermodynamics

Z. Lu and O. Raz, PNAS **144**, 5803 (2017)





The mechanism is the metastable state (for finite state system)

heuristic for continuous-state systems

the warm initial state is trapped by the metastable state

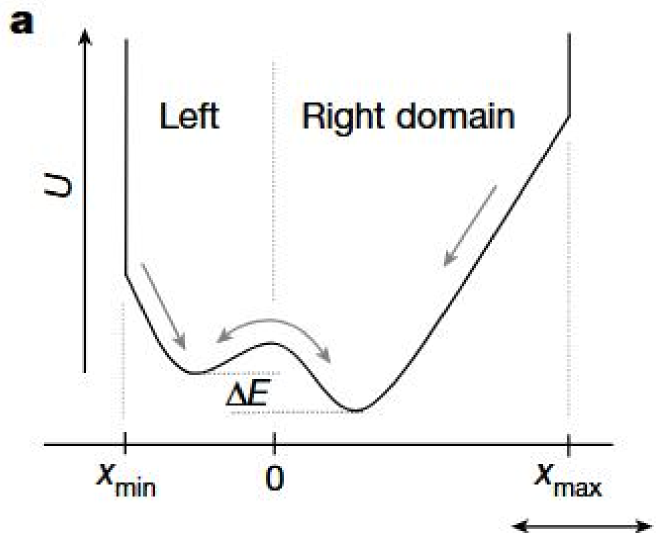
the hot initial state escape the metastable state

Experiment for the double-well potential

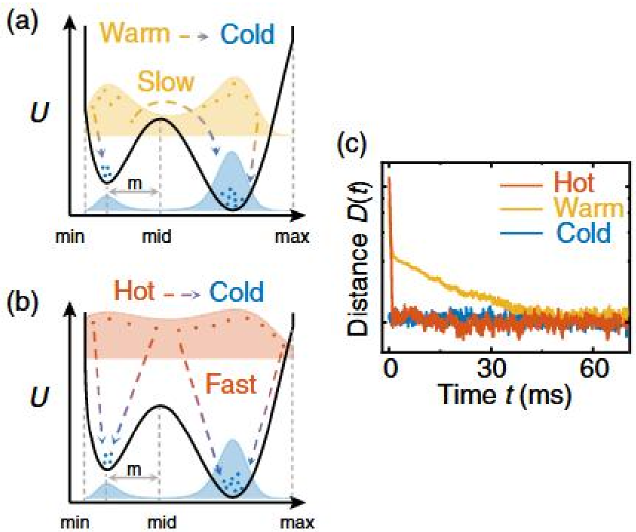
metastable state

mimic water-ice transition

long-time scale



A. Kumar and J. Bechhoefer, Nature 584, 64 (2020).

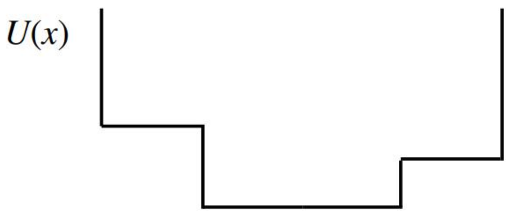


Y. Tian, et al, Phys. Rev. Res. 7, L042020 (2025)

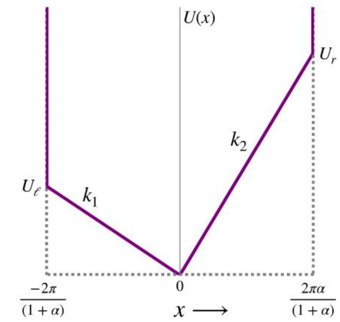
optical tweezers

levitated nanoparticles in vacuum

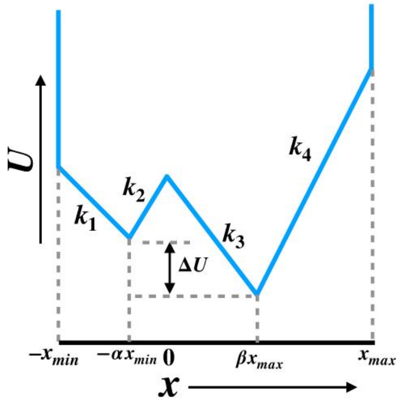
Many other potential

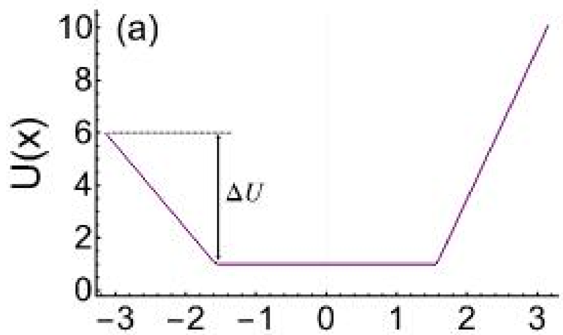


M. R. Walker and M. Vucelja, J. Stat. Mech. 2021, 113105 (2021)



A. Biswas and R. Rajesh, Phys. Rev. E 108, 024113 (2023)





A. Biswas and R. Rajesh, J. Chem. Phys. 159, 044120 (2023)

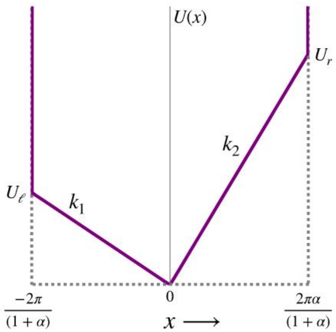
mutual comparison is often cumbersome

too much parameter: wells, widths, curvatures, wells depth, barrier height, slopes.....

