The Mpemba effect occurs when a system prepared at a hot temperature cools down faster than its warm temperature copy. We derive the necessary conditions for the Mpemba effect in the small diffusion limit of one-dimensional overdamped Langevin dynamics on a double-well potential. The conditions depend on the means of first passage times and potential energy and their pair correlation. Our results agree with the recent experimental findings, which shows the strong Mpemba effect occurs when the probability of being in a well at initial and bath temperature matches.

Keywords: Anomalous thermal relaxation, Mpemba effect, overdamped Langevin dynamics, Double-well potential, Kramer’s escape rate, Mean first passage time.

Rapid cooling or heating of a physical system to its environment can lead to unusual thermal relaxation phenomena. A prime example of such anomalous thermal relaxation is the Mpemba effect. The phenomenon occurs when a system prepared at a hot temperature over-takes an identical system prepared at a warm temperature and equilibrates faster to the cold environment [1]. A related effect exists in heating [1, 2]. Comparing two identical physical systems in their relaxation to the environment, we would expect that the system with a smaller mismatch between its own and the environment’s temperature would thermalize faster — yet it is not always the case. Thus far, the Mpemba effect has been observed in various physical systems, including water [3, 4], clathrate hydrates [5], magnetic systems [6], polymers [7], and colloidal particle systems [8]. Numerically it has been also seen in spin-glasses [9], systems without equipartition [10], driven granular gasses [11–18], cold gasses [19], quantum systems [20–22], and antiferromagnets [1, 23–26]. The copious observations imply that the effect is general, which was studied in several theoretical works [1, 23, 27–31].

We study the Mpemba effect in overdamped Langevin dynamics on a double-well potential to better understand the phenomena. The overdamped Langevin dynamics of a double-well potential is a model with wide applications, spanning chemical reactions, escapes of metastable states, models of quantum tunneling, and scalar field theories. For a classical point particle, this problem is well-studied and goes by the name of Kramers’ escape problem [32–34]. However, even in the context of this simple problem, it is not known when we have such anomalous relaxations as the Mpemba effect. This letter derives the necessary conditions for the Mpemba effect, adding intuition to understanding anomalous thermalization in this model.

In particular, our analytical results support the experimental findings of Kumar and Bechoeffer [8] of when the strong variant of the Mpemba effect occurs. The so-called strong Mpemba effect was theoretically predicted by Klich, Raz, Hirschberg, and Vucelja in [23], and it was experimentally first observed by Kumar and Bechoeffer [8]. It is characterized by a jump in the relaxation time and, thus, an exponential speed up to the relaxation, which essentially happens for initial conditions that are orthogonal to the slowest relaxation mode. In the case of overdamped Langevin dynamics in a double-well potential, Kumar and Bechoeffer observed that the strong Mpemba effect happens when the probability of the particle being in a well is the same for the initial and the bath temperature. The observation implies that in some cases, the effect happens when all of the probability of being in a well is already there — just “drapes” differently — corresponding to the bath temperature.

We introduce the model and the Mpemba effect. We derive the necessary conditions for the Mpemba effect in terms of the properties of the potential and the mean first passage times (Kramers’ escape rates). Our analytical results are within the limit of small diffusion — the limit where Kramers’ escape rate can be analytically determined.

Model — We consider an overdamped Langevin dynamics for a particle with trajectory \(x(t)\) in a double-well potential \(U\) (see insets of Fig. 1 and Fig. 2)

\[
\frac{\gamma}{\text{d}t} x(t) = -U'[x(t)] + \xi(t),
\]

where \(U' \equiv dU/dx\), \(\gamma\) is the damping coefficient, \(\xi(t)\) is thermal noise with Gaussian statistics — mean is \(\mathbb{E}[\xi(t)] = 0\) and the variance is \(\mathbb{E}[\xi(t)\xi(t')] = 2\gamma k_B T_0 \delta(t - t')\). Below, we set the Boltzmann constant to unity, i.e., \(k_B = 1\). The corresponding Fokker-Planck (FP) equation describes the evolution of a probability density, \(p(x, t)\), of having a particle at time \(t\) at coordinate \(x(t) = x\)

\[
\partial_t p(x, t) = \partial_x \left[ \frac{1}{\gamma} U'(x) + \frac{T_0}{\gamma} \partial_x \right] p(x, t) \equiv \mathcal{L} p(x, t),
\]

where \(\mathcal{L}\) is the Fokker-Planck operator. We also denote the probability current density, \(j(x, t)\), as \(\partial_x j(x, t) \equiv -\partial_t p(x, t)\). We assume that our system is closed; thus, the probability is conserved, and we have reflective boundary conditions. The stationary distribution with
zero probability current everywhere is the Boltzmann equilibrium probability distribution,
\[ \pi_{T_b}(x) = \frac{1}{Z(T_b)} e^{-\frac{U(x)}{T_b}}, \]
where \( Z(T_b) \equiv \int_{x_{min}}^{x_{max}} \exp[-U(x)/T_b] dx \) is the partition sum.

