

# Flexible accelerated molecular dynamics with a hybrid metadynamics/hyperdynamics method

Kristof M. Bal and Erik C. Neyts

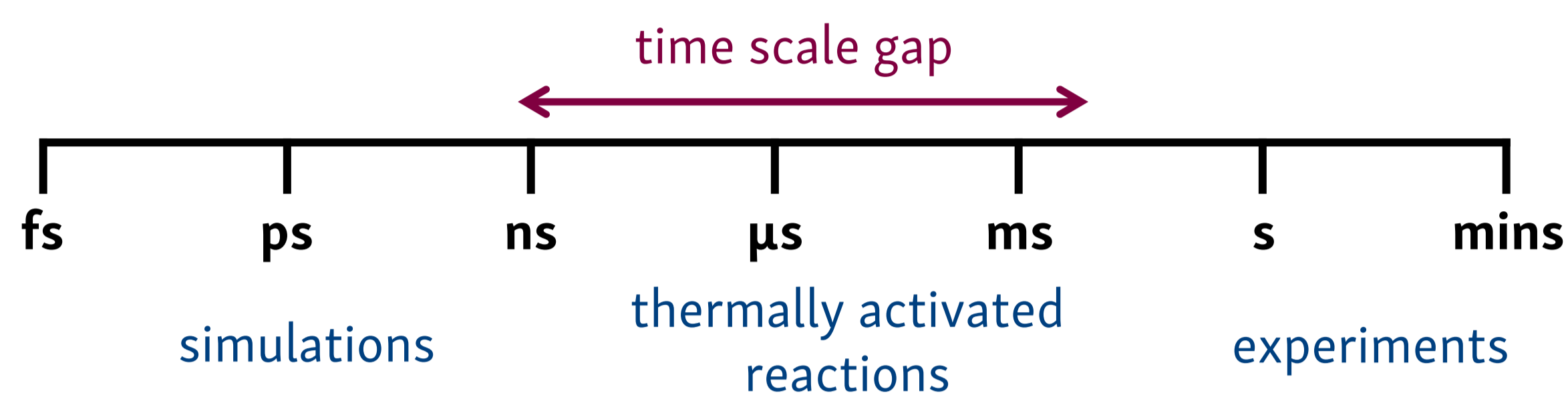
Research Group PLASMAN, Department of Chemistry, University of Antwerp,  
Universiteitsplein 1, 2610 Wilrijk, Antwerp, Belgium

kristof.bal@uantwerpen.be

## Introduction

### The MD time scale problem

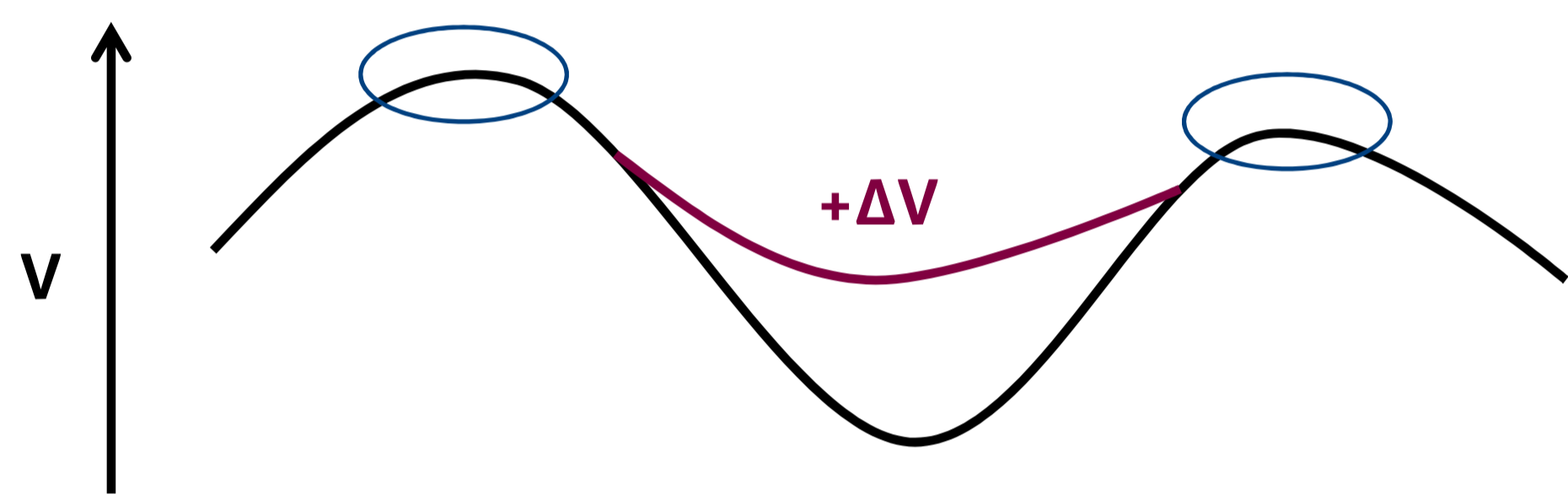
Molecular Dynamics (MD) simulations give atomic-level insight in static/dynamic properties of matter, but have a limited time scale.



