Atomistic Modeling of Carbon Nanostructures: Challenges and Opportunities

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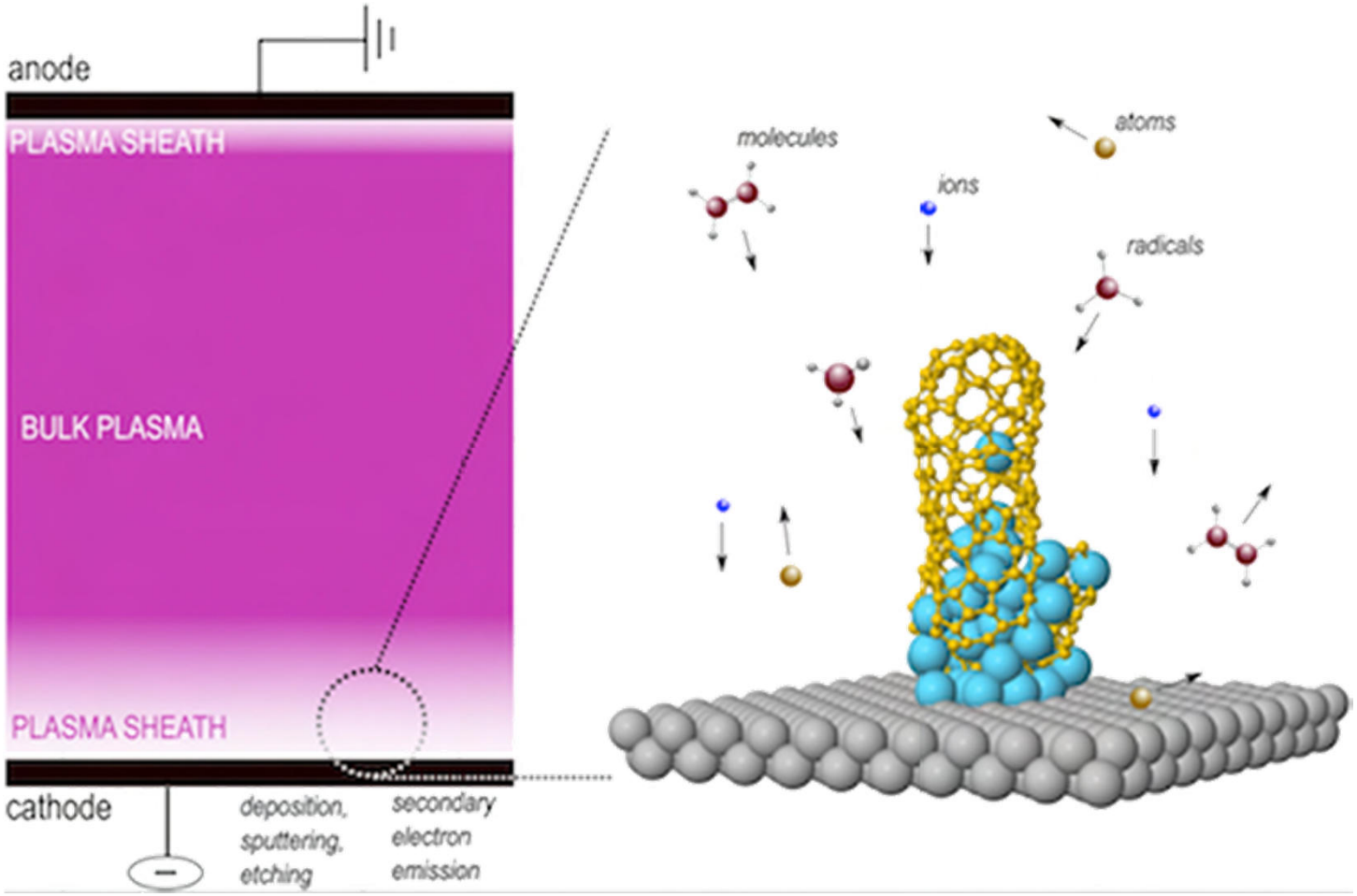
INTRODUCTION

ATOMISTIC SIMULATIONS

Plasma-based synthesis or modification of carbon nanostructures is a very complex process

ATOMISTIC SIMULATIONS



Neyts *J. Vac. Sci. Technol. B* **30,** 030803 (2012)

ATOMISTIC SIMULATIONS

Plasma-based synthesis or modification of carbon nanostructures is a very complex process

We wish to known the atomic-level mechanisms!

