The phenomenon that a system at a hot temperature cools faster than at a warm temperature, referred to as the Mpemba effect, has recently been realized for trapped colloids. Here, we investigate the cooling and heating process of a self-propelled active colloid using numerical simulations and theoretical calculations with a model that can be directly tested in experiments. Upon cooling, activity induces a Mpemba effect and the active particle transiently escapes an effective temperature description. At the end of the cooling process the notion of temperature is recovered and the system can exhibit even smaller temperatures than its final temperature, a surprising phenomenon which we refer to as activity-induced overcooling.

When water is cooled down to be frozen, it seems intuitive that the cooler the water, the faster it will freeze. Contrary to that, about 2300 years ago, Aristotle already noticed that “to cool hot water quickly, begin by putting it in the sun” [1], observing that hot water can be cooled and also frozen faster than warm water. The first systematic study to investigate this effect was conducted in the 1960s by Mpemba [2]. Thereafter, numerous experimental studies followed, but no consensus on the cause of the “Mpemba effect” for water was found, so far [3–8]. Recently, the Mpemba effect was discovered for colloidal particles that are subjected to a thermal quench [9], where the colloids were confined to a double well potential, mimicking the liquid and frozen state of water. The experimental findings match theoretical predictions giving a clear explanation of the underlying effect [10,11] and provide an experimental road to recent theoretical advances in understanding principles of the Mpemba effect [12–17].

Active colloids that are self-propelling, constantly pump energy into the system and, therefore, are inherently out of equilibrium [18]. Active colloidal particles have been realized in various experimental systems [18] and can show fascinating effects such as wall accumulation [19–21], activity induced ratchet motion [22,23], motility induced phase separation [24,25], or vortex formation [26]. Here, we investigate the cooling and heating process of trapped active colloids and find that they exhibit, not only a Mpemba effect, but also overcooling, i.e., they transiently reach a temperature that is lower than its final steady state temperature [Fig. 1(d)]. However, before overcooling happens, the system deviates significantly from any reference system at a prescribed temperature, i.e., it escapes an effective temperature description [Fig. 1(d)]. Irrespective of the validity of the effective temperature concept during relaxation, the active colloids can show a Mpemba effect.

To illustrate the Mpemba effect, imagine two systems, one of which is at an initial warm temperature, and the second is at an initial hot temperature. Both systems are then cooled down to an imposed cold temperature [Fig. 1(a)]. Normally, the warm system cools faster than the hot system and a Mpemba effect occurs if the hot system

![Diagram](https://via.placeholder.com/150)

**FIG. 1.** (a) Cooling and heating scenarios, where each colored arrow represents a cooling or heating process. The arrows’ length displays the time that the system needs to cool down (left) or heat up (right). (b) Asymmetric potential with walls $U(x)$ as a function of space that the active colloid (blue circle) is subjected to. (c) Occupation probability $\pi(x)$ of an active (black line) and passive (green line) colloid in the external potential shown in (b). (d) An overcooling scenario, where during the cooling process the system escapes an effective temperature description (black represents the regime without a temperature definition) and then goes to lower temperatures than the final temperature. The color code of the arrow represents the temperature.
cools faster than the warm one. Analogously, a cold system can heat up faster than the warm one [Fig. 1(a)], which is referred to as the inverse Mpemba effect [12,27]. The Mpemba effect for a passive colloid [9] in an asymmetric potential [similar to Fig. 1(b)] can be understood as follows: a hot particle cooling down has enough residual energy to overcome the barrier and, subsequently, quickly relaxes to the cold state. On the other hand, a warm particle, having effectively less residual energy, will take a longer time overcoming the potential barrier.

We investigate the cooling and heating process of active colloids in a confining asymmetric potential [Fig. 1(b)]. An active Brownian particle subjected to fluctuations with a temperature $T$ and performing overdamped motion is modeled in one spatial dimension by the following equation:

$$\frac{dx}{dt} = v_0 n - \frac{1}{\gamma} \partial_x U(x) + \eta(t), \quad (1)$$

where $v_0$ is the self-propulsion speed, and $n$ is the direction of propulsion. The propulsion direction is inverted after a time $t_p$. The temperature quench is applied at this time. (b) Distributions at $t_p$.

