Faster uphill relaxation in equidistant temperature quenches

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We uncover an unforeseen asymmetry in relaxation – for a pair of thermodynamically equidistant temperature quenches, one from a lower and the other from a higher temperature, the relaxation at the ambient temperature is faster in case of the former. We demonstrate this finding on hand of two exactly solvable many-body systems relevant in the context of single-molecule and tracer-particle dynamics. We prove that near stable minima and for all quadratic energy landscapes it is a general phenomenon that also exists in a class of non-Markovian observables probed in single-molecule and particle-tracking experiments. We hypothesize that the asymmetry is a general feature of reversible overdamped diffusive systems with single-well and sufficiently symmetric multi-well energy landscapes.

Figure 1. Instantaneous excess free energy after a temperature quench $T \rightarrow T_{eq}$ (i.e. at time $t = 0^+$) in units of $k_B T_{eq}$. $D[\mathcal{P}_\Psi(t = 0^+)|\mathcal{P}_{\Psi}^{eq}]$ (see Eq. 3), as a function of the relative pre-quench temperature $\tilde{T} = T/T_{eq}$ (note the logarithmic scale); a) refers to the end-to-end distance of a Gaussian chain with 100 beads and b) to the 7-th in a single file of 10 particles in a linear potential with slope 10 confined to a unit box. The blue and red points depict a pair of equidistant temperature quenches, $T^{-} \rightarrow T^{+}$, with corresponding excess potential energies $\langle \Delta U \rangle_{\tilde{T}^{\pm}} \equiv \langle U(0^+) \rangle_{\tilde{T}^{\pm}} - \langle U \rangle_{1}$, in a manner that is not Markovian.

Here, we address relaxation from an instantaneous temperature quench $T \rightarrow T_{eq}$ at time $t = 0$ with respect of its directionality, $T^{-} \uparrow T_{eq}$ versus $T^{+} \downarrow T_{eq}$. We uncover an unforeseen dependence on the direction of the quench – for a given pair of temperatures $T^{-} < T_{eq} < T^{+}$ yielding equidistant displacements from equilibrium at $t = 0^+$ (see Fig. 1), relaxation evolves, contrary to intuition, faster 'uphill' than 'downhill' the energy landscape. This holds for single-well and sufficiently symmetric multi-well energy landscapes, under Markovian dynamics as well as most non-Markovian observables typically probed by single-molecule and particle-tracking experiments. We demonstrate the asymmetry on hand of the Gaussian polymer chain [12], single-file diffusion in a tilted box [4] and for diffusion in a symmetric double-well potential. For relaxation near a stable minimum and thus for all reversible Ornstein-Uhlenbeck processes we prove that the asymmetry, albeit counter-intuitive, is general.

**Theory.** We consider $d$-dimensional Markovian diffusion with a $d \times d$ diagonal, positive-definite diffusion matrix $\mathbf{D}$ and mobility tensor $\mathbf{M}_T = \mathbf{D}/k_B T$ in a po-
The evolution of the probability density at temperature $T$ is governed by the Fokker-Planck operator $\mathcal{L}_T \equiv \nabla \cdot \mathbf{D} \nabla + \nabla \cdot \mathbf{M}_T \nabla U(x)$. We let $\mathcal{G}_T(x, t|x_0)$ be the Green’s function of the initial value problem $(\partial_t - \mathcal{L}_T)\mathcal{G}_T(x, t|x_0) = \delta(x - x_0)$, and assume that the potential $U(x)$ is confining (i.e. $\lim_{|x| \to \infty} U(x) = \infty$). This assures the existence of an invariant Maxwell-Boltzmann measure with density $\lim_{|x| \to \infty} \mathcal{G}_T(x, t|x_0) \equiv \mathcal{P}_T^{\text{eq}}(x) = \frac{Q^*_T e^{-U(x)/k_B T}}{\mathcal{Z}^*_T}, \forall x_0$ with partition function $\mathcal{Q}_T^* = \int e^{-U(x)/k_B T} \, dx \ [43]$. The system is prepared at equilibrium with the Kullback-Leibler divergence $\Delta^\beta_T(x, t|x_0) \equiv \mathcal{P}_T^{\text{eq}}(x) - \mathcal{P}_1^{\text{eq}}(x)$, whereupon an instantaneous temperature quench is performed to the ambient temperature $T_{\text{eq}}$ at $t = 0$. The relaxation evolves at $T_{\text{eq}}$ according to $\mathcal{L}_{T_{\text{eq}}}$ and for a given system it is uniquely characterized by $T$. For convenience we define $\mathcal{T} \equiv T/T_{\text{eq}} \ [44]$, such that

$$P_T(x, t) = \int dx_0 \mathcal{G}_T(x, t|x_0) \mathcal{P}_T^{\text{eq}}(x_0) \xrightarrow{t \to \infty} \mathcal{P}_1^{\text{eq}}(x). \ (1)$$

The instantaneous entropy and mean energy are given by $S_T(t) = -k_B \int dx \mathcal{P}_T(x, t) \ln \mathcal{P}_T(x, t)$ and $\langle U(t) \rangle_T = \int dx \mathcal{P}_T(x, t) U(x)$, respectively, where $\langle \cdot \rangle_T$ denotes an average over all paths $x(t)$ starting from $\mathcal{P}_T^{\text{eq}}(x_0)$. Let the measured physical observable be $q = \Gamma(x)$. Its probability density function corresponds to

$$\mathcal{P} \equiv \mathcal{P}_T(q, t) = \int dx \delta(\Gamma(x) - q) \mathcal{P}_T(x, t), \ (2)$$

which in general displays non-Markovian dynamics as soon as $q$ corresponds to a low-dimensional projection. Once equilibrium is reached we have $\lim_{t \to \infty} \mathcal{P}_T(q, t) = \mathcal{P}_T^{\text{eq}}(q)$, or, expressed via the so-called potential of mean force $U(q)$ \ [45], $\mathcal{P}_T^{\text{eq}}(q) = e^{-\beta_q U(q)} \ [14, 17, 46]$. Obviously, when $\Gamma(x) = x$ we have $\mathcal{P}_T(q, t) = \mathcal{P}_T(x, t)$. We quantify the instantaneous displacement from equilibrium with the Kullback-Leibler divergence \ [47, 52]

$$\mathcal{D}(\mathcal{P}_T(t)||\mathcal{P}_T^{\text{eq}}) = \int dq \mathcal{P}_T(q, t) \ln(\mathcal{P}_T(q, t)/\mathcal{P}_T^{\text{eq}}(q)). \ (3)$$

Writing this out for the Markovian case we find, upon identifying $S_T(t)$ and $\langle U(t) \rangle_T$:

$$\mathcal{D}(\mathcal{P}_T(t)||\mathcal{P}_T^{\text{eq}}) = -S_T(t) + k_B + \beta_q \langle U(t) \rangle_T + \ln Q_{T_{\text{eq}}}. \ (4)$$

Recalling the definition of free energy $F = -\beta_q \ln Q_{T_{\text{eq}}}$ and defining the generalized instantaneous free energy as $F_T(t) = \langle U(t) \rangle_T - T_{\text{eq}} S_T(t)$ we see, upon multiplying by $\beta_q = k_B T_{\text{eq}}$ that in the Markovian case Eq. \ [3] is the instantaneous generalized excess free energy in units of $k_B T_{\text{eq}}$, i.e. \ $\mathcal{D}(\mathcal{P}_T(t)||\mathcal{P}_T^{\text{eq}}) = \beta_q (F_T(t) - F) = \beta_q \delta F_T(t) \ [43, 50]$. Writing out Eq. \ [3] for the non-Markovian case and identifying $S_T(t)$ and $\langle U(t) \rangle_T$ (we use calligraphic letters for thermodynamic potentials of projected observables) we find

$$\mathcal{D}(\mathcal{P}_T(t)||\mathcal{P}_T^{\text{eq}}) = -S_T(t) + k_B + \beta_q \langle U(t) \rangle_T. \ (5)$$

delivering the instantaneous generalized excess free energy for non-Markovian observables $\delta F_T(t) = -T_{\text{eq}} \delta S_T(t) + \langle U(t) \rangle_T$, such that $D_T = \beta_q \delta F_T(t)$ (with an obvious abuse of notation). We henceforth express energies in units of $k_B T_{\text{eq}}$. If (and only if) latent degrees of freedom (i.e. those integrated out) relax much faster than $q(t)$, Eqs. \ [4] and \ [5] are equivalent and $q(t)$ is a Markovian diffusion in the free energy landscape $U(q) \ [4]$. In absence of a complete time-scale separation, however, both $S_T(t)$ and $\langle U(t) \rangle_T$ contain contributions from the (hidden) relaxation of the latent degrees of freedom.