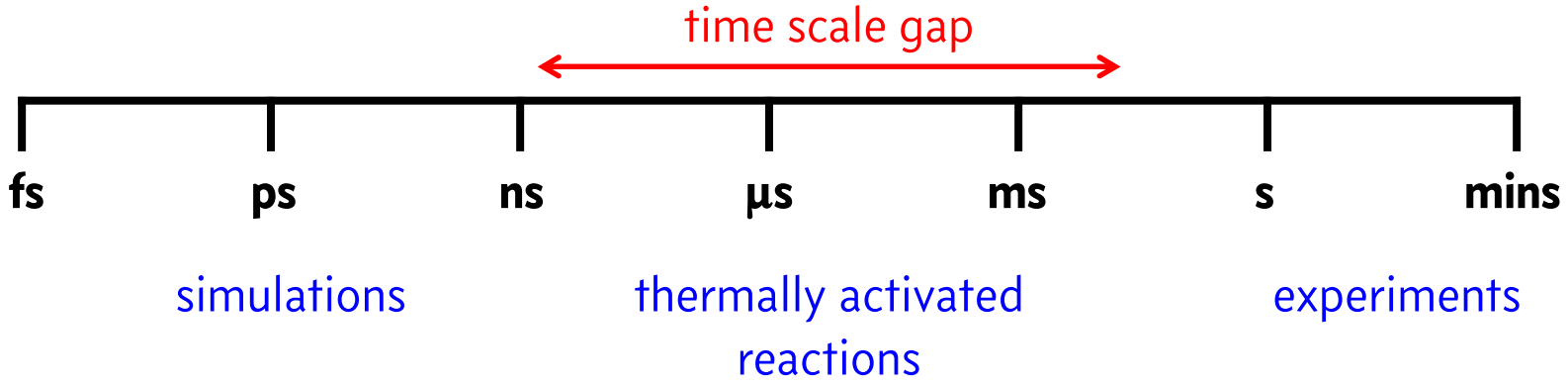
Molecular dynamics (MD) simulations seem perfect

- Explicit dynamics from equations of motion
- Atomistic detail
- Fully self-consistent system evolution
- Truly exploratory

Direct simulation should be fairly straightforward

- *CNT growth:* catalyst NP + C_xH_y precursors
- *Nanostructure etching:* material + etchant species (ions, radicals)

THE TIME SCALE PROBLEM



But MD has a severe time scale limitation!

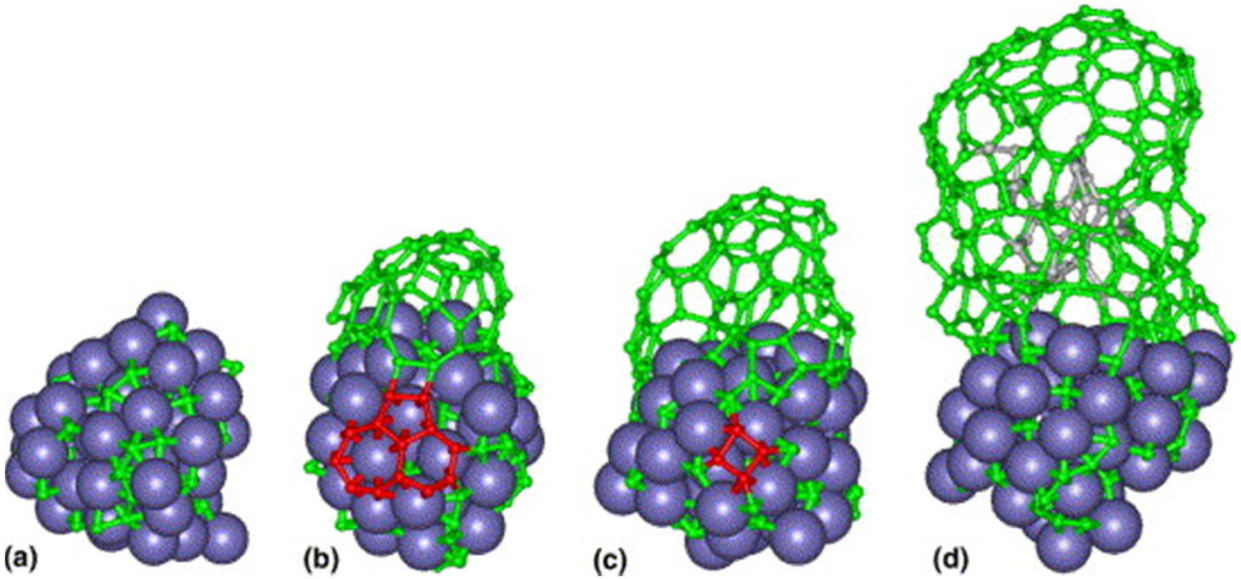
Many interesting processes occur at much longer time scales

e.g., CH_4 splitting on Ni

Average reaction time is ~1 µs at 800 K…

…but MD will only get you to ns!

THE TIME SCALE PROBLEM



MD requires inter-impact times of ~ps → pressures of ~100 atm!