### Hyperdynamics

To accelerate transitions, a bias potential  $\Delta V$  can be added to destabilize minima.<sup>1</sup> If  $\Delta V$  does not cover transition states:

- correct relative dynamics is retained.
- acceleration (boost) is proportional to  $e^{\beta\Delta V}$ .



### The CVHD method

How to construct a suitable, efficient hyperdynamics bias  $\Delta V$ ?  
→ The *collective variable-driven hyperdynamics (CVHD) method*<sup>2</sup> simplifies the application of hyperdynamics by using:

1. A single collective variable (CV) transparently abstracting the full reactivity of the system into one variable. E.g., the breaking of any bond in the system is represented by the same change in this CV.

$$\chi_i = \frac{r_i - r_i^{\min}}{r_i^{\max} - r_i^{\min}} \longrightarrow \chi_t = \left( \sum_i \chi_i^p \right)^{1/p} \longrightarrow \eta = \frac{1}{2} (1 - \cos(\pi \chi_t^2))$$

2. A self-learning bias potential, generated by a metadynamics procedure<sup>3</sup> as a history-dependent sum of repulsive Gaussian hills.

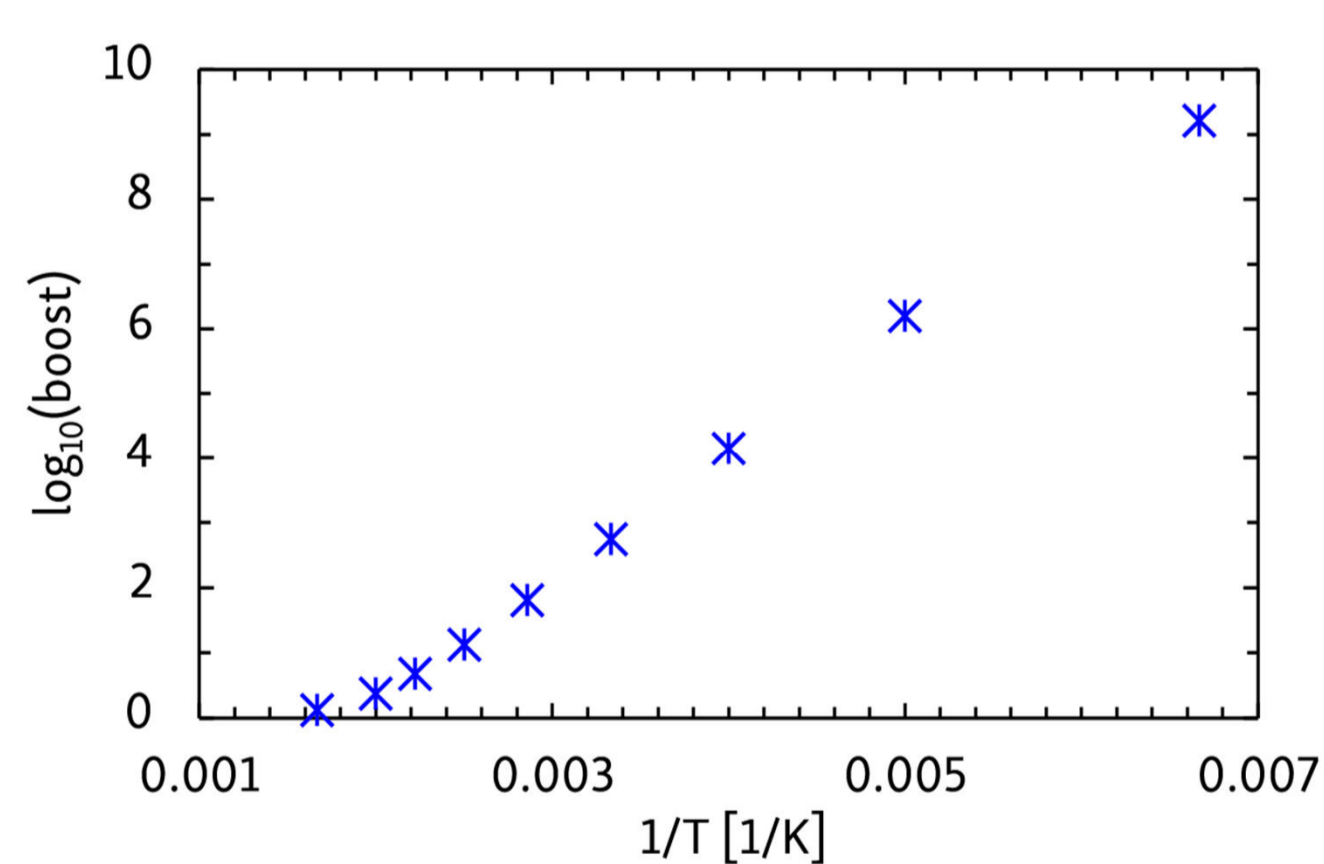
$$\Delta V = \sum_i w_i e^{-\frac{(\eta - \eta(t_i))^2}{2\delta^2}}$$

