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## Supplementary information

# Exponentially faster cooling in a colloidal system

In the format provided by the authors and unedited natureresearch

**Peer Review File**

**Manuscript Title: Exponentially faster cooling in a colloidal system**

**Redactions – Mention of other journals**

This document only contains reviewer comments, rebuttal and decision letters for versions considered at *Nature*. Mentions of the other journal have been redacted.

**Reviewer Reports on the Initial Version:**

Dear Editor,

The manuscript "Exponentially faster cooling in a colloidal system" by Avinash Kumar and John Bechhoefer, describes a very careful and thoughtful experiment, where a Mpemba effect was measured in a colloidal system.

The Mpemba effect is a long standing, highly debatable problem, where a hot system cools (or freezes) faster than a colder copy of the same system. It is a rare cases where the problem itself can be understood (and even be observed) by almost anyone, but a fundamental understanding of the mechanism behind it is still lacking. For several decades it attracted mainly the science-teaching community, but recently it is getting much attention in a growing number of disciplines, from numerical chemistry to theoretical physics. A crucial missing part in the Mpemba puzzle is some link between the numerical or theoretical ideas, which are usually limited to small, mesoscopic systems, and experimental observations which up until now where done on macroscopic systems. This is piece of the puzzle is now well addressed in the manuscript under review, and in a remarkable way that I am sure will be useful to further shed light on this interesting but not that simple effect.

The main important findings and consequences of this manuscript, in my view, are:

1. Statistics. Probably the best well controlled experiment done prior to the current manuscript is the one done on clathrate hydrates (ref. 21 of the manuscript), where each realization of the system was repeated 8 times. Although that experiment was done on a macroscopic system, where naively we expect the statistical distribution to be insignificant and to arise mainly from experimental inaccuracies, this was not the case, and the variance in the measured relaxation times is much broader than that. This observation, which repeated itself in most of the reported experimental results (see the data spread of many experiments discussed in Ref. 8), highly suggests that there is an important statistical factor in the effect. However, it was never explored in any experiment so far. In the manuscript by Kumar and Bechhoefer, the number of realizations is 1000 for each set of experimental parameters, which ensures accurate statistics. To my knowledge, this is the first experiment where the number of realizations is so high. As a result, the significant of the reported results is beyond any question, in contrast to all other experiments done before.

2. Correspondence to theory. In all previous studies of the Mpemba effect, no quantitative connection between theory and experiment was made, except for some very specific calculations for water (e.g. evaporation rate). Even detailed numerical studies on water or spin-glass systems did not

lead to any quantitative comparison to experimental results. The current manuscript is the first experiment ever to relate the observed effect to any of the theories.

3. Observation of the“strong” Mpemba effect. The author report the first ever experimental observation of two different “strengths” of the effect. This, by itself, is a very important result. Not only does it demonstrate a theoretically suggested idea, but it also demonstrates a possible way to relate other experimental observations to the theory: by looking 1 for similar effect in macroscopic systems it will be possible to understand if the mechanism is similar or not.

4. Repeatability and reproducibility: A major problem with many of the previous experiments is that the macroscopic systems used are never “identical”, and it is never clear what is the origin of the observed effect, nor that it can be reproduced. And indeed, some manuscripts claim not to observe any effect under “identical” conditions, which are clearly not identical. The current manuscript is easily reproducible, and moreover its agreement with theory suggests that no such problem can occur.

In addition to the above, the manuscript is very well written and therefore is accessible to a wide range of readers. The experiment itself seems to be very carefully made, and in fact was planned in a truly remarkable way to address many experimental problems: from data quantization rate to the required thermal range needed. Based on all the above considerations, I strongly support on publication of this manuscript in Nature. In the next page I attached a set of comments and questions, which I hope the authors can address.

1. Page 2, line 26: Ref. 8 and 9 where already discussed in the abstract where you mentioned the Mpemba being controversial. Indeed, these references are great to demonstrate how controversial the effect is, but not to point out that it often occurs when there is a phase transition (which is the context on page 2). Ref. 8 actually defines the effect without the phase transition.