Many examples prove that is too fast

Ding et al., *Chem. Phys. Lett.* **393,** 309 (2004)

TOWARDS BETTER MODELS

FORCE-BIAS MONTE CARLO

$$p(x \rightarrow x') \sim \exp\left(\frac{\beta F_x (x' - x)}{2}\right) \text{ instead of } \mathbf{F} = m \cdot \mathbf{a}$$

fbMC is a stochastic method

- Atomic movements sampled from distribution
- No "true" dynamics, but system evolution similar to MD
- Average atomic displacement (~0.1 Å) larger than MD (~0.01 Å)

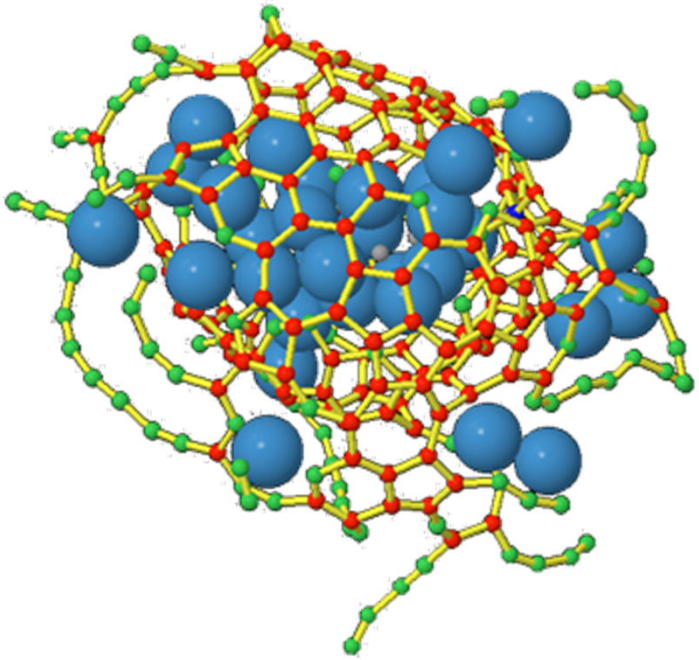
Easy to implement & very generic

Practical realisation:

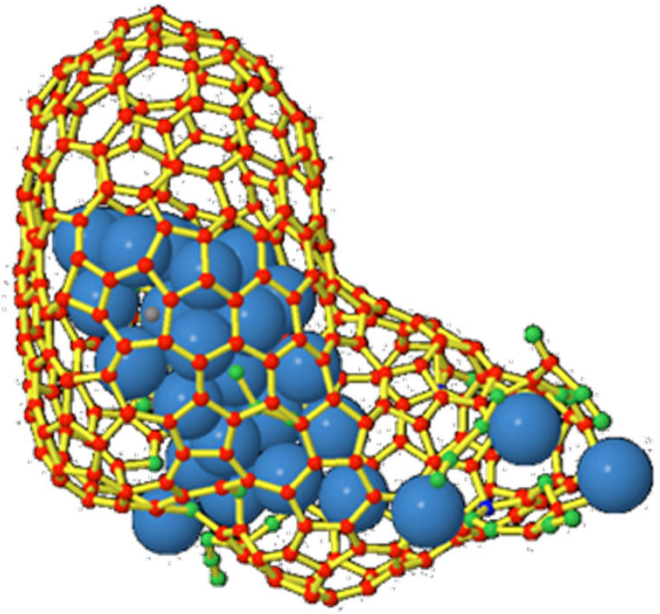
- Perform impacts with MD
- Mimic inter-impact relaxation with fbMC