## Applications

### Comparison with a reference hyperdynamics method

If bond stretching is used as local reactivity index:

- Compare with "Bond Boost" hyperdynamics.
- Diffusion on the Cu(001) surface as test system.
- Large boosts: time scales up to 500 seconds are obtained.

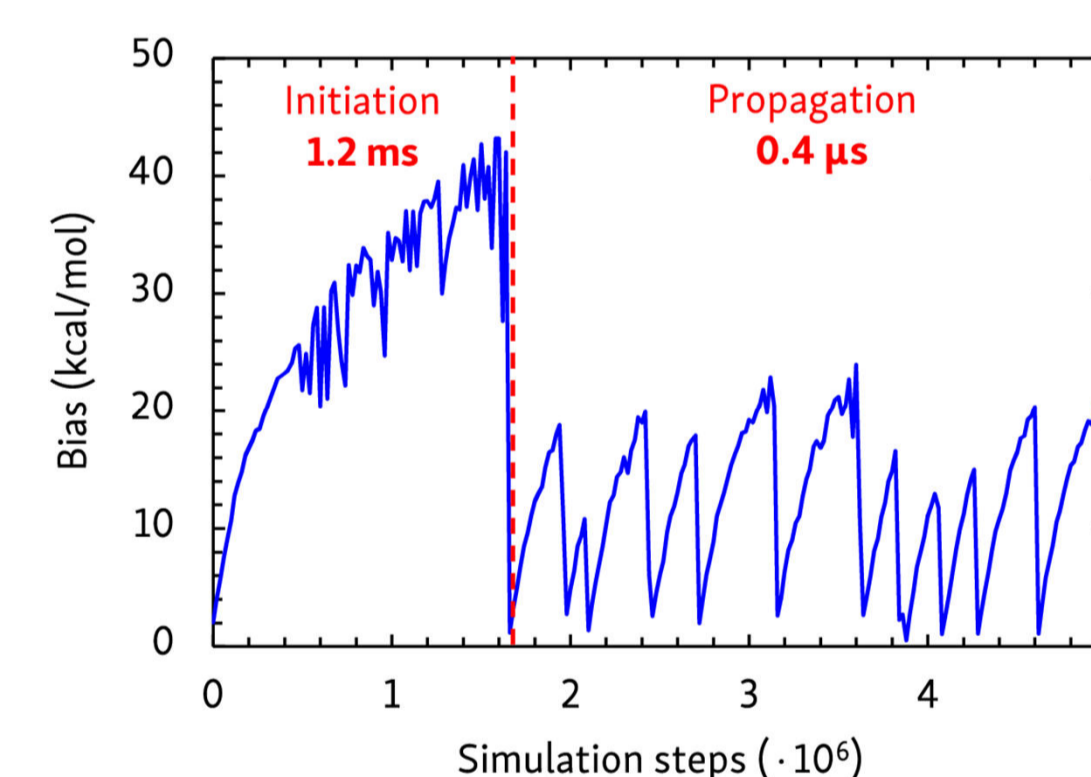


Process \ E <sub>A</sub> (eV)	CVHD	BB
Vacancy hop	0.44 ± 0.01	0.44 ± 0.03
Adatom hop	0.53 ± 0.01	0.52 ± 0.03
Adatom exchange	0.76 ± 0.04	0.73 ± 0.04
Dimer hop	0.51 ± 0.01	0.47 ± 0.03
Dimer Exchange	0.74 ± 0.06	0.71 ± 0.06

### Complex systems need multi-time scale methods

Real systems possess an unpredictable potential energy surface and wildly varying barrier heights.

- E.g., for alkane pyrolysis, from 30 to 80 kcal/mol.
- CVHD's dynamic bias always has the "right" strength.