2. Page 2, line 29: In addition to Refs. 14-16, there is a newer numerical study that support the same results – PRE 100, 032103 (2019).

3. Page 5, line 63: ”As we will see below...” - this sentence is not clear at this stage of the manuscript. It is true that in second read, after the reader understand the overall picture, its makes perfect sense, but maybe the author should consider to explain a bit more at this stage.

4. Page 5, line 65: Defining $\alpha = |xmax/xmin|$ has a very small (and probably insignificant) approximation in it, since by Eq.(1) of the method, the maximum of the potential is not exactly at $x = 0$. It is probably clearer to leave the definition of $\alpha$ as it is, but a small comment on this point (probably in the Method) can help the reader.

5. Label of Fig.4: In b, it should probably be “ for Tc = 1 (black)” instead of “for Tc = 1 (red)”.

6. Page 10, line 118: Formally, this is true when $a2 \neq 0$ (which is the common case).

7. Page 30, line 415: Can you quantify in how many experimental realizations have you actually measured such a violation? I think this would be reassuring to see that this is indeed a very small fraction.

8. Page 30, lines 425-426: At first, this looks like a “red light” over the results – in what realistic system other than cold atoms will a factor of 1000 in the temperature be relevant?

Then after giving it some thought, I realized that in fact this is a problem which is specific to this system. Let me explain why: in most systems, the relaxation is dictated by the free energy landscape rather than the energy landscape itself, as is the case in a single body system like the present one. In many-body systems, the change in the Boltzmann distribution can be quite dramatic even with a small change in the temperature. For example, consider the Ising model, whose Landau free energy looks, for some range of temperatures and magnetic fields, just like the potential in Fig. 1. Moreover, the dynamic of the system under quench is, in some cases, very similar to the dynamic of the colloidal system, where the free energy replaces the actual energy. However, in many-body systems as the Ising model, the free-energy landscape is by itself a function of the temperature, and near the phase transition it changes dramatically. This can easily lead to a similar effect in such systems, for a much smaller temperature changes, which are relevant experimentally. I do not expect this to appear in the text, but mention it here because it might be useful for the author.

9. Page 30, section ”Imposing an instantaneous quench via initial condition”: it is not clear how the specific initial condition is forced on the system. I can think of three ways this can be done: (i) After a specific location was chosen, a strong force is applied on the particle via the OT, and stir it to the desired position. My guess is that this is what was actually been done. (ii) An alternative way is to record many long trajectories, and post-select a specific trajectory (and possibly an initial time) such that the location is the desired location. If this is the case, then some careful is needed: to avoid correlations, the same trajectory cannot be used more than once. Lastly (iii) It is possible to calculate a potential whose Boltzmann distribution is the desired distribution, and let the system relax into equilibrium in this potential. It will be useful for the reader to understand which of the above (or maybe some other method) is actually used in the experiment.

Dear Editor,

I am very glad to review this manuscript titled "Exponentially faster cooling in a colloidal system". I strongly recommend accepting this manuscript with minor revisions. Please see my detailed comments below.

In this manuscript, the authors demonstrated the first clean experimental demonstration of the Mpemba effect -- a counterintuitive cooling effect where a hot system may cool faster than a warm one.

In the past, this counterintuitive effect - mostly discussed in terms of cooling/freezing water - was under massive debate due to the difficulties of providing a perfectly controlled experiment. Additionally, the early attempts in explaining the original Mpemba effect (for freezing water) were extremely complicated due to the many anomalous behaviors of water (e.g., supercooled liquid phase, hydrogen bond network, and decreased melting point pressure increase). This manuscript chose a perfect experimental set up to get rid of all of the ambiguities. Using a feed-back trap system, where a Brownian particle in a thermal bath feels an engineered energy landscape, this work demonstrated not only the Mpemba effect but also the strong Mpemba effect proposed in the theory literature.