Bal & Neyts *J. Chem. Phys.* **141,** 204104 (2014) and references therein

FORCE-BIAS MONTE CARLO



MD

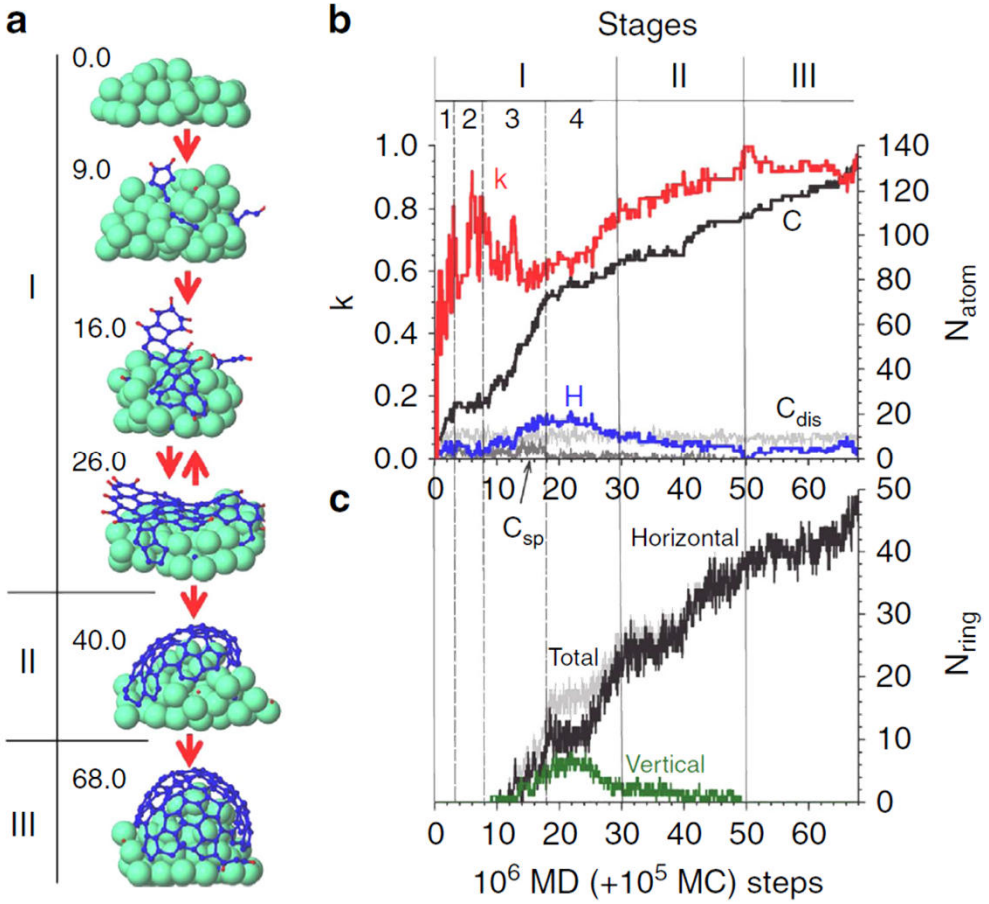


MD + fbMC

fbMC makes the simulation more physically sensible

Neyts et al. *ACS Nano* **4,** 6665 (2010)

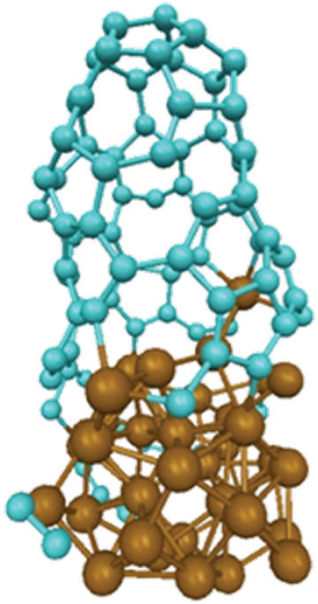
FORCE-BIAS MONTE CARLO



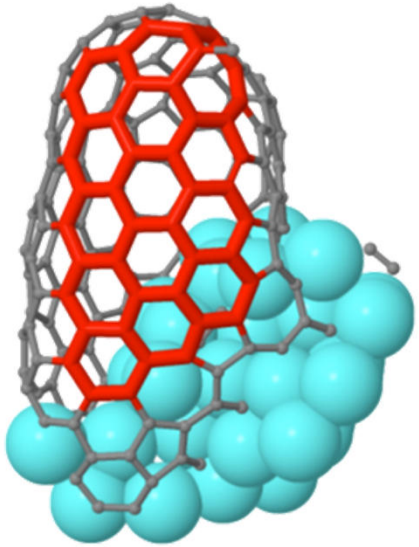
One can even study nucleation from C_xH_y feedstock

Khalilov et al. *Nat. Commun.* **6,** 10306 (2015)

FORCE-BIAS MONTE CARLO



MD simulation
Bad CNT
Time scale: 40 ps



MD + fbMC
Good CNT
Time scale: ???

Page et al., *Acc. Chem. Res.* **43,** 1375 (2010)

Neyts et al., *JACS* **133,** 17225 (2011)

