Flexible accelerated molecular dynamics with a hybrid metadynamics/hyperdynamics method

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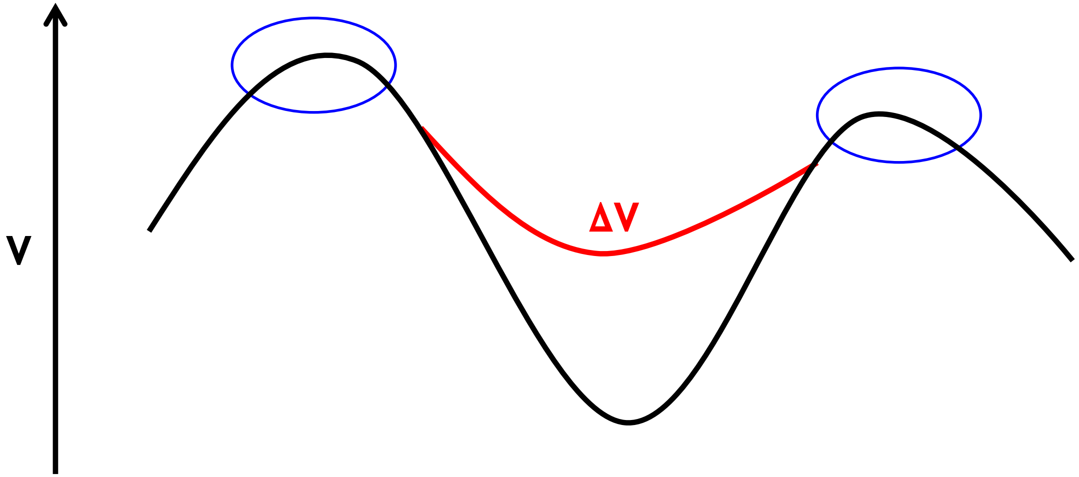
INTRODUCTION TO THE CVHD METHOD

HYPERDYNAMICS



Add a bias potential ΔV to the potential energy surface (PES)

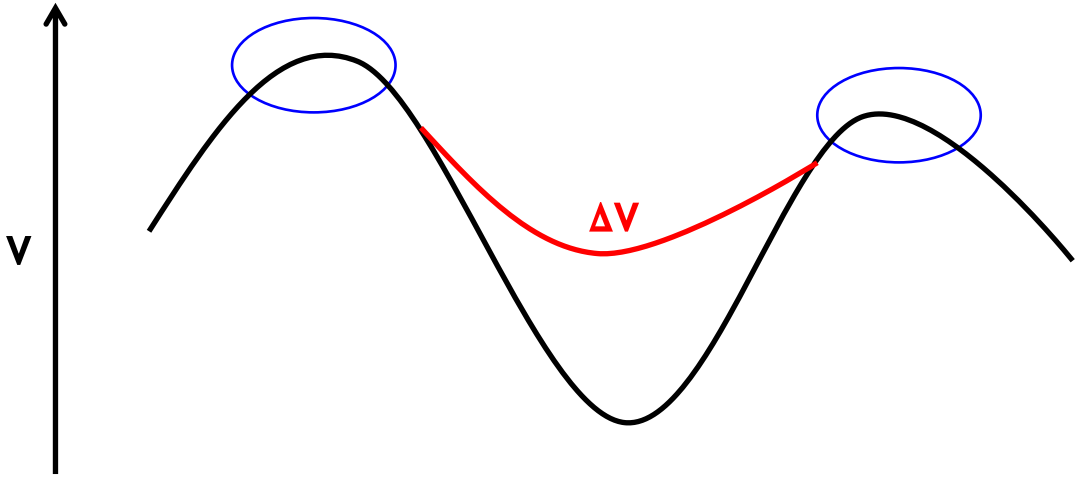
- "Fill" and destabilize minima
- Leave dividing surfaces untouched

Simulations on the modified PES $V^*(\mathbf{R}) = V(\mathbf{R}) + \Delta V(\mathbf{R})$ exhibit

- Faster state-to-state transitions…
- …but correct relative dynamics…
- …and global system evolution equivalent to (much slower) MD

Time becomes a statistical quantity, this **hypertime** is related to the MD time through the **boost factor** $\langle e^{\beta \Delta V} \rangle$.

HYPERDYNAMICS



How to construct a suitable and efficient bias potential?

→ What should ΔV be a function of?

- The lowest eigenvalue of the Hessian (Voter)
- The potential energy V (Steiner; Fichthorn et al.; Hamelberg et al.; …)
- Bond distortions (Miron & Fichthorn)
- Collective variables (Tiwary & van de Walle)

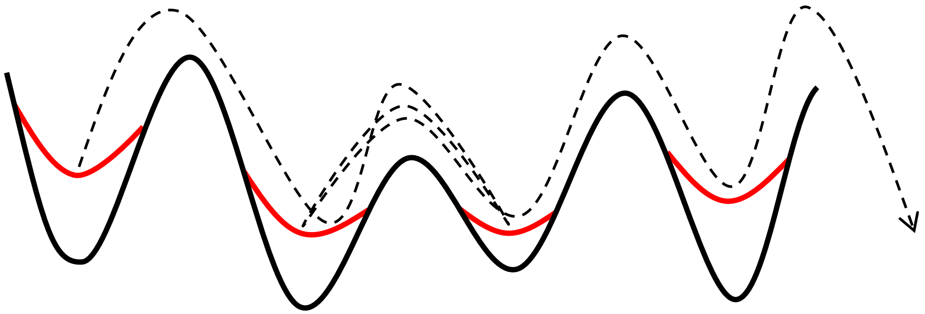
→ How to parameterize ΔV?

- Use *a priori* knowledge of the PES (most methods)
- Apply a self-learning method

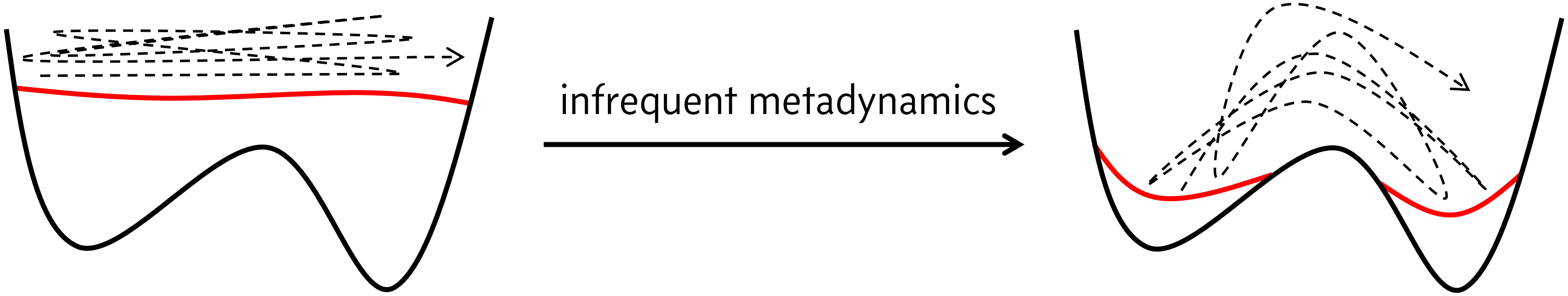
HYPERDYNAMICS & METADYNAMICS

To some extent, metadynamics is already self-learning hyperdynamics, as it also enhances sampling through a bias potential, but with a different focus

Hyperdynamics: “natural” unconstrained sequence of state-to-state transitions, without much a priori information on the possible pathways.



