Relaxation shortcuts through boundary coupling

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When a hot system cools down faster than an equivalent cold one, it exhibits the Mpemba Effect. This counterintuitive phenomenon was observed in several systems including water, magnetic alloys and polymers. In most experiments the system is coupled to the bath through its boundaries, but all theories so far assumed bulk coupling. Here we build a general framework for boundary coupling relaxation and show that the Mpemba effect persists in these cases. Surprisingly, it can survive even an arbitrarily weak couplings. An example is given in the Ising antiferromagnetic chain.

When coupled to a thermal bath, most systems relax towards equilibrium. The precise details of the relaxation are determined by many factors, including the intrinsic properties of the specific system, its initial condition, the bath’s properties and the exact nature of the coupling between the system and the bath. However, it is commonly expected that in the weak coupling limit a macroscopic system that is initiated in equilibrium state corresponding to some initial temperature $T_0$ relaxes quasi-statically towards the bath temperature $T_b$, such that the system can be described at each instance as in equilibrium for some temperature. This is a consequence of the self-thermalization being much faster then the heat exchange with the thermal bath. In a strong coupling, on the other hand, the self-thermalization process through which the system equilibrates is not fast enough, and the energy exchange with the environment drives the system into a relaxation trajectory that can reach far from any equilibrium distributions where anomalous relaxations might arise. Such far from equilibrium relaxation trajectories can be counterintuitive, and show interesting phenomena that are unexpected near equilibrium [1–3]. An important example for such a phenomenon is the Mpemba Effect (ME) [4, 5], where a hot system, under proper conditions, cools down faster than an initially cold one when quenching both to an even colder bath. The ME was observed experimentally in a variety of setups, including water [6], magnetic alloys [7], polymers [8], clathrate hydrates [9] and very recently in small size systems like colloids diffusing in a potential [10, 11]. In addition to these experimental observations, it was also observed in a variety of numerical and theoretical models for water molecules [12, 10], driven granular gases [17, 20], inertial suspensions [21], gas of visco-elastic particles [22], diffusing in a potential [2, 23] and classical as well as quantum spin models [26, 31].

Theoretical models proposed so far to explain the ME assumed that all the relevant degrees of freedom (e.g. all spins, or all molecules) are directly coupled to the thermal bath. However, in most experiments demonstrating the ME (with colloidal system [10, 11] being the only exception), the system is coupled to the heat bath only through its boundaries, potentially hindering the adequacy of such models for large sized systems. Similarly, the dependence of the effect on the coupling strength is unknown. Intuitively, one expects the effect to become visible as the coupling with the thermal bath strengthens, while a weak coupling, on the other hand, is expected to make the effect harder to observe.

In this letter we construct a general theoretical framework for boundary coupling with the bath, and use it to demonstrate the existence of the ME even in such systems. We do so by combining two types of dynamics: heat exchange through the boundaries and an energy conserving self-thermalization dynamic for the thermally isolated bulk. The ratio between the characteristic timescales of the two dynamics tunes the coupling strength, and allows us to explore the limiting cases of arbitrary weak and strong couplings. We then demonstrate this general construction in the 1D Ising antiferromagnet, and show that it exhibits a ME even at arbitrarily weak boundary coupling with the bath. An exact coarse-graining of the system [22, 33] enables exploring the infinite and zero coupling strength limits, and somewhat surprisingly shows that the effect survives the arbitrarily weak coupling limit.

We begin by introducing a general formulation of the setup. To model boundary coupling with the thermal

![Inset: the ME exists if $a_2(T_0, T_b) = 0$ and is non-monotonic in $T_0$.](attachment:fig1.png)

**FIG. 1.** (a) The system: an antiferromagnet Ising chain, with a single spin coupled to the thermal bath. Transitions are allowed only if energy is conserved, except for flipping the spin coupled to the bath. (b) Minimal coupling strength $C$ (colorbar) for which there exists some type of a ME at the corresponding bath temperature $T_b$ (x axis) and $H$ (y axis). In the white areas there is no ME at any coupling strength. Inset: the ME exists if $a_2(T_0, T_b)$ is non-monotonic in $T_0$. 

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environment, which is stochastic in nature, we consider the probability distribution $\tilde{p}$ where the component $p_i(t)$ is the probability to be in a microstate $i$, that has energy $E_i$, at a given time $t$. $\tilde{p}(t)$ evolves in time according to the master equation

$$\partial_t \tilde{p}(t) = W(\beta_b)\tilde{p}(t),$$

(1)

where the rate matrix $W$ encodes the specific model and depends on the bath (inverse) temperature $\beta_b = 1/T_b$ (for simplicity we use units where $k_B = 1$). The off-diagonal terms $W_{ij}$ are the jumping rates from state $j$ to state $i$, while the diagonal term $W_{ii} = -\sum_{j\neq i} W_{ji}$ represents the escape rate from the state $i$. We assume that detailed balance and ergodicity hold, so that regardless of the initial condition the system relaxes towards the (unique) Boltzmann distribution $\pi(\beta_b)$.

where $Z(\beta_b) = \sum_i e^{-\beta_b E_i}$ is the partition function of the system at the bath temperature.

