nature portfolio

Peer Review File

Long-term memory induced correction to Arrhenius law

Reviewer #1 (Remarks to the Author):

In this paper the authors consider the Kramers escape problem, which for Markovian dynamics leads to the famous Arrhenius law. They address a controversy that arose when considering Kramers escape for non-Markovian dynamics. Two analytical approaches claimed that the mean first passage time (MFPT) for non-Markovian Langevin dynamics becomes infinite while numerical results, as well as more hidden mathematical results from the 1960's, yielded finite MFPTs. By generalising previous theoretical approaches and applying them to a simple example of non-Markovian Kramers escape, the authors calculate the MFPT by analytical approximations and compare their results with simulations. The agreement is excellent and provides convincing evidence that the MFPT for this process is indeed finite. This is demonstrated in detail by an analytical formula for the MFPT derived by the authors that generalises the conventional Arrhenius result by elucidating in detail the non-Markovian contributions to the escape dynamics.

I find the paper very well written. The introduction amply outlines the problem at hand, its general importance and the embedding of the present research into previous literature. The minimal model studied in this paper is well presented, and the key ingredients of the theoretical approach are clearly explained. The matching between analytical and numerical results gives confidence in the quality of the analytical approximation for which, moreover, basic assumptions are checked numerically. Accordingly, in terms of scientific soundness and quality I have nothing to criticise; see just my very brief list of minor comments included below. To me, the main question is whether the presented research features sufficient novelty, importance and impact to justify publication in Nat. Comm.

As the authors nicely discuss in their introduction, studying non-Markovian Kramers escape has already attracted quite some attention in the literature. They develop a new technique for solving this important problem in a special case. For this they draw to quite some extent on own previous work, see Eqs.(6),(8), as is adequately pointed out in the ms. While their new approach is well outlined on the first few pages, I find the final discussion of the rare event limit leading to their central result Eq.(13) a bit technical. On the other hand, I do very much appreciate that the authors make an important contribution to this particular field, which should help to resolve the stated controversy about infinite MFPTs for non-Markovian dynamics. And their central formula beautifully dissects the different contributions to a non-Markovian result for a MFPT beyond Arrhenius' law.

In summary, what the authors present here is a very nice, important result that undoubtedly will be much appreciated by scientists working on MFPTs and non-Markovian stochastic processes. It addresses, and solves at least to some extent, a long-standing open problem in this field. The developed theory looks sound and promising for further applications but is to quite some extent based on previous work by the authors. This is reflected in the paper partially appearing a bit technical, especially to the end. Altogether my impression is that in terms of novel methods, importance and impact on physics research this paper is not strong enough to excite the more general readership of Nat. Comm. I am absolutely sure this work will find its place, and appreciation, in the more specialised literature, but I am afraid I cannot recommend publication in this journal.

minor remarks:

p.2, Eq.(2): For their dynamics, they assume the validity of the fluctuation-dissipation theorem. If I am not mistaken, this seems to be directly reflected in Eq.(9), which forms an important ingredient in the whole theory. Could the theory still be worked out for dynamics without fluctuation-dissipation theorem, which in this sense may relate to a case of (anomalous, fractional) active Brownian motion? Scenarios like this have recently been considered, e.g., in Ref.[A]. Surely, this question goes considerably beyond the framework of the present paper. But it might be interesting whether the theory could be further generalised along these lines, connecting the conventional Kramers scenario for a passive particle with the big, different field of active particles. Future work along these lines could make the research of this paper much stronger.

p.3: There seems to be a mismatch for defining the factor A in Eq.(1): Using the definition of $\Phi(t)$ via the Mittag-Leffler function, the subsequent definition of τ_d and the approximation of ML for large arguments and plugging the result into Eq.(1) yields an expression for A where k and K_α are swapped compared to the authors' definition on p.3. Please check, perhaps there is a little typo.

[A] K.Goswami, R.Metzler, J. Phys. Complex. 4, 025005 (2023)

Reviewer #2 (Remarks to the Author):

In their work entitled “Long-term memory induced correction to Arrhenius law”, the authors address a fundamental question in the context of stochastic processes, that is, is the Arrhenius law still valid for long-term memory processes? The impact of long-term memory on the kinetics of rare events has been previously investigated (both analytically and numerically) with inconsistent results. A crucial point concerns the first-passage time (FPT) to a target configuration, that provides a quantitative characterization of the kinetics of rare events and whose finiteness is controversial.

Here the authors work out an analytical approach that allows them to quantify the impact of long-term memory on the kinetics of rare events and state that the mean FPT is finite. Their predictions are quantitatively and convincingly supported by numerical simulations. The underlying physics is also described by explaining that, in the rate event limit, the Arrhenius law holds but the long-term memory induces a second effective energy barrier, implying corrections that are quantitatively estimated.

I find that this work makes essential steps towards the comprehension of complex, widespread phenomena. Also, the authors introduce analytical tools which can have a significant impact on future research.

As for the presentation, the authors succeed in balancing expository clarity and scientific rigour, maintaining fluency and referring to the appendices for the more technical parts. Thus, the manuscript is overall accessible to a wide audience.

Therefore, as for scientific content and presentation, in my opinion this work fully deserves publication in Nature Communications.