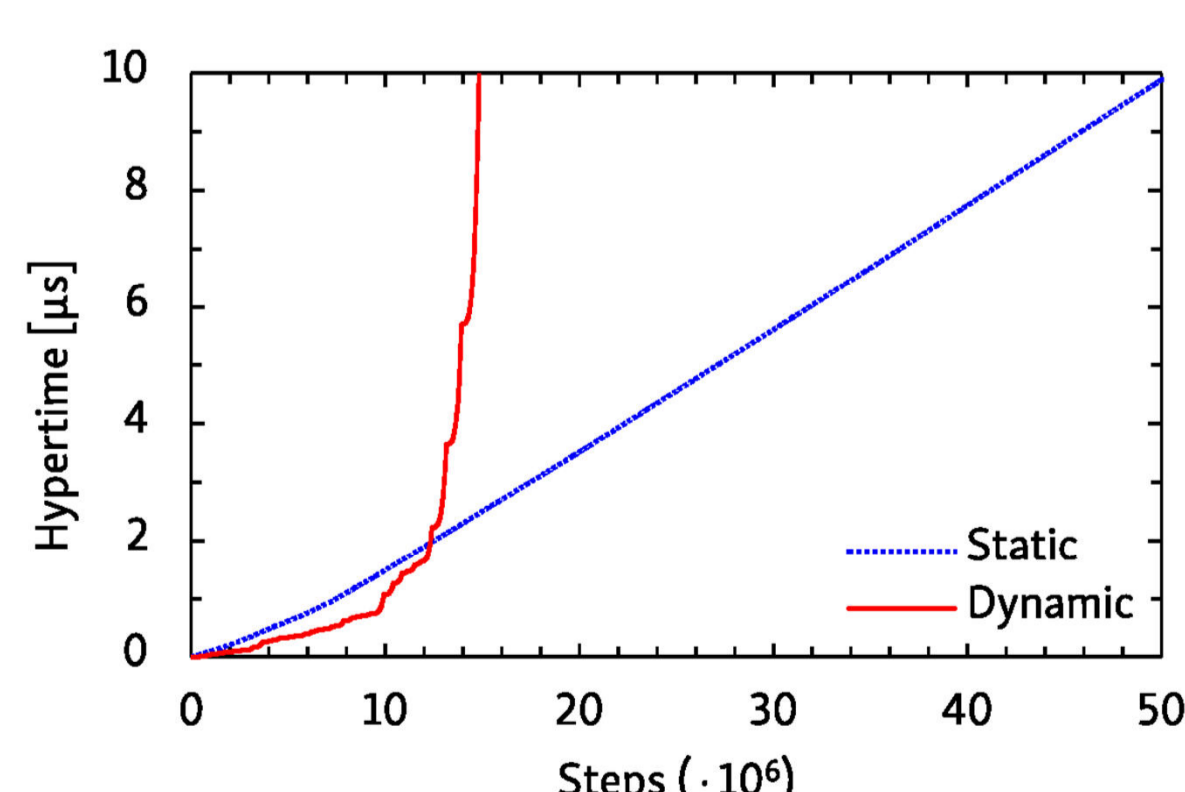
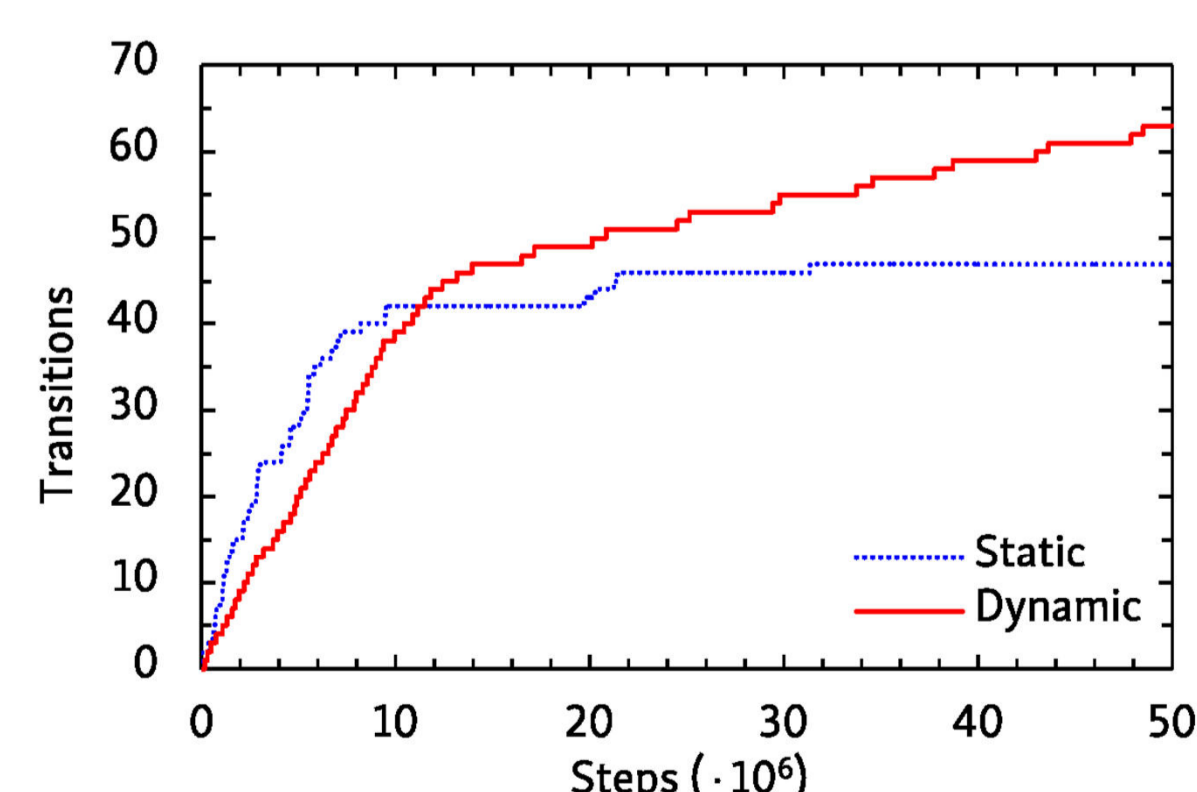