Consider now a pair of temperatures $T^+ > 1$ and $T^- < 1$ corresponding to equal displacements immediately after the quench: $D_{T^+} \equiv \langle 0^+ \rangle = D_{T^-} \equiv \langle 0^+ \rangle$. The existence of (at least) two such temperatures is guaranteed within an interval $T \in (T_{\text{min}}, T_{\text{max}})$ where $D_T \equiv f(T)$ has no local maximum. The central question of this Letter addresses the relative speed of the ‘uphill’ ($T^+ < 1$) versus ‘downhill’ ($T^+ > 1$) relaxation.

**Gaussian Chain.** — In the context of single-molecule experiments we consider a chain of $N + 1$ beads with coordinates $\mathbf{R} = \{r_i\}$ connected by harmonic springs with potential $U(\mathbf{R}) = \sum_{i=1}^{N+1} (r_{i+1} - r_i)^2 / 2$ (general Gaussian networks are analyzed in the SM). We introduce the $\mathbb{R}^{3(N+1)} \times \mathbb{R}^{3(N+1)}$ triagonal super-matrix $\Xi$ with elements $\Xi_{ii} = 1$ and $\Xi_{i+1,i} = \Xi_{i,i+1} = (-1-\delta_i + \delta_i N+1) \mathbb{I}$, where $\mathbb{I}$ is the $3 \times 3$ identity matrix. The corresponding Itô equation of motion reads $d\mathbf{R}(t) = \Xi \mathbf{R}(t) dt + \sqrt{2} d\mathbf{W}_t$, where $d\mathbf{W}_t$ is the $(3(N+1))$-dimensional super-vector of independent Wiener increments with zero mean and unit variance, $\mathbb{E}[d\mathbf{W}_t d\mathbf{W}_t^T] = \delta_{ij} \delta(t - t')$. We pass to normal coordinates $\mathbf{R} \equiv \mathbf{x} \equiv \{x_i\}$, i.e. $\mathbf{A}^T \mathbf{X} = \text{diag}(\mu)$ with elements $\mu_k = 4 \sin^2(2\pi k / (2N+1))$, such that $\mathbf{R} = \mathbf{A} \mathbf{X}$ with the $\mathbb{R}^{3(N+1)} \times \mathbb{R}^{3(N+1)}$ orthogonal super-matrix with elements $\mathbf{A}_{ij} = (2^i \epsilon_{ij}) / 2^{(2i+1)N+1}$. In normal coordinates probability densities factorize:

$$P_T(x, t) = \prod_{k=1}^{N} \frac{\mu_k}{2 \pi \Lambda_k^T(t)} \exp \left( -\frac{\mu_k x_k^2(t)}{2 \Lambda_k^T(t)} \right), \ (6)$$

where we have introduced $\Lambda_k^T(t) = 1 + (\tilde{T} - 1)e^{-2\mu_k t}$. Since $\tilde{T}(0) = \tilde{T}$, we have $P^{eq}(x) = P_T(x, 0)$, while $\lim_{t \to \infty} P_T(x, t) = P^{eq}(x)$. In single-molecule experiments (e.g. FRET \ [53, 54] or optical tweezers \ [40, 41]) one typically tracks a single (e.g end-to-end) distance within the macromolecule, $d = |r_1 - r_N| = |\sum_{k=1}^{N} (A_{1k} - A_{Nk}) x_k|$. The dynamics of $d$ is a non-Markovian problem according to Eq. \ [2] with $q = d$. The time-dependent probability density function of $d$ can be calculated exactly (see derivation in SM) and, introducing $A_{ij}^N(t) \equiv \sum_{k=1}^{N} \Lambda_k^T(t) (A_{1k} - A_{Nk}) x_k$, the reads

$$P_T(d, t) = \frac{d^2}{2\pi} A_{11}^{(N)}(t)^{-3/2} e^{-d^2/4A_{11}^{(N)}(t)}. \ (7)$$
Note that immediately after the quench \( P_T(d,0) = P_T^{eq}(d) \), whereas in equilibrium \( \lim_{t \to \infty} P_T(d, t) = P_T^{eq}(d) \). In the Markovian setting all eigenmodes relax independently (see Eq. (3)), whereas the projection onto a single distance mixes the modes in a non-trivial manner (see Eq. (7)). The instantaneous displacement from equilibrium is given exactly by

\[
\mathcal{D}[P_T(t) || P_T^{eq}] = 3 \sum_{k=1}^{N} \left[ A_k^T(t) - 1 - \ln A_k^T(t) \right] \tag{8}
\]

\[
\mathcal{D}[P_T(t) || P_T^{eq}] = 3 \left[ \frac{A_1^N(t) - 1 + \ln A_1^N(t)}{A_1^N(0) - 1 + \ln A_1^N(0)} \right], \tag{9}
\]

whereas the initial excess free energies read

\[
\delta \mathcal{F}_T(0) = \mathcal{D}[P_T(0) || P_T^{eq}] = 3N(\hat{T} - 1 - \ln \hat{T})/2 \tag{10}
\]

and \( \delta \mathcal{F}_T(t) = \mathcal{D}[P_T(t) || P_T^{eq}] / N \), which are both convex in \( \hat{T} \). The latter is also the only surviving variable. The instantaneous potential energy of the full system in turn reads \( \langle U(t) \rangle_{\hat{T}} = \frac{1}{2} \sum_{k=1}^{N} A_k^T(t) \), while the potential of mean force is given by \( U(d) = -\ln P_T^{eq}(d) \). Note that aside from the specific values of \( \mu_k \) and \( A \) Eqs. (8-10) hold for any reversible Ornstein-Uhlenbeck process, that is for any \( \hat{T} \), symmetric matrix \( \Xi \), and tagged distance.

The results for \( \mathcal{D}[P_T(t) || P_T^{eq}] \) and corresponding \( \langle U(t) \rangle_{\hat{T}}, \langle U(d) \rangle_{\hat{T}}, \langle S_T(t) \rangle_{\hat{T}} \) and \( S_T(t) \) for a pair of equidistant temperature quenches are shown in Fig. 2 and demonstrate that the uphill relaxation is always faster than downhill relaxation. As we prove below this is true for any reversible Ornstein-Uhlenbeck process (OUp) quenched arbitrarily far from equilibrium.

In Fig. 2b we depict energy and entropy differences \( \langle \Delta U(t) \rangle_{\hat{T}+} = \langle U(t) \rangle_{\hat{T}+} - \langle U \rangle_1 \) and \( \Delta S_T(t) = S_T(t) - S_1 \), which highlight that uphill relaxation is dominated by entropy and downhill relaxation by potential energy differences. Surprisingly, entropy pushing the Markovian system up the energy landscape is more efficient. Curiously, in the non-Markovian setting we find \( \langle U \rangle_{\hat{T}} \) to be the dominant driving force for uphill relaxation and \( S_T(t) \) for downhill relaxation – a consequence of the relaxation of hidden, latent degrees of freedom, which generally depends on the details of the projection.

