

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.

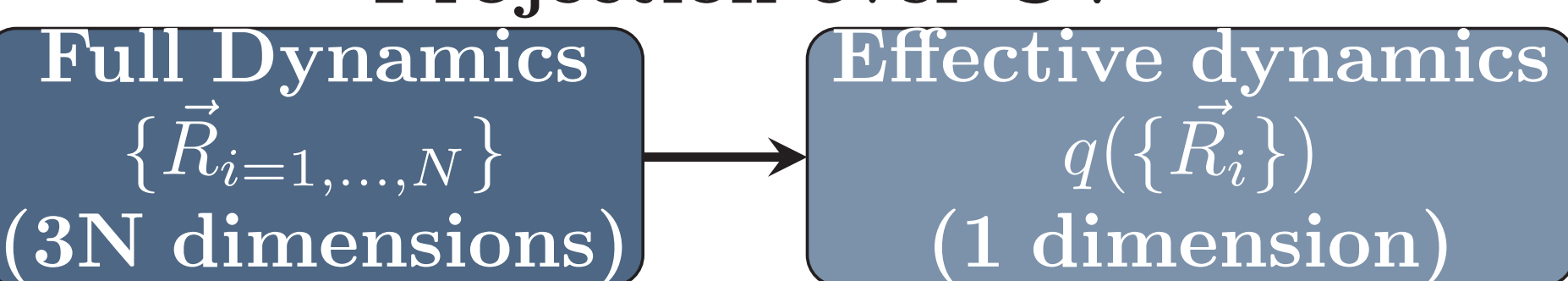
Optimal RCs are essential to the understanding of the underlying **mechanisms of a transformation**. Projecting onto an accurate RC helps to **accurately and efficiently** estimate **reaction rates** and identify the common properties of transition states.

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 [2]. It is based on the fact that sub-optimal RCs yield kinetic rates higher than optimal ones.

THEORETICAL FRAMEWORK

In 2016, Zhang et. al. [3] investigated the repercussions on the reaction rate k of **projecting** the full dynamics onto a **low-dimensional space** defined by the collective variable (CV).

Projection over CV



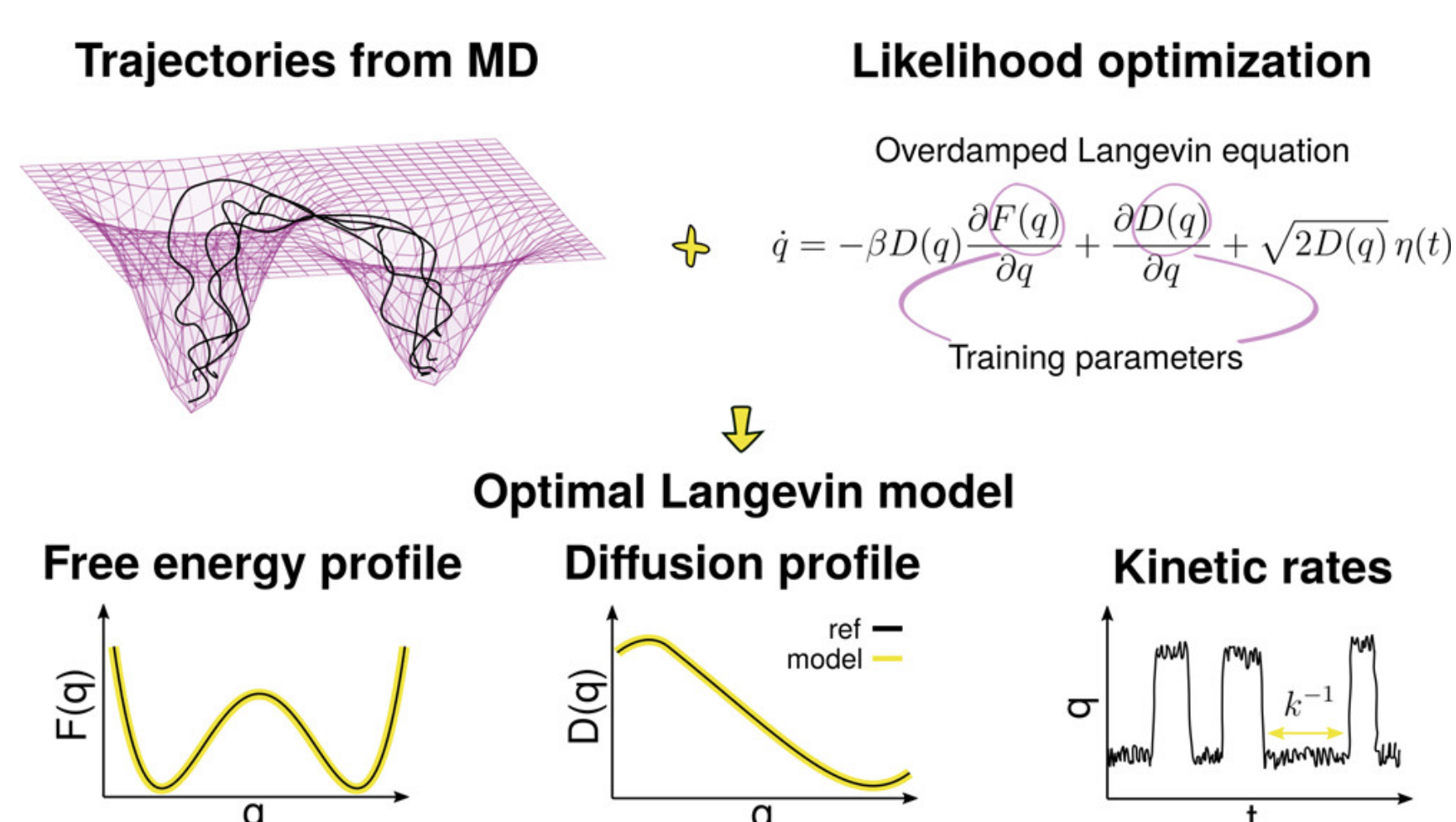
The rate of the full dynamics is less than or equal than the one computed using effective dynamics.

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

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

TRAINED LANGEVIN MODEL

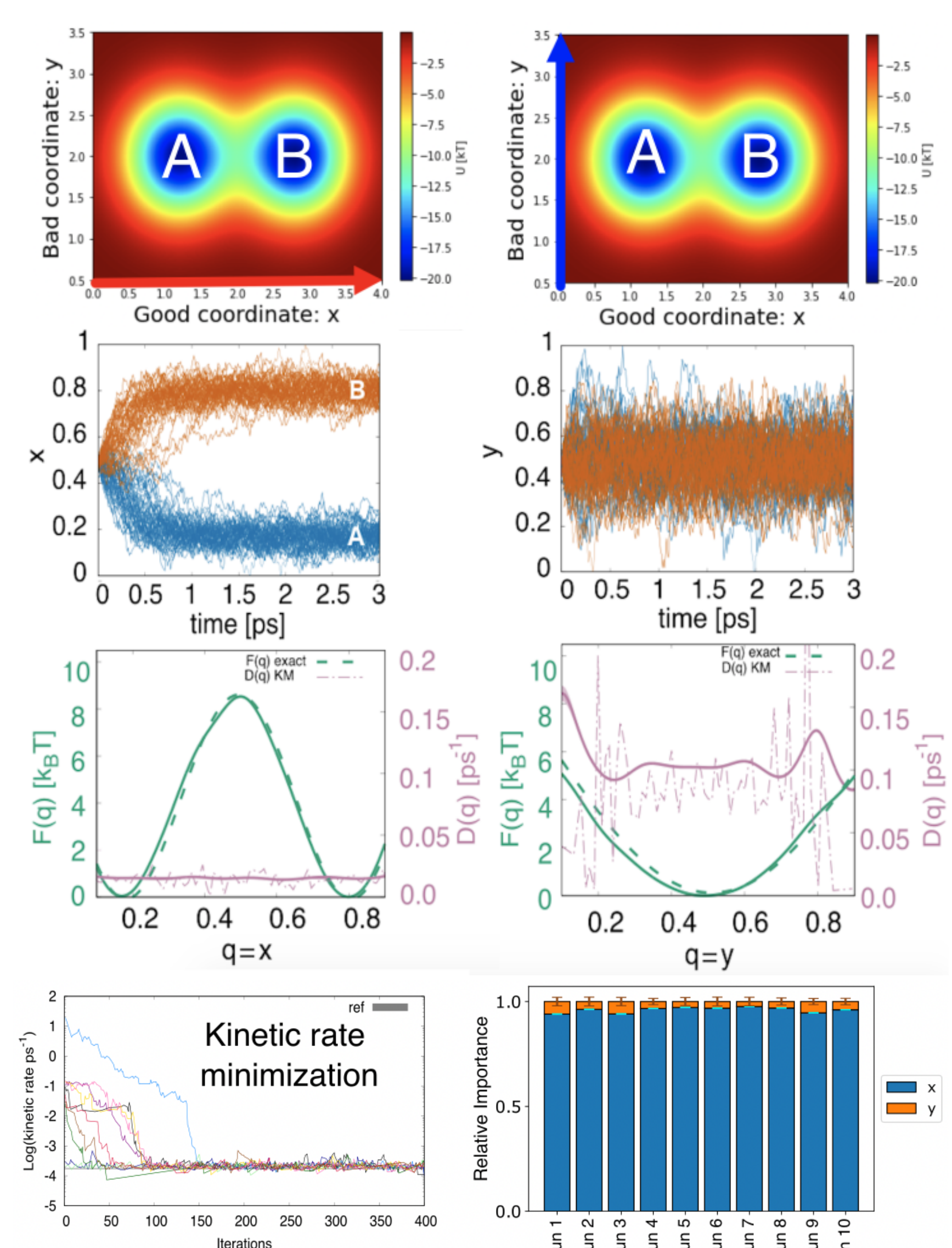
The free energy $F(q)$ and diffusion $D(q)$ are obtained by training an overdamped Langevin model via **likelihood maximization** [4].



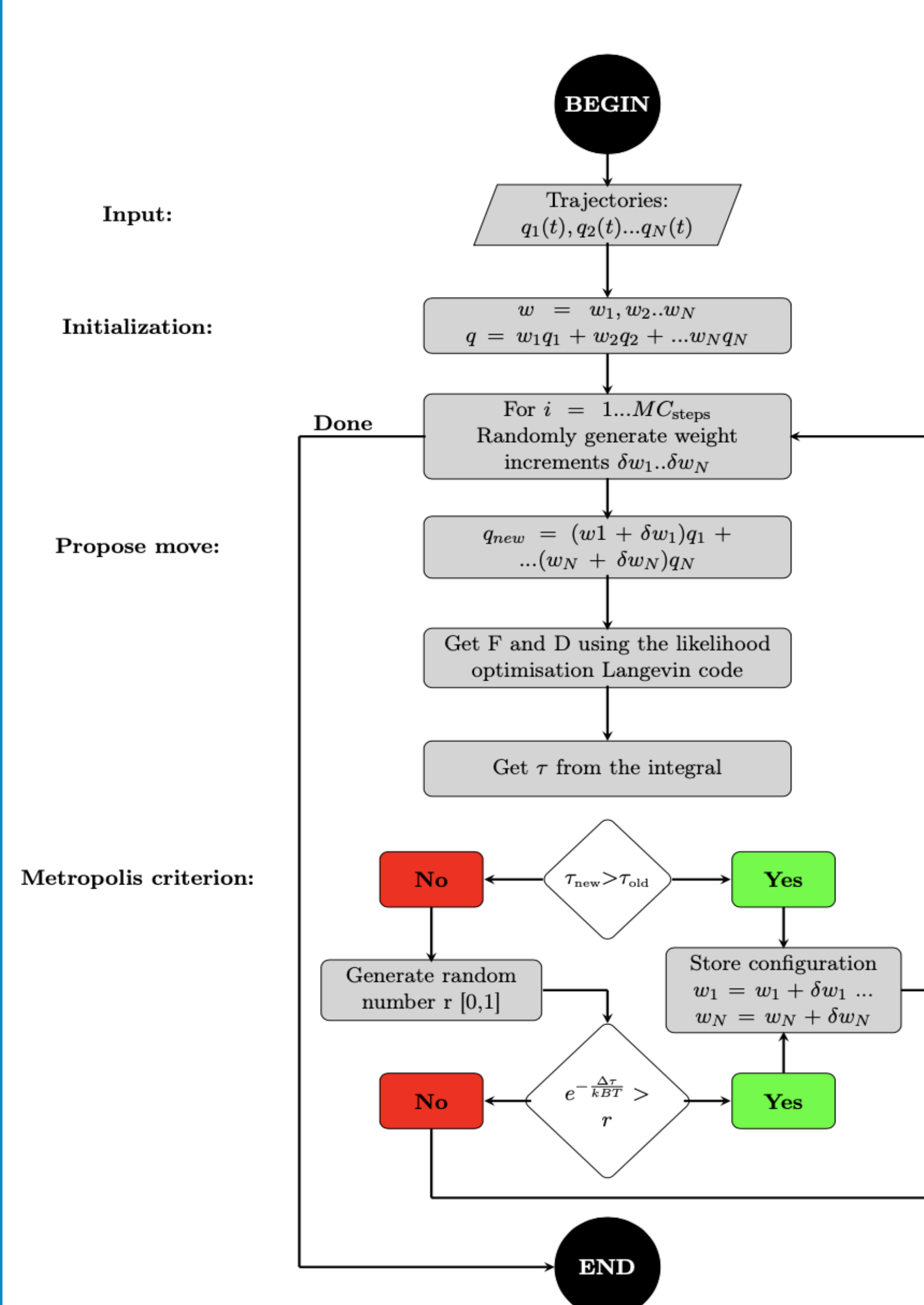
The kinetic rate is calculated as the following

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

RESULTS: 2-D DOUBLE WELL



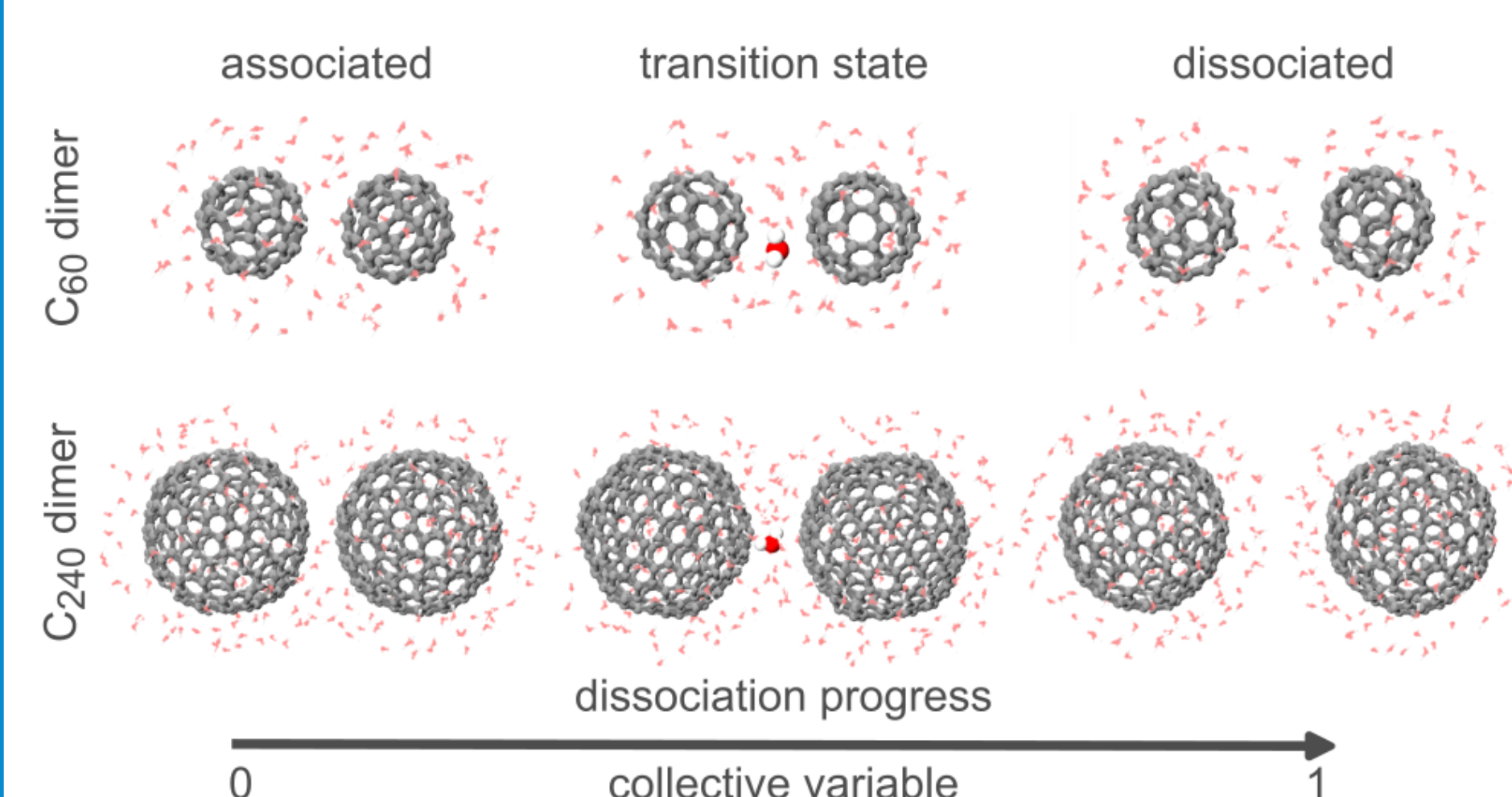
COMPUTATIONAL METHODS



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

- 1 **Input**: 100 short MD trajectories
- 2 Construct a trial RC as linear combination of CVs
- 3 Optimize an overdamped Langevin model via likelihood maximization [4]
- 4 Compute the rate and accept move based on a *Metropolis* criterion
- 5 Repeat steps 2 \rightarrow 4 until convergence

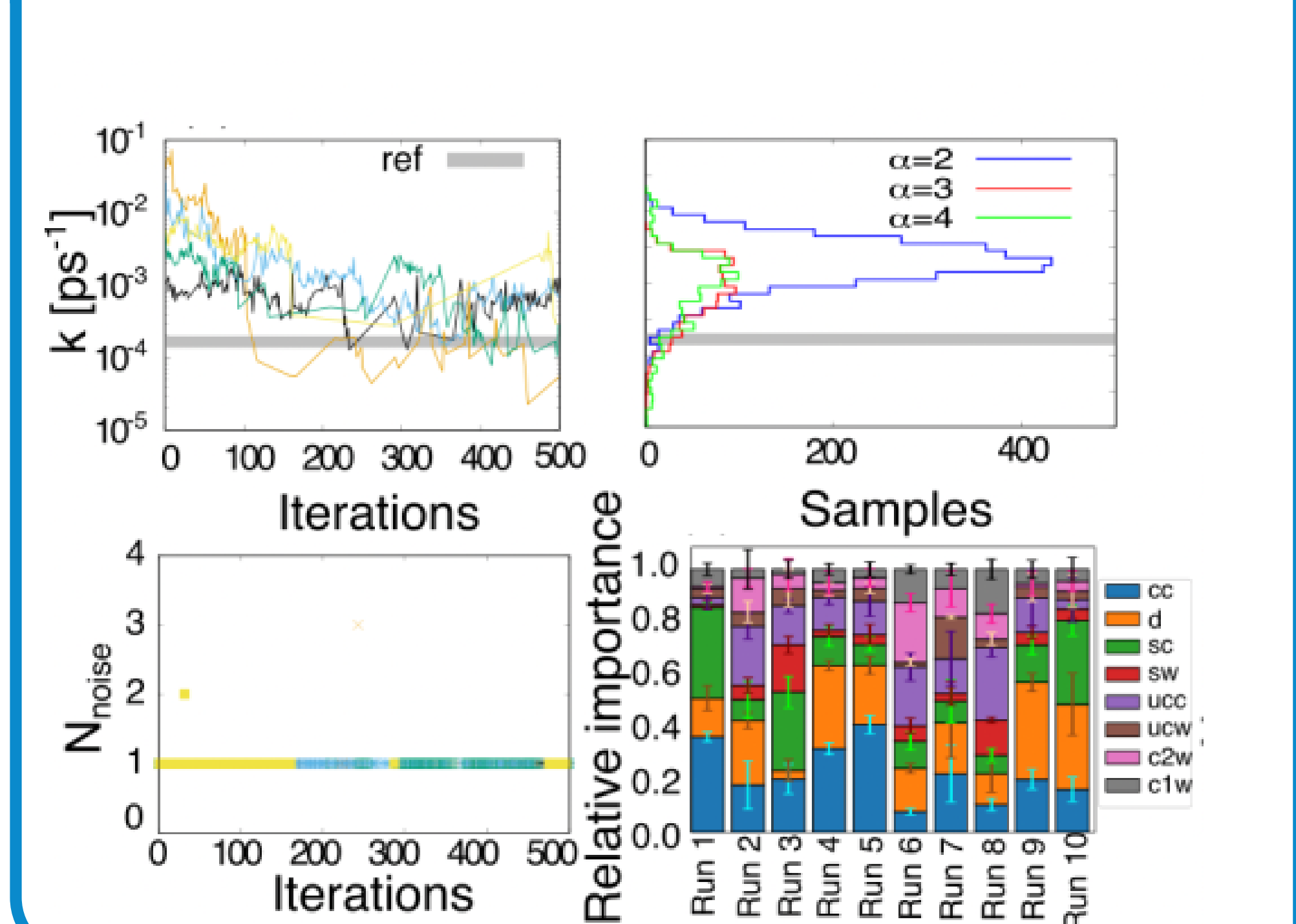
FULLERENE DIMER IN WATER



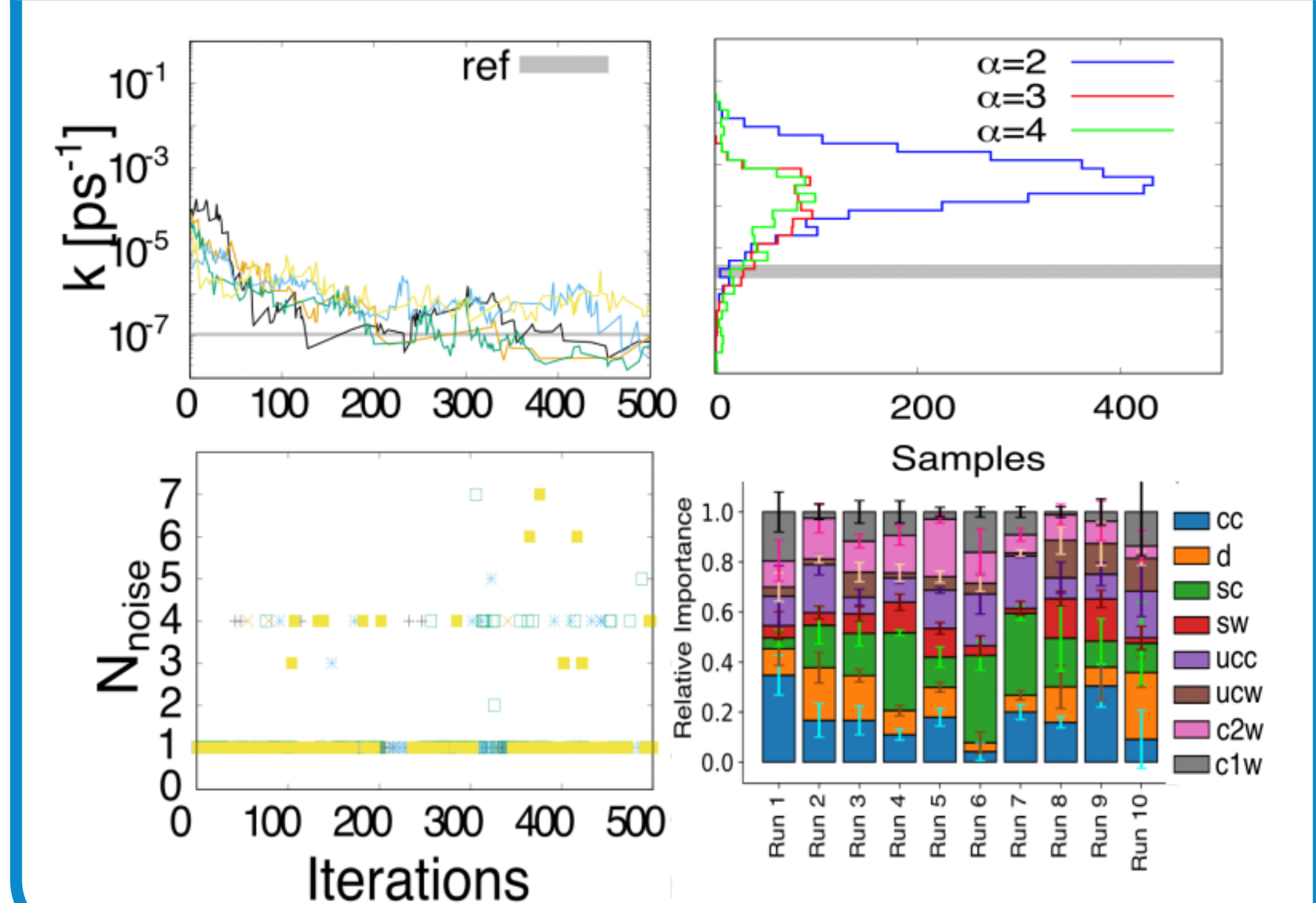
Basis set of collective variables:

1. **d**: distance between centers of mass
2. **cc**: C-C contacts
3. **c2w**: C- H_2O contacts for 2 fullerene
4. **c1w**: C- H_2O contacts for 1 fullerene
5. **sc**: C pair entropy
6. **sw**: H_2O pair entropy
7. **ucc**: VdW C-C potential energy
8. **ucw**: VdW C- H_2O potential energy

RESULTS C_{60} FULLERENE



RESULTS C_{240} FULLERENE



CONCLUSION

We developed an efficient and computationally affordable method that automates the optimization of RCs for complex systems. Currently, our method is limited to linear combinations of CVs, our aim is to go beyond it using neural networks

REFERENCES

References

- [1] J. Lu and E. Vanden-Eijnden *J. Chem. Phys.*, 2014.
- [2] L. Mouaffac, K. Palacio-Rodriguez, and F. Pietrucci *arXiv preprint arXiv:2302.12497*, 2023.
- [3] W. Zhang, C. Hartmann, and C. Schütte *Faraday discuss.*, 2016.
- [4] K. Palacio-Rodriguez and F. Pietrucci *J. Chem. Theory Comput.*, 2022.