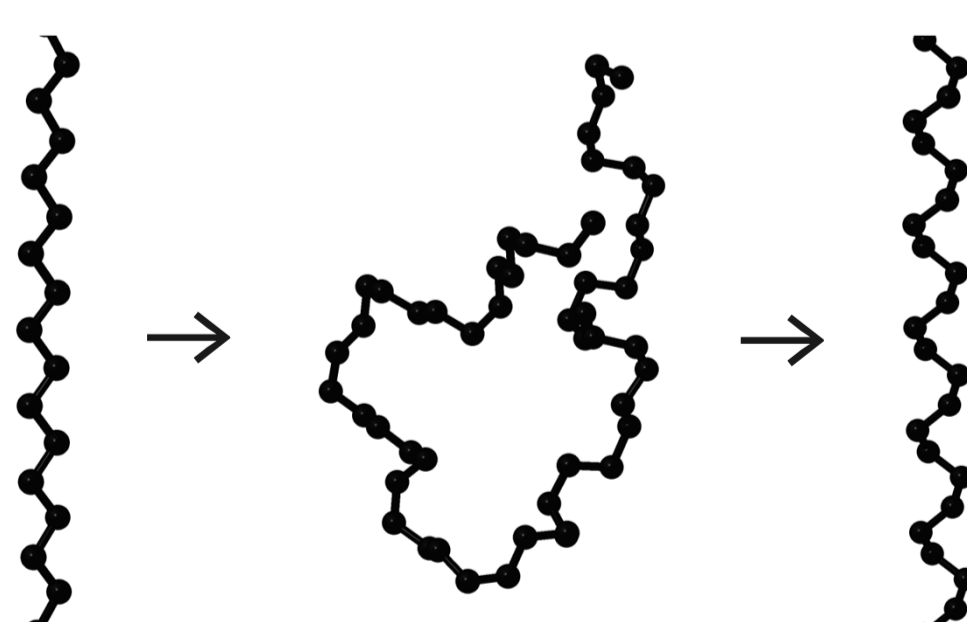