**Tilted Single File.** In the context of tracer-particle dynamics we consider \( N \) hard-core Brownian point particles (the extension to a finite diameter is straightforward) diffusing in a box of unit length \( (D = L = 1) \) in the presence of a linear potential (e.g. the gravitational field), \( U(x_i) = \sum_{i=1}^{N} g x_i \). We solve the full system’s dynamics via the coordinate Bethe ansatz. In dimensionless units the Boltzmann-Gibbs density of a single particle at temperature \( \hat{T} \) corresponds to \( P_T^{eq}(x) = g \hat{T}^{-1} e^{-g x / \sqrt{2}} \). For the full single file we have

\[
P_T^{eq}(x) = N ! \hat{O}_x \prod_{i=1}^{N} P_T^{eq}(x_i), \quad \hat{O}_x \equiv \prod_{i=2}^{N} \theta(x_i - x_{i-1})
\]

the Heaviside function. We expand the Green’s function for a single particle at \( \hat{T} = 1 \) in a bi-orthonormal eigenbasis, \( \zeta(x_i, t|x_0) = \sum_{k=0}^{\infty} \phi_k^R(x) \phi_k^L(x_0) e^{-\lambda_k t} \), where \( \lambda_0 = 0 \), \( \lambda_k = \pi^2 k^2 + g^2 / 4 \) and

\[
\phi_k^L(x) = e^{\frac{g x^2}{2 \sqrt{2 \lambda_k}}} (g \sin(k \pi x) - 2k \pi \cos(k \pi x)), \quad k > 0 \tag{11}
\]

and \( \phi_k^R(x) = e^{-g x / \sqrt{2 \lambda_k}} \phi_k^L(x) \), whereas for \( k = 0 \) we have \( \phi_0^R(x) = 1 \), \( \phi_0^L(x) = P_T^{eq}(x) \).

As before we assume that the system is quenched at \( t = 0 \). The surrounding many-body probability density can be shown to read (see SM) \( P_T(x, t) = N ! \hat{O}_x \prod_{i=1}^{N} P_T(x_i, t) \), where we introduced \( P_T(x_i, t) = \int_{x_0}^{1} dx_0 \zeta(x_i, t|x_0) P_T^{eq}(x_0) \) and \( \hat{O}_x \) guarantees that the non-crossing conditions are satisfied at all times.

We are interested in the diffusion of a tagged particle \( x_T(t) = z(t) \) as the non-Markovian observable (i.e. \( \tilde{H}_x(z) = \tilde{O}_x \prod_{i=1}^{N} \int_{x_0}^{1} dx_0 \delta(x_T - z(t)) \)). Introducing the auxiliary function \( \Omega_T^z(x, y) \equiv e^{-g x / \sqrt{T}} - e^{-g y / \sqrt{T}} \) the equilibrium tagged particle probability density at \( \hat{T} \) can be shown to read (see SM)

\[
P_T^{eq}(z) = \frac{g N ! \Omega_T^z(0, z)^N \Omega_T^z(z, 1)^N}{N! N! T \Omega_T^z(0, 1)} e^{-g z / \sqrt{T}}, \tag{12}
\]

where \( \frac{N_L}{N_R} = \frac{T-1}{T-1} \) and \( N_L = N - N_T \) are the total number of particles to the left and to the right of the tagged particle, respectively. The time-dependent probability density \( P_T(z, t) \) is in turn obtained with the coordinate Bethe-ansatz and reads

\[
P_T(z, t) = \sum_{k} \nu_k(z) \nu_k^T e^{-\lambda_k t}, \tag{13}
\]

where \( \sum_k \) denotes the sum over all possible permutations of a \( N \)-tuple of non-negative integers, \( k = \{ k_i \} \), and \( \lambda_k = \sum_{i=1}^{N} \lambda_{k_i} \) are Bethe eigenvalues of the operator \( \tilde{L}_1 = \sum_{i=1}^{N} (\partial_x^2 + g \partial_x) \) in a unit box under non-crossing conditions. The expressions for \( \nu_k(z), \nu_k^T \), and the potential energy, \( \langle U(t) \rangle_{\hat{T}} = g N \langle x(t) \rangle \), are somewhat lengthy and are hence deferred to the SM (Eqs. (S33-S39)). As the integrals in Eqs. (3-7) cannot be carried out exactly we resort to efficient numerical quadratures.

The results for \( \mathcal{D}[P_T(t) || P_T^{eq}] \) and corresponding \( \langle \Delta U(t) \rangle_{\hat{T}}, \langle U(d) \rangle_{\hat{T}}, \Delta S_T(t) \) and \( S_T(t) \) for the the Markovian \( N \)-particle diffusion as well as the non-Markovian tagged particle dynamics are shown in Fig. 2. Similar to the results for the Gaussian chain, in the tilted single file ‘uphill’ relaxation, both full as well as for a tagged particle, seems to always be faster than ‘downhill’ relaxation, irrespective of which particle we tag and for any \( \hat{T}, N \) and tilting strength \( g > 0 \) (see also SM).

The dominant driving force for uphill relaxation of the full system is \( \Delta S_{T-} \), whereas downhill relaxation is
dominated by $\langle \Delta U(t) \rangle_{\tilde{T}_-}$ (see Fig. 2)). Conversely, in the tagged-particle case the precise partitioning between $\langle U(t) \rangle_{\tilde{T}_-}$ and $S(t)_{\tilde{T}_-}$ depends on which particle we tag. The reason lies in the shape of $U(z)$ and the dependence of $\mathcal{P}_z(0,0')$ on $\tilde{T}$, which in turn both depend on the tagged particle as well as $\tilde{T}$, $N$ and tilting strength $g$.

Is the asymmetry universal?—We first focus on dynamics near a stable minimum $R_0$, $\delta R(t) = R(t) - R_0$, which is well described by an Ornstein-Uhlenbeck process (OUp), i.e. $d\delta R(t) = \mathbf{H} \delta R(t) dt + \sqrt{2dW_t}$, where $(\mathbf{H})_{ij} = \sum_{ij} \partial_{R_i} \partial_{R_j} U(R)|_{R_0}$ is the Hessian.

**Theorem 1.** For a general diffusion sufficiently close to a stable minimum and for any stable reversible OUp the relaxation from a pair of equidistant quenches of arbitrary magnitude (as defined above) is always faster uphill.

**Proof.** For any $0 < \tilde{T}_- \leq 1$ and $1 \leq \tilde{T}_+ < \infty$ satisfying $D_{\tilde{T}_+}(0^+) = D_{\tilde{T}_-}(0^+)$ we have by construction $\tilde{T}_+ - \tilde{T}_- = \ln(\tilde{T}_+/\tilde{T}_-)$. We first prove the claim for the Markovian setting, where Eq. [2] has the structure $D(t) = \sum_{k=1}^N D_k(t)$. We set $\varphi \equiv \tilde{T}_+ / \tilde{T}_- > 1$, $\delta_z \equiv \tilde{T}_+ - 1$, and write $\Delta D_k(t) = D_k^\varphi(t) - D_k^\delta_z(t) = \ln Z(\varphi, \mu_k)$, such that

\[
Z(\varphi) = \varphi^{e^{-\delta_z}(1 + \delta_+ e^{-\tau})/(1 + \delta_+ e^{-\tau})} = [\varphi(1 + \delta_- e^{-\tau})^\tau e^{-\tau} / (1 + \delta_+ e^{-\tau})] \geq [\varphi(1 + \delta_-) / (1 + \delta_+)]^\tau e^{-\tau} \geq 1,
\]

where we have used the generalized Bernoulli inequalities, i.e. for any real $0 \leq y_1 \leq 1$, $y_2 \geq 1$ and $x \geq -1$ we have $(1 + x)^{y_1} \geq 1 + y_1 x$ and $(1 + x)^{y_2} \leq 1 + y_2 x$. Recalling the definition of $\Delta D_k(t)$ completes the proof.