For the scalar product \( \langle u, v \rangle \equiv \int_{x_{min}}^{x_{max}} u(x)v(x) dx \), the adjoint operator of the Fokker-Plank operator is \( L^* = \gamma^{-1}[-U''(x) + \partial_x \partial_t] \). The corresponding eigenvalue problems are \( \mathcal{L}v_i = \lambda_i v_i \) and \( \mathcal{L}^* u_i = \lambda_i u_i \), where the two eigenfunctions are related as \( u_i(x) = \exp[U(x)/T_b]v_i(x) \). The probability density \( p(x,t) \) can be expressed as
\[ p(x,t) = \pi_{T_b}(x) + \sum_{i>1} a_i e^{\lambda_i t} v_i(x), \]
with overlap coefficients
\[ a_i = \frac{\langle u_i, p_{\text{init}} \rangle}{\langle u_i, v_i \rangle}, \]
where \( p_{\text{init}} \) is the initial condition.

**Strong and weak Mpemba effect** – We consider that our system starts from Boltzmann equilibrium at temperature \( T \), \( \pi_T \), and consider cases with a gap between the second and the third eigenvalue, \( \lambda_2 > \lambda_3 \). The strong Mpemba effect happens when the overlap \( a_2 \), defined in Eq. (5), is zero, i.e., when
\[ \langle u_2 U \rangle_T = \langle u_2 \rangle_T \langle U \rangle_T = 0. \]

To study the Mpemba effects, strong and weak, we need the eigenfunction \( u_2 \), which is what we find below.

**Spectrum of the adjoint FP operator** – For the spectrum of the adjoint FP operator we look at the following eigenvalue problem
\[ \partial_x e^{-\frac{U(x)}{T_b}} \partial_x u_i(x) = \frac{\gamma \lambda_i}{T_b} e^{-\frac{U(x)}{T_b}} u_i(x), \]
for details see supplementary material [35]. Integrating the equation from \( x_{min} \) to \( x \) twice, and using the boundary condition, \( u'_i(x_{min}) = 0 \), we have
\[ u_i(x) = u_i(x_{min}) \times \left[ 1 + \frac{\gamma \lambda_i}{T_b} \int_{x_{min}}^{x} e^{\frac{U(y)}{T_b}} dy \int_{x_{min}}^{y} e^{-\frac{U(z)}{T_b}} u_i(z) dz \right]. \]
Similarly integrating twice from \( x \) to \( x_{max} \) and using the boundary condition \( u'_i(x_{max}) = 0 \), we get another expression for \( u_i \),
\[ u_i(x) = u_i(x_{min}) \alpha_i \times \left[ 1 + \frac{\gamma \lambda_i}{T_b} \int_{x_{min}}^{x} e^{\frac{U(y)}{T_b}} dy \int_{x_{min}}^{y} e^{-\frac{U(z)}{T_b}} u_i(z) dz \right], \]
with
\[ \alpha_i = \frac{u_i(x_{max})}{u_i(x_{min})}. \]

In the small-diffusion limit the eigenfunction \( u_i \) over \( D_L = [x_{min}, 0] \) is better approximated starting from Eq. (9) than Eq. (10), and over \( D_R = [0, x_{max}] \) it is best to use Eq. (10). By demanding \( u_i \) is continuous at \( x = 0 \) we get the eigenvalue
\[ \gamma \lambda_i = (1 - \alpha_i) \left[ \int_{x_{min}}^{x_{max}} e^{\frac{U(y)}{T_b}} dy \int_{x_{min}}^{y} e^{-\frac{U(z)}{T_b}} u_i(z) dz \right]^{-1}. \]

Below we derive the first nonzero eigenvalue, \( \lambda_2 \), and the corresponding left eigenfunction, \( u_2 \). The magnitude \( -\lambda_2 \) signifies the transition rate between the two wells. Its analogs for diffusion over a barrier are the Kramers escape time and the mean first passage time, c.f. [36, 37]. The so-called Kramers problem is analytically solvable in the limit of small diffusion and large barriers, that is, when \( |\Delta U| / T_b \gg 1 \), where \( \Delta U \equiv U(x_L) - U(x_R) \) is the barrier height, and \( x_L \) and \( x_R \) are the positions of the left and right potential minima. In this limit, the transition rate between the wells is small, i.e., \( -\gamma \lambda_2 L^2 / T_b \ll 1 \), with width between the wells \( L \equiv |x_L - x_R| \). Hence we can use an iterative procedure to find the first nonzero eigenvalue \( \lambda_2 \) and corresponding eigenfunction \( u_2 \). Namely, in the zeroth approximation, diffusion is so small that there are no jumps between the wells,
\[ \lambda_2^{(0)} = 0, \]
this implies, that \( u_2 \), defined in Eqs. (9) and (10), is
\[ u_2^{(0)} = \begin{cases} u_2(x_{min}), \quad x \in D_L \\ u_2(x_{max}), \quad x \in D_R \end{cases}. \]