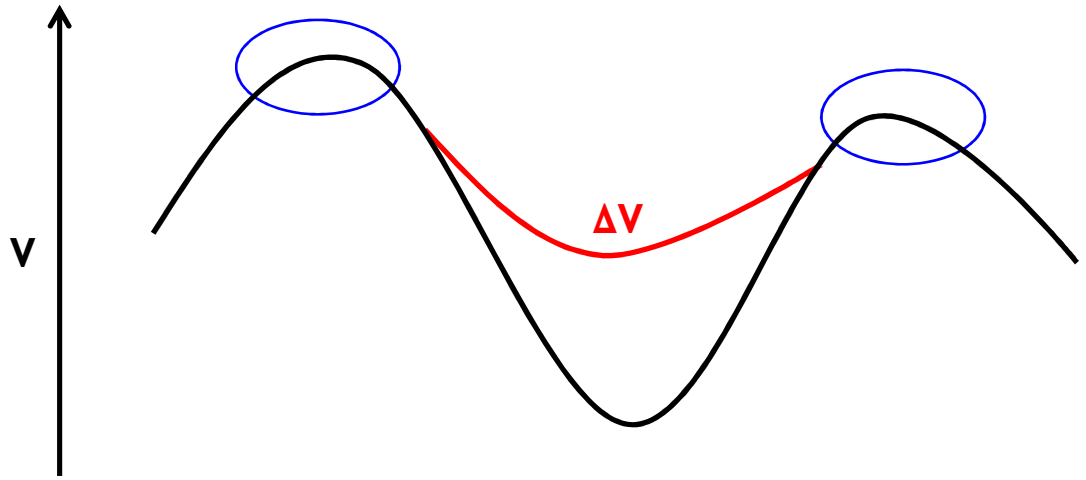
fbMC is still not good enough

No "real" dynamics and unclear time scale

We want rigorously correct methods with real time scales

HYPERDYNAMICS

$$t_{\text{real}} = t_{\text{MD}} \left\langle e^{\Delta V/kT} \right\rangle$$



Slow processes can be accelerated with the **hyperdynamics** method

A **bias potential** lowers the apparent barrier of a escape process

→ arbitrarily slow process become accessible

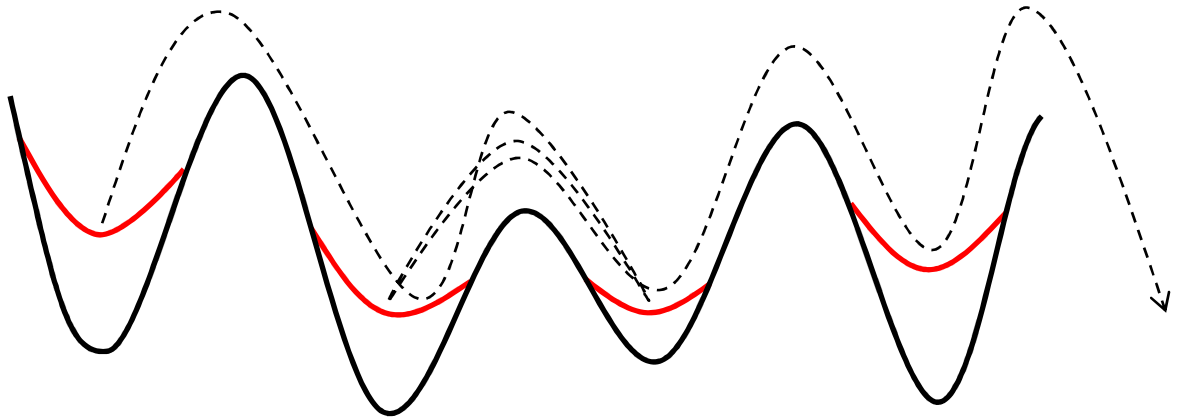
If transition states remain unbiased

Correct **relative dynamics** is preserved (k_1/k_2 = constant)

Time scales can be recovered!

Voter *J. Chem. Phys.* **106,** 4665 (1997)

THE CVHD METHOD



Unfortunately, implementing hyperdynamics requires a lot of *a priori* information

→ functional form of ΔV?

We developed a method, collective variable-driven hyperdynamics (CVHD) that

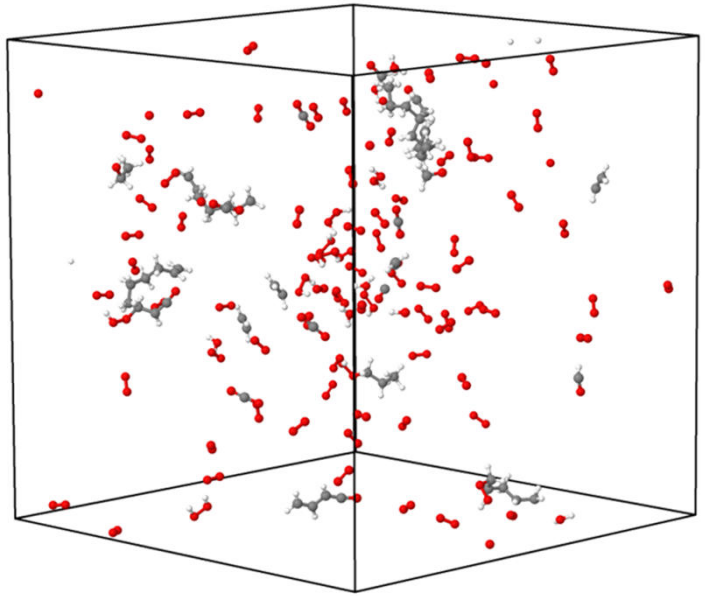
- Can automatically generate ΔV on the fly
- Requires few system-specific details

One needs to know what type of reaction coordinate = the CV

- Bond breaking? Conformational change?