To prove the claim in the non-Markovian setting for projections of type $g = |\delta R_i - \delta R_j|$ we first realize that $\hat{A}_{ij}^\varphi(t) \leq 0$ and $\hat{A}_{ij}^\delta_z(t) \geq 0$, where $f(t) \equiv d f(t)$. Setting $\Delta D(t) \equiv D[\mathcal{P}_{\tilde{T}_+}(t)] - D[\mathcal{P}_{\tilde{T}_-}(t)]$ and using Eq. [9] we find, upon taking the derivative

\[
\Delta \dot{D}(t) = \frac{\hat{A}_{ij}^\varphi(t)}{A_{ij}^\varphi(t)} - \frac{\hat{A}_{ij}^\delta_z(t)}{A_{ij}^\delta_z(t)} - \frac{\hat{A}_{ij}^{\varphi -}(t)}{A_{ij}^{\varphi -}(0)} + \frac{\hat{A}_{ij}^{\delta_z -}(t)}{A_{ij}^{\delta_z -}(0)}, \tag{15}
\]

Eq. [15] implies $\Delta \dot{D}(t) \geq 0$ because $A_{ij}^{\varphi +}(t) \geq A_{ij}^{\delta_z +}(t)$ while $A_{ij}^{\delta_z -}(t) \leq A_{ij}^{\varphi -}(t)$, which completes the proof. □

The fact that tilted single-file diffusion, being anharmonic with non-perturbative interactions, still displays the asymmetry for quenches of arbitrary magnitude and for any steepness of the potential hints that the asymmetry might be more general. Note that tagging different particles in different slopes $g > 0$ we can construct $U(z)$ with arbitrary asymmetry. Taken alongside Theorem 1 this strongly suggest that uphill relaxation in single-well potentials could be universally faster. Since the projection [2] is independent of $T$ these statements should naturally extend also to non-Markovian observables, in particular those probed in many single-molecule and particle-tracking experiments. The asymmetry apparently prevails even in symmetric double-well potentials (see SM), but not in general energy landscapes (counterexamples are shown in the SM).

**Conclusion.**—We uncovered an unforeseen asymmetry in the relaxation to equilibrium in equidistant temperature quenches. Uphill relaxation was found to be faster – a phenomenon we proved to be universal for quenches of dynamics near stable minima. We hypothesize that it is a general phenomenon in reversible overdamped diffusion in single-well potentials that may extend to symmetric multi-well potentials. The dependence on directionality of the displacement from equilibrium, which so far seems to have been overlooked, implies a systematic asymmetry in the dissipation of the system’s entropy $\dot{S}_T(t)$ versus heat $\langle U(t) \rangle_T$ [12], or the modified entropy $\tilde{S}_T(t)$ and strong coupling counterpart of heat $\langle \dot{U}(t) \rangle_T$ [14] during relaxation of Markovian and
non-Markovian observables, respectively. Our results can readily be tested by existing single-molecule [40, 41] and particle-tracking [4] experiments. To gain a deeper understanding of the asymmetry on the level of individual trajectories it would be particularly interesting to analyze relaxation from equidistant quenches in terms of occupation measures [4, 7] and from the perspective of stochastic thermodynamics [12, 14].

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Supplementary Material for:
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Abstract
In this Supplementary Material (SM) we present detailed derivations of the main results for the Gaussian-Chain and tilted single-file diffusion model presented in the main Letter, as well as several supplementary figures. We present counterexamples demonstrating that the uphill-downhill asymmetry is not universal as it vanishes in asymmetric multi-well potentials. Finally, we also discuss the non-Markovian Mpemba effect.

GAUSSIAN CHAIN AND ORNSTEIN-UHLENBECK PROCESS

We consider a Gaussian Chain with N+1 beads with coordinates \( \mathbf{R} = \{ \mathbf{r}_i \} \) connected by harmonic springs with potential energy \( U(\mathbf{R}) = \frac{1}{2} \sum_{i=1}^{N} |\mathbf{r}_i - \mathbf{r}_{i+1}|^2 \). The overdamped Langevin equation governing the dynamics of a Gaussian Chain with N+1 beads connected by ideal springs with zero rest-length and diffusion coefficient \( D \) is given by the set of coupled Itô equations

\[
\begin{align*}
\text{d}\mathbf{r}_1(t) &= [-\mathbf{r}_1(t) + \mathbf{r}(t)]dt + \sqrt{2D}\mathbf{\xi}_1(t) \\
\text{d}\mathbf{r}_i(t) &= [\mathbf{r}_{i-1}(t) - 2\mathbf{r}_i(t) + \mathbf{r}_{i+1}(t)]dt + \sqrt{2D}\mathbf{\xi}_i(t) \\
\text{d}\mathbf{r}_{N+1}(t) &= [-\mathbf{r}_{N+1}(t) + \mathbf{r}_N(t)]dt + \sqrt{2D}\mathbf{\xi}_{N+1}(t),
\end{align*}
\]

(S1)

where \( \mathbf{\xi}_i(t) \) stands for zero mean Gaussian white noise, i.e.

\[
\langle \mathbf{\xi}_i(t) \rangle = 0, \quad \langle \mathbf{\xi}_{i,k}(t)\mathbf{\xi}_{i,l}(t') \rangle = \delta_{ii}\delta(t-t').
\]

(S2)

It is straightforward to generalize these formulas to any reversible \( 3(N+1) \)-dimensional Ornstein-Uhlenbeck process \( \mathbf{R}(t) \equiv \{ \mathbf{r}_i(t) \} \) with some \( \mathbb{R}^{3(N+1)} \times \mathbb{R}^{3(N+1)} \) symmetric force matrix \( \mathbf{\Xi} \) and potential energy function \( U(\mathbf{R}) = \frac{1}{2}\mathbf{R}^T\mathbf{\Xi}\mathbf{R} \)

\[
d\mathbf{R}(t) = \mathbf{\Xi}\mathbf{R}(t)dt + \sqrt{2D}\mathbf{dW}_t,
\]

(S3)

where \( d\mathbf{W}_t \) is the \( 3(N+1) \)-dimensional super-vector of independent Wiener increments with zero mean and unit variance, \( \mathbb{E}[dW_{i,t}dW_{j,t'}] = \delta_{ij}\delta(t-t') \). In this super-vector/super-matrix notation the Gaussian is recovered by introducing \( \mathbb{R}^{3(N+1)} \times \mathbb{R}^{3(N+1)} \) tridiagonal super-matrix \( \mathbf{\Xi} \) with elements

\[
\mathbf{\Xi}_{ii} = 1, \quad \mathbf{\Xi}_{ii+1} = \mathbf{\Xi}_{ii-1} = (-1 - 1^\delta_{i,1}^\delta_{i,N+1})\mathbb{1},
\]

(S4)

where \( \mathbb{1} \) is the \( 3 \times 3 \) identity matrix. This leads to the equations of motion presented in the Letter. Since \( \mathbf{\Xi} \) is supposed to be symmetric these equations can be decoupled by diagonalizing \( \mathbf{\Xi} \) i.e. by passing to normal coordinates \( \mathbf{R} \to \mathbf{X} \equiv \{ x_i \} \):

\[
\mathbf{A}^T\mathbf{\Xi}\mathbf{A} = \text{diag}(\mu)
\]

(S5)

where the diagonal super-matrix has elements \( \text{diag}(\mu)_{kk} = \mu_k\mathbb{1} \). This yields eigenvalues \( \mu_i \) and orthogonal super-matrices \( (\mathbf{A}_{ij})_{ij} \equiv \mathbf{A}_{ij}\mathbb{1} \), where the \( i \)th row \( \mathbf{A}_{ij} \), \( j = 0, \ldots, N \) corresponds to an eigenvector of the 1-dimensional contraction of \( \mathbf{\Xi} \) (see e.g. Eq. (S4)) for the Gaussian chain, i.e. \( \mathbf{\Xi}_{ii} \to 1 \) and \( \mathbf{\Xi}_{ii-1} \to (-1 - 1^\delta_{i,1}^\delta_{i,N+1}) \).