For what follows, it is important to note that we centered the potential so it has a local maximum at \( x = 0 \). The coefficient \( \alpha_2^{(0)} \) we get from demanding \( u'_2(x) \) is continuous at \( x = 0 \). In the zeroth-order approximation we
have
\begin{equation}
\alpha_2^{(0)} = -\frac{\int_0^{\tau_{\min}} e^{-\frac{\lambda \tau}{\gamma}} d\tau}{\int_0^{\tau_{\max}} e^{-\frac{\lambda \tau}{\gamma}} d\tau} \equiv \frac{\Pi_L(T_b)}{\Pi_R(T_b)}.\tag{15}
\end{equation}

where we label with \( \Pi_X(T_b) \) the probability of the particle being in well \( X \), where \( X = L \) or \( R \), at temperature \( T_b \). Plugging in \( u_2^{(0)} \), Eq. (14), in the exact expression for \( \lambda_2 \), Eq. (12), we get
\begin{equation}
\frac{\gamma \lambda_2^{(1)}}{T_b} = -\frac{\Pi_L(T_b)}{\Pi_R(T_b) \lambda_L(0) + \Pi_L(T_b) \lambda_R(0)} \frac{Z(T_b)}{T_b},\tag{16}
\end{equation}

where we denoted
\begin{align}
\lambda_L(x) &\equiv \int_x^{\tau_{\max}} e^{-\frac{U(\tau)}{\gamma \rho}} d\tau \int_y^{\tau_{\max}} e^{-\frac{U(\tau)}{\gamma \rho}} d\tau, \\
\lambda_R(x) &\equiv \int_x^{\tau_{\min}} e^{-\frac{U(\tau)}{\gamma \rho}} d\tau \int_y^{\tau_{\max}} e^{-\frac{U(\tau)}{\gamma \rho}} d\tau.\tag{17}
\end{align}

The eigenvector is
\begin{equation}
u_2^{(1)}(x) \propto \begin{cases} 
1 + \frac{\lambda_2^{(1)}}{T_b} A_L(x), & x \in D_L, \\
\alpha_2^{(1)} + \alpha_2^{(0)} \frac{\lambda_2^{(1)}}{T_b} A_R(x), & x \in D_R 
\end{cases}.\tag{19}
\end{equation}

From continuity of \( u_2(x) \) at \( x = 0 \), we have \( \alpha_2^{(1)} = \alpha_2^{(0)} \). Note that alternatively, the results for \( \lambda_2 \) and \( u_2^{(0)} \) could have been obtained by solving for the ground state and the lowest eigenfunction of the adjoint FP operator with the inverted potential \( -U(x) \) and absorbing boundary conditions since there is an exact mapping between the two problems, see e.g. \[36\].

Below we remain with the first approximation in \( -\gamma \lambda_2 L^2 / T_b \ll 1 \); however, for simplicity, we drop writing the superscripts above \( u_2 \), \( \lambda_2 \), and \( \alpha_2 \). Before proceeding further, it is instructive to express \( A_L(x) \) and \( A_R(x) \) in terms of mean first passage times.

**Mean First Passage Time** – A typical Mean First Passage Time (MFPT) scenario tracks particles that leave a domain for the first time and do not come back to it, see e.g. \[37\]. Suppose we look at the domain \( D_R \). The motion of particles is governed by the Langevin equation Eq. (1). Also, suppose our initial point \( x_0 \in D_R \). The first passage time is the time it leaves the domain. To find the MFPT, we focus on the trajectories that have not left the domain \( D_R \) before time \( t \). The distribution of such particles obeys the Fokker-Planck equation
\begin{equation}
\partial_t \tilde p = \tilde L \tilde p,\tag{20}
\end{equation}

where \( \tilde L = \mathcal{L} \), and we added the tilde symbol to signify different initial and boundary conditions from the rest of the paper. Here the initial condition is \( \tilde p(x,0) = \delta(x-x_0) \) for \( x_0 \in D_R \) and the boundary conditions are: \( \tilde p(x_{\max}) = [\tilde p' + U' \tilde p]_{x=x_{\max}} = 0 \) and \( \tilde p(0,t) = 0 \). The number of points that are still in \( D_R \) at time \( t \) is
\begin{equation}
\tilde P(t,x_0) = \int_{D_R} \tilde p(x,t) dx.\tag{21}
\end{equation}

The number of points that have not left before time \( t \) but have left during time integral \( (t,t+dt) \) is
\begin{equation}
P(t,x_0) - \tilde P(t+dt,x_0) = \rho(t,x_0) dt,
\end{equation}

where \( \rho(t,x_0) \) is the distribution of first passage times. MFPT is the first moment of \( \rho(t,x_0) \), i.e.,
\begin{equation}
\tau_R(x_0) = \int_0^\infty \rho(t,x_0) dt = \int_0^\infty \tilde P(t,x_0) dt.\tag{23}
\end{equation}