Metadynamics: extensive sampling of a limited part of the phase space.
Tiwary & Parrinello: get correct kinetics within this region if you’re careful.



HYPERDYNAMICS & METADYNAMICS

With infrequent metadynamics, a self-learning sampling method has been given the ability to generate correct kinetics.

→ Metadynamics getting some hyperdynamics aspects

Can we go the other way?

→ *Make hyperdynamics self-learning by adopting parts of metadynamics*

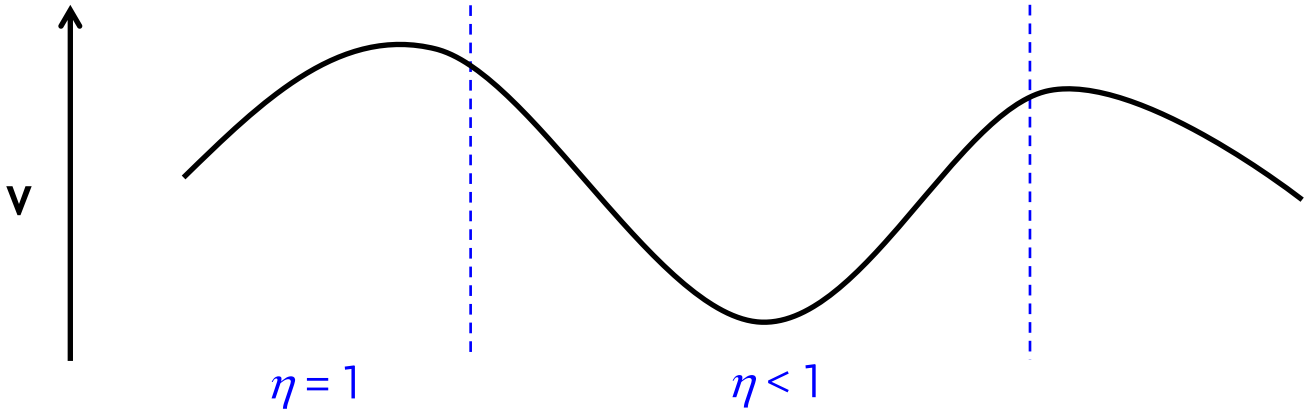
Required ingredients:

Suitable collective variable (CV)

History-dependent bias constructed from a sum of repulsive Gaussians

→ The *collective variable-driven hyperdynamics method* (CVHD)

CVHD – THE CV



In metadynamics, the used CV(s) must be able to distinguish between all relevant states one wishes to visit.

In a true hyperdynamics method, we preferably shouldn't need to know in advance where we're going, but this complicates the choice of CVs.

In CVHD, as in the SISYPHUS method (Tiwary & van de Walle), we use a single CV, η, centered around the current state:

- If $0 < \eta < 1$: system is well within current state
- If $\eta > 1$: system is close to dividing surface or has crossed it
- i.e., only distinguish between "current state" and "rest of the universe"

CVHD – THE CV

Most chemical processes involve bond breaking, so as a first CV it makes sense to use a bond distortion (cf. Bond Boost):

$$\chi_i = \frac{r_i - r_i^{\min}}{r_i^{\max} - r_i^{\min}}$$

Which can yield a single CV (cf. SISYPHUS):

$$\chi_t = \left(\sum_i \chi_i^p \right)^{1/p}$$

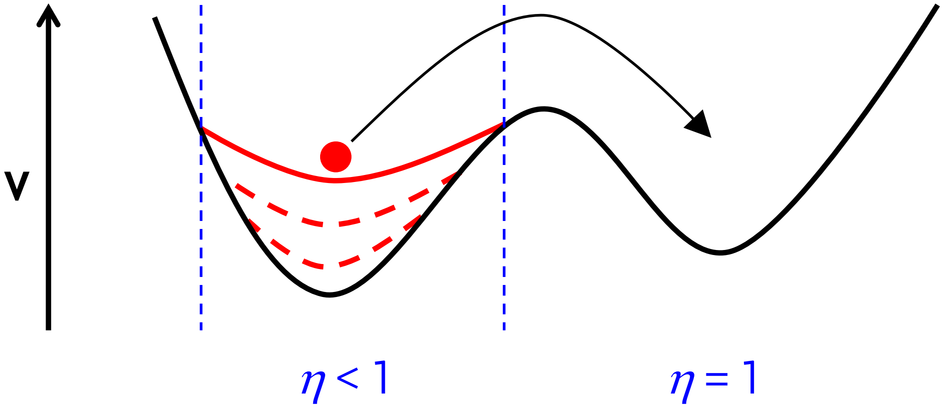
And in order to get vanishing derivatives:

$$\eta = \frac{1}{2}\left(1 - \cos(\pi \chi_t^2)\right)$$

Generalizable to other χ, other definitions of η, multiple CVs…

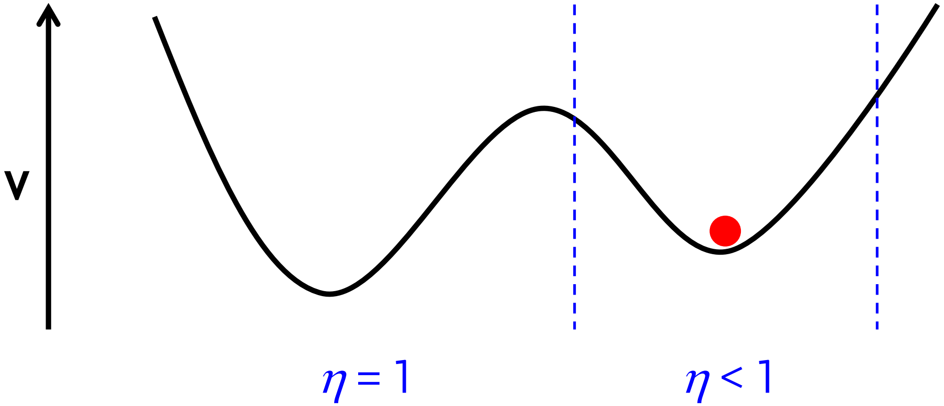
CVHD – THE BIAS

A bias potential is easily generated through a metadynamics procedure, i.e., as a history-dependent sum of Gaussians.



$$\Delta V = \sum_{i}^{hills} e^{-\frac{(\eta-\eta(t_i))^2}{2\delta^2}}$$

But because the CV can only resolve the current state, we have to reset it after each transition, and “throw away” the bias.