Target of this study

What is the dominant mechanism for the Mpemba effect in overdamped system?

The mechanism of metastable state can not explain
why some cases can show the Mpemba effect
such as the single well potential



A unified mechanism beyond the metastable state is needed

Setup

overdamped Langevin equation

$$\dot{x} = -\frac{\partial V}{\partial x} + \xi(t)$$

corresponding Fokker-Planck equation

$$\frac{dp(x,t)}{dt} = \frac{\partial}{\partial x}\left[\frac{\partial V(x)}{\partial x}p(x,t) + \beta^{-1}\frac{\partial p(x,t)}{\partial x}\right] = \mathcal{W}p(x,t)$$

general solution of Fokker-Planck equation

$$p(x,t) = \sum_n a_n e^{-\lambda_n t} r_n(x)$$

right eigenvector $\mathcal{W}r_n(x) = \lambda_n r_n(x)$

left eigenvector $\mathcal{W}^\dagger l_n(x) = \lambda_n l_n(x)$

$$\int r_n(x) l_m(x) dx = \delta_{nm}$$

overlap coefficient

$$a_n = \int dx\, l_n(x) p(x,0)$$

Long-time limit

Note that $\lambda_1 = 0 \quad r_1(x) = \pi(\beta, x) \quad l_1(x) = 1$

Gibbs distribution $\pi(\beta, x) = \frac{e^{-\beta V(x)}}{\int e^{-\beta V(x)} dx}$

In long-time limit

$$p(x,t) \approx \pi(\beta, x) + a_2 r_2 e^{-\lambda_2 t}$$

smaller $|a_2|$
→faster relaxation

We consider the case that the initial state is a equilibrium state

temperature quench $T_{\mathrm{i}} \to T_{\mathrm{b}}$

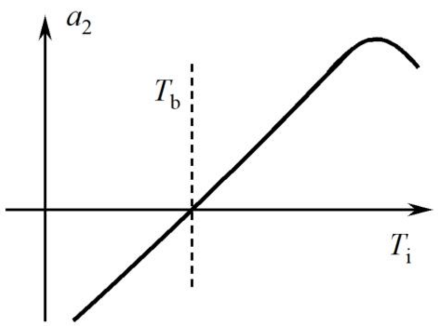
$$a_2 = \int dx\, l_2(x) \pi(\beta_{\mathrm{i}}, x)$$

Mpemba effect for $T_{\mathrm{i}}^{\mathrm{h}} > T_{\mathrm{i}}^{\mathrm{w}} > T_{\mathrm{b}}$ we have $|a_2^{\mathrm{h}}| < |a_2^{\mathrm{w}}|$

inverse Mpemba effect for $T_{\mathrm{i}}^{\mathrm{c}} < T_{\mathrm{i}}^{\mathrm{w}} < T_{\mathrm{b}}$ we have $|a_2^{\mathrm{c}}| < |a_2^{\mathrm{w}}|$

Some remarks

(i)



l_2 (x) is the eigenvector, but -l_2 (x) also is the eigenvector

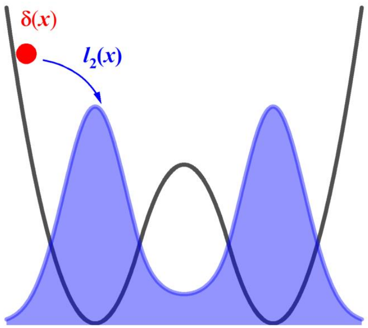
and note the $a_2(T_b)$=0 due to the biorthogonal

We choose a "gauge" that a_2>0 in cooling process and a_2<0 in heating process

(ii)