In the 1D case, \( \tau_R \) can be calculated explicitly, see e.g. \[37\]. In the supplementary material we reproduce the main steps leading to the differential equation
\begin{equation}
\frac{T_b}{\gamma} e^{-\frac{U(x)}{\gamma \rho}} \partial_x e^{-\frac{U(x)}{\gamma \rho}} \partial_x \tau_R(x) = -1,
\end{equation}

with boundary condition \( \tau_R(0) = 0 \), which means that any initial point on the boundary will leave immediately. Next, we assume that MFPT at \( x = x_{\max} \) approaches a constant, i.e., \( \tau'(x_{\max}) = 0 \). Integrating the MFPT differential equation, Eq. (24), twice for the right domain, we get
\begin{equation}
A_R(x) = \frac{T_b}{\gamma} \left[ \tau_R(x_{\max}) - \tau_R(x) \right], \quad x \in D_R.\tag{25}
\end{equation}

An analogous derivation can be done for the left domain, \( D_L \), where MFPT \( \tau_L \) satisfies
\begin{equation}
\frac{T_b}{\gamma} e^{-\frac{U(x)}{\gamma \rho}} \partial_x e^{-\frac{U(x)}{\gamma \rho}} \partial_x \tau_L(x) = -1,
\end{equation}

with boundary conditions \( \tau'_L(x_{\min}) = 0 \) and \( \tau_L(0) = 0 \). We integrate the equation twice and for \( x \in D_L \) get
\begin{equation}
A_L(x) = \frac{T_b}{\gamma} \left[ \tau_L(x_{\min}) - \tau_L(x) \right].\tag{27}
\end{equation}

Now, using Eqs. (27) and (25) we can write the eigenvalue as
\begin{equation}
\lambda_2 = \frac{Z(T_b)}{\Pi_R(T_b) \tau_L(x_{\min}) + \Pi_L(T_b) \tau_R(x_{\max})}.
\end{equation}

In the small-diffusion limit the exponential integrals in \( Z(T_b) \), \( \tau_R(x_{\max}) \) and \( \tau_L(x_{\min}) \) are readily approximated by Laplace’s method. In this limit, the eigenvalue reduces to the sum of Kramer’s rates from one well to another (see supplementary material \[35\] and c.f. \[36\]).

Now that we have obtained the expression for \( u_2 \) and know the meaning of integrals \( A_R \) and \( A_L \) in terms of the MFPTs, we are ready to write down the conditions for the Mpemba effect.
Conditions for the strong Mpemba effect – Plugging in the expression for $u_2$, Eq. (19), in Eq. (6), we get the condition for the strong Mpemba effect

$$0 = \left( \frac{\Pi_L(T)}{\Pi_L(T_b)} - \frac{\Pi_R(T)}{\Pi_R(T_b)} \right) + \frac{\gamma \lambda_2}{T_b} \left( \langle A_L \rangle_{L,T} \frac{\Pi_L(T)}{\Pi_L(T_b)} - \frac{\Pi_R(T)}{\Pi_R(T_b)} \langle A_R \rangle_{R,T} \right), \quad (29)$$

where $\langle \cdot \rangle_{X,T}$ is the average over $\mathcal{P}_X$ with probability distribution $\pi(T) Z(T) / \Pi_X(T)$, where $X$ is $L$ or $R$. For vanishing small $|\lambda_2|/T_b$, and using $\Pi_L + \Pi_R = 1$, the above expression reduces to

$$\Pi_L(T) = \Pi_L(T_b), \quad (30)$$

which is what Kumar and Bechhoeffer observed to be fulfilled for the temperature at which they saw the strong Mpemba effect [8]. Corrections linear in $|\lambda_2|/T_b$ in the case of strong Mpemba effect give us the dependence on MFPT $\tau_L$ and $\tau_R$. An example of the strong Mpemba effect and use of Eq. (29) is on Fig. 1.

Conditions for the weak Mpemba effect - After plugging in $u_2$, Eq. (19), in Eq. (7), the necessary condition for the “weak” Mpemba effect can be written as

$$0 = W^{(0)} + \frac{\gamma \lambda_2}{T_b} W^{(1)}, \quad (31)$$

where we defined

$$W^{(0)} \equiv \langle U \rangle_{L,T} \frac{\Pi_L(T)}{\Pi_L(T_b)} - \frac{\Pi_R(T)}{\Pi_R(T_b)} \langle U \rangle_{R,T} - \langle U \rangle_{T} \left( \frac{\Pi_L(T)}{\Pi_L(T_b)} - \frac{\Pi_R(T)}{\Pi_R(T_b)} \right), \quad (32)$$

and

$$W^{(1)} \equiv \langle U A_L \rangle_{L,T} \frac{\Pi_L(T)}{\Pi_L(T_b)} - \frac{\Pi_R(T)}{\Pi_R(T_b)} \langle U A_R \rangle_{R,T} - \langle U \rangle_{T} \left( \langle A_L \rangle_{L,T} \frac{\Pi_L(T)}{\Pi_L(T_b)} - \frac{\Pi_R(T)}{\Pi_R(T_b)} \langle A_R \rangle_{R,T} \right). \quad (33)$$

For vanishingly small $|\lambda_2|/T_b$ the condition for the Mpemba effect, Eq. (31), approximates to $W^{(0)} = 0$. The dependence on MFPT is the first order term, and it comes through $\lambda_2$, $A_L$, and $A_R$. An example of the Mpemba effect and use of Eq. (31) is on Fig. 2.