	Pyrolysis	Combustion
Lowest T	1000 K	700 K
Longest time	57 ms	39 s
Largest boost	6.3 · 10 <sup>6</sup>	1.3 · 10 <sup>9</sup>

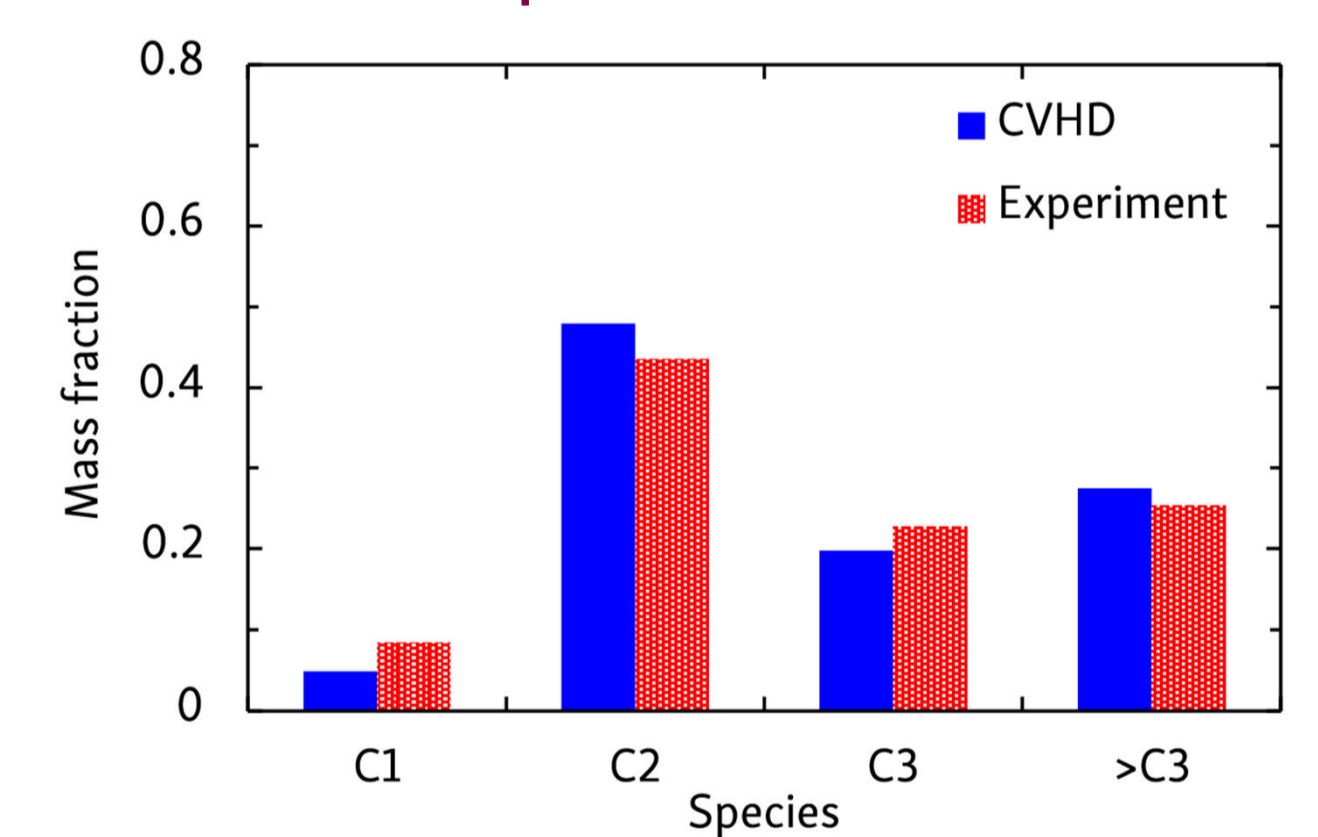