To characterize the relaxation process one formally integrates Eq. (1). Starting from equilibrium conditions at an initial temperature $\beta_0$, we get:

$$\tilde{p}(t, \beta_0, \beta_b) = e^{W(\beta_b)t}\tilde{\pi}(\beta_b) =$$

$$= \tilde{\pi}(\beta_b) + \sum_{i>1} a_i(\beta_0, \beta_b)e^{\lambda_i(\beta_b)t}\bar{v}_i(\beta_b),$$

(2)

where $0 = \lambda_1 > \lambda_2 \geq \lambda_3 \geq \ldots$ and $\bar{v}_i$ are respectively the (real) eigenvalues and right eigenvectors of the rate matrix $W$, while the coefficients $a_i$ are the projection of the left eigenvectors of $W$ over the initial equilibrium distribution $\tilde{\pi}(\beta_0)$. The existence of the ME is encoded in the slowest relaxation, regulated by the second dominant eigenvalue $\lambda_2$ [3]: a non-monotonic dependence of the coefficient $a_2(\beta_0, \beta_b)$ with respect to the initial temperature $\beta_0$ guarantees the possibility of observing the effect when quenching the system to that specific bath temperature $\beta_b$. For simplicity, in this work we do not distinguish between the different types of the Mpemba effects (inverse vs. direct, strong vs. weak, etc) [3].

In many experimental setups, the thermal bath is not directly coupled to all the degrees of freedom composing the system: heat can be transferred only through those sitting on the boundaries. All other transitions between microstates are “bulk transitions”, and as no energy is exchanged with the bath in such transitions they can only happen between states with the same energy. These bulk transitions serve as a self-thermalization (ST) mechanism, whereas the boundary transitions (BT) couple the system to the bath and enable transitions between different energy shells. This structure can be modeled by

$$W(\Gamma^{ST}, \Gamma^{BC}) = \Gamma^{ST} W^{ST} + \Gamma^{BC} W^{BC}.$$  

(3)

Here $W^{ST}$ and $W^{BC}$ are normalized rate matrices corresponding to the self thermalization and boundary coupling transitions respectively, and $\Gamma^{ST, BC}$ are coupling constants modulating the rates amplitude. Their ratio, $C = \Gamma^{BC}/\Gamma^{ST}$, dictates the coupling strength [33]: in the limit $C \ll 1$ boundary flips – regulating the energy exchange with the bath – occur rarely compared to thermalization flips, so the system thermalizes quickly after each energy exchange with the bath. In the $C \gg 1$ limit, the boundaries (in thermal equilibrium with the bath) exchange heat much faster than the thermalization and the diffusion of energy within the system sets the timescale for the relaxation. We refer to the former limit as the weak coupling and to the latter as strong coupling.

By construction, $W^{ST}$ is a rate matrix that contains only transitions between states that have the same energy. Generically, it is a reducible matrix with a zero eigenvalue degeneracy equal to the number of different energy shells. As for $W^{BC}$, it is generically a sparse matrix, as most transitions involve more than the boundary spins. The interaction of the system with a thermal bath at inverse temperature $\beta_b$ satisfies detailed balance, therefore $W^{BC}_{ij} = W^{BC}_{ji} e^{-\beta_b (E_j - E_i)}$, where $E_{(i,j)}$ are the energy corresponding to the two states.

In the weak coupling limit, a naive perturbation scheme with $C \ll 1$ would not prove useful: for $C = 0$ the matrix $W$ is reducible and its zero eigenvalue is highly degenerate, so one cannot apply the standard analysis. Instead, it is constructive in this case to aggregate all the microstates that share the same energy into a single macrostate and construct the effective dynamics by summing all the microscopic transitions between them [32, 33]. In this case, the dynamics is dictated only by the boundary flips, and the diffusion within each energy shell is assumed to happen instantaneously. Similarly, in the strong coupling limit, micro-states can be aggregated into macrostates by combining all the microstates connected by boundary flips. Mathematically, the two aggregation procedures can be done by arranging the states such that $W^{BC}$ or $W^{ST}$ is block diagonal where each block corresponds to transitions within a macrostate, and coarsening over these blocks.