The necessary conditions for the Mpemba effect, Eqs. (29) and (31), express the relation between the mean free passage times, mean energy, and the pair correlation of the mean free passage time and energy that must hold if the effect is to occur. These equations are the main result of this letter. Notice that in the small-diffusion limit, we sometimes neglect entirely the $\gamma \lambda_2/T_b$ terms for Eqs. (29) and (31), in which case the condition for the effects depend on the average energy and probabilities to be in a well, i.e., Eq. (30) and $W^{(0)} = 0$.

Generalizations – Our results generalize to the case of spatially-dependent diffusion and predict the Mpemba effect for potentials that are a multiple of the original potential. The two are described next.

Spatially dependent diffusion – For a one-dimensional FP equation by a suitable transformation, the coordinate dependent diffusion coefficient can be transformed to an arbitrary constant $D(T_b) > 0$, see e.g. [36]. In our case, the diffusion coefficient is set to $D(T_b) = T_b/\gamma$. For a one-dimensional case if in the original coordinates, $x$, the diffusion was $\tilde{D}(\tilde{x}, T_b)$, then in the new coordinates, $\tilde{x}$, the diffusion constant is $D(T_b) = (dx/d\tilde{x})^2 \tilde{D}(\tilde{x}, T_b)$. The transformation is $x(\tilde{x}) = \int_{\tilde{x}_0}^{\tilde{x}} d\tilde{y} (\tilde{D}(T_b)/\tilde{D}(T_b, \tilde{y}))^{1/2}$,
\[ \langle u_2 U \rangle_T - \langle u_2 \rangle_T \langle U \rangle_T \]

temperature \( T/T_b \)

\[ \langle u_2 U \rangle_T - \langle u_2 \rangle_T \langle U \rangle_T \]

temperature \( T/T_b \)

FIG. 2. (top) The overlap coefficient \( a_2(T, T_b) \) is obtained numerically (green line), and by using the approximated eigenfunction \( u_2 \), Eq. (19), (red circles). This is an example of the Mpemba effect since here \( a_2 \) is a non-monotonic function of the initial temperature \( T \) (it has a local maximum at \( T \approx 19 T_b \)). The small-diffusion parameter is \( |\Delta U|/T_b \approx 0.2 \). The eigenvalue is \( \lambda_2 \approx -0.92 \) numerically and \( \lambda_2^{(1)} \approx -0.89 \) with our approximation. The inset shows the potential. (bottom) The condition for the Mpemba Effect stated in Eq. (7) and approximated with Eq. (31) (zeroth order: orange circles and first order: teal triangles). In the ”zeroth” order, we neglected terms proportional to \( \gamma |\lambda_2|/T_b \) in Eq. (31). Both orders agree well with the numerics.

where choice of \( \tilde{x}_0 \) determines the value of \( D \). The transformed potential is

\[ -\frac{1}{\gamma} U'(\tilde{x}) = \frac{d\tilde{x}}{dx} \left( -\frac{1}{\gamma} U'(\tilde{x}) \right) + \left( \frac{d^2\tilde{x}}{dx^2} \right) \tilde{D}(\tilde{x}, T_b). \] (34)

Hence by knowing a Mpemba effect for pair of temperatures \( \{T_{\text{init}} = T, T_b\} \), force \(-U'\), and diffusion coefficient \( D(T_b) \), we also know that there will be a Mpemba effect for the same temperature pair, \( \{T_{\text{init}} = T, T_b\} \), force \(-U'\), and diffusion constant \( \tilde{D}(\tilde{x}, T_b) \).

Scaling argument – Since the temperature always appears in a ratio of potential vs. temperature, we have the same expression for the Boltzmann distribution \( \pi \) and the second left eigenfunction \( u_2 \) the FP operator for \( \{U, T\} \) and for \( \{\kappa U, \kappa T\} \), where \( \kappa \) is a constant. Thus a Mpemba effect for potential \( U \), diffusion constant \( T_b/\gamma \), and temperature pair \( \{T_{\text{init}} = T, T_b\} \) implies a Mpemba effect for potential \( \kappa U \), diffusion constant \( \kappa T_b/\gamma \) and temperatures \( \{T_{\text{init}} = \kappa T, \kappa T_b\} \).

Discussion – We derive the necessary conditions for the Mpemba effect and its strong variant in the case of one-dimensional overdamped Langevin dynamics on a double-well potential. Our results predict the initial temperature that will lead to the Mpemba effect via integral equations that contain probabilities to be in each of the wells averaged MFPTs over a well, average potential energy in the well, and the average pair-correlation of the potential and the MFPT over a well. These are exponential integrals and are readily evaluated by Laplace’s method. In particular, for the strong Mpemba effect, our findings match the experimental results of Kumar and Bechhoefer [8], who saw that the effect when the probabilities of being in a well at the initial temperature and at the bath temperature matched. In particular, like in [8], we also observed that it is easier to find occurrences of the strong Mpemba effect in asymmetric domains.