The system described by Eq. (1) can be realized using a Janus colloid [18,28], yielding a self-propulsion together with optical [9,29] or acoustic [30] traps that establish an external potential and a half channel that confines the motion of the colloid into one spatial dimension [31,32] (see the Supplemental Material [33] for a sketch) [34–41].

In the following, we generate the probability distribution $P(x, t)$ to find the particle at position $x$ and time $t$ from Eq. (1). Typical steady state distributions denoted by $\pi(x)$ for a passive ($v_0 = 0$) and an active particle ($v_0 \neq 0$) are shown in Fig. 1(c), where the particles are localized around the two minima of the external potential. Additionally, the distribution of the active particle is enhanced toward the wall regions due to the wall accumulation effect that arises from the persistence and active motion of the particle [42–52].

Now, consider two systems which are initially in their steady state at a hot $T_{\text{hot}}$ (hot particle) and warm temperature $T_{\text{warm}}$ (warm particle) with $T_{\text{hot}} > T_{\text{warm}}$ [Fig. 2(a)]. Figures 2(a)–2(c) reveal how the distributions of the warm and hot particles relax and finally reach their new steady state distributions $\pi_{\text{cold}}(x)$ after an instantaneous thermal quench to $T_{\text{cold}}$ [Fig. 2(c)]. The hot particle relaxes faster [Fig. 2(b)] than the warm particle [Fig. 2(c)], which is an anomalous cooling referred to as the Mpemba effect. The intuitive underlying reason for the Mpemba effect is related to the fact that the distribution of the warm particle is localized into the minima of the external potential [Eq. (2)], such that the particle needs to hop over the potential barrier to relax to the cold distribution. On the other hand, the distribution of the hot particle is not

$$U(x) = \begin{cases} 
-F_0 x, & \text{if } x < x_{\text{min}}, \\
F_B [(1 - x^2)^2 - \frac{1}{2} x], & \text{if } x_{\text{min}} < x < x_{\text{max}}, \\
F_0 x, & \text{if } x > x_{\text{max}}.
\end{cases} \quad (2)$$

This potential is displayed in Fig. 1(b), where the terms in Eq. (2), proportional to $F_0$, represent repulsive walls at positions $x_{\text{min}}$ and $x_{\text{max}}$, and the term proportional to $F_B$ models an asymmetric potential with two minima of different height. The size of the box confining the particle, $l = |x_{\text{max}} - x_{\text{min}}|$, provides a natural unit of length, and combined with the translational diffusion constant, there is a natural unit of time $\tau_D = l^2/D_T$ and velocity $v_D = l/\tau_D$.

FIG. 2. (a)–(c) Probability distributions of active colloids. A hot (red dotted line, $T_{\text{hot}} = 2500T_{\text{cold}}$), a warm (blue dashed line, $T_{\text{warm}} = 50T_{\text{cold}}$), and cold (black solid line) colloid is shown. (a) Initial steady state distributions at $t = 0$. A temperature quench is applied at this time. (b) Distributions at $t = 3 \times 10^{-3} \tau_D$. The hot colloid has relaxed close to $T_{\text{cold}}$. (c) Distributions at $t = 50 \times 10^{-3} \tau_D$. The warm colloid has also relaxed close to $T_{\text{cold}}$. (d) Relaxation dynamics of the “distance” $D(t)$ measured by the partitioning between probability distributions and the steady state distribution of a cold colloid for an initially hot, warm, and cold colloid. [Parameters: $F_0/(\gamma v_D) = 1.5 \times 10^5$, $F_B/(\gamma v_D) = 24$, $x_{\text{min}}/l = -1/3$, $x_{\text{max}}/l = 2/3$, $v_0/v_D = 120$, $\tau_p/\tau_D = 2 \times 10^{-4}$.]
To get further insight into the relaxation process, the distance between the cooled steady state distribution $\pi_{\text{cold}}(x)$ and the probability distribution $P(x, t)$ of a particle during the cooling process is quantified. In order to construct such an abstract distance measure, the spatial components of both $\pi_{\text{cold}}(x)$ and $P(x, t)$ are discretized into $N$ grid points, giving $\pi_{\text{cold}}$ and $P_i(t)$, respectively, resulting in the following distance measure:

$$D(t) = \frac{1}{N} \sum_{i=0}^{N} |P_i(t) - \pi_{\text{cold}}|.$$  \hspace{1cm} (3)

Figure 2(d) shows the distance measure Eq. (3), which quantifies the cooling process of the hot and warm particles. From this measure, a cooling time $t_c$ can be extracted, defined as the time at which $D(t)$ has decayed to zero, or, here, to the noise level.

Exploring a range of initial temperatures $T$ yields the cooling curves shown in Fig. 3(a). For active particles ($v_0 \neq 0$), the cooling curve is nonmonotonic, giving rise to a Mpemba effect that is induced by activity. Here, activity changes the probability distributions of the particles by inducing a wall accumulation [Fig. 1(c)], which, in turn, enables the Mpemba effect. For the parameters chosen, passive particles ($v_0 = 0$) show normal cooling [Fig. 3(a)], that is, the cooling time increases monotonically with initial temperature. Figure 3(b) shows the dependence of the active Mpemba effect on the self-propulsion and persistence of the particle, see the Supplemental Material [33] for details. For low persistence and self-propulsion, there is no Mpemba effect for our choice of parameters, while at higher self-propulsion and persistence, activity induces a Mpemba effect.

A statistically equivalent version of Eq. (1) in terms of a probability $P(x, t)$ to find the particle at position $x$ and time $t$ and its polarization $P^*(x, t)$ is given by the Smoluchowski equation

$$\partial_t P = -v_0 \partial_x P^* + \frac{1}{\gamma} \partial_x \{\partial_x U(x)\} P + D_T \partial_x^2 P, \hspace{1cm} \text{for passive particles}$$

$$\partial_t P^* = -v_0 \partial_x P^* + \frac{1}{\gamma} \partial_x \{\partial_x U(x)\} P^* + D_T \partial_x^2 P^* - \frac{2}{\tau_p} P^*, \hspace{1cm} \text{for active particles}$$

which is solved using an eigenfunction expansion (see the Supplemental Material [33]). The resulting cooling curves agree with the numerical approach using Eq. (1) (see the Supplemental Material [33]) and the transition line (black line) from normal cooling to active Mpemba effect is shown in Fig. 3(b). The dependence of the Mpemba effect on the compartment size and persistence length is discussed in the Supplemental Material [33].

Recently, the inverse Mpemba effect, where a cold particle heats faster than a warm one, has been discovered for passive colloids [27]. Figure 3(c) shows the heating curves of passive and active particles toward the temperature $T_{\text{hot}}$. Here, a passive particle has a nonmonotonic heating curve, an inverse Mpemba effect [27], which is eliminated by the active motion [see, also, Fig. 3(d)].

An effective temperature is defined based on the distance measure $D(t)$ that can be traced in time. At a given time $t$ the probability distribution $P(x, t)$ is compared to all possible steady states $\pi_{\text{eff}}(x)$ with effective temperatures $T_{\text{eff}}$, explicitly

$$D_{\text{eff}}(t) = \sum_i |P_i(t) - \pi_{i,\text{eff}}|,$$  \hspace{1cm} (6)