In the particular case of the Gaussian chain the eigenvalues and eigenvectors read

\[
\mu_k = 4\sin^2\left( \frac{k\pi}{2(N+1)} \right), \quad \mathbf{A}_{ij} = \sqrt{\frac{2^1-\delta_{j,0}}{N+1}} \cos \left( \frac{(2i-1)j\pi}{2(N+1)} \right).
\]

(S6)

The back-transformation corresponds to \( \mathbf{r}_i = \sum_{k=0}^{N} A_{ik}x_k \). In normal coordinates the the potential energy function \( U(\mathbf{X}) = \frac{1}{2}\sum_{k=0}^{N} \mu_kx_k^2 \) while the corresponding Fokker-Planck equation for the evolution of the Green’s function at a temperature \( T \), \( G_T(x,t|x_0) \), reads

\[
\left[ \frac{\partial}{\partial t} - \sum_{k=0}^{N} \left( \mu_k \frac{\partial^2}{\partial x_k^2} + \beta\mu_k \frac{\partial}{\partial x_k} \right) \right] G_T(x,t|x_0) = \delta(x-x_0),
\]

(S7)
where \( \beta = 1/k_B T \). Note that we are interested only in internal dynamics and not on the center-of-mass dynamics, therefore we will henceforth ignore the \( k = 0 \) contribution, as the zero mode with \( \mu_0 = 0 \) pertains only to the center-of-mass motion. Without any loss of generality we henceforth set \( D = 1 \) and measure energies in units of \( k_B T_{\text{eq}} \), where \( T_{\text{eq}} \) is the equilibrium (post-quench) temperature as defined in the manuscript. Moreover, since we are only interested in the evolution at temperature \( T_{\text{eq}} \), we further express temperature relative to \( T_{\text{eq}} \), i.e. \( \tilde{T} \equiv T/T_{\text{eq}} \), such that \( \tilde{T} = 1 \) corresponds to \( T_{\text{eq}} \). The stationary solution of Eq. (S7) corresponds to the Boltzmann-Gibbs density

\[
P^\text{eq}_T(X) = \frac{1}{\prod_{k=1}^{N} \left( \frac{\mu_k}{2\pi} \right)^{3/2} \exp \left( -\frac{\mu_k X_k^2}{2T} \right)}.
\]  

(S8)

The probability density of \( X \) starting from an initial probability density function \( P^\text{eq}_T(X_0) \) is obtained from the Green’s function via

\[
P_T(X, t) = \int dX_0 G_1(X, t|X_0) P^\text{eq}_T(X_0),
\]  

(S9)

where

\[
G_1(X, t|X_0, 0) = \frac{1}{\prod_{k=1}^{N} \left( \frac{\mu_k}{2\pi(1 - e^{-\mu_k t})} \right)^{3/2} \exp \left[ -\frac{\mu_k X_k^2}{2(1 - e^{-\mu_k t})} \left( x_k^2 - 2x_k \cdot x_{0k} e^{-\mu_k t} + x_{0k}^2 e^{-2\mu_k t} \right) \right].
\]  

(S10)

is the well-known Green’s function of an Ornstein-Uhlenbeck process. Note that \( \lim_{t \to \infty} G_T(X, t|X_0, 0) = P^\text{eq}_T(X) \).

The integral Eq. (S9) can easily be performed analytically and yields

\[
P_T(X, t) = \frac{1}{\prod_{k=1}^{N} \left( \frac{\mu_k}{2\pi[1 + (\tilde{T} - 1)e^{-\mu_k t}]} \right)^{3/2} \exp \left( -\frac{\mu_k X_k^2}{2[1 + (\tilde{T} - 1)e^{-\mu_k t}]} \right)}.
\]  

(S11)

Eq. (S11) can now be used to calculate the Kullback-Leibler divergence (Eq. (3) in the Letter) to yield the first of Eqs. (8) in the Letter. Furthermore, the average potential energy and the system’s entropy are defined as

\[
\langle U(t) \rangle_T \equiv \int dx P_T(x, t) U(x), \quad S_T(t) = -\int dx P_T(x, t) \ln P_T(x, t)
\]  

(S12)

and read, upon performing the integration and introducing \( \Lambda_k^T(t) = 1 + (\tilde{T} - 1)e^{-\mu_k t} \),

\[
\langle U(t) \rangle_T = \frac{3}{2} \sum_{l=1}^{N} \Lambda_k^T(t), \quad S_T(t) = \frac{3}{2} \sum_{k=1}^{N} \left[ 1 - \ln \left( \frac{\mu_k}{2\pi \Lambda_k^T(t)} \right) \right].
\]  

(S13)

In the projected, non-Markovian setting we are interested in the dynamics of an internal distance \( d_{ij}(t) \equiv |r_i(t) - r_j(t)| \). In normal coordinates this corresponds to

\[
d_{ij} \equiv |r_i - r_j| = \sum_{k=1}^{N} |(A_{ik} - A_{jk}) x_k|.
\]  

(S14)

By doing so we project out \( 3(N-1) \) latent degrees of freedom and track only \( d_{ij} \). The ‘non-Markovian Green’s function’, that is, the probability density of \( d_{ij} \) and time \( t \) given that the full system evolves from \( P^\text{eq}_T(X_0) \) is defined as

\[
P_T(d, t) = \int d\Omega \int dX_0 \delta \left( \sum_{k=1}^{N} [A_{ik} - A_{jk}] x_k - d \right) G_1(X, t|X_0, 0) P^\text{eq}_T(X_0)
\]  

\[
= d^2 \int_{d_0}^{\infty} dl_0 \int d\Omega \int dX_0 \delta \left( \sum_{k=1}^{N} [A_{ik} - A_{jk}] x_k - d \right) \delta \left( \sum_{k=1}^{N} [A_{ik} - A_{jk}] x_{k,0} - l_0 \right) G_1(X, t|X_0, 0) P^\text{eq}_T(X_0)
\]  

\[
= \int_{0}^{\infty} dl_0 P_T(d, t|l_0; P^\text{eq}_T),
\]  

(S15)
where we first line project onto the vectors \( \mathbf{d} \) and \( \mathbf{d}_0 \) and afterwards marginalize over all respective angles \( \Omega \) and \( \Omega_0 \). Note that the step in line 2 of Eq. (S15) is actually not necessary but is preferable if one also wants to access the general non-Markovian two-point joint density \( \mathcal{P}_T(d, t; d_0; P_{eq}^T) \). The calculation proceeds as follows.

We first preform two 3-dimensional Fourier transforms \( \mathbf{d}_0 \rightarrow \mathbf{u} \) and \( \mathbf{d} \rightarrow \mathbf{v} \):

\[
\mathcal{P}_T^d(\mathbf{u}, t; \mathbf{v}, 0; P_{eq}^T) = \frac{1}{(2\pi)^6} \int d\mathbf{d} e^{-i\mathbf{v} \cdot \mathbf{d}} \int d\mathbf{d}_0 e^{-iw \cdot \mathbf{d}_0} \mathcal{P}_T(d, t; d_0; P_{eq}^T)
\]

\[
= \frac{1}{(2\pi)^6} \prod_{k=1}^N \exp \left[ -\frac{\delta A_k^2}{2\mu_k} (1 + (\tilde{T} - 1)e^{-2\mu_k t}) \mathbf{v}^2 - \frac{\delta A_k^2}{2\mu_k} \mathbf{u}^2 - 2\frac{\delta A_k^2}{2\mu_k} e^{-\mu_k t} \mathbf{v} \cdot \mathbf{u} \right],
\]

where we have introduced the short-hand notation \( \delta A_k \equiv A_{ik} - A_{jk} \). Now we define, as in the main text, \( \Lambda_k^T(t) \equiv 1 + (\tilde{T} - 1)e^{-2\mu_k t} \) as well as