Lastly, given that the Kramer’s escape problem is a basic model in a wide variety of physical scenarios, it would be interesting to see the interpretation of the derived necessary conditions for the strong and ”weak” Mpemba effects in specific cases.

ACKNOWLEDGEMENTS

This material is based upon work supported by the National Science Foundation under Grant No. DMR-1944539. MV and MRW acknowledge discussions with Gregory Falkovich, David Mukamel, Baruch Meerson, Oren Raz, Gianluca Teza, Roi Holzmann, Aaron Winn, Shlomi Reuveni, Eli Barkai, and Peter Arnold. This work would not have been possible had MV not been invited to coffee at a critical moment to discuss anything and everything except the work of this paper.

* mvucelja@virginia.edu

[1] Z. Lu and O. Raz, Proceedings of the National Academy of Sciences 114, 5083 (2017).
[2] A. Kumar, R. Chétrite, and J. Bechhoefer, Proceedings of the National Academy of Sciences 119, e2118484119 (2022).
[3] M. Jeng, American Journal of Physics 74, 514 (2006).
[4] E. B. Mpemba and D. G. Osborne, Physics Education 4, 172 (1969).
[5] Y.-H. Ahn, H. Kang, D.-Y. Koh, and H. Lee, Korean Journal of Chemical Engineering 33, 1903 (2016).
[6] P. Chaddah, S. Dash, K. Kumar, and A. Banerjee, ArXiv e-prints (2010).
[7] C. Hu, J. Li, S. Huang, H. Li, C. Luo, J. Chen, S. Jiang, and L. An, Crystal Growth & Design 18, 5757 (2018).
[8] A. Kumar and J. Bechhoefer, Nature 584, 64 (2020).
[9] M. Baity-Jesi, E. Calore, A. Cruz, L. A. Fernandez, J. M. Gil-Narvión, A. Gordillo-Guerrero, D. Iníguez, A. Lasanta, A. Maiorano, E. Marinari, V. Martin-Mayor, J. Moreno-Gordo, A. Muñoz Sudupe, D. Navarro, G. Parisi, S. Perez-Gaviro, F. Ricci-Tersenghi, J. J. Ruiz-Lorenzo, S. F. Schifano, B. Seoane, A. Tarancón, R. Tripiccione, and D. Yllanes, Proceedings of the National Academy of Sciences 116, 15550 (2019).
[10] A. Gijón, A. Lasanta, and E. R. Hernández, Phys Rev E 100, 032103 (2019).
[11] R. Gómez González and V. Garzó, Physics of Fluids 33, 093315 (2021).
[12] E. Mompó, M. A. López-Castaño, A. Lasanta, F. Vega Reyes, and A. Torrente, Physics of Fluids 33, 062005 (2021).
[13] A. Lasanta, F. Vega Reyes, A. Prados, and A. Santos, Phys. Rev. Lett. 119, 148001 (2017).
[14] A. Megías and A. Santos, Frontiers in Physics 10 (2022).
[15] A. Biswas, V. V. Prasad, and R. Rajesh, Journal of Statistical Physics 186, 45 (2022).
[16] A. Biswas, V. V. Prasad, and R. Rajesh, Europhysics Letters 136, 46001 (2022).
[17] A. Torrente, M. A. López-Castaño, A. Lasanta, F. V. Reyes, A. Prados, and A. Santos, Phys. Rev. E 99, 060901 (2019).
[18] A. Biswas, V. V. Prasad, O. Raz, and R. Rajesh, Phys. Rev. E 102, 012906 (2020).
[19] T. Keller, V. Torggler, S. B. Jäger, S. Schütz, H. Ritsch, and G. Morigi, New Journal of Physics 20, 025004 (2018).
[20] A. Nava and M. Fabrizio, Phys. Rev. B 100, 125102 (2019).
[21] S. Kochsiek, F. Carollo, and I. Lesanovsky, Phys. Rev. A 106, 012207 (2022).
[22] F. Carollo, A. Lasanta, and I. Lesanovsky, Phys. Rev. Lett. 127, 060401 (2021).
[23] I. Klich, O. Raz, O. Hirschberg, and M. Vucelja, Phys. Rev. X 9, 021060 (2019).
[24] G. Teza, R. Yaacoby, and O. Raz, arXiv preprint arXiv:2112.10187 (2021), 10.48550/ARXIV.2112.10187.
[25] G. Teza, R. Yaacoby, and O. Raz, arXiv preprint arXiv:2203.11644 (2022), 10.48550/ARXIV.2203.11644.
[26] G. Teza, R. Yaacoby, and O. Raz, arXiv preprint arXiv:2209.09307 (2022), 10.48550/ARXIV.2209.09307.
[27] M. R. Walker and M. Vucelja, J. Stat. Mech. 2021, 113105 (2021).
[28] D. M. Busiello, D. Gupta, and A. Maritan, New Journal of Physics 23, 103012 (2021).
[29] J. Degünther and U. Seifert, Europhysics Letters 139, 41002 (2022).
[30] J. Lin, K. Li, J. He, J. Ren, and J. Wang, Phys. Rev. E 105, 014104 (2022).
[31] R. Holtzman and O. Raz, Communications Physics 5, 280 (2022).
[32] H. A. Kramers, Physica 7, 284 (1940).
[33] V. Mel’nikov, Physics Reports 209, 1 (1991).
[34] J. Langer, Annals of Physics 54, 258 (1969).
[35] M. R. Walker and M. Vucelja, “Supplementary material "Mpemba effect in terms of mean first passage times of overdamped Langevin dynamics on a double-well potential"”, (2022), supplement.
[36] H. Risken, *The Fokker-Planck Equation* (Springer, 1989).
[37] R. Zwanzig, *Nonequilibrium statistical mechanics* (Oxford University Press, New York, NY, USA, 2000).
Eigenvalue problem of the adjoint FP operator