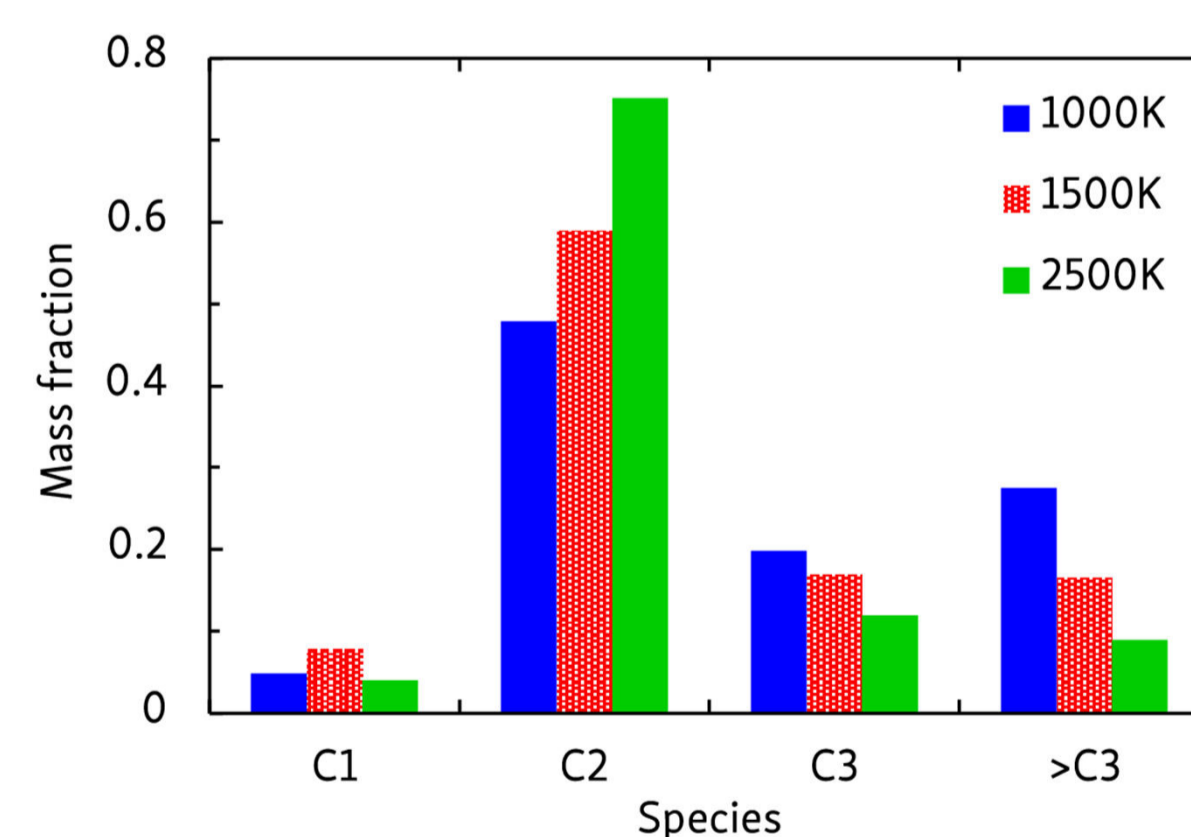
### Something different: conformational sampling

CVHD is not confined to one kind of process.