\[
\Lambda_k^T(t) \equiv \sum_{k=1}^N \Lambda_k^T(t) \delta A_k^2/2\mu_k, \quad \mathcal{B}_ij^T(t) \equiv \tilde{T} \sum_{k=1}^N \delta A_k^2 \exp(-\mu_k t)/2\mu_k,
\]

and rewrite Eq. (S16) as

\[
\mathcal{P}_T^d(\mathbf{u}, t; \mathbf{v}, 0; P_{eq}^T) = \frac{1}{(2\pi)^6} \exp \left( -\Lambda_k^T(t) \mathbf{v}^2 - \Lambda_k^T(0) \mathbf{u}^2 - 2\mathcal{B}_ij^T(t) \mathbf{v} \cdot \mathbf{u} \right),
\]

which can be easily inverted back to give

\[
\mathcal{P}_T(d, t; d_0; P_{eq}^T) = (4\pi)^{-3} |\Lambda_k^T(t)\Lambda_k^T(0) - \mathcal{B}_ij^T(t)|^{-3/2} \exp \left( -\frac{1}{4} \Lambda_k^T(0) \mathbf{d}^2 - 2\mathcal{B}_ij^T(t) \mathbf{d} \cdot \mathbf{d}_0 + \Lambda_k^T(t) \mathbf{d}_0^2 \right).
\]

The marginalization is henceforth straightforward and yields

\[
\mathcal{P}_T(d, t; d_0; P_{eq}^T) = \frac{(dd_0)^2}{2\pi |\Lambda_k^T(t)\Lambda_k^T(0) - \mathcal{B}_ij^T(t)|^{-3/2}} \int_0^\pi d\cos \theta \exp \left( \frac{1}{2} \frac{dd_0 \mathcal{B}_ij^T(t) \cos \theta}{\Lambda_k^T(t)\Lambda_k^T(0) - \mathcal{B}_ij^T(t)} \right)
\]

\[
= \frac{dd_0}{2\pi \mathcal{B}_ij^T(t)} \left| \Lambda_k^T(t)\Lambda_k^T(0) - \mathcal{B}_ij^T(t) \right|^{1/2} \sinh \left( \frac{1}{2} \frac{dd_0 \mathcal{B}_ij^T(t) dd_0}{\Lambda_k^T(t)\Lambda_k^T(0) - \mathcal{B}_ij^T(t)} \right).
\]

The probability density of \( d \) at time \( t \) after having started from an initial density \( P_{eq}^T(X_0) \) (i.e. the pre-quench equilibrium) follows by simple integration and finally reads

\[
\mathcal{P}_T(d, t) = \int_0^{\infty} dt_0 \mathcal{P}_T(d, t; t_0; P_{eq}^T) \equiv \frac{d^2}{2\sqrt{\pi}} \Lambda_k^T(t)^{-3/2} e^{-d^2/4\Lambda_k^T(t)},
\]

which is precisely Eq. (7) in the manuscript. The average potential of mean force, \( \langle \mathcal{U}(t) \rangle_T \equiv -\langle \ln \mathcal{P}_T(d, t) \rangle_T \) and entropy, \( \mathcal{S}_T(t) \equiv -\langle \ln \mathcal{P}_T(d, t) \rangle_T \) (in units of \( k_B T \)), where \( \langle f(d) \rangle_T \equiv \int dP_T(l, t) f(l) \), in turn read

\[
\langle \mathcal{U}(t) \rangle_T = \ln \left( 2\sqrt{\pi} \Lambda_k^T(t) \right) - \Lambda_k^T(t)^{1/2}(2 - \gamma_e + \ln \Lambda_k^T(t)) + \frac{3}{2} \Lambda_k^T(t) \]

\[
\mathcal{S}_T(t) = \ln \left( 2\sqrt{\pi} \Lambda_k^T(t) \right) - \Lambda_k^T(t)^{1/2}(2 - \gamma_e + \ln \Lambda_k^T(t)) + \frac{3}{2}
\]

where \( \gamma_e \) denotes Euler’s gamma. Using the results in Eq. (S22) as well as the definition of the equilibrium free energy, \( F = -\ln Q_1 \equiv -\int dX e^{-U(X)} \), (where all potentials are in units of \( k_B T_{eq} \)) we arrive at

\[
\mathcal{D}[\mathcal{P}_T^d(t)||P_1] = \langle \mathcal{U}_T(t) \rangle - \mathcal{S}_T(t) - F, \quad \mathcal{D}[\mathcal{P}_T(d)||P_1] = \langle U_T^H(t) \rangle - \mathcal{S}_T(t),
\]

which are exactly Eqs. (4) and (5) in the Letter. For any stable symmetric matrix \( \Xi \) the condition of equidistant quenches \( \mathcal{D}[\mathcal{P}_T^d(0)||P_1] = \mathcal{D}[\mathcal{P}_T^d(0)'||P_1] \) is satisfied by

\[
\tilde{T}^+ - \tilde{T}^- = \ln(\tilde{T}^+/\tilde{T}^-) \rightarrow \tilde{T}^+(\tilde{T}^-) = -W_{-1}(\tilde{T}^- e^{-\tilde{T}^+}),
\]
where $W_{-1}(x)$ defined for $x \in [-e^{-1}, 0)$ denotes the second real branch of the Lambert-W function, which in turn satisfies the following sharp two-sided bound \[ \frac{2}{3} \left[ 1 + \sqrt{2(\bar{T} - 1 - \ln \bar{T}) + \bar{T} - 1 - \ln \bar{T}} \right] \leq \bar{T}^+(\bar{T}^-) \leq 1 + \sqrt{2(\bar{T} - 1 - \ln \bar{T}) + \bar{T} - 1 - \ln \bar{T}.} \] (S25)

**Kullback-Leibler divergence and uphill/downhill asymmetry in relaxation of a random Gaussian network**

In the Letter we prove that for any reversible ergodic Ornstein-Uhlenbeck process uphill relaxation (i.e. for a quench from $\bar{T}^- \uparrow 1$) for which $\langle U(0^+) \rangle_{\bar{T}^-} - \langle U \rangle_1 < 0$ is always faster than downhill relaxation (i.e. for a quench from $\bar{T}^+ \downarrow 1$) for which $\langle U(0^+) \rangle_{\bar{T}^-} - \langle U \rangle_1 > 0$, where the pair of equidistant quenches $\bar{T}^+$ and $\bar{T}^-$ is defined in the Letter. To visualize this on hand of an additional instructive example, we generated a random Gaussian network with 10 beads by filling elements of the upper-triangular part of the connectivity matrix with a $-1$ according to a Bernoulli distribution with $p = 0.7$. The resulting matrix was then symmetrized and the diagonal elements chosen to assure sure mechanical stability (i.e. 'connectedness'). The resulting connectivity matrix $\Gamma$ is related to the general Ornstein-Uhlenbeck matrix in Eq. (S3) via $\Xi = \Gamma \otimes \mathbb{1}$, where

$$
\Gamma = \begin{pmatrix}
5 & -1 & -1 & 0 & -1 & 0 & 0 & 0 & -1 & -1 \\
-1 & 5 & -1 & 0 & -1 & -1 & 0 & 0 & 0 & -1 \\
-1 & -1 & 8 & -1 & -1 & 0 & -1 & -1 & -1 & -1 \\
0 & 0 & -1 & 7 & -1 & -1 & -1 & -1 & -1 & -1 \\
-1 & -1 & -1 & -1 & 9 & -1 & -1 & -1 & -1 & -1 \\
0 & -1 & 0 & -1 & -1 & 7 & -1 & -1 & -1 & -1 \\
0 & 0 & -1 & -1 & -1 & 7 & -1 & -1 & -1 & -1 \\
0 & 0 & -1 & -1 & -1 & -1 & 7 & -1 & -1 & -1 \\
-1 & 0 & -1 & -1 & -1 & -1 & -1 & 8 & -1 \\
-1 & -1 & -1 & -1 & -1 & -1 & -1 & -1 & 9
\end{pmatrix}.
$$

(S26)

The corresponding results for $\mathcal{D}[\mathcal{P}_f(t)||\mathcal{P}_1]$, whereby we tagged the distance between the 1st and 10th bead, i.e. $d = |r_1 - r_{10}|$, are shown in Fig. S3.