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

PYROLYIS & COMBUSTION

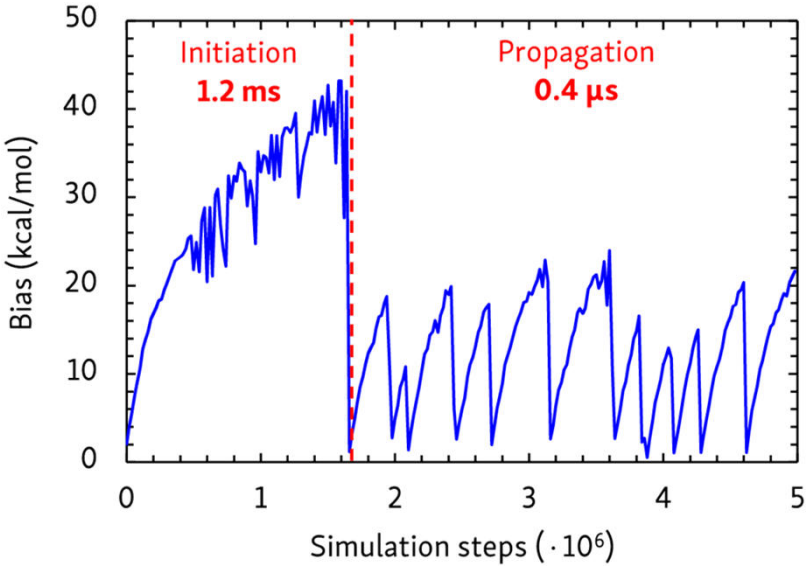


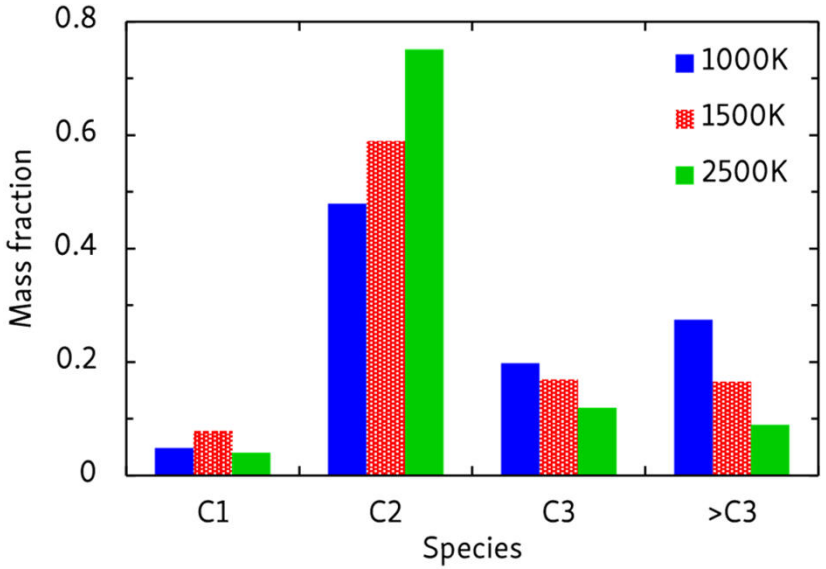
n-Dodecane pyrolysis and combustion is a great test system

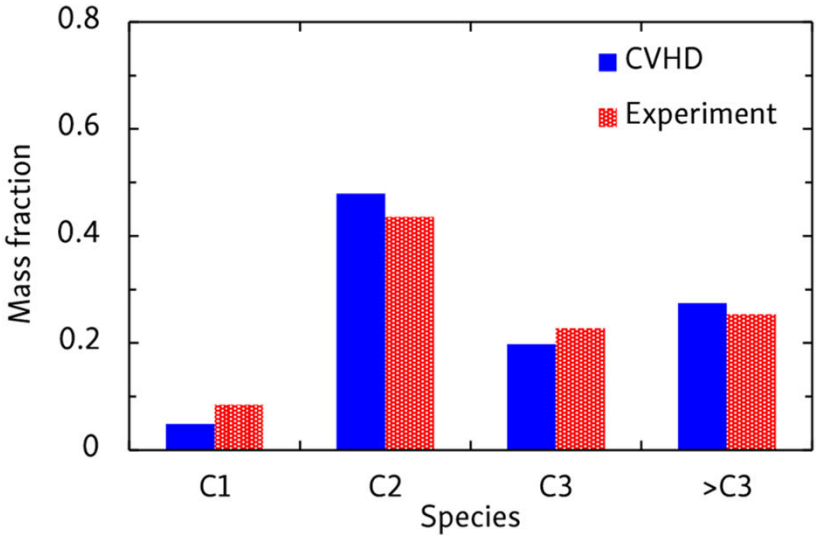
- Many reactions
- We don't define any pathways, only bias bond breaking

Bal & Neyts *Chem. Sci.* **7,** 5280 (2016)

PYROLYIS & COMBUSTION







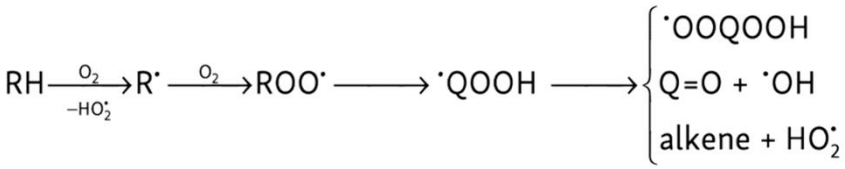
On the fly bias

Temperature-dependent pyrolysis products

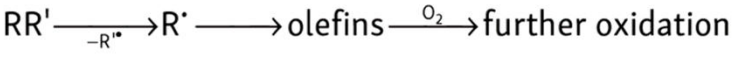
Remarkable agreement with recent experiments @ 1000 K