We start with the adjoint Fokker-Planck equation and get the following eigenvalue problem

\[ \mathcal{L}^t u_i(x) = \frac{1}{\gamma} \left[ -U' \partial_x + T_b \partial_x^2 \right] u_i(x) = \frac{T_b}{\gamma} e^{\frac{U(x)}{T_b}} \partial_x e^{\frac{-U(x)}{T_b}} \partial_x u_i(x) = \lambda_i u_i(x), \]  

(35)

which we can write as

\[ \partial_x e^{\frac{-U(x)}{T_b}} \partial_x u_i(x) = \frac{\gamma \lambda_i}{T_b} e^{\frac{U(x)}{T_b}} u_i(x). \]  

(36)

Approximations to exponential integrals

In the small-diffusion limit the exponential integrals in \( Z(T_b) \), \( \tau_R(x_{\text{max}}) \) and \( \tau_L(x_{\text{min}}) \) are readily approximated by the Laplace method, leading to

\[ Z(T_b) \approx \sqrt{\frac{2\pi T_b}{|U''(x_L)|}} e^{-\frac{U(x_L)}{T_b}} + \sqrt{\frac{2\pi T_b}{|U''(x_R)|}} e^{-\frac{U(x_R)}{T_b}}, \]  

(37)

\[ \tau_R(x_{\text{max}}) \approx \frac{\gamma}{T_b} \frac{1}{2} \sqrt{\frac{2\pi T_b}{|U''(0)|}} e^{\frac{U(0)}{T_b}} \sqrt{\frac{2\pi T_b}{|U''(x_R)|}} e^{-\frac{U(x_R)}{T_b}}, \]  

(38)

\[ \tau_L(x_{\text{min}}) \approx \frac{\gamma}{T_b} \frac{1}{2} \sqrt{\frac{2\pi T_b}{|U''(0)|}} e^{\frac{U(0)}{T_b}} \sqrt{\frac{2\pi T_b}{|U''(x_L)|}} e^{-\frac{U(x_L)}{T_b}}. \]  

(39)

In this limit, the eigenvalue reduces to the sum of Kramer’s rates from one well to another (c.f. [36]). Hence we have

\[ \lambda_2 \approx \frac{1}{2\pi \gamma} \left[ e^{\frac{U(0) - U(x_L)}{T_b}} \sqrt{|U''(0)||U''(x_L)|} + e^{\frac{U(0) - U(x_R)}{T_b}} \sqrt{|U''(0)||U''(x_R)|} \right]. \]

Mean First Passage Time

In the 1D case, \( \tau_R \) can be calculated explicitly, see e.g. [37]. Here we reproduce the main steps

\[ \tau_R(x_0) = \int_0^\infty dt \int_{D_R} e^{t \tilde{L}_1} \delta(x - x_0) \, dx \]

(40)

\[ = \int_0^\infty dt \int_{D_R} \delta(x - x_0) e^{t \tilde{L}_1} \, dx. \]  

(41)

Thus we have

\[ \tau_R(x) = \int_0^\infty e^{t \tilde{L}_1} \, dt, \]  

(42)

\[ \tilde{L}_1 \tau_R(x) = \int_0^\infty dt \tilde{L}_1 e^{t \tilde{L}_1} = \int_0^\infty \frac{d}{dt} e^{t \tilde{L}_1} \, dt = -1. \]  

(43)
where the upper limit vanishes because of the absorbing boundary condition. Thus mean first passage time fulfills the following differential equation

\[- \frac{U'}{\gamma} \partial_x \tau_R + \frac{T_b}{\gamma} \partial_x^2 \tau_R = \frac{T_b}{\gamma} e^{-\frac{U(x)}{T_b}} \partial_x e^{-\frac{U(x)}{T_b}} \partial_x \tau_R(x) = -1. \tag{44}\]