- Not all processes require biasing bond stretching & breaking.
- Dihedrals are key in the folding of chain-like structure.

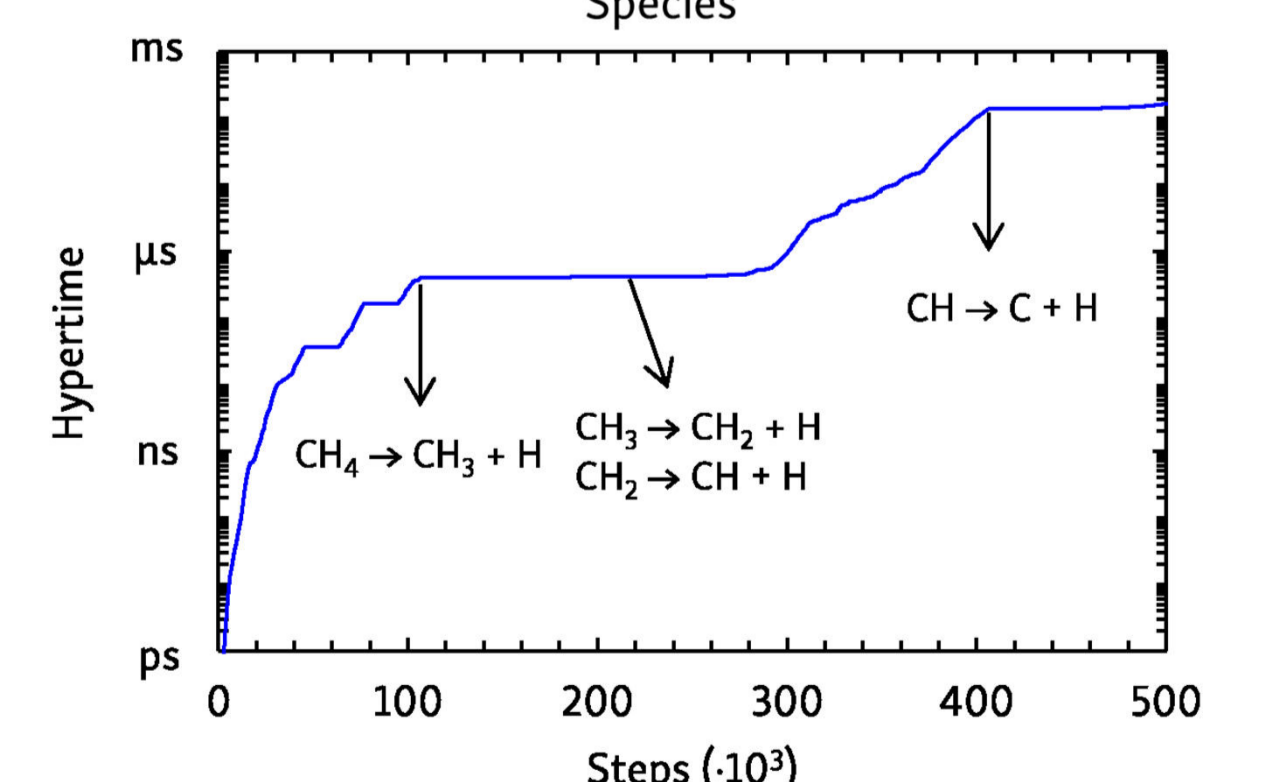


- MD is limited to much higher T and cannot match experimental conditions and results. CVHD recovers the experiment @ 1000 K.<sup>4</sup>



Multi-time scale abilities are also particularly useful to study catalytic reactions on surfaces.

→ CH<sub>4</sub> dehydrogenation on Ni(111)



## Conclusion

CVHD can describe the atomic-level dynamics of complex processes over realistic timescales, bridging the gap between simulations and experiments.

## Acknowledgements & References

[1] A.F. Voter, Phys. Rev. Lett. **78**, 3908 (1997).

[2] K. M. Bal & E. C. Neyts, J. Chem. Theory Comput. **11**, 4545 (2015).

[3] A. Laio & M. Parrinello, Proc. Natl. Acad. Sci. USA **99**, 12562 (2002).

[4] K. M. Bal & E. C. Neyts, Chem. Sci. **7**, 5280 (2016).