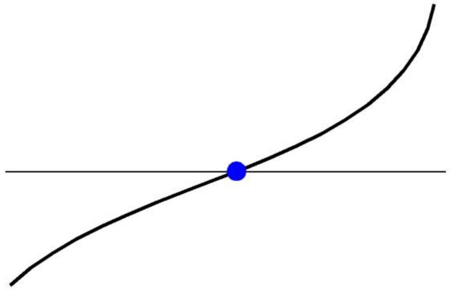
$$a_2 = \int dx\, l_2(x) p(x,0)$$

l_2 (x) measures how microscopestate δ(x) excite the slowest mode



smaller |l_2 (x)|
→faster relaxation from microscope state δ(x) to final state

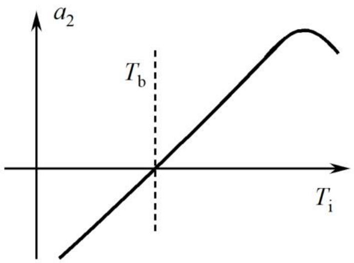
(iii)



l_2 (x) is a monotonic function according to the Sturm-Liouville Theorem

Mpemba effect

For the "gauge" we choosing, the condition for Mpemba effect



$$\frac{\partial a_2}{\partial T_{\rm i}} < 0 \quad \Longrightarrow \quad \int \frac{\partial l_2(x)}{\partial x} J_{T_{\rm i}}(x) \mathrm{d}x < 0$$

here we define J_{Ti}

$$\frac{\partial \pi(T_{\rm i})}{\partial T_{\rm i}} = -\frac{\partial J_{T_{\rm i}}}{\partial x} \quad \Longrightarrow \quad J_{T_{\rm i}}(x) = -\int_{-\infty}^{x} \frac{\partial \pi(y,T_{\rm i})}{\partial T_{\rm i}} dy$$

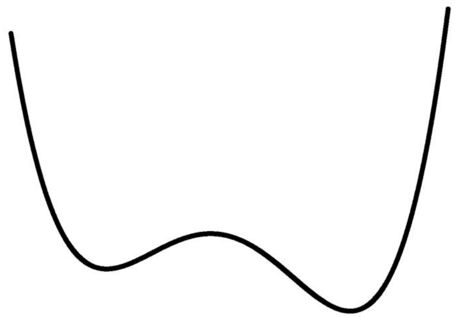
describe how population transfers
as temperature increase at T_i

$$\int \frac{\partial l_2(x)}{\partial x} J_{T_{\rm i}}(x) \mathrm{d}x < 0$$

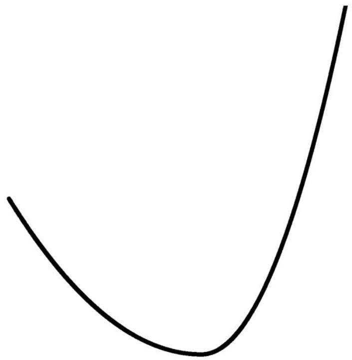
there are enough region where
population transfer to small l_2

The Mpamba effect is essentially that, as initial temperature increase,
the population transfer from large l_2 (x) state to small l_2 (x) state.