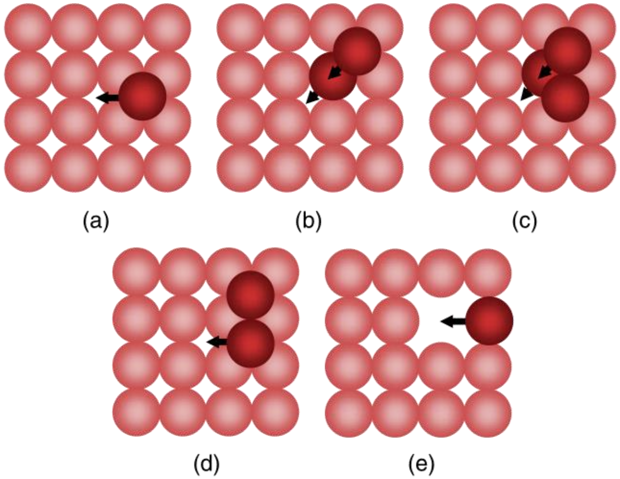


Sometimes more efficient to not use a “dynamic” bias, but rather a predifined one

$$\Delta V = V^{\max}(1-\eta)$$

APPLICATIONS

DIFFUSION ON CU(001)



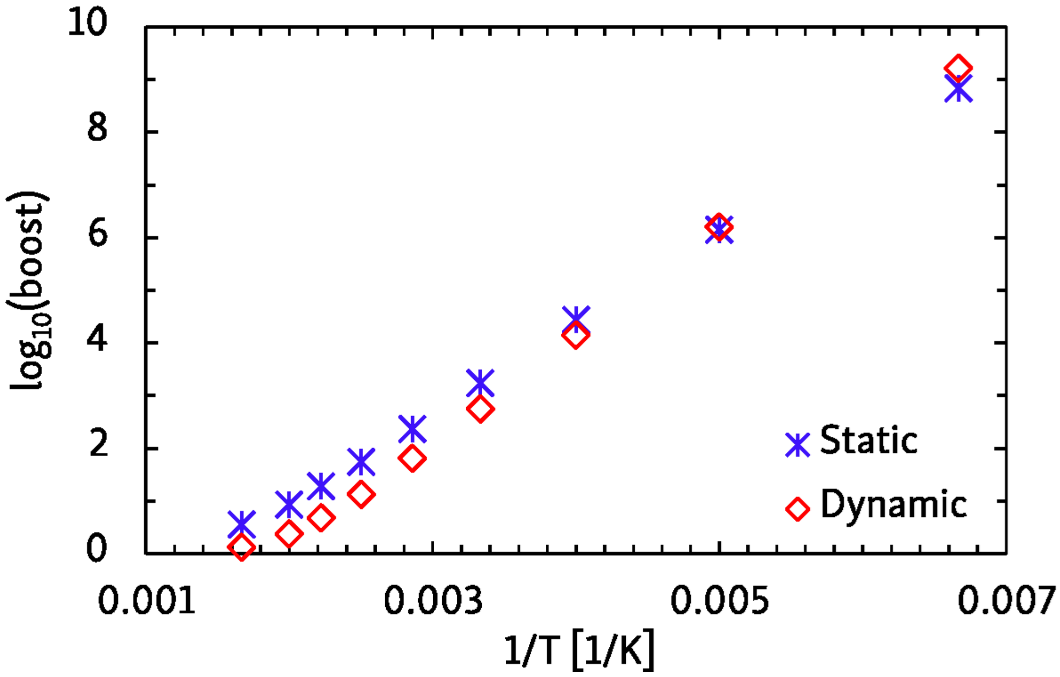
process	E_A^{DB} (eV)	E_A^{SB} (eV)	E_A^{BB} (eV)
vacancy hop	0.44 ± 0.01	0.43 ± 0.02	0.44 ± 0.03
adatom hop	0.53 ± 0.01	0.51 ± 0.01	0.52 ± 0.03
adatom exchange	0.76 ± 0.04	0.71 ± 0.05	0.73 ± 0.04
dimer hop	0.51 ± 0.01	0.49 ± 0.02	0.47 ± 0.03
dimer exchange	0.74 ± 0.06	0.76 ± 0.05	0.71 ± 0.06

Opportunity to compare CVHD with “Bond Boost” (BB) hyperdynamics

BB ~ static CVHD with bond length distortion CV

Excellent recovery of Arrhenius-type diffusion parameters

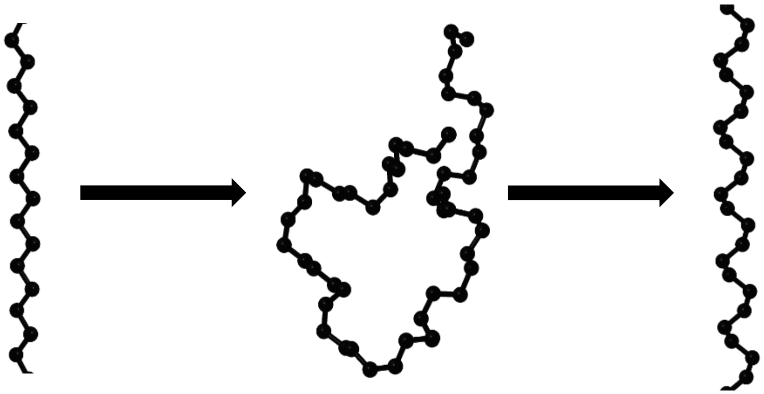
DIFFUSION ON CU(001)



Performance of dynamic bias improves at lower rates

Temperatures as low as 150 K (time up to 500 seconds)