Let us demonstrate the above construction with a specific example, depicted in the cartoon of Fig. 1(a). It consists in a 1-dimensional ring of $N$ Ising spins with nearest neighbour antiferromagnet interactions. Each spin $\{\sigma_s\}_{s=1,...,N}$ in the chain can either be in an up or down (±1) state, giving a total of $M = 2^N$ different microstates, identified by the $N$-dimensional vector $\vec{\sigma}$. The energy of a microstate $\vec{\sigma}$ is provided by the Hamiltonian functional

$$\mathcal{H}(\vec{\sigma}) = -J \sum_s \sigma_s \sigma_{s+1} - H \sum_{s=1}^N \sigma_s,$$

(4)

where $J < 0$ is the coupling constant, $H$ is an external magnetic field and $\sigma_{N+1} \equiv \sigma_1$. For simplicity, we set $J = -1$.

To model boundary coupling in this system, we choose a specific spin (say $\sigma_1$), which is coupled to the bath. This implies that a general microstate $\vec{\sigma}$ is connected through thermal flips only with a single state $\vec{\sigma'}$ in which the first spin is flipped, $\sigma_1 \rightarrow -\sigma_1$, while the remaining
spins are unaltered. For two general microstates $\vec{s}^i$ and $\vec{s}^j$ the transition is therefore
\[
W_{ij}^{BC} = \frac{\delta_{\vec{s}^i,\vec{s}^j} \prod_{s>1} \delta_{\vec{s}^i,\vec{s}^j}^s}{1 + e^{\beta_b(\mathcal{H}(\vec{s}) - \mathcal{H}(\vec{s}^j))}}
\]  
(5)
where $\delta_{ij}$ is the Kronecker delta, $\sigma_j^i$ is the $s$ spin in the microstate $\vec{s}^i$ and we used standard Glauber dynamics as the transition weight $\mathcal{W}_{ij}^{ST}$ that counts the number of spins that has to be flipped between the two configurations, as suggested by decimation-like procedures operated on Markov jump processes. We therefore formalize bulk transitions between two states $i \neq j$ as
\[
W_{ij}^{ST} = \delta_{\mathcal{H}(\vec{s}^i),\mathcal{H}(\vec{s}^j)} 2^{-d_{ij}}.
\]  
(6)

The full transition matrix for the model is finally built as a linear combination of the two rate matrices as in Eq. 3.

With this construction, let us consider the persistence of the ME in a boundary coupling setup. In Fig. 1(b) we plot the minimal coupling constant $C$ for which some type of a ME exists in the system, for $N = 10$ (implying $M = 1024$ microstates) and as a function of bath temperature $\beta_b$ and external magnetic field $H$. The strength of the coupling affects only quantitatively the regions where the ME can be observed (the larger $C$, the larger the area). In particular, we see that for any $|H| \leq 2$ the effect exists for any bath temperature above a critical $T_b^* = 1/\beta^*$ (highlighted with a red arrow).

In the weak coupling case ($C \ll 1$), the coarse-grained rate matrix is given by
\[
W_{ij}^{\text{weak}} = \frac{G_{ij}}{\Omega_j} \frac{1}{1 + e^{\beta_b(E_i - E_j)}}
\]  
(7)
where the indices $i, j$ now refer to the energies $E_i$ and $E_j$, the (symmetric) matrix $G_{ij}$ counts the number of transitions connecting microstates in the two energy shells, and $\Omega_j$ is the number of microstates with energy $E_j$. This coarsening considerably reduces the size of the matrix, allowing to numerically analyze longer chains assessing the stability of the phase diagram in the thermodynamic limit. The total number of energy shells grows quadratically as $2 + (N/2)^2$, as opposed to the exponential growth of the number of microstates. As an example, at $N = 50$ (Fig. 2b,d) there are $\sim 10^{15}$ microstates, but only 627 macrostates in the coarse-grain representation.

The case of extremely strong coupling ($C \gg 1$) can be similarly analyzed. In our model only a single spin is coupled to the bath, therefore the clustering of a $N$ spin chain model results in an effective $N - 1$ long chain with an additional “superposed” spin oscillating infinitely fast between the two $\pm 1$ states. Indicating with $i$ one of the possible $2^{N-1}$ configurations of the bulk chain, we set $\delta_{\vec{s}^i,\vec{s}^j}$ to be the Hamiltonians of each of the two possible states in the $i$-th cluster. The two states composing a cluster are not equivalent as in the weak coupling case. To correctly define the transition rates in the coarse-grained model we therefore need to introduce a Glauber weight: $w_{ij}^\sigma = e^{-\beta_b\mathcal{H}_i^\sigma}/(e^{-\beta_b\mathcal{H}_{i-1}^\sigma} + e^{-\beta_b\mathcal{H}_{i+1}^\sigma})$ with $\sigma = \pm 1$ depending on the microstate from which the original transition occurred. This provides us with:
\[
W_{ij}^{\text{strong}} = \sum_{\sigma, \sigma'} w_{ij}^\sigma \delta_{\mathcal{H}_j^\sigma, \mathcal{H}_j^{\sigma'}} 2^{-(d_{ij} + \delta_{\sigma, -\sigma'})}
\]  
(8)
where the Kronecker delta corrects the Hamming distance for the coupled spin. The area in which an effect can be observed is wider (Fig. 2a): a stronger coupling should indeed ease the undertake of anomalous relaxation paths.