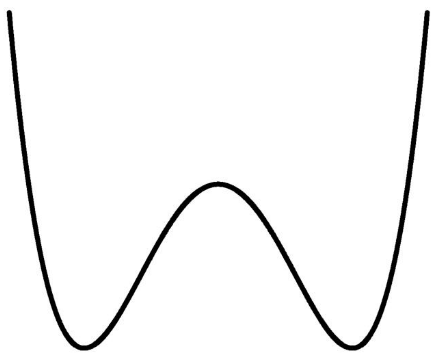
Different type of potential



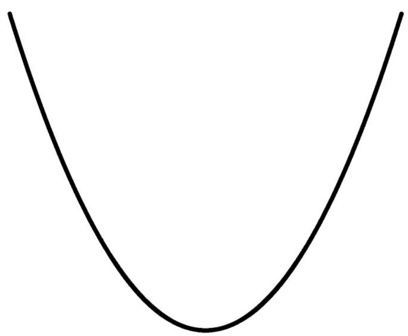
asymmetrical double-well potential



asymmetrical single-well potential



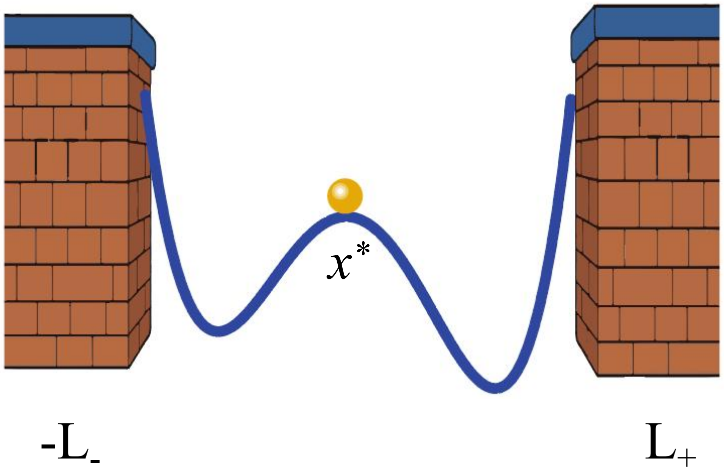
symmetrical double-well potential



symmetrical single-well potential

with and without boundary

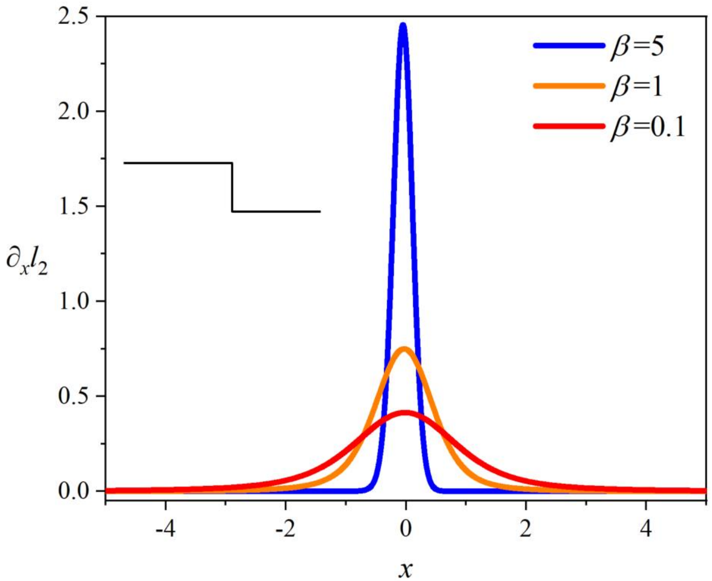
Asymmetrical double-well potential



we first consider low bath temperature

due to the experiment and time scale

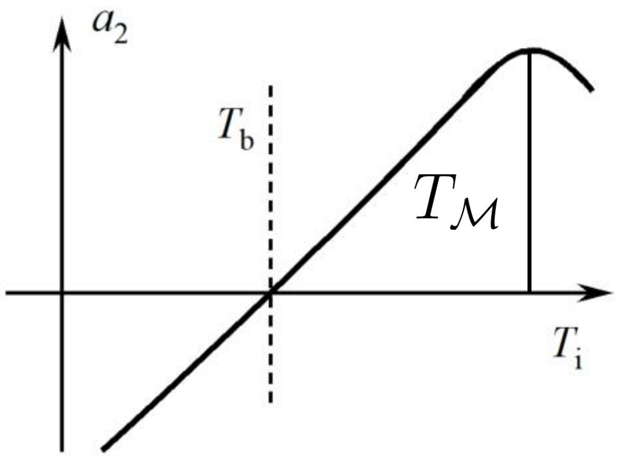
$$\tau = 1/\lambda_2 \sim e^{-\beta \Delta V}$$



$$\ell_2(x) \simeq \frac{1-e^{-\beta\Delta E}}{2} - \frac{1+e^{-\beta\Delta E}}{2} \mathrm{erf}\left[\sqrt{\frac{\beta|V''(x^*)|}{2}}(x-x^*)\right]$$

In low bath temperature, it is a jump function from 1 to 0

Asymmetrical double-well potential



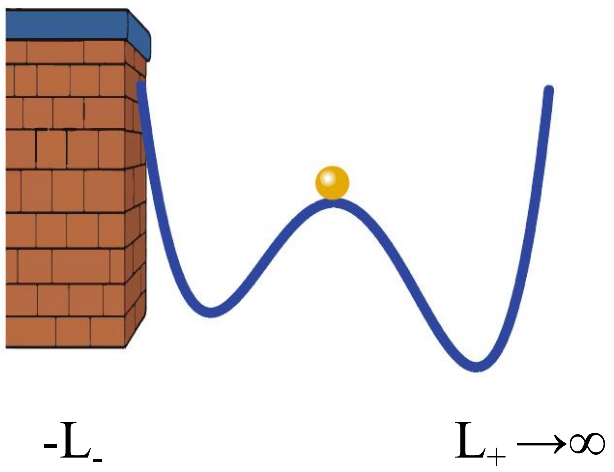
polynomial potential

$$V(x) = (x - x^*)^n + \sum_{k=0}^{n-1} v_k (x - x^*)^k$$

⇓

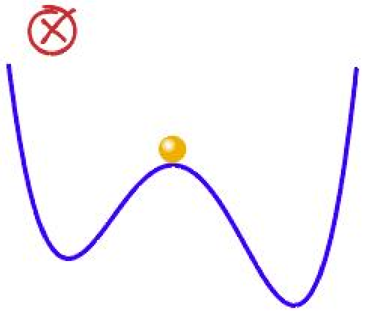
$$\beta_{\mathcal{M}} \simeq \mathrm{Cst}\frac{\ln L_-}{L_-^n} + \frac{1}{L_-^n} \ln\left[1 - \frac{L_+}{L_-} e^{-\beta_{\mathcal{M}}(L_+^n - L_-^n)}\right]$$