which is discretized as before. The temperature $T_{\text{eff}}$ for which $D_{\text{eff}}(t)$ is minimal, is then defined as the effective temperature.
temperature of the system. When cooling down to \( T_{\text{cold}} \), the effective temperature of a passive system decays monotonically, until it reaches its steady state [Fig. 4(a)]. Turning on activity, the particles probability distribution quickly enters a regime where it is not captured by a steady state distribution. Hence, the effective temperature description breaks down. This is quantified by the distance measure, which has to be sufficiently small to define a temperature, here, \( D_{T_{\text{eff}}}^{T_{\text{eff}}}(t) < 0.1 \) is used (see, also, the Supplemental Material [33]). Even if no effective temperature can be assigned to the active colloid at time \( t \), \( D_{T_{\text{eff}}}^{T_{\text{eff}}}(t) \) can still show how far the instantaneous distribution is from the final, steady-state cold distribution. In this sense, irrespective of the validity of the effective temperature concept during relaxation, Fig. 2(d) does show a Mpemba-type effect: the initially hot active colloid does, indeed, approach the cold state faster than the initially warm colloid. However, toward the end of the cooling process, the effective temperature description is recovered and takes values that are lower than the final steady state temperature [Fig. 4(a)]. This surprising effect is an activity induced overcooling of the system. The probability distributions [Fig. 4(c)] show how the distribution \( P(x, t) \) is closer to an effective distribution \( \pi_{T_{\text{eff}}}(x) \) than to the distribution of the cold state \( \pi_{\text{cold}} \), meaning that the particle has an effective temperature \( T_{\text{eff}} \) \( < T_{\text{cold}} \). The theoretical approach using Eqs. (4) and (5) also shows an overcooling [Fig. 4(a), (inset)], where the probability distribution was numerically evaluated in the long time limit, which was used to find the effective temperature with Eq. (6). Intuitively, overcooling is related to the particle hopping over the potential barrier to achieve the correct partitioning needed in the final steady state. The barrier separates two regions, and if the probability to find the particle in the right region is higher than required for the final steady state, the particle needs to hop over the barrier. Hopping processes are typically slow and, therefore, will dominate the final relaxation. During this relaxation the absolute peak height is higher than needed for the final steady state, which corresponds to a lower effective temperature just before final relaxation. Activity helps to achieve this imbalance of occupancy, since it enhances the probability of finding the particle at the wall.
enabling a strong peak in the right region. This overcooling mechanism is qualitatively different than that found for a mean-field Ising model [13].

Figure 4(d) displays the dependence of the overcooling effect on the active motion of the particle. At low self-propulsion and persistence, monotonous cooling is recovered, while increasing both leads to an overcooling.

Our choice for an effective temperature is not unique, and we computed the effective temperature using several other definitions (see the Supplemental Material [33]), which display the same overcooling effect. Here, as an alternative measure for the effective temperature [53], the lag diffusion defined as

\[
D(t, \Delta t) = \left(1/N_r\right) \sum_{i=1}^{N_r} [x_i(t + \Delta t) - x_i(t)]^2 / \Delta t
\]

is computed, where \(t\) is the time at which we start measuring the diffusion and \(\Delta t\) is the lag time. \(N_r\) is the number of realizations of trajectories \(x_i(t)\) that are simulated. By computing the reduced lag diffusion \(D(t, \Delta t) - D_{\infty}(\Delta t)\), where \(D_{\infty}(\Delta t)\) is the diffusion at the end of our simulations, it is observed that the diffusion shows lower values than its final steady state value [Fig. 4(c)], which is an overcooling of the system. This effect is purely induced by activity, it is not present for the corresponding passive system (see the Supplemental Material [33]).

We have investigated the interplay of two nonequilibrium phenomena, the cooling or heating process of a colloid, and its active motion, showing that the active motion of a particle can fundamentally change the relaxation process. In principle, our model allows for a direct experimental verification with active colloids. In the future, it will be interesting to see how this translates to higher dimensions, and many particle systems. Overcooling enables a refrigerator to transiently cool a system to lower temperatures than the prescribed temperature, which raises the question how the effect optimizes the function of heat engines [54,55]. While we focused on active colloids in this Letter, similar effects might arise for biological microswimmers, such as bacteria or microalgae, which can change their motility pattern and, therefore, their effective temperature in response due to external stimulus [56].

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