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Introduction

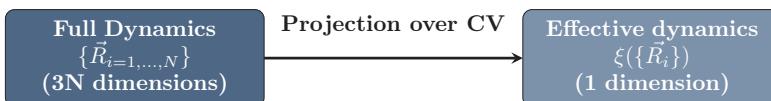
While **collective variables** (CV) are ubiquitously used to model physico-chemical transformations, finding **optimal reaction coordinates** (RC) that yield accurate thermodynamic and kinetic properties is a **fundamental challenge** in the field of atomistic simulations.

Optimal RCs are essential to the understanding of the underlying **mechanisms of a transformation**. Projecting onto an accurate RC helps to **accurately and efficiently estimate reaction rates** and identify the common properties of transition states.

Customarily, optimal RCs are defined as monotonic one-to-one functions of the **committor** [1]. We are proposing an original computationally affordable method to optimize reaction coordinates. It is based on the fact that sub-optimal RCs yield kinetic rates higher than optimal ones.

Theoretical framework

In 2016, Zhang et. al. [2] investigated the repercussions on the reaction rate of projecting the full dynamics onto a low dimensional space defined by the reaction coordinates.

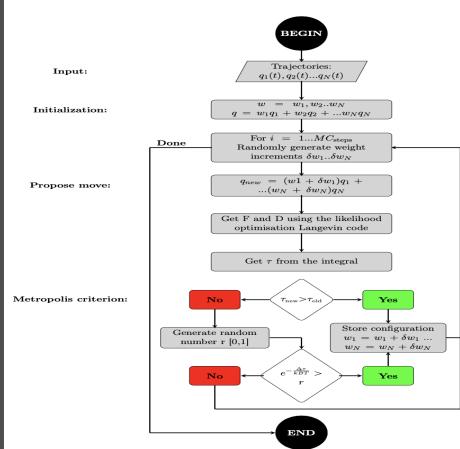


They proved that the reaction rate of the full dynamics is always less than or equal than the one computed using effective dynamics.

$$k_{\text{true}} \leq k_{\text{effective}}$$

How can you tell if a CV is optimal? \Rightarrow Optimal CV yields minimal kinetic rate

Computational methods

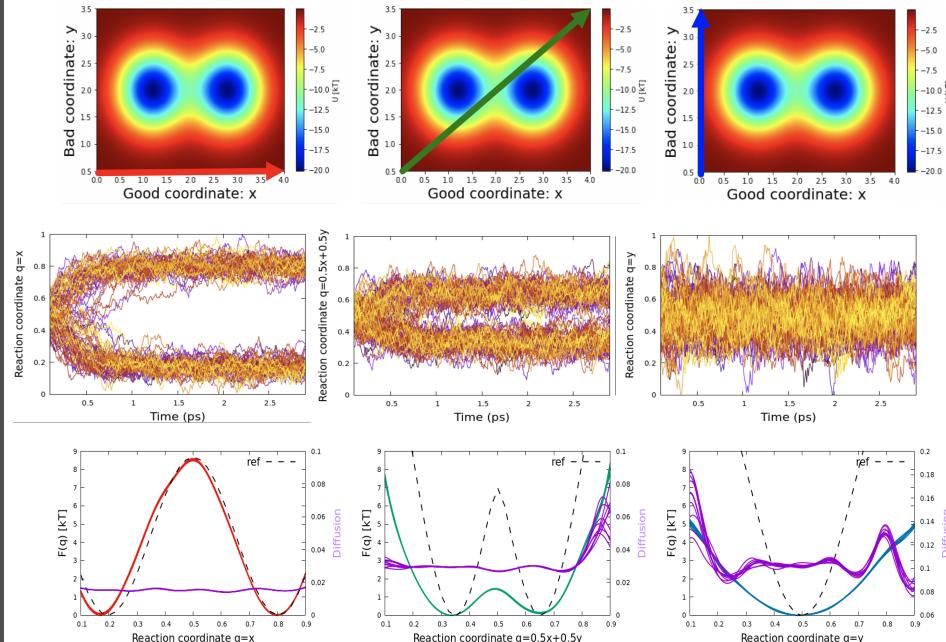


The stochastic algorithm developed is based on a Monte Carlo optimization and it does the following:

- 1 **Input:** Proposed pool of CVs
- 2 Construct a trial move using linear combinations of CVs
- 3 Build a Langevin model via likelihood maximization [3]
- 4 Compute the rate and accept move if the rate is minimized based on a **Metropolis criterion**
- 5 Repeat steps 2 → 4 until convergence

The RC optimization is a post-process method, where the only computationally expensive step is the generation of the MD trajectories. This makes the method computationally affordable.

Benchmark: 2-D double well

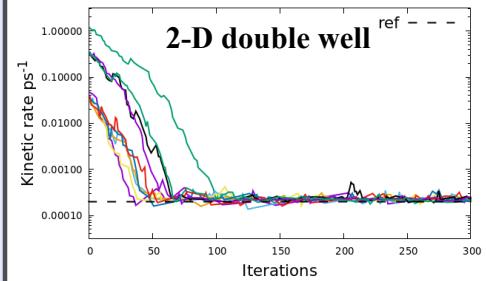


Kinetic rate calculation

The kinetic rate is computed in the following way:

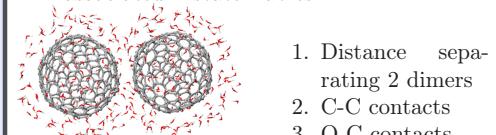
$$k^{-1} = \int_{q_0}^b dy \frac{e^{\beta F(y)}}{D(y)} \int_a^y dz e^{-\beta F(z)} \quad (1)$$

With a and b being the reflecting and absorbing boundaries respectively.

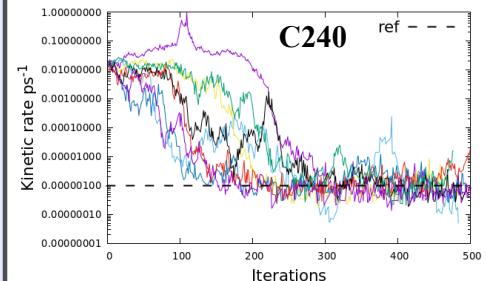


C_{240} fullerene dimers in water

C_{240} fullerene dimers Pool of collective variables:



- 1 Distance separating 2 dimers
- 2 C-C contacts
- 3 O-C contacts



Distance is found to be the optimal RC

Conclusions

Optimal RCs yield minimal kinetic rates. An efficient and computationally affordable algorithm based on this optimality criterion is developed. Kinetic rates are minimized and optimal RCs are retrieved at the end of each run.

References

- [1] Lu and Vanden-Eijnden *The Journal of chemical physics*, 2014.
- [2] W. Zhang, C. Hartmann, and C. Schütte *Faraday discussions*, 2016.
- [3] Palacio-Rodriguez and Pietrucci *arXiv preprint arXiv:2106.05415*, 2021.