MODEL FOLDING

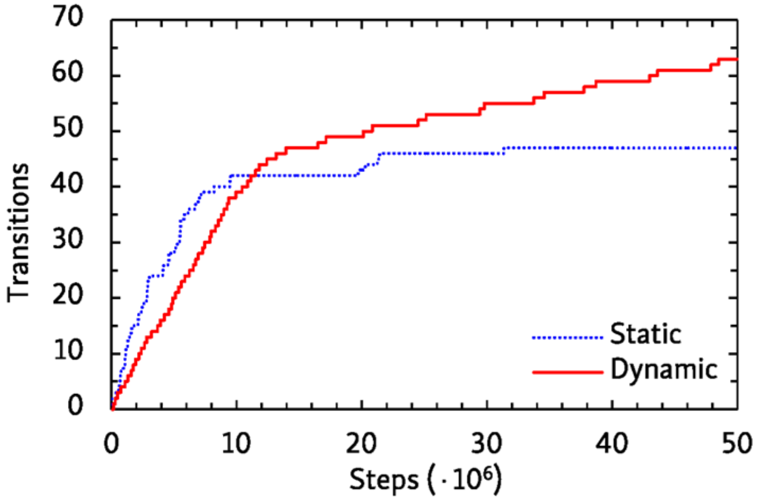


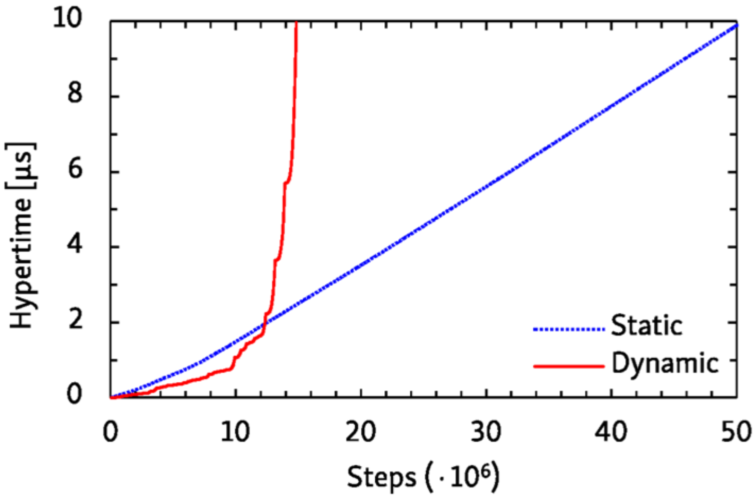
Use dihedral distortion instead of bonds!

Model potential with helix state as minimum

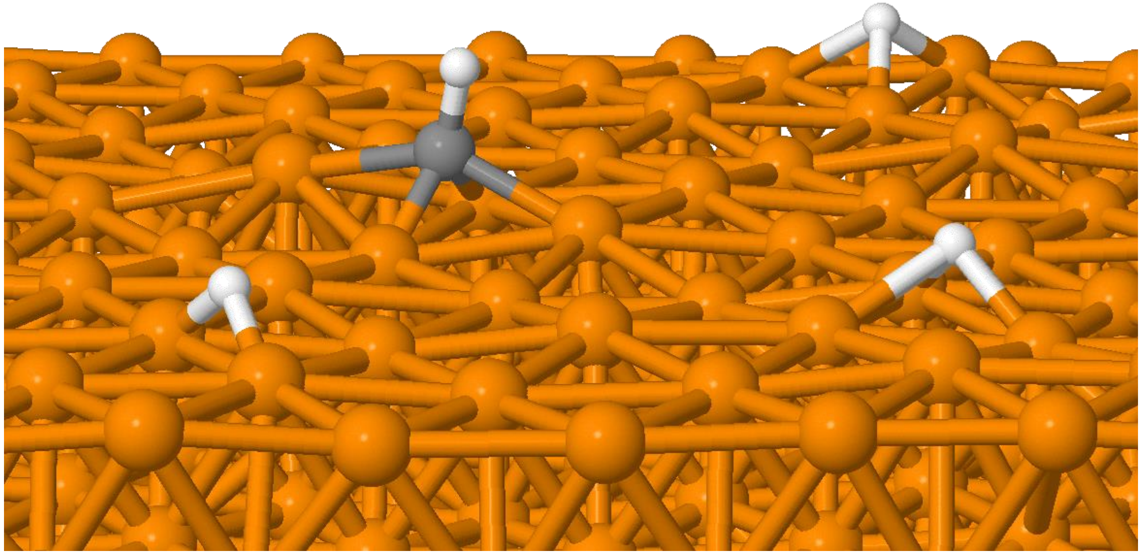
- ~ 8 kcal/mol barrier for a single dihedral
- Start with 50 bead extended chain at 300 K

Dynamic bias is adaptable and eventually beats the static option





HETEROGENEOUS CATALYSIS



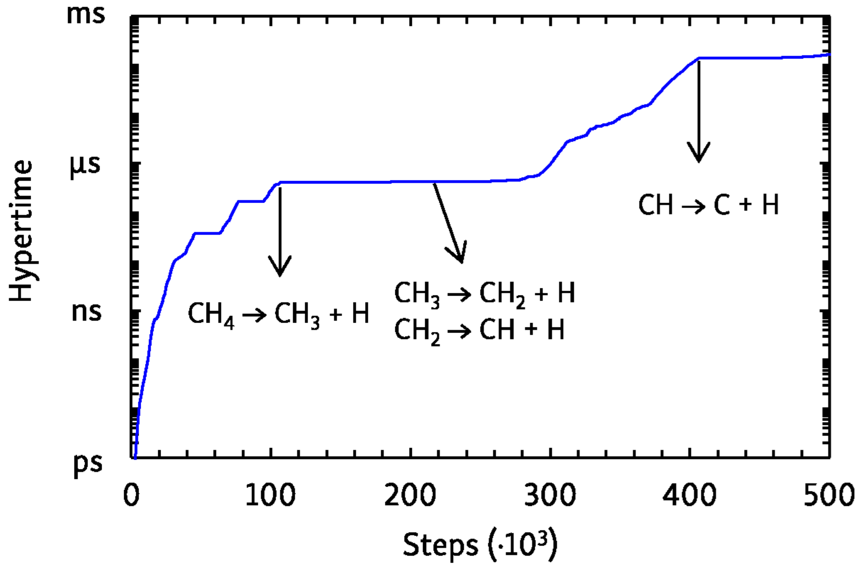
Dissociation of CH_4 on Ni(111): barriers for individual decomposition steps differ strongly:

Only ~8 kcal/mol for $CH_2 \rightarrow CH + H$

More than 30 kcal/mol for $CH \rightarrow C + H$

→ Can’t use a predifined bias

HETEROGENEOUS CATALYSIS



process	reaction time
$CH_4(g) \rightarrow CH_3(ad) + H(ad)$	4–9 μs
$CH_3(ad) \rightarrow CH_2(ad) + H(ad)$	0.09–0.22 μs
$CH_2(ad) \rightarrow CH(ad) + H(ad)$	37–91 ps
$CH\ (ad) \rightarrow C(ad) + H(ad)$	0.3–0.8 ms