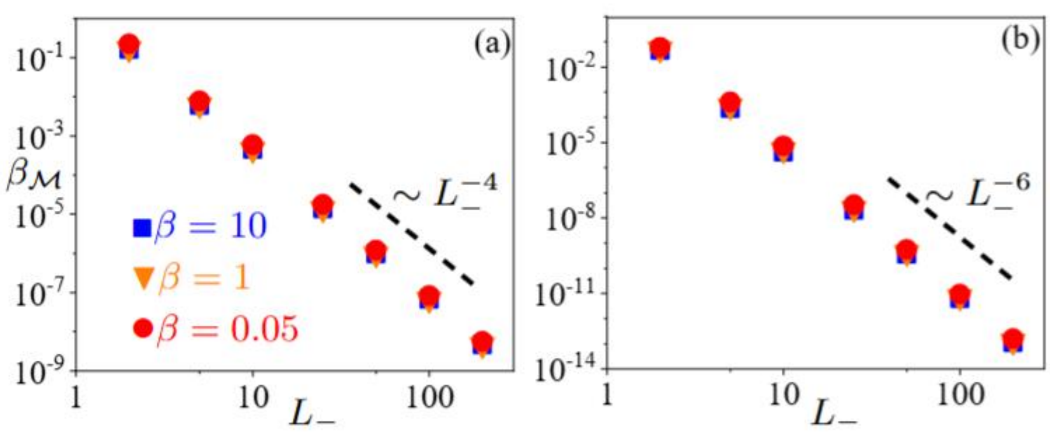
Asymmetrical double-well potential



$$\beta_{\mathcal{M}} \simeq \mathrm{Cst}\frac{\ln L_-}{L_-^n} + \frac{1}{L_-^n}\ln\left[1 - \frac{L_+}{L_-}e^{-\beta_{\mathcal{M}}(L_+^n - L_-^n)}\right]$$