The result presented in this manuscript will have a significant impact on the fields of physics,

chemistry, biology, and material sciences. It shows clear evidence that we need to transform the way we consider cooling, heating, and other processes/dynamics, where systems are driven out of equilibrium by environmental changes (e.g., changes in temperature, pH, mechanical stress, external electrical field, or concentration of signaling molecules). By demonstrating the Mpemba effect in a simple experimental system other than the "mysterious" substance like water, this experiment indicates that the "intuition" rooted in equilibrium or near-equilibrium (linear response) theory can be misleading when we try to predict the far-from-equilibrium responses of a driven material.
Overall, this work is original and transformative. The conclusion is clearly stated and solid. The data acquisition, statistics, and error analysis are made correctly and well presented. I strongly recommend accepting this manuscript after minor revisions on wordings (see listed suggestions at the end of this report).

A brief summary of the content:
This manuscript described an experimental setup of a one-dimensional (asymmetric) double-well potential. A single Brownian particle immersed in a thermal bath sits in this potential, and it represents the system for quenched cooling. The Brownian particle is prepared at an initial hot/warm temperature and is cooled to the cold bath's temperature. By repeating this experiment multiple times, an ensemble representation (probability distribution) of the particle can be obtained, and the authors study the relaxation of the initial Boltzmann distribution at initial hot/warm temperatures as they are cooled to the final cold temperature. Then they defined the "L1 norm" to characterize the "distance" between the system and its final equilibrium to keep track of the cooling process. They demonstrate that for certain asymmetric potentials, there exists a range of initial temperatures where it takes a shorter time to cool hot systems than warm systems (indicating the Mpemba effect). Their experiment is perfectly controlled so that the two systems are identical in every way except for their initial temperature. Thus, their experiment provides the first clear demonstration of the Mpemba effect without any hidden complications (like supercooling for water). Additionally, their analysis agrees with the general theory predicted by Lu and Raz in 2017. The authors then went beyond and explored the relationship between this Mpemba effect and the geometrical shape of the energy landscape, where they found an experimental verification of the strong Mpemba effect (Klich and coworkers, 2019).

Suggested minor revisions:
1) In Fig.2 a-c. It may be helpful if the authors could state in the caption that the x-axis (time) is on the log scale for a more transparent comparison between the hot and the cold system. If the readers are careless, they may ignore this log scale and get confused by the panel c. One would expect the panel c to show an equilibrated system. Thus one should expect the feature of the noisy trajectory to not change over time. It is the case, but plotting it in the log scale may make the curve look different - at a log scale, the curve seems less noisy at a short time than at a longer time. There is nothing wrong here, but it may help avoid confusion for the readers if the authors mention this and reassure the readers that Fig. 5c is definitely in equilibrium even though the curves at the log scale looks less noisy on the left than the right.

2) At lines 102 and 103, as well as lines 120 and 121, the authors may want to refer to the Section of Strong Mpemba effect.

3) More of a suggestion: the notation "\Delta D" defined at line 125 may be confusing for some readers since it is not a difference in D. It is okay if the authors would like to stay with the current notation.

4) It would be helpful if legends are provided in Fig. 5c ("\Delta D", |a_2|, etc.)

5) Legends in Extended Data Fig.3 would be helpful.

6) Between line # 523 and 524, there is a typo in equation (12). The authors must have meant to

write "...*v_k(...)" rather than "...* v_2(...)". The same typo is found for the "v_2(...)" at line # 524. This does not affect the conclusion.

7) For line 561 to 563, technically, there is no fixed sign required for eigenfunctions here. I assume that the authors choose a sign for a better illustration of the two functions?

8) At line 568, it may be helpful for the authors to mention that <u_2|\pi>=0 as explicitly.

9) At line 576 and 577, maybe the sentence can be restated to emphasize that the terms of k>2 are negligible at the long time limit.

10) Minor suggestion for line 580 and equation (23). The notation v_i may be confusing since it is v_2(x_i), and people may confuse it with a vector-like v_k for k=i. This is a minor point, and authors can judge if a better notation is necessary.

11) At line 582, while introducing the equation (24), it may be helpful if the authors say that the terms for k>2 are negligible.

12) I do not quite get the point of the sentence, "The result is effectively an upper bound on the size of a_2." at line 602.

The manuscript demonstrates the Mpemba effect using a microparticle trapped by feedback optical tweezers. The Mpemba effect, which is an old story in original, is attracting growing interest recently. This effect is counter-intuitive and intriguing. However, the Mpemba effect has not been clearly defined and has not been clearly demonstrated. This paper used an ingenious setting and a sophisticated technique and demonstrated the Mpemba effect. The logic and story of the manuscript are readable to non-expert people. The paper would make a significant progress in the field.
However, the core idea of this experiment has been already demonstrated theoretically and numerically elsewhere Lu and Raz, PNAS (2017). And, my impression is that the experiment is a little bit artificial and is rather like a simulation. Therefore, I would say that the paper is more suitable for more specific journals like [redacted].

Some minor comments are

1. The feedback trap is a fascinating technique to construct a potential with such a nanometer-sized resolution. However, it kicks the particle every 10 us. And, I am concerned that the kicking affects the dynamics. Did you check if the particle motion satisfies the local detailed balance condition at like 0.1-ms or 1-ms time scale?

2. The authors mention "exponentially faster cooling" several times, including the title and abstract. But, the definition of "exponentially faster" was not very clear to me. Please define this term explicitly.

3. It would be better to make Fig. 1 more intuitive so that the readers could better understand the idea shown in this paper.

4. Typo
Eq.(3): p_0 -> p_{r_0} ?

**Author Rebuttals to Initial Comments:**

## Reviewer 1

1. Page 2, line 26: Ref. 8 and 9 where already discussed in the abstract where you mentioned the Mpemba being controversial. Indeed, these references are great to demonstrate how controversial the effect is, but not to point out that it often occurs when there is a phase transtion (which is the context on page 2). Ref. 8 actually defines the effect without the phase transition. We have replaced Refs. 8 and 9 with one that discusses the Mpemba effect in the context of phase transitions.

2. Page 2, line 29: In addition to Refs. 14-16, there is a newer numerical study that support the same results – PRE 100, 032103 (2019). We thank the Reviewer for pointing out this recent article. Because its focus is on a mechanism depending on different time scales for kinetic- and potential-energy degrees of freedom, we felt it more appropriate to include in a sentence on line 33.

3. Page 5, line 63: “As we will see below...” - this sentence is not clear at this stage of the manuscript. It is true that in second read, after the reader understand the overall picture, it makes perfect sense, but maybe the author should consider to explain a bit more at this stage. We understand the concern here. In trying to explain more at this stage, we thought that presenting a lot of detail early on might confuse the reader. Moreover, we are pretty much at the limit of length. Perhaps the Editor can decide on this.

4. Page 5, line 65: Defining $\alpha = |x_{max}/x_{min}|$ has a very small (and probably insignificant) approimation in it, since by Eq.(1) of the method, the maximum of the potential is not exactly at $x = 0$. It is probably clearer to leave the definition of $\alpha$ as it is, but a small comment on this point (probably in the Method) can help the reader. It is correct that the naive estimate of α in our definition is slightly biased. We have checked that the value of α calculated including the offset in the barrier position, is off by 5%. However, the probability distribution corresponding to the bath temperature changes only by <1%. We have added a note about this in the manuscript (lines 357-362).

5. Label of Fig.4: In b, it should probably be “for $T_c = 1$ (black)” instead of “for $T_c = 1$ (red)”. We have fixed the typo.

6. Page 10, line 118: Formally, this is true when $a_2 \neq 0$ (which is the common case). We have added the mentioned condition on a2 to clearly state the point (line 119).

7. Page 30, line 415: Can you quantify in how many experimental realizations have you actually measured such a violation? I think this would be reassuring to see that this is indeed a very small fraction. The total time that a particle spends outside the box [xmin, xmax] seems a better estimate of such violations. From the trajectory of a system starting at temperature = 1000, we measure that the total time spent outside the box is 2.09 ms for a 70 s long experiment. Thus,

such excursions account for only ~0.003% of the total time of the experiment. We have added a note in the section “Infinite potential vs. finite potential” in Methods (lines 428-430).

8. Page 30, lines 425-426: At first, this looks like a “red light” over the results– in what realistic system other than cold atoms will a factor of 1000 in the temperature be relevant? Indeed, we also worried about this point and offer Extended Data Fig. 3 and its associated discussion of how we create a fast experimental time scale as one response. However, the Reviewer gives another reason (based on free energy changes) that the large temperature ranges required by our system would correspond to more moderate changes in other systems. This is an interesting point that deserves to be followed up in future work.

9. Page 30, section “Imposing an instantaneous quench via initial condition”: it is not clear how the specific initial condition is forced on the system. I can think of three ways this can be done: (i) After a specific location was chosen, a strong force is applied on the particle via the OT, and stir it to the desired position. My guess is that this is what was actually been done. (ii) An alternative way is to record many long trajectories, and post-select a specific trajectory (and possibly an initial time) such that the location is the desired location. If this is the case, then some careful is needed: to avoid correlations, the same trajectory cannot be used more than once. Lastly (iii) It is possible to calculate a potential whose Boltzmann distribution is the desired distribution, and let the system relax into equilibrium in this potential. It will be useful for the reader to understand which of the above (or maybe some other method) is actually used in the experiment. We have used the first technique, as surmised by the referee, to instantaneously quench the particle from a desired probability distribution. We have added a sentence about that in the in the section “Imposing an instantaneous quench via initial conditions” in Methods (lines 439-440).

## Reviewer 2

**1.** In Fig.2 a-c. It may be helpful if the authors could state in the caption that the x-axis (time) is on the log scale for a more transparent comparison between the hot and the cold system. If the readers are careless, they may ignore this log scale and get confused by the panel c. One would expect the panel c to show an equilibrated system. Thus, one should expect the feature of the noisy trajectory to not change over time. It is the case, but plotting it in the log scale may make the curve look different - at a log scale, the curve seems less noisy at a short time than at a longer time. There is nothing wrong here, but it may help avoid confusion for the readers if the authors mention this and reassure the readers that Fig. 5c is definitely in equilibrium even though the curves at the log scale looks less noisy on the left than the right. We have added some information about the logarithmic time scale in the caption to Fig. 2. There is already a sentence later on in the caption asserting that 2c is in equilibrium: “The cold distance plot is a control experiment where the particle is released from the equilibrium distribution at the bath’s temperature.”

2. At lines 102 and 103, as well as lines 120 and 121, the authors may want to refer to the Section of Strong Mpemba effect. We have added a note to refer to the section "Strong Mpemba effect" at both places.

3. More of a suggestion: the notation "\Delta D" defined at line 125 may be confusing for some readers since it is not a difference in D. It is okay if the authors would like to stay with the current notation. We have modified the sentence (lines 128–129) to indicate that ΔD is calculated by subtracting the noise from the D values (t = 0) found by fitting the long-time asymptotic regime of the distance curve. We also note that, as discussed in the Methods section on the L1 distance (lines 488-503), the quantity D is always positive. Measurements that are then "in the noise" actually have a positive value (given by Eq. 9) and need to be subtracted before fitting an exponential to extract a2. (The subtracted offset, however, is, in practice, quite small.)

4. It would be helpful if legends are provided in Fig. 5c ("\Delta D", |a_2|, etc.) We are not quite sure what the Reviewer would like here. The two curves in 5c are already labeled as "warm" or "hot". If the Reviewer thinks these should instead be put in a legend, we can leave that with the Editor as to which style is preferred.

5. Legends in Extended Data Fig.3 would be helpful. Extended Fig. 3 is just a qualitative representation of the double-well potential with different slopes. In the section "Choice of potential energy landscape", we talk briefly about how different slopes can affect the equilibration time. We feel that adding more quantitative information about the slopes is not needed here.

6. Between line # 523 and 524, there is a typo in equation (12). The authors must have meant to write "...*v_k(...)" rather than "...* v_2(...)". The same typo is found for the "v_2(...)" at line # 524. This does not affect the conclusion. We have corrected the typo in Eq. (12) and the sentence immediately afterward.

7. For line 561 to 563, technically, there is no fixed sign required for eigenfunctions here. I assume that the authors choose a sign for a better illustration of the two functions? Yes, the sign is chosen for clarity. However, although the overall sign of the eigenfunctions is arbitrary, once we choose the sign of one of them, the sign of the other eigenfunctions is decided accordingly. We have added a small note about this in the manuscript (lines 573– 575).

8. At line 568, it may be helpful for the authors to mention that =0 as explicitly. We do not understand what the referee is referring to here.

9. At line 576 and 577, maybe the sentence can be restated to emphasize that the terms of k>2 are negligible at the long time limit. We have added a sentence mentioning that we neglect terms for k>2 (lines 589–590).

10. Minor suggestion for line 580 and equation (23). The notation v_i may be confusing since it is v_2(x_i), and people may confuse it with a vector-like v_k for k=i. This is a minor point, and authors can judge if a better notation is necessary. We understand that it may be confusing to

some readers, but we immediately state after Eq. 23 that vi = v2(iΔx) . We did consider alternate combinations such as *Vi*2 *V*{2} *i*, but each has inconsistencies with the notations we have been using in the manuscript. Overall, we think the current notation strikes the best compromise between readability and consistency.

11. At line 582, while introducing the equation (24), it may be helpful if the authors say that the terms for k>2 are negligible. We have added a sentence in the manuscript mentioning this (line 595).

12. I do not quite get the point of the sentence, "The result is effectively an upper bound on the size of a_2." at line 602. We have removed this sentence to avoid ambiguity; it was not an important point.

## Reviewer 3

1. The feedback trap is a fascinating technique to construct a potential with such a nanometer-sized resolution. However, it kicks the particle every 10 us. And, I am concerned that the kicking affects the dynamics. Did you check if the particle motion satisfies the local detailed balance condition at like 0.1-ms or 1-ms time scale? We have checked that particle trajectories do satisfy local detailed balance. For two arbitrary points, (x, y) in the trajectory separated by times of 0.01 and 0.1 ms, we measured the ratio P(x) k(x,y) / P(y) k(y,x), where is the probability density at position , and the transition rate between points x and y. For better statistics, we considered a 5 s long trajectory, sampled at 10 μs. For 0.01 ms, we found a typical ratio of 0.999 and for 0.1 ms, a typical ratio was 0.971. For longer time scales, the statistics were poor. In previous work [Jun *et al*., Phys. Rev. E 86, 061106, 2012], we had considered this issue in a different way. For a feedback trap, the force exerted on a particle at a position xn is created by moving the trap position with respect to the particle position and is given as Fn = − βxn. The proportionality constant β = Δt /t is similar to the spring constant in a real trap, where Δt is the sampling time and tr the relaxation time. For β ≪ 1, the dynamics of the particle in a feedback trap are similar to the dynamics in a real potential [Jun *et al*., Phys. Rev. E 86, 061106, 2012]. In our experiment, for Δt = 10 μs and tr = 0.4ms, the dynamics of the particle are negligibly affected by the discrete kicks for β = 0.025. We have added a paragraph clarifying this at the end of the section “Set up” in Methods (lines 324–335).

2. The authors mention "exponentially faster cooling" several times, including the title and abstract. But, the definition of "exponentially faster" was not very clear to me. Please define this term explicitly. We have added a sentence in the section “Strong Mpemba effect” at line 159. We mention that in the case of strong Mpemba effect where a2 = 0 , the relaxation is dominated by λ3( > λ2). Thus, the relaxation ~e−λ3t is exponentially faster than the relaxation ~e−λ2t.

3. It would be better to make Fig. 1 more intuitive so that the readers could better understand the idea shown in this paper. We have modified Fig. 1b to show more clearly how the probabilities “fall" into the two macrostates. We colour code probabilities that (approximately)

are transformed from the initial hot state to the cold state and also match the areas. We hope these changes make the figure more intuitive.

4. Typo Eq.(3): p_0 -> p_{r_0} ? We have corrected the typo.