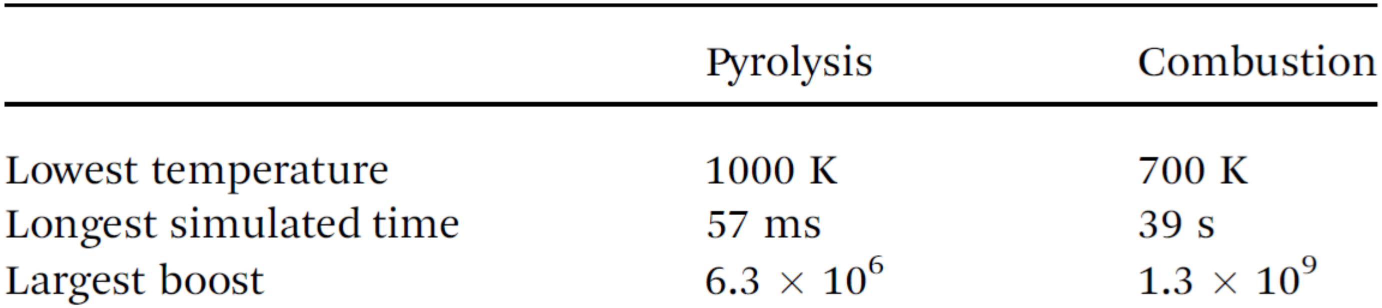
CVHD in dynamic mode is really flexible

Multi-timescale abilities

PYROLYSIS & COMBUSTION

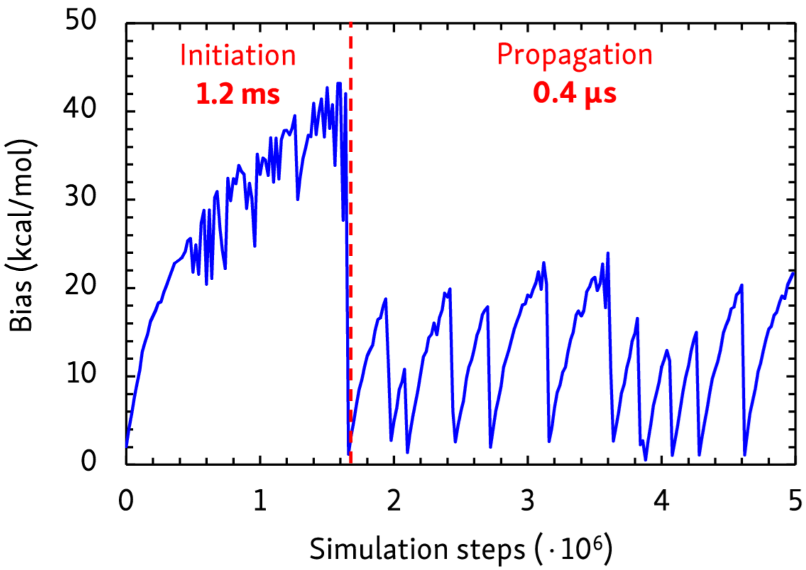
- We want to use CVHD as a predictive tool
- Pyrolysis/combustion is an interesting option
    - Many MD studies (and good ReaxFF potential) available…
    - … but at high temperatures (>2000 K instead of ~1000 K)
    - Complex temperature-dependent pathways and products
    - Barriers from ~30 kcal/mol (propagation) to ~80 kcal/mol (initiation)
    - Parallel replica only got to 1 μs at 1350 K (Joshi et al.)

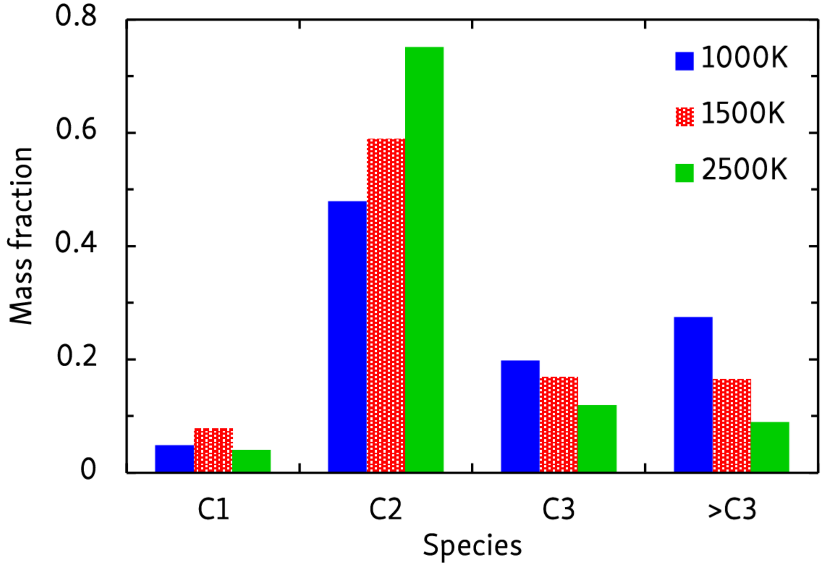
For the *n*-dodecane test system, CVHD can reach longer times (ms and beyond)

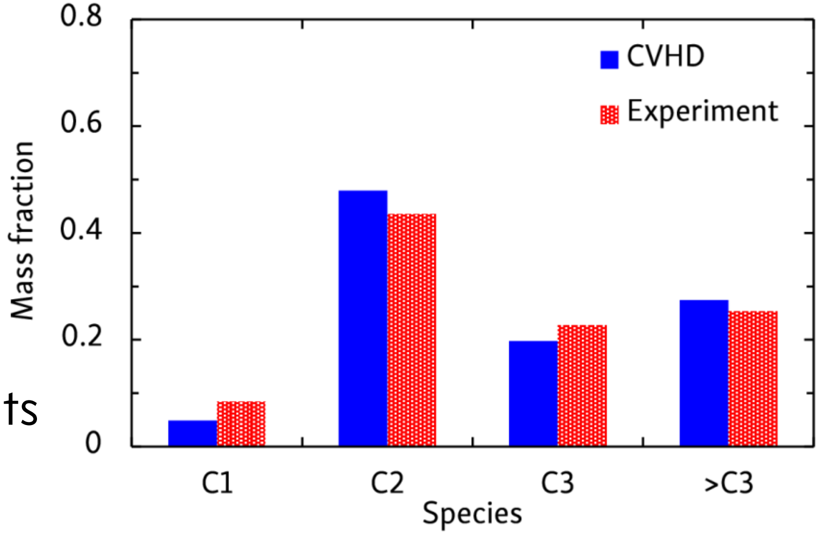


	Pyrolysis	Combustion
Lowest temperature	1000 K	700 K
Longest simulated time	57 ms	39 s
Largest boost	6.3×10^6	1.3×10^9

PYROLYSIS







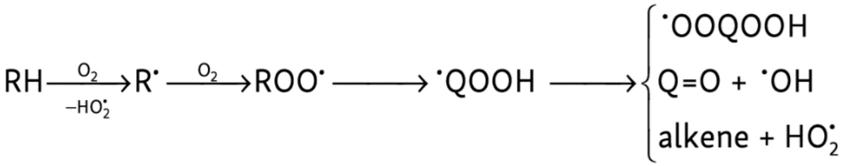
Use of dynamic bias in practice

Temperature-dependent pyrolysis products

Remarkable agreement with recent experiments

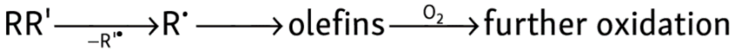
OXIDATION

Low temperature:

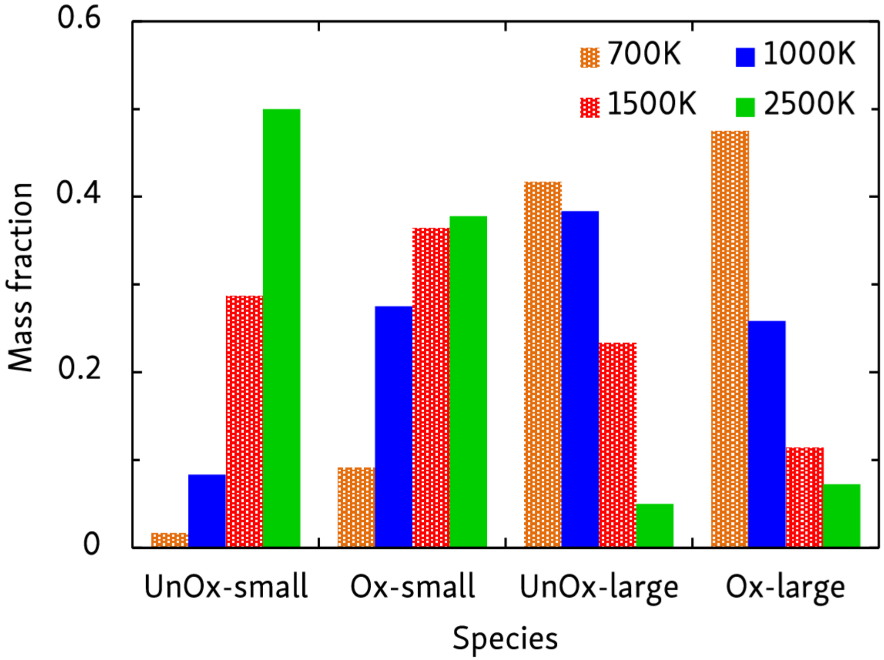


$$RH \xrightarrow[-HO_2^{\bullet}]{O_2} R^{\bullet} \xrightarrow{O_2} ROO^{\bullet} \longrightarrow {}^{\bullet}QOOH \longrightarrow \begin{cases} {}^{\bullet}OOQOOH \\ Q{=}O + {}^{\bullet}OH \\ \text{alkene} + HO_2^{\bullet} \end{cases}$$

High temperature:

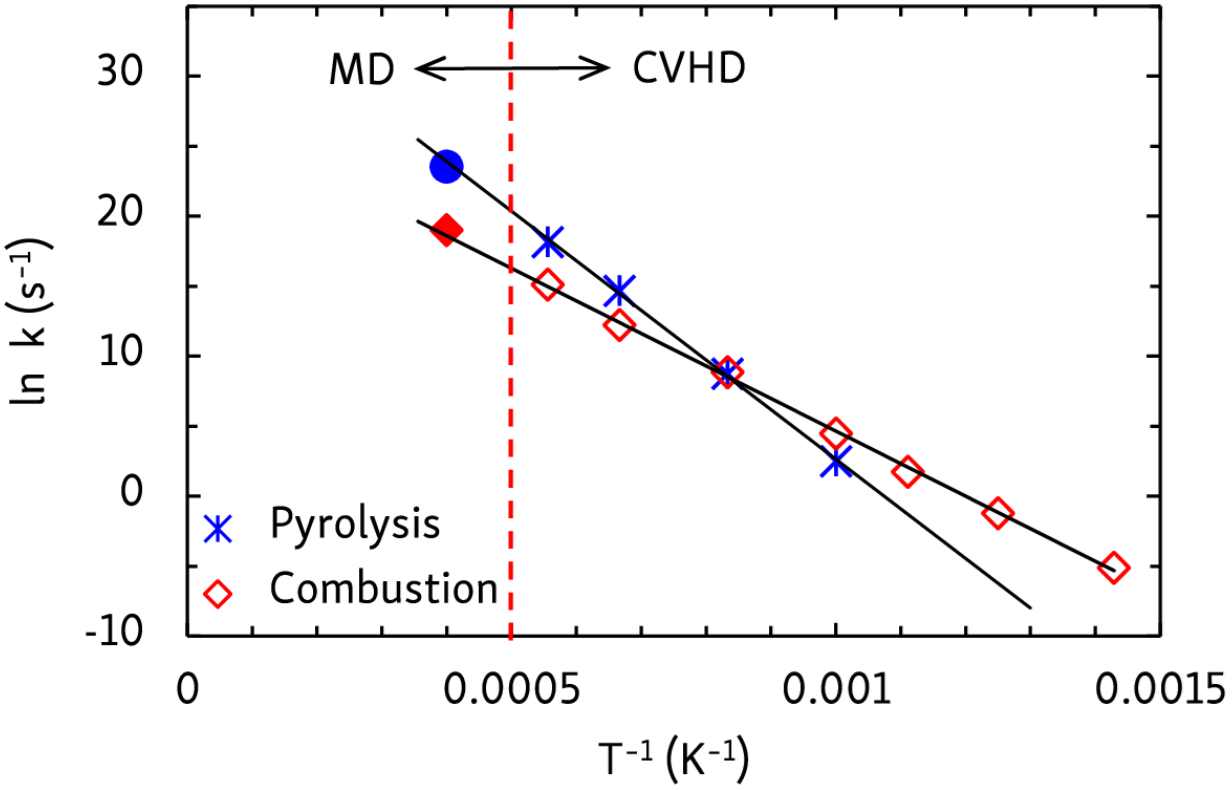


$$RR' \xrightarrow[-R'^{\bullet}]{} R^{\bullet} \longrightarrow \text{olefins} \xrightarrow{O_2} \text{further oxidation}$$