$$\beta_{\mathcal{M}} \simeq \mathrm{Cst}\frac{\ln L_-}{L_-^n}$$

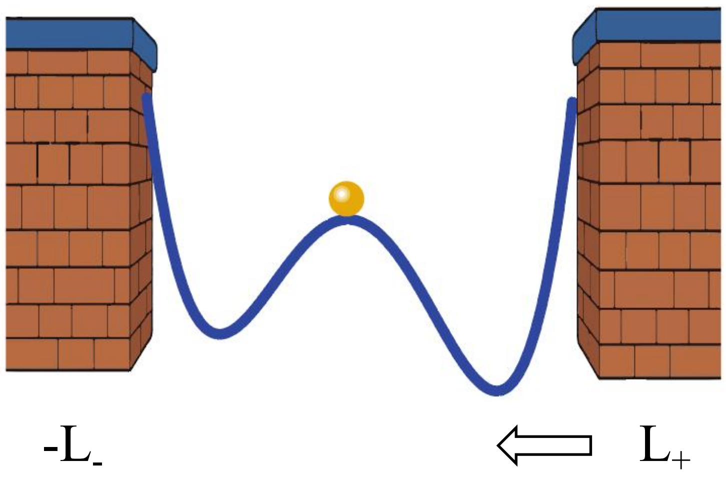




$V(x) = (x^2-1)^2 - 0.2x$

$V(x) = (x^2-1)^2(x^2+1) - 0.2x$

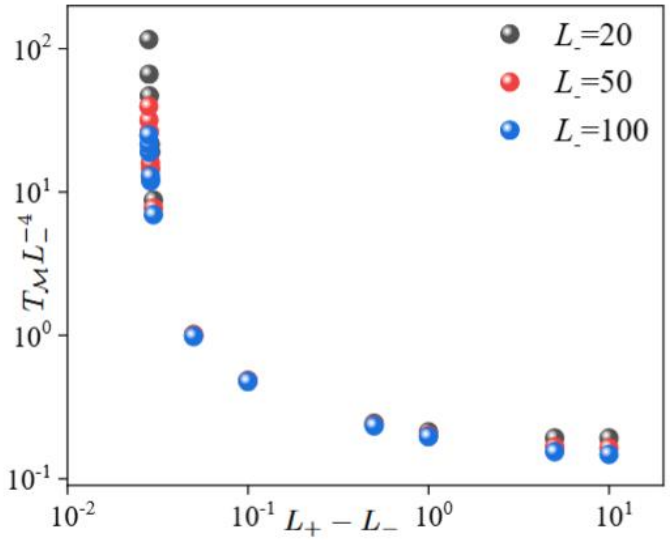
Asymmetrical double-well potential



for $L_+ \leq L_-$

$\beta_{\mathcal{M}}$ do not have a solution

no Mpemba effect



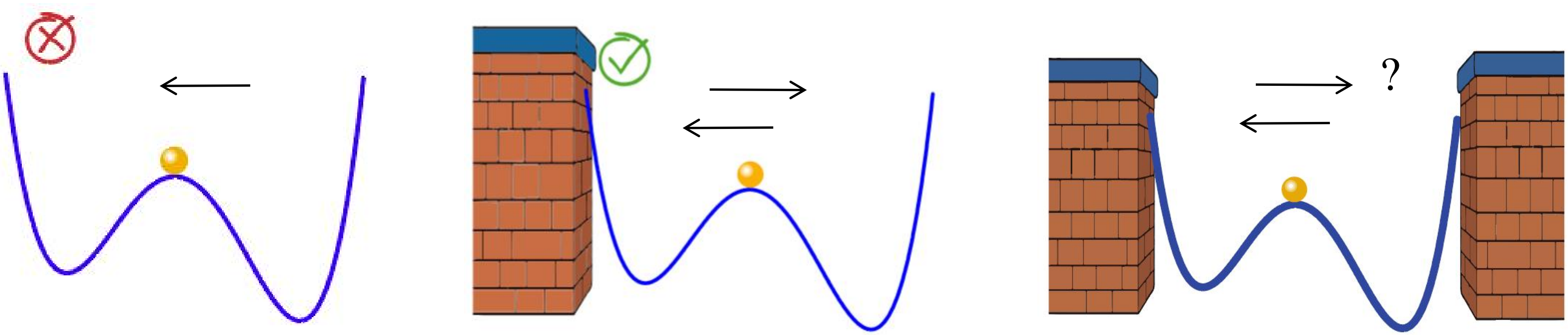
the left boundary is necessary for Mpemba effect, but not suffient

Asymmetrical double-well potential

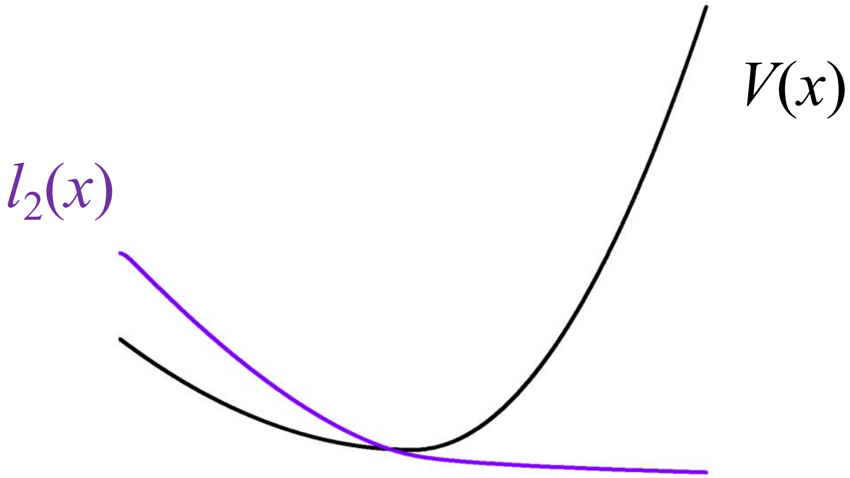
$$\int \frac{\partial l_2(x)}{\partial x} J_{\mathrm{T_i}}(x)\mathrm{d}x < 0$$

for low bath temperature $\partial_x \ell_2(x) \simeq -\delta(x - x^*)$

the sign of $J_{\mathrm{T_i}}(x^*)$ determines the Mpemba effect



Asymmetrical single-well potential



For any initial temperature, the population transfer to soft side (l_2 increase) is more than hard side (l_2 decrease)

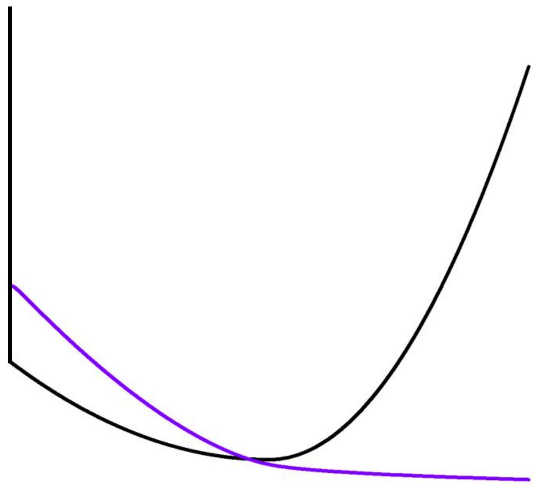
$$\frac{da_2}{dT_{\mathrm{i}}} = \int \frac{\partial l_2(x)}{\partial x} J_{\mathrm{T_i}}(x)\mathrm{d}x > 0$$

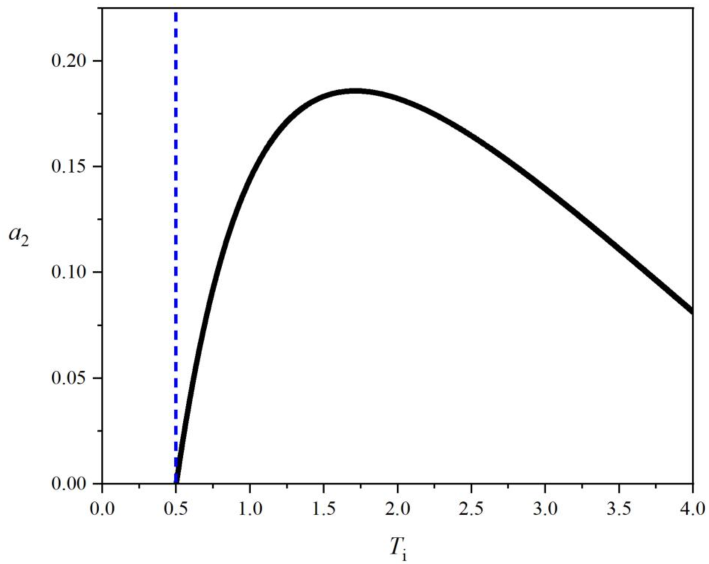
there is no Mpemba

How to make the population transfer to hard side more than soft side?