I only have a couple of remarks that the authors might consider in their review:

- The authors focus on a particular class of friction kernels, as defined in Eq. (3). This choice is very reasonable and well motivated from a physical point of view; moreover, the analytical framework can take into account different choices. The question then arises as to what extent the results obtained by the authors are robust to varying the definition of the friction kernel. Of course, this question is beyond the scope of this paper, but any comment the authors would like to share on this point would be appreciated by the reader.

- The authors find unambiguous evidence for the finiteness of the mean FPT and this implies that previous results obtained with the generalised Fokker-Planck equation or with the Wilemski-Fixman approximation display some flaws. As far as I understood from the lines after eq. (9), the motivation given by the authors is that those approaches assume that the process is at all times in an equilibrium state and this, ultimately, yields a wrong estimate for the mean FPT. If possible, the authors could extend their comments on the reasons why the previous approaches are expected to fail as this would not only further clarify the physical process under study but would also make the reader better aware of the pitfalls behind these notoriously-complex, long-term memory processes.

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We thank the referee for these overall very positive comments and for acknowledging that our theory « solves a long-standing open problem…». The negative recommendation for publishing in Nat Com seems to be based on the facts that some derivations could be made more accessible, and that our results are based to some extent on previous works.

First, we have revised the manuscript to make the explanation of Eq(13) more accessible. Second, we would also like to mention that, although a general method to analyse memory effects for first passage processes was indeed introduced before (as was mentioned in the manuscript), this method did not cover the case of long-term memory, which is the focus of this manuscript. In fact, our central results (13), which relies on a complex multiscale analysis, is completely new, and could by no means be deduced from previous works. Furthermore, given the importance and impact of Arrhenius laws and of long-term memory processes in various fields, including beyond physics, we do believe that our simple predictions (13) will be of interest for the wide audience of Nat. Com. (as stated by referee #2, who finds that the present problem is « a fundamental question in the context of stochastic processes»). We hope, in view of these arguments, and of the clarifications that we provide, that the new version of the manuscript is now suitable for publication in Nat. Comm.

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We thank the referee for this remark. In fact, our approach does not require that fluctuation dissipation holds. For such non equilibrium processes, if defined via a Langevin equation as given in the text (Eq. 2, with no restriction on the friction kernel and correlation of the noise), one could calculate the properties of the walk without target (phi, l, p_s, A,…, as done in Ref 35 for example), and then use our formalism to calculate the mean FPT. This is now mentioned in the conclusion. We have also cited the reference [A].

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In principle the theory can be extended to non-thermal cases. Indeed, one could calculate for such active models the properties of the motion without target (as is done, e.g. in Ref [35]), and then use our formalism to deduce the first passage properties. This has been clarified in the conclusion.

- The authors find unambiguous evidence for the finiteness of the mean FPT and this implies that previous results obtained with the generalised Fokker-Planck equation or with the Wilemski-Fixman approximation display some flaws. As far as I understood from the lines after eq. (9), the motivation given by the authors is that those approaches assume that the process is at all times in an equilibrium state and this, ultimately, yields a wrong estimate for the mean FPT. If possible, the authors could extend their comments on the reasons why the previous approaches are expected to fail as this would not only further clarify the physical process under study but would also make the reader better aware of the pitfalls behind these notoriously-complex, long-term memory processes.

We thank the referee for this suggestion. We have added a sentence in the conclusion on the failure of these « standard » approximations, they are indeed linked to the fact that they rely on a kind of equilibrium assumption at all times for the additional degrees of freedom, which in the present case of long-term memory is too strong to predict correctly first passage properties.

REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author):

I thank the authors for their constructive reply to my report. As I wrote in my previous report, I acknowledge again that the authors solve `a long-standing open problem', or, as the other referee formulates it, `a fundamental question in the context of stochastic processes'. However, there is perhaps a little bit of a misunderstanding in that the negative conclusion in my first report does not only relate to making `some derivations [...] more accessible', and that the presented results `are based to some extent on previous works'. My concern is further strengthened by the rather substantial amount of important literature, published in other journals, that is already available on right this topic. In this respect I disagree with the other referee on the novelty of the present research. In my view, addressing an important problem is not enough to justify publication in a highly prestigious journal. The performed research should, in my view, also consist of a distinct level of novelty, both technically in view of previous work as well as in terms of delivering substantially novel physics, that warrants publication in such a journal.

I appreciate that the authors modified their ms. to address my previous criticism, but their modifications are rather marginal. I emphasize again that this ms. contains research of high quality that undoubtedly will be of interest to experts in this field. But I am afraid I do not see any reason to change my previous conclusion that this ms. does not contain enough breakthrough new results to justify publication in Nat. Comm.

Reviewer #2 (Remarks to the Author):

The authors have satisfactorily addressed all the points raised in my previous report and I am now happy to recommend publication in Nature Communications.

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The authors introduce an analytical approach that allows them to show that the first-passage time of rare events is finite, which by itself is an important finding. These predictions agree with numerical simulations done by the authors. The underlying mechanism is clearly explained. I find this work to be elegant and to make an important contribution in the field of statistical physics, I therefore recommend publication as is.

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We thank the referee for evaluating our work and the statement that the work contains research of « high quality ». We think that the analytical prediction of the modification of Arrhenius laws by long-term memory (for which no analytical result was available), by identifying analytically the multi-scale structure of the problem (which is by no means identified in previous studies), is important enough to justify the publication of these results in Nat. Com. (although we understand that such a recommendation can be subject to debate).

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