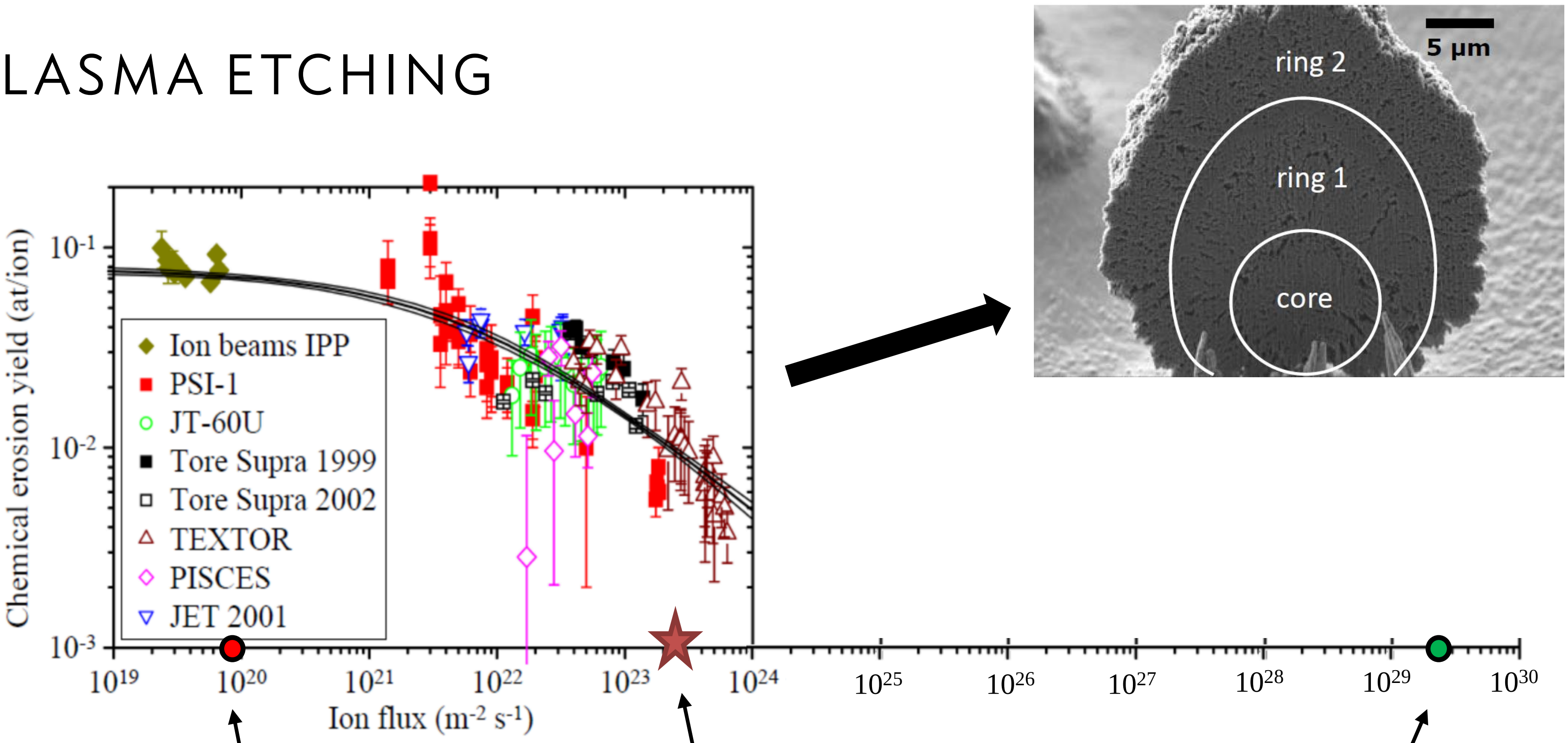
Temperature-dependent oxidation pathways and products can also be captured

PYROLYSIS & COMBUSTION



A posteriori validation through direct MD

PLASMA ETCHING



ICP plasma reactor

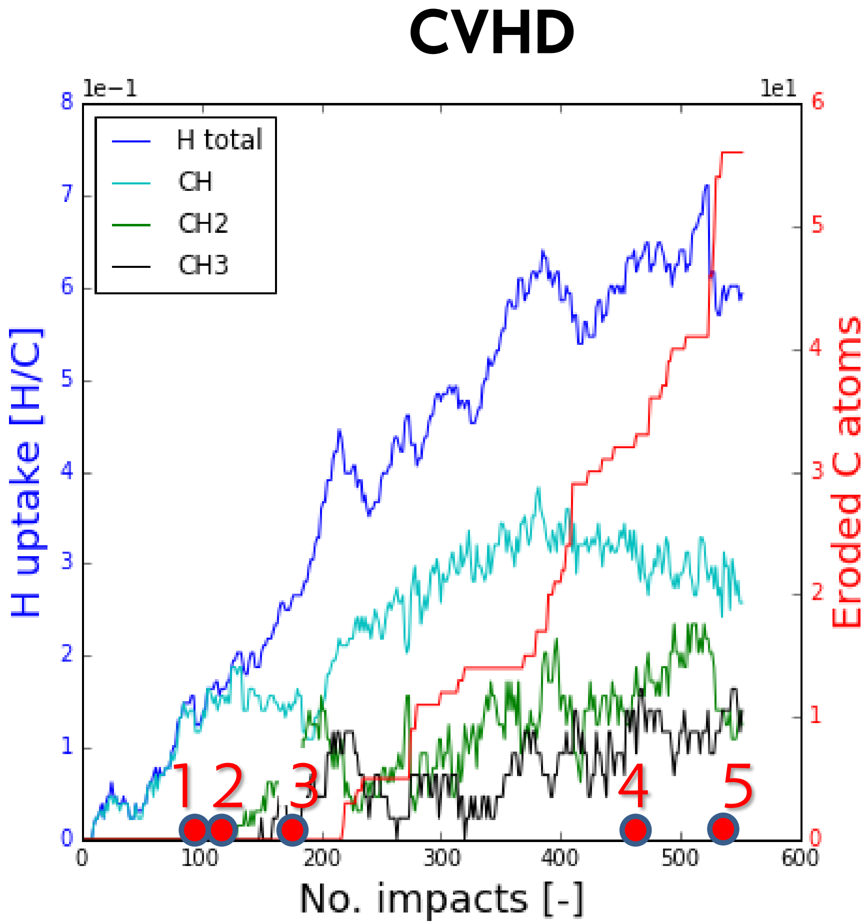
CVHD (1 µs)

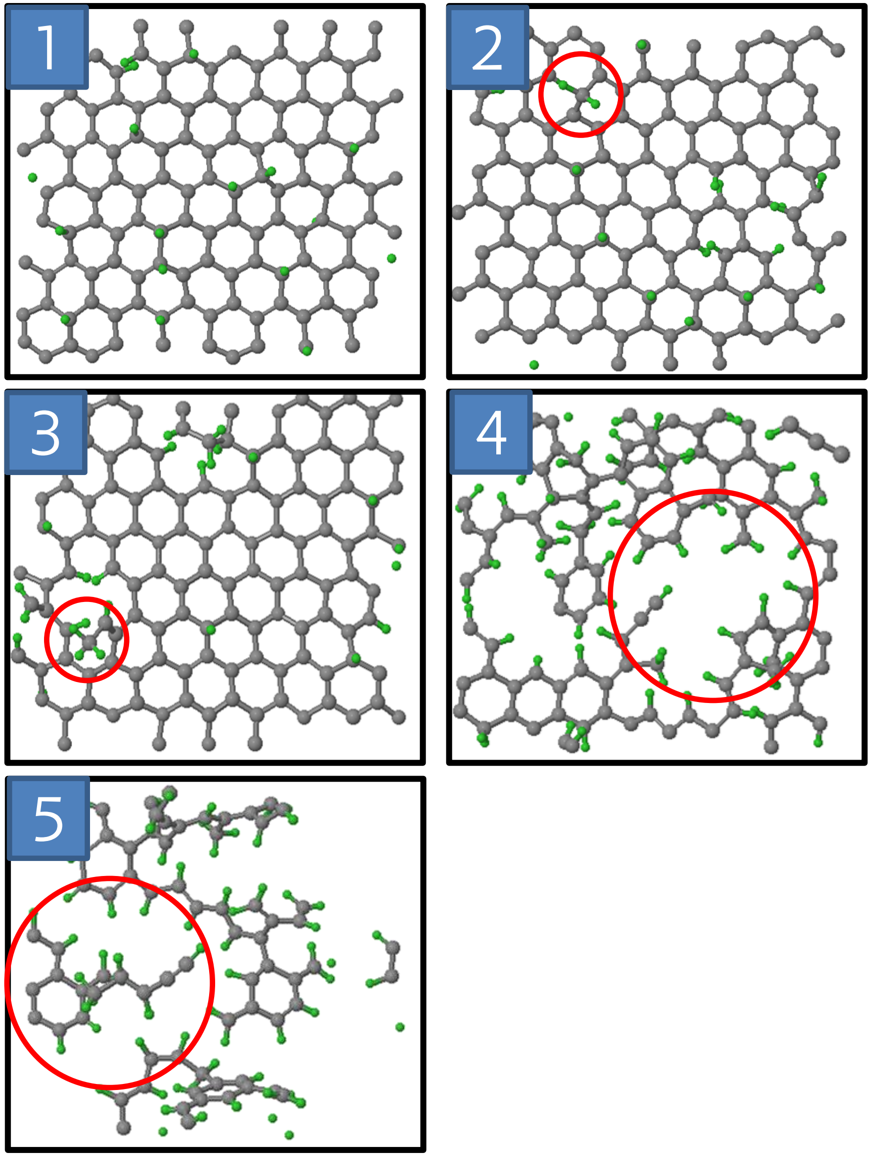
normal MD (1 ps)