Asymmetrical single-well potential

add a boundary in the soft side



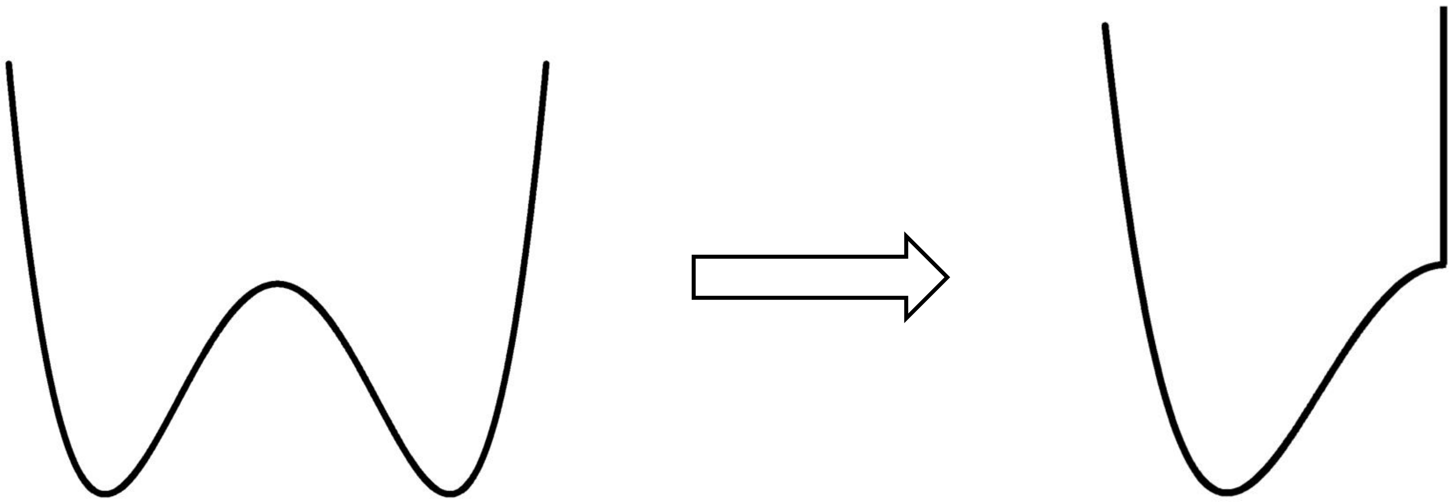


$$\frac{da_2}{dT} = \int \frac{\partial l_2(x)}{\partial x} J_{\mathrm{T_i}}(x)\mathrm{d}x < 0$$

When temperature is high enough, the population meet the boundary in the soft side, and transfers to hard side

if the boundary is in the hard side,
there is no Mpemba

Symmetric double-well potential



For symmetric potential, a_2=0, so we should consider a_3.

the symmetric potential is equivalent to considering only one half

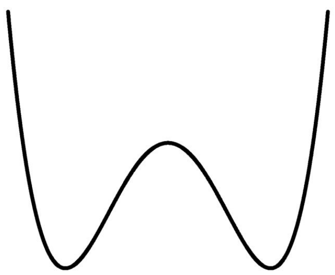
$$a_3^{\text{double}} = a_2^{\text{single}}$$

