Reactive Machine-learned potentials: optimal active learning strategies development and application to HMX energetic material

Mathilde Kretz[1,2], Clément Wespiser[2,3], Damien Laage[1], Jean-Bernard Maillet[2,3], Guillaume Stirnemann[1]
[1]Chimie Physique et Chimie du Vivant Laboratory, ENS, PSL, Sorbonne Univ., CNRS, Paris, France
[2]DAM, DIF, CEA, Arpajon, France
[3]Matière sous Conditions Extrêmes Laboratory, CEA, Paris-Saclay Univ., Bruyères-le-Chatel, France

mathilde.kretz@ens.psl.eu

While Machine Learning Interatomic Potentials (MLIPs) have added a new perspective to molecular dynamics these recent years – offering interesting balance between accuracy and computational cost, compared to ab-initio or empirical methods – methodological questions remain regarding the ideal strategy for their application to reactive systems. It is indeed necessary to optimize the construction of the dataset used for model training to reduce the computational cost of ab-initio calculations while comprehensively exploring the configuration space to accurately describe the transition pathways [1, 2]. These pathways, critical for predicting reaction kinetics, are in fact underrepresented in unbiased dynamics, while stable structures are often over-sampled. This leads to significant redundancy in the training dataset.

These issues are particularly relevant for the study of energetic materials, which are prone to spontaneous decompositions in addition to exhibiting complex reactivity with multiple decomposition pathways. Furthermore, recent studies suggest that this chemical reactivity can be significantly altered by intramolecular deformations induced by events such as the passage of a shock wave. Strain-induced reactions – or mechanochemistry – may play a critical role, beyond thermal activation [3, 4].

It is therefore particularly interesting to focus on determining the optimal methodology for constructing a dataset representative of these effects. Indeed, these strained states obtained from large scale shock simulations cannot be directly characterized by DFT calculation, and a specific alternative must be proposed.

An initial application involved investigating the gas phase decomposition of the HMX molecule. By exploring the nitro-group scission and the ring opening using biased molecular dynamics methods, we were able to construct free energy surfaces for these initial decomposition channels. Furthermore, it is particularly interesting to observe the differences resulting from the choice of sampling methods (Steered-MD, MetaD, Well-Tempered MetaD), as well as the uncertainty arising from the choice of model architectures, whether a dense network (such as DeepMD), or an equivariant graph network (such as MACE [5]).

References

[1] Unke et al., Chem. Rev., 121 (2016) 10142.
[2] Smith et al., J. Chem. Phys., 148 (2018) 241733.
[3] Hamilton et al., J. Phys. Chem. Lett., 13 (2022) 6657.
[4] Zhang et al., J. Phys. Chem. A, 130(13) (2026) 2778.
[5] Batatia et al., J. Chem. Phys., 163 (2025) 184110.

Figures

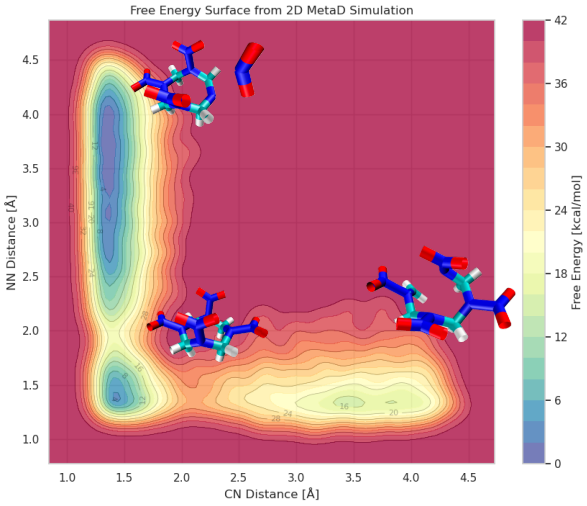

Figure 1. Free energy surface obtained from a 2D well-tempered metadynamic simulation, biased toward the nitro group scission and ring-opening of HMX. Force field used was MACE MP-0b3 foundation model.