In Fig. 2a we plot the regions in which some ME can be observed in the limiting coupling setups discussed above, and compare them with the intermediate $C = 1$ case. Somewhat surprisingly, the ME can be observed even for $C \ll 1$, demonstrating that the effect survives the limit of arbitrarily weak coupling.

Additional analysis that can demonstrate the ME in this setup can be obtained by projecting the relaxation paths in the (high-dimensional) probability space on two order parameters: the average $\langle n \rangle$ and staggered magnetization $\langle n_j \rangle$. This method enables to use Monte-Carlo simulation in large systems where direct calculation of $\langle n \rangle$ is impractical, and nevertheless compare the relaxation trajectory with the equilibrium distributions at different temperatures. In Fig. 3 we illustrate differ-
FIG. 3. Relaxation paths for a weakly coupled system ($N = 50$) on the $(m_1)- (m_2)$ plane. Initial temperatures are chosen before (red), at (blue) and after (green) the zero of $a_2(T_0)$ as shown in the inset. Red and green paths approach the equilibrium locus along the same vector with opposite direction, indicating the existence of a ME

ent relaxation paths in a weakly coupled chain of $N = 50$ spins, in comparison to the equilibrium line. Initial temperatures are chosen before, at and after the zero of $a_2$ at $T_0 \sim 0.6 < T_b$. The hot (green) and cold (red) relaxation paths approach the bath equilibrium at $T_b = 5$ along the same direction, which is the projection of $\vec{v}_2$ into the observable space, but with opposite direction. This corresponds to a sign-change in $a_2$, which indeed vanishes at the blue trajectory implying non-monotonicity of $a_2(T_0)$ (inset of Fig. 3) and consequently a ME in the system.

An important feature emerging from the weak coupling limit analysis links the ME with a degeneracy in the spectrum of the rate matrix $W$. The ME is defined through the monotonicity of $a_2(\beta_0, \beta_b, H)$ as a function of $\beta_0$, which in general is expected to change continuously. However, at $H = 0$ and a specific bath temperature which we denote by $T_b^*$, the first non-zero eigenvalues overlap: $\lambda_2 = \lambda_3$ (See Fig. 2a,d). At this point, $\vec{v}_2$ and $\vec{v}_3$ exchange their role as the slowest direction in the system, and consequently $a_2$ changes discontinuously and the ME appears [39]. Analysis at different sizes (Fig. 4) shows a polynomial convergence of this $T_b^*$ towards an asymptotic value $T_b^* \sim 2.91$. This suggests that the ME survives the thermodynamic limit and that $N = 50$ is a large enough system to capture some properties in the thermodynamic limit of the model.

Finally, let us explain the counter-intuitive survival of the Mpemba effect in the weak coupling limit. The self-thermalization matrix $W^{ST}$ defined in Eq. 6 allows only transitions within an energy shell, since the bulk is assumed to be isolated from the thermal bath. Transitions between energy shells are realized through $W^{BC}$ only. However, in the thermodynamic limit, energy shells that have a microscopic energy difference (namely $\Delta E \sim 1$ even though $E \sim N$), might be separated by many boundary, thrusting a slow relaxation among them. As a result, the self thermalization in the thermodynamic limit has the same characteristic timescale as that of the boundary transitions. It is thus the ideal thermal isolation that is responsible for the far from equilibrium trajectories in the weak coupling limit (Fig. 3) [10].

Summarizing, we constructed a theoretical framework to characterize the evolution of a system coupled to the thermal bath only through its boundaries, and proved how anomalous relaxation phenomena can survive such an apparently strong limitation. The proposed modelization is quite general, and in principle can be applied to any memoryless system exchanging heat with the thermal bath through limited degrees of freedom. Our results corroborate the validity of the ME as an out-of-equilibrium phenomena, proving that it is not an artifact induced by a full coupling. Rather, it seems that it is related to the frustration-like microscopic interactions associated with antiferromagnets. The far-from-equilibrium relaxations in the weak coupling limit are yet another counter-intuitive result, not necessarily related with the ME but linked with the ideal isolation of the bulk of the system [11]. The possibility of tuning the coupling strength through $C$, together with the thermodynamics limit analysis (Fig. 2) clearly point towards the possibility of experimentally observing the inverse effect in magnetic alloys setups as those utilized in Ref. [7].

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