automatically introduce a invisible wall in the soft side

there is Mpemba effect

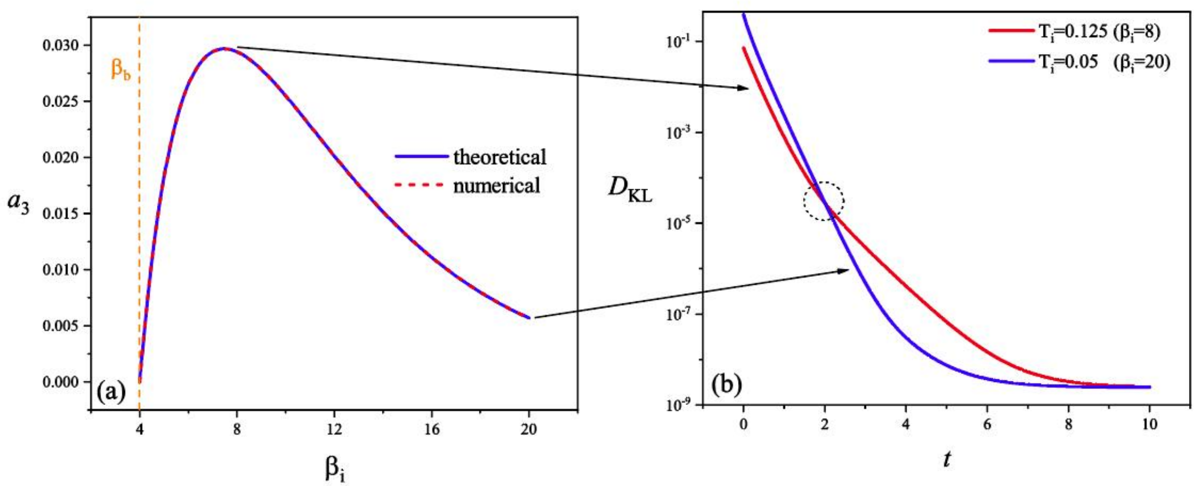
Symmetric double-well potential

connected harmonic potential (C^1)

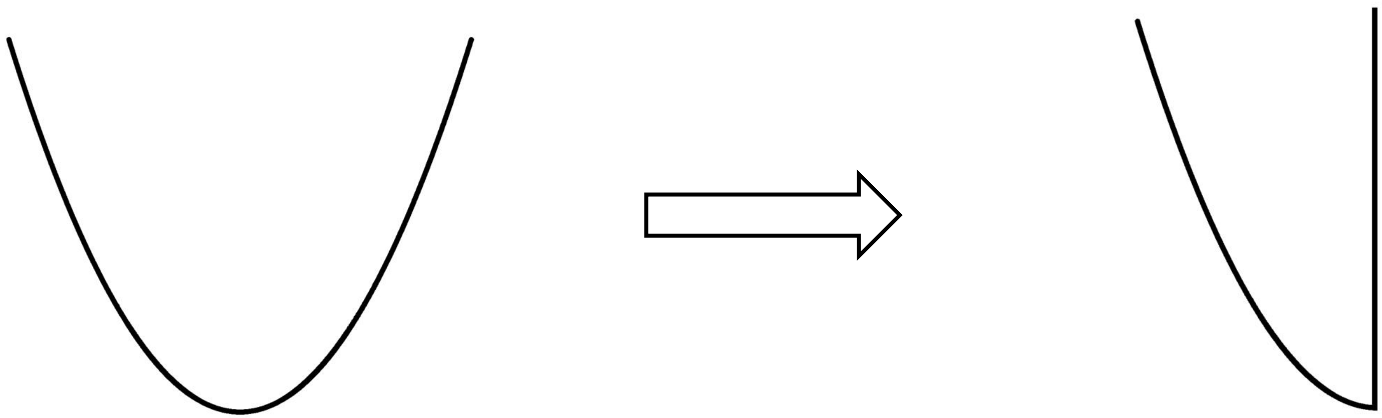


$$V(x) = \begin{cases} \frac{k}{2}(x+a)^2 & x \in (-\infty, -x_c] \\ V_m - \frac{k}{2}x^2 & x \in (-x_c, x_c] \\ \frac{k}{2}(x-a)^2 & x \in (x_c, \infty) \end{cases}$$

$$a_3(\beta_i) = \begin{cases} \frac{2C_2}{Z(\beta_i)}\left(-e^{V_m\left(\frac{\beta_f}{2}-\beta_i\right)}\frac{1}{2}\sqrt{\frac{2\pi}{k|\beta_f-\beta_i|}}\mathrm{erf}\left[\frac{a}{2}\sqrt{\frac{k|\beta_f-\beta_i|}{2}}\right] + \frac{\sqrt{\beta_f k}}{\beta_i k}e^{-\frac{\beta_i k a^2}{8}}\right) & \text{for} \quad \beta_i < \beta_b \\ \frac{2C_2}{Z(\beta_i)}\left(-e^{V_m\left(\frac{\beta_f}{2}-\beta_i\right)}\frac{1}{2}\sqrt{\frac{2\pi}{k|\beta_f-\beta_i|}}\mathrm{erfi}\left[\frac{a}{2}\sqrt{\frac{k|\beta_f-\beta_i|}{2}}\right] + \frac{\sqrt{\beta_f k}}{\beta_i k}e^{-\frac{\beta_i k a^2}{8}}\right) & \text{for} \quad \beta_i > \beta_b \end{cases}$$



Symmetric single-well potential



Similar, we should consider a_3.

the symetric potential is equivalent to considering only one half

The population always transfer to out side
where $l_{3(2)}$ increase

there is no Mpemba effect

Take home message

1. Mpemba effect results from the population transfer from large l_2 to small l_2. $\frac{da_2}{dT} = \int \frac{\partial l_2(x)}{\partial x} J_{\mathrm{T_i}}(x)\mathrm{d}x < 0$

2. A wall (or large steepness) is necessary for Mpemba effect.

3. The metastable state is not the dominant mechanism even for the asymmetric double-well potential.

Thanks For Your Attention!

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