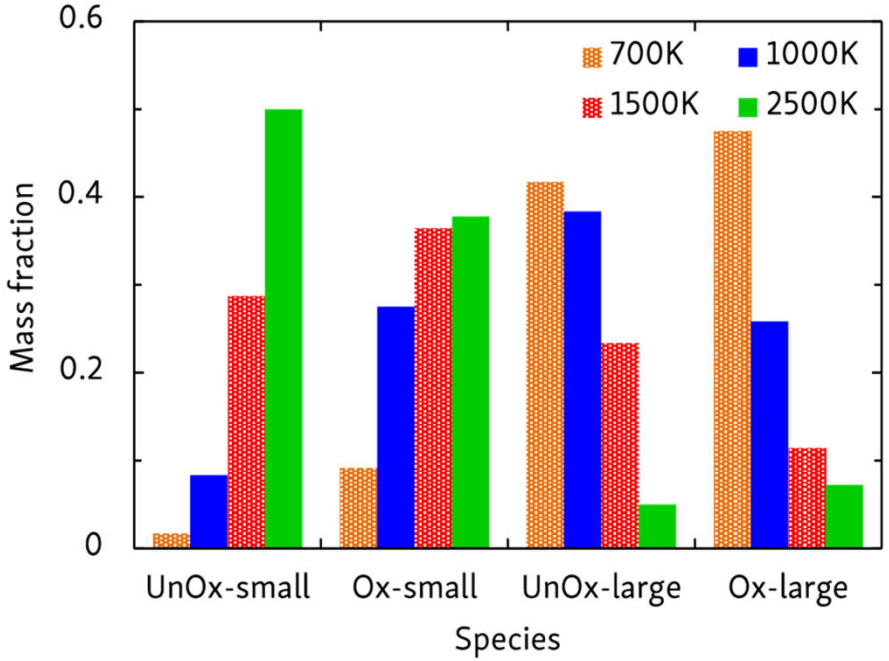
PYROLYIS & **COMBUSTION**

Low temperature:



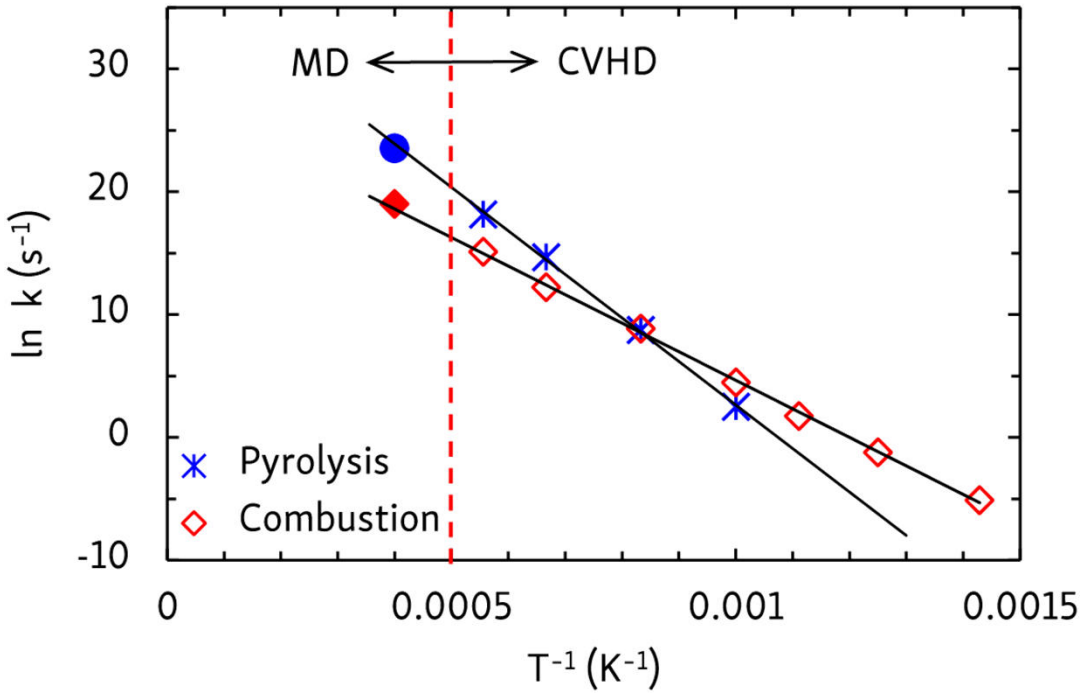
High temperature:





Temperature-dependent oxidation pathways and products can also be captured

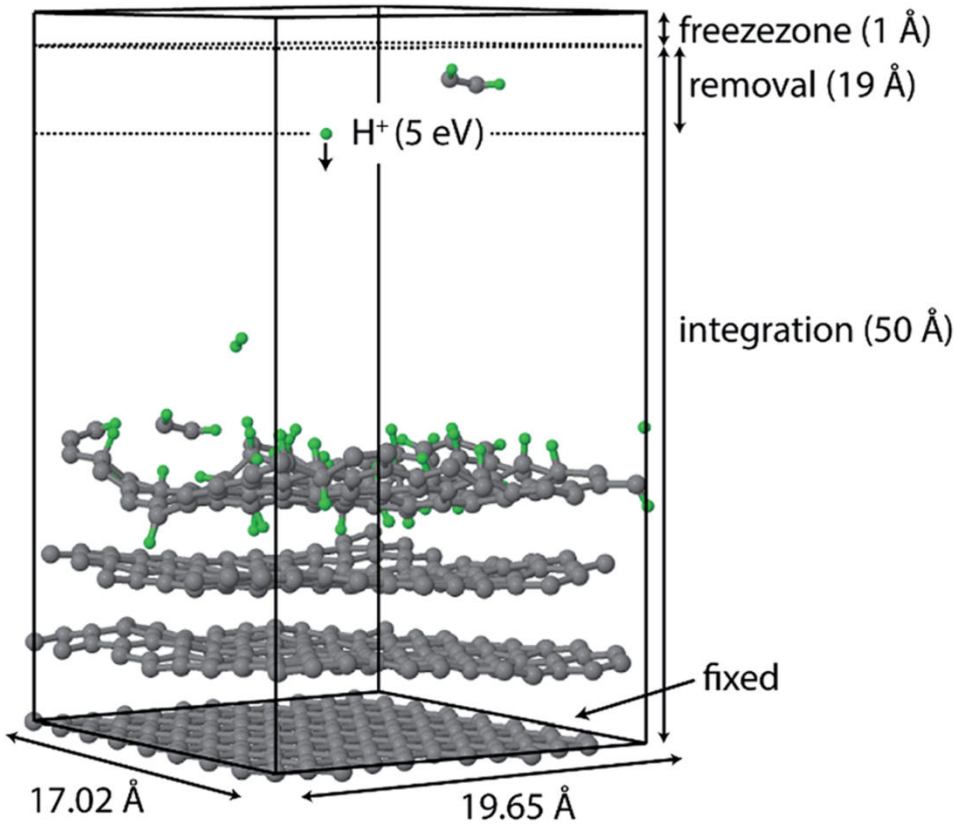
PYROLYIS & COMBUSTION



A posteriori validation through direct MD

	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

CARBON NANOSTRUCTURES: H ETCHING

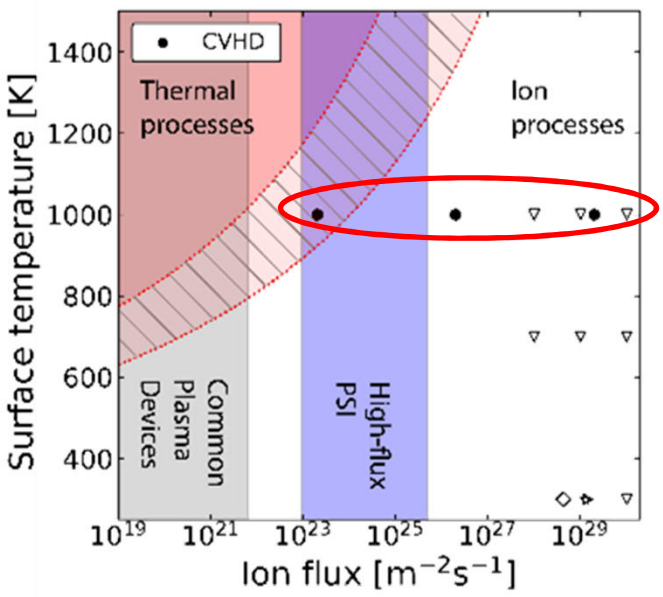


Graphite etching with H ions in a high-density fusion plasma

CVHD between impact allows for arbitrary inter-impact times

Aussems et al. *Chem. Sci.* **8,** 7160 (2017); *Carbon*, in press

CARBON NANOSTRUCTURES: GRAPHITE ETCHING



Experimentally relevant regimes in CVHD

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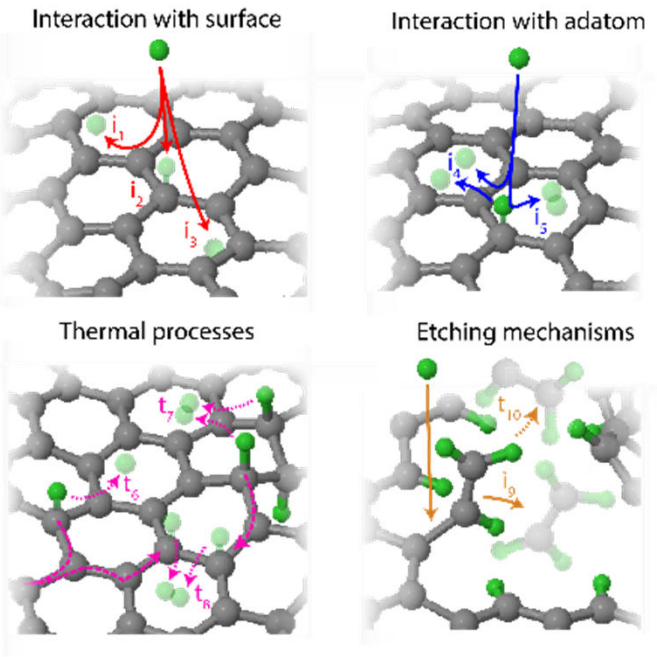