* mvucelja@virginia.edu

[1] Z. Lu and O. Raz, Proceedings of the National Academy of Sciences **114**, 5083 (2017).
[2] A. Kumar, R. Chétrite, and J. Bechhoefer, Proceedings of the National Academy of Sciences **119**, e2118484119 (2022).
[3] M. Jeng, American Journal of Physics **74**, 514 (2006).
[4] E. B. Mpemba and D. G. Osborne, Physics Education **4**, 172 (1969).
[5] Y.-H. Ahn, H. Kang, D.-Y. Koh, and H. Lee, Korean Journal of Chemical Engineering **33**, 1903 (2016).
[6] P. Chaddah, S. Dash, K. Kumar, and A. Banerjee, ArXiv e-prints (2010).
[7] C. Hu, J. Li, S. Huang, H. Li, C. Luo, J. Chen, S. Jiang, and L. An, Crystal Growth & Design **18**, 5757 (2018).
[8] A. Kumar and J. Bechhoefer, Nature **584**, 64 (2020).
[9] M. Baity-Jesi, E. Calore, A. Cruz, L. A. Fernandez, J. M. Gil-Narvión, A. Gordillo-Guerrero, D. Iñiguez, A. Lasanta, A. Maiorano, E. Marinari, V. Martin-Mayor, J. Moreno-Gordo, A. Muñoz Sudupe, D. Navarro, G. Parisi, S. Perez-Gaviro, F. Ricci-Tersenghi, J. J. Ruiz-Lorenzo, S. F. Schifano, B. Seoane, A. Tarancón, R. Tripiccione, and D. Yllanes, Proceedings of the National Academy of Sciences **116**, 15350 (2019).
[10] A. Gijón, A. Lasanta, and E. R. Hernández, Phys Rev E **100**, 032103 (2019).
[11] R. Gómez González and V. Garzo, Physics of Fluids **33**, 093315 (2021).
[12] E. Mompó, M. A. López-Castaño, A. Lasanta, F. Vega Reyes, and A. Torrente, Physics of Fluids **33**, 062005 (2021).
[13] A. Lasanta, F. Vega Reyes, A. Prados, and A. Santos, Phys. Rev. Lett. **119**, 148001 (2017).
[14] A. Megías and A. Santos, Frontiers in Physics **10** (2022).
[15] A. Biswas, V. V. Prasad, and R. Rajesh, Journal of Statistical Physics **186**, 45 (2022).
[16] A. Biswas, V. V. Prasad, and R. Rajesh, Europhysics Letters **136**, 46001 (2022).
[17] A. Torrente, M. A. López-Castaño, A. Lasanta, F. V. Reyes, A. Prados, and A. Santos, Phys. Rev. E **99**, 060901 (2019).
[18] A. Biswas, V. V. Prasad, O. Raz, and R. Rajesh, Phys. Rev. E **102**, 012906 (2020).
[19] T. Keller, V. Torggler, S. B. Jäger, S. Schütz, H. Ritsch, and G. Morigi, New Journal of Physics **20**, 025004 (2018).
[20] A. Nava and M. Fabrizio, Phys. Rev. E **100**, 125102 (2019).
[21] S. Kochsiek, F. Carollo, and I. Lesanovsky, Phys. Rev. A **106**, 012207 (2022).
[22] F. Carollo, A. Lasanta, and I. Lesanovsky, Phys. Rev. Lett. **127**, 060401 (2021).
[23] I. Klch, O. Raz, O. Hirschberg, and M. Vucelja, Phys. Rev. X **9**, 021060 (2019).
[24] G. Teza, R. Yaacoby, and O. Raz, arXiv preprint arXiv:2112.10187 (2021), 10.48550/ARXIV.2112.10187.
[25] G. Teza, R. Yaacoby, and O. Raz, arXiv preprint arXiv:2203.11644 (2022), 10.48550/ARXIV.2203.11644.
[26] G. Teza, R. Yaacoby, and O. Raz, arXiv preprint arXiv:2209.09307 (2022), 10.48550/ARXIV.2209.09307.
[27] M. R. Walker and M. Vucelja, J. Stat. Mech. **2021**, 113105 (2021).
[28] D. M. Busiello, D. Gupta, and A. Maritan, New Journal of Physics **23**, 103012 (2021).
[29] J. Degünther and U. Seifert, Europhysics Letters **139**, 41002 (2022).
[30] J. Lin, K. Li, J. He, J. Ren, and J. Wang, Phys. Rev. E **105**, 014104 (2022).
[31] R. Holtzman and O. Raz, Communications Physics **5**, 280 (2022).
[32] H. A. Kramers, Physica **7**, 284 (1940).
[33] V. Mel’nikov, Physics Reports **209**, 1 (1991).
[34] J. Langer, Annals of Physics **54**, 258 (1969).
[35] M. R. Walker and M. Vucelja, “Supplementary material ”Mpemba effect in terms of mean first passage times of overdamped Langevin dynamics on a double-well potential”,” (2022), supplement.
[36] H. Risken, *The Fokker-Planck Equation* (Springer, 1989).
[37] R. Zwanzig, *Nonequilibrium statistical mechanics* (Oxford University Press, New York, NY, USA, 2000).