

Supplementary Information for Comparison of Predictive Approaches to the Dynamics of Activated Catalytic Processes

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Estimation of the computational cost of RGO algorithm

In the main paper we have already estimated the worst-case cost of the RGO algorithm in the present implementation, equal to $500 \times (3N - 6) \times 2$ Hessian calculations. Here we explore the impact of numerical versus analytical schemes. To do so, we use a different case study, i.e., a system described by a potential that is available both in the OPTIM code (thus linked to analytical Hessian), and the LAMMPS code (so we can use the approach with numerical second derivatives pretending that analytic second derivatives are not available). We focus on the $\text{Cu}_5\text{Ag}_{27}$ cluster published in Ref. 1, described by a second-moment tight-binding potential. The first iteration of the RGO algorithm requires approximately 6 minutes with the analytical Hessian compared to 50 minutes for the seminumerical (with analytical gradients) LAMMPS version, that is roughly an increase by a factor of 8. Also, the seminumerical Hessian scales quadratically with respect to the number of atoms, bringing a factor of ≈ 2 when switching from the considered 32-atom system to the 58-atom system considered in main text. Altogether, this brings in a factor of 16. On top of this factor, we note that in the semi-numerical approach there are $6N$ extra calls of LAMMPS by OPTIM and every time that LAMMPS is called the code has to read the data and initialize the calculation, which takes up significant extra CPU time. For these reasons, we estimate an increase of 1-2 orders of magnitude in computational effort due to the use of numerical rather than analytical second derivatives.

References

- [1] M. Asgari, F. R. Negreiros, L. Sementa, G. Barcaro, H. Behnejad and A. Fortunelli, *The Journal of chemical physics*, 2014, **141**, 041108.

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