![Figure S3](image.png)

Figure S3. $\mathcal{D}[\mathcal{P}_{f\pm}(t)||\mathcal{P}_1]$ as a function of time for a pair of equidistant quenches with $\bar{T}^+ = 2.64$ and $\bar{T}^- = 0.24$, which illustrates the asymmetry in the thermal relaxation holds for any Gaussian Network (according to our proof).

**TILTED SINGLE FILE**

We consider a system of $N$ hard-core point-particles (the extension to a finite diameter is straightforward \[2, \textit{3}\]) diffusing in a box of unit length with a diffusion coefficient $D$, which we set equal to 1 and express energies in units of $k_B T_{\text{eq}}$ without any loss of generality. The particles with positions $x = \{x_i\}$ feel the presence of a linear potential
\[ U(\{x_i\}) = \sum_{i=1}^{N} g x_i. \] The Green’s function of the system obeys the many-body Fokker-Planck equation

\[ (\partial_t - \tilde{\mathcal{L}}_{\tilde{T}}) G_{\tilde{T}}(x, t | x_0) \equiv \left( \partial_t - \sum_{i=1}^{N} (\partial_{x_i}^2 + g \tilde{T}^{-1} \partial_{x_i} \right) G_{\tilde{T}}(x, t | x_0) = \delta(x - x_0) \] (S27)

The confining walls are assumed to be perfectly reflecting, i.e. \( J(x_i) |_{x_i=0} = J(x_i) |_{x_i=1} = -D(g/\tilde{T} - \partial_{x_i}) G_{\tilde{T}}(x, t | x_0) = 0, \forall i \). Moreover, particles are not allowed to cross, which introduces the following set of internal boundary conditions

\[ (\partial_{x_i+1} - \partial_{x_i} ) G_{\tilde{T}}(x, t | x_{i+1} = x_i = 0, \forall i. \] (S28)

Eq. (S27) with reflecting external boundary conditions \( J(x_i) |_{x_i=0} = J(x_i) |_{x_i=1} = 0, \forall i \) and internal boundary conditions in Eq. (S28) is solved exactly using the coordinate Bethe ansatz (we do not repeat the results here as they can be found in [4]). It is convenient to introduce the particle-ordering operator

\[ \hat{O}_x \equiv \prod_{i=2}^{N} \theta(x_i - x_{i-1}), \] (S29)

where \( \theta(x) \) is the Heaviside step-function. Let \( \zeta_{\tilde{T}}(x_i, t| x_{0i}) \) be the Green’s function of the corresponding single-particle problem and \( P_{\tilde{T}}^{eq}(x_i) = \lim_{t \to \infty} \zeta_{\tilde{T}}(x_i, t| x_{0i}) \) the density of the equilibrium measure at temperature \( \tilde{T} \), then the Green’s function can be written directly as

\[ G_1(x, t | x_0) = N! \hat{O}_x \prod_{i=1}^{N} \zeta_1(x_i, t | x_{0i}) \to P_{\tilde{T}}(x, t) = N! \hat{O}_x \prod_{i=1}^{N} \int_0^t dx_{0i} \zeta_1(x_i, t | x_{0i}) P_{\tilde{T}}^{eq}(x_{0i}), \] (S30)

where the normalization factor \( N! \) assures a correct re-weighing of non-crossing trajectories [4].

A key simplification in the calculation of order-preserving integrals as well as all projected, tagged-particle observables (incl. functionals; see e.g. [4]) is the so-called ‘extended phase space integration’ introduced by Lizana and Ambjörnsson [2, 3], according to which for any \( 1 \leq M \leq N \) and some function \( f(x) \) that is symmetric with respect to permutation of coordinates \( x_i \),

\[ \hat{O}_x \prod_{i=1}^{N} \int_0^{\infty} dx_{0i} f(x) \delta(z - x_M) = \prod_{i=1}^{M-1} \int_0^{\infty} dx_{0i} \prod_{j=M+1}^{N} \int_0^{\infty} dx_{0j} \frac{f(x_M = z, \{ x_{i\neq M}\})}{(M-1)! (N-M)!}. \] (S31)

With the aid of Eq. (S31) it is possible to calculate the Kullback-Leibler divergence as

\[ D[P_{\tilde{T}} | P_1] = \int dx P_{\tilde{T}}(x, t) \ln(P_{\tilde{T}}(x, t) / P_1(x)) = N \int_0^{\infty} dx P_{\tilde{T}}^1(x, t) \ln(P_{\tilde{T}}^1(x, t) / P_1^1(x)), \] (S32)

where \( P_{\tilde{T}}^1(x, t) = \int_0^{\infty} dx_0 \zeta_1(x, t | x_0) P_{\tilde{T}}^{eq}(x_0) \), and the second equality is a result of applying Eq. (S31). The result in Eq. (S32) for a single file of 10 particles is depicted in Fig. (3a) in the Letter. For the sake of completeness, we also present the exact explicit result for \( \langle U(t) \rangle_{\tilde{T}} = g N (x(t))_{\tilde{T}} \), which reads

\[ \langle U(t) \rangle_{\tilde{T}} = g N \left( \frac{1 - e^{g T} + g^2}{g (1 - e^{g T})} + 8 \sum_{k=1}^{\infty} \frac{g k \pi}{\lambda_k} \right)^2 \left( 2(\tilde{T} - 1)(e^{g/\tilde{T}} - (1)^k) (e^{g/\tilde{T}} - (1)^k)^2 \right) e^{-\lambda_k t}. \] (S33)

The results for the non-Markovian tagged-particle dynamics can be derived analogously. The probability density function for tagging the \( M \)th particle is defined as

\[ P_{\tilde{T}}(z, t) = \Pi_x(z) P_{\tilde{T}}(x, t) \equiv \hat{O}_x \prod_{i=1}^{N} \int_0^{\infty} dx_{0i} \delta(z - x_{\tau}) P_{\tilde{T}}(x, t) \] (S34)

and since \( P_{\tilde{T}}(x, t) \) is symmetric to permutation of particle indices Eq. (S31) can be applied. The exact result has the form of a spectral expansion (Eq. (13) in the Letter) and reads

\[ P_{\tilde{T}}(z, t) = \sum_k V_{0k}(z) V_{k0} e^{-\lambda_k t}, \] (S35)
where \( \mathbf{k} = \{ k_i \} \) is a \( N \)-tuple of non-negative integers and \( \lambda_k = \sum_{i=1}^{N} \lambda_{k_i} \) are Bethe eigenvalues of the operator 
\[ \hat{L}_1 = \sum_{i=1}^{N} (\partial_{x_i}^2 + g \partial_{x_i}) \] in a unit box under non-crossing conditions with \( \lambda_0 = 0 \) and \( \lambda_k = \pi^2 k_i^2 + g^2 / 4, \forall k > 0 \). Let \( N_L = T - 1 \) and \( N_R = N - T \) be the total number of particles to the left and to the right of the target particle, respectively. Then \( V_{0k}(z) \) and \( V^F_{0k} \) in Eq. \( \text{(S33)} \) are defined as

\[
V_{0k}(z) = \frac{m_k}{N_L! N_R!} \frac{2g\alpha}{T \Omega_T^2(0, 1)} \sum_{\{k_i\}} N_k \left( \sum_{i=1}^{N_k} L_1^T(z) \right) \left( \sum_{i=N_k+2}^{N} L_1^T(z) \right) \quad (S36)
\]