Graphite etching and redeposition in a fusion-like plasma generates carbon microstructures

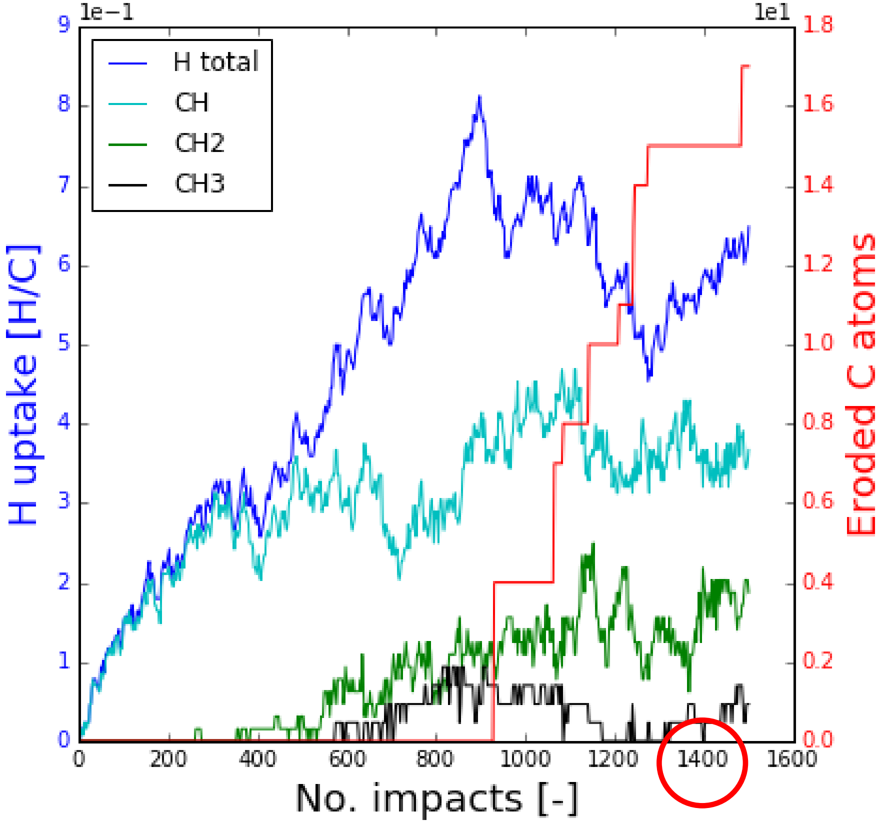
Very high H fluxes: experiment approaching simulation!

PLASMA ETCHING

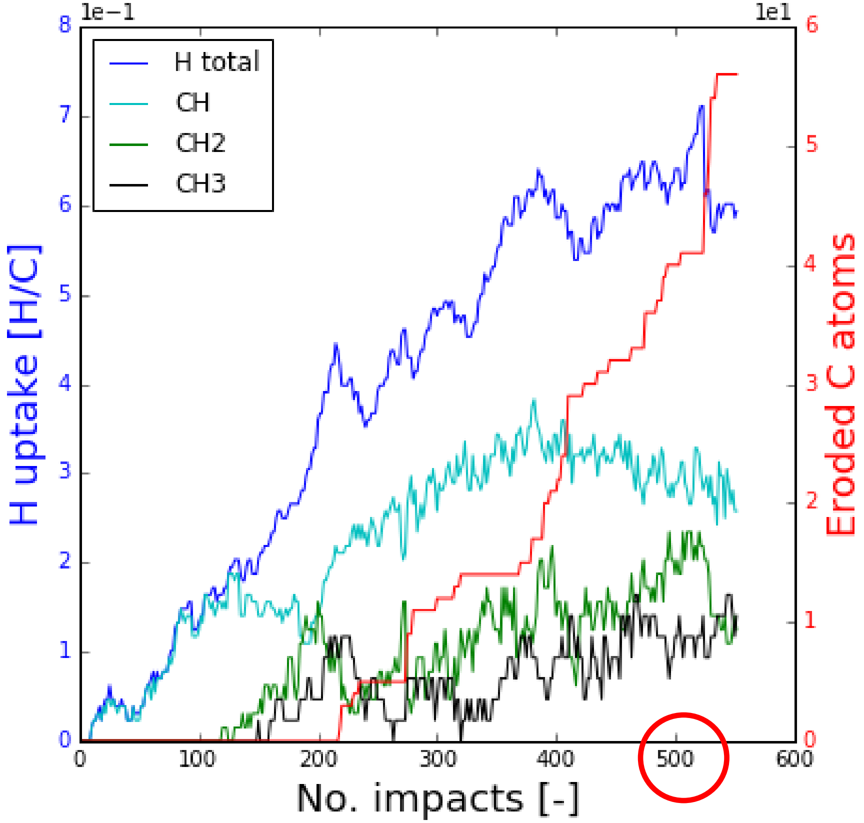




PLASMA ETCHING



MD (2 ps)



CVHD (1 μs)

Much more efficient erosion at lower fluxes + CVHD

CLOSING REMARKS

CONLUSION

The CVHD method combines aspects from different well-established biasing methods (hyperdynamics and metadynamics)

  Quite easy to apply to different systems

  Does not require much system-specific optimization

  Spans a broad range of time scales

Probably not useful (for now?) if

  You want to recycle states/barriers

  Low-barrier events are a problem

The future

  Apply to different and more complicated systems (like nanoscale growth)

  Applications will lead to new CVs being used in CVHD

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References

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Bal & Neyts, J. Chem. Theory Comput. **11**, 4545 (2015).