Dr Andrea Taroni
Chief Editor
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Dear Dr Taroni,

I would like to submit for your consideration the attached manuscript entitled *"Justification for the use of Markovian Langevin statistics in the modelling of activated surface diffusion"* by J. Wilkinson and J. Ellis, for publication as an Article in Nature Physics. I am thrilled to share our progress in understanding the role of the Markovian Langevin equation in surface diffusion with you. The conclusions of our work justify the standard data analysis technique in the field of surface dynamics in a most unexpected way, with far-reaching insights applicable to the diverse application of Kramers' theory of low-friction reaction rates.

Main Points

Our paper focuses on helium spin-echo experiments, which are almost exclusively analysed using simulated solutions to the Markovian Langevin equation. This approach is immensely popular thanks to the Langevin equation's computational efficiency, simplicity of form, and ease of implementation. However, we argue that a careful evaluation of the assumptions used to arrive at the Markovian Langevin equation, uncovers them to be at best not-justifiable and at worst profoundly unrealistic in the context of surface diffusion.

We resolve the apparent issue through the identification of a new generalised energy exchange rate parameter that specifies the hopping rate of an adatom extremely well, regardless of the statistical nature of the thermal forces involved. This realisation indicates that the only non-equilibrium quantity of interest in low friction activated surface diffusion is the generalised energy exchange rate, which may be evaluated using any stochastic model of adatom motion that satisfies Boltzmann statistics. To a reader active in the field of surface dynamics, this conclusion is a re-assuring one that eases any concerns over the use of the Markovian Langevin equation in their field. We however believe the paper appeals to a far broader audience as we provide a general overview of the various aspects of fluctuation and dissipation that affect the rate of energy exchange with a heat bath. In particular, we analytically derive an expression for the energy exchange of a particle in a harmonic potential under the influence of thermal forces with an arbitrary coloured noise spectrum. This provides a simple non-Markovian generalisation of Kramers' low-friction theory of reaction rates which is already broadly applied to activated processes outside of surface dynamics.

Other matters

We declare that this manuscript has not been published before, in whole or in part, and is not currently being considered for publication elsewhere. We will however make the final draft of this manuscript accessible on the arXiv, in line with your pre-print policy described on the Nature Physics website. My co-author and I have approved the final version of this manuscript and we have no conflict of interests to declare.

For peer-review, we recommend the following distinguished individuals in the field of surface dynamics:

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Thank you for your consideration.

Yours sincerely,

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