\[
V^F_{0k} = \frac{N!}{N_L! N_R!} \frac{2g\alpha}{T \Omega_T^2(0, 1)} \int_0^1 dz \sum_{\{k_i\}} N_k \left( \sum_{i=1}^{N_k} L_1^T(z) \right) \left( \sum_{i=N_k+2}^{N} L_1^T(z) \right) \quad (S37)
\]

where \( \alpha = \tilde{T}/(2 - \tilde{T}) \), \( \Omega_T^2(x, y) = e^{-gx/\tilde{T}} - e^{-gy/\tilde{T}} \), and \( m_k = \prod_i n_{k_i} \) is the multiplicity of the Bethe eigenstate corresponding to the \( N \)-tuple \( \mathbf{k} \), and the number \( n_{k_i} \) counts how many times the eigenindex \( k_i \) appears in the Bethe eigenstate \( \Phi \). In Eq. \( \text{(S37)} \) we have introduced the auxiliary functions

\[
T^T_\tilde{T}(z) = P^\text{eq}_T(z) \frac{e^{\alpha z/2} (g \sin(k_T \pi z) - 2k_T \pi \cos(k_T \pi z))}{\sqrt{2\lambda_{k_T}}} \quad \forall k_T > 0 \quad (S38)
\]

and \( T^\text{eq}_T(z) = P^\text{eq}_T(z) \) for \( k_T > 0 \) (where \( P^\text{eq}_T(z) \) is defined in Eq. (12) in the Letter), as well as

\[
L_i^\tilde{T}(z) = \begin{cases} \Omega_T^2(0, z)/\Omega_T^2(0, 1), & k_i = 0 \\ \sqrt{\lambda_{k_i}}, & k_i \neq 0 \end{cases} \quad (S39)
\]

\[
R_i^\tilde{T}(z) = \begin{cases} \Omega_T^2(z, 1)/\Omega_T^2(0, 1), & k_i = 0 \\ \sqrt{\lambda_{k_i}}, & k_i \neq 0 \end{cases} \quad (S39)
\]

Note that \( \lambda_{k \pm} = \pi^2 (x k_i)^2 + g^2 / 4, \forall k > 0 \), and \( \{k_i\} \) denotes the sum over all possible permutations of \( \mathbf{k} \) and the functions \( \Phi_k^{\alpha, \alpha}(x, y) \) and \( \Psi_k^{\alpha, \alpha}(x, y) \) are defined as

\[
\Phi_k^{\alpha, \alpha}(x, y) = \frac{e^{-gx/2\alpha} \sin(k \pi x) - e^{-gy/2\alpha} \sin(k \pi y)}{\lambda_{k \pm} \sqrt{2\lambda_{k \pm}}} \quad (S39)
\]

\[
\Psi_k^{\alpha, \alpha}(x, y) = \frac{e^{-gx/2\alpha} \cos(k \pi x) - e^{-gy/2\alpha} \cos(k \pi y)}{\lambda_{k \pm} \sqrt{2\lambda_{k \pm}}} \quad (S39)
\]

Details of the calculations can be found in [4]. The evaluation of Kullback-Leibler divergence, \( S_T(t), S_F(t) \) as well as \( \langle \mathcal{U}(t) \rangle \) cannot be carried out analytically and we therefore resort to efficient and accurate numerical quadratures. The results are presented in Fig. (3) in the Letter.

We performed extensive systematic calculations for different values of \( g \) and \( N \), various combinations of \( \tilde{T} \pm \) as well as for different choices for tagged particles. All these calculations gave the same qualitative picture – without any exceptions ‘uphill’ relaxation was always faster. However, we are not able to prove rigorously that this is indeed always the case. Therefore, for the single file the universally faster uphill relaxation is only a conjecture.

**NON-EXISTENCE OF A UNIQUE RELAXATION ASYMMETRY IN MULTI-WELL POTENTIALS**

In the letter we demonstrated that the relaxation in single-well potentials is faster uphill than downhill. We have proven that this is always the case near stable minima and for any reversible Ornstein-Uhlenbeck process. Based on additional physical arguments we hypothesized that the asymmetry is a general feature of diffusion in single-well potentials. However, as we remarked in the Letter, it is not difficult to construct counterexamples proving that the asymmetry is not a general phenomenon in all reversible ergodic diffusion processes.

To that end we consider markovian diffusion in rugged, multi-well potentials parametrized by

\[
U(x) = e(ax^6 + bx^4 + cx^2 + dx^2), \quad (S40)
\]

with some appropriately chosen constants \( a, b, c, d \) and \( e \). Let the dynamics evolve according to \( \hat{L}_F = \partial_x^2 - \tilde{T}^{-1}\partial_x F(x) \), where \( F(x) = -6e(ax^5 + 4bx^3 + 3cx^2 + 2dx) \) in a finite domain \( a \leq x \leq b \) with reflecting boundaries, and let the corresponding Green’s function be the solution of the following boundary value problem

\[
(\partial_t - \hat{L}_F)G_F(x, t|x_0) = \delta(x - x_0), \quad -\partial_x F(x)G_F(x, t|x_0)|_{x=a} = -\partial_x F(x)G_F(x, t|x_0)|_{x=b} = 0. \quad (S41)
\]
We solve the boundary problems by means of numerical diagonalization using a finite element routine. The results for three distinct parameter sets is shown in Fig. (S4). We did not perform a systematic analysis of all the possible potentials. However, based on our observations it seems that the different uphill/downhill relaxation patterns depend on how different entropic contributions (i.e. intra-well entropy versus inter-well configuration entropy) change qualitatively with temperature for potentials with several minima. It seems that the asymmetry observed in single-well potentials persists in symmetric potentials and ceases to exists as soon as the potential becomes asymmetric with sufficiently deep wells, where entropy attains an additional inter-well configurational component.

**GENERALIZED MPEMBA EFFECT FOR NON-MARKOVIAN DYNAMICS**

A phenomenon closely linked to relaxation from a quench is the so-called Mpemba effect \[5–7\], according to which a liquid upon cooling can freeze faster if its initial temperature is higher. Meanwhile the phenomenon has been extended to cover relaxation processes in different systems: magneto-resistors \[8\], carbon-nanotubes \[9\], polymers crystallization \[10\], clathrate hydrates \[11\], granular systems \[12\] and spin glasses \[13\]. Recently theoretical generalizations of it for Markovian observables have been published \[14–16\]. Not long ago the phenomenon was also addressed in more detail in the context of Markovian stochastic dynamics \[14, 16\].

Here we further extend the concept of the Mpemba effect to projected, non-Markovian observables. As before we focus on the distance of two different generic configurations displaced from equilibrium at \(t = 0\), such that one is displaced further away than the other, whereas the time-evolution of the entire system is governed by the same Fokker-Planck operator. In this setting, there are cases, where the more distant initial configuration reaches equilibrium faster that the closer one. One can observe this effect in the two systems analyzed in the Letter (see Fig. S5). It is worth to stress that the presence of the generalized Mpemba effect not only depends on the system and the initial condition (like in the Markovian case) but also on the particular type of projection In Fig. S6 we demonstrate, on hand of the same system (a tilted single file of 5 particles) from the same pair of pre-quench temperatures, that we can switch the generalized Mpemba effect on and off by simply changing the particle we are tagging.
Figure S5. In the left panel we show time dependence of the Kullback-Leibler divergence for a Gaussian Chain of 100 beads, while the right panel depicts a Single File of 10 particles ($g = 5$). In both cases we focus on non-Markovian observables, the end-to-end distance for the Gaussian chain and on the 7th particle of the single file, respectively. For some pairs of initial temperatures we notice the generalized Mpemba effect: systems that start further away from the equilibrium approach the equilibrium configuration faster.

Figure S6. Kullback-Leibler divergences for a single file of 5 particles with $g = 1$. If we tag the 2nd particle (solid lines) or the 5th (dashed lines) for the same pair of pre-quench temperatures one projection displays the generalized Mpemba effect while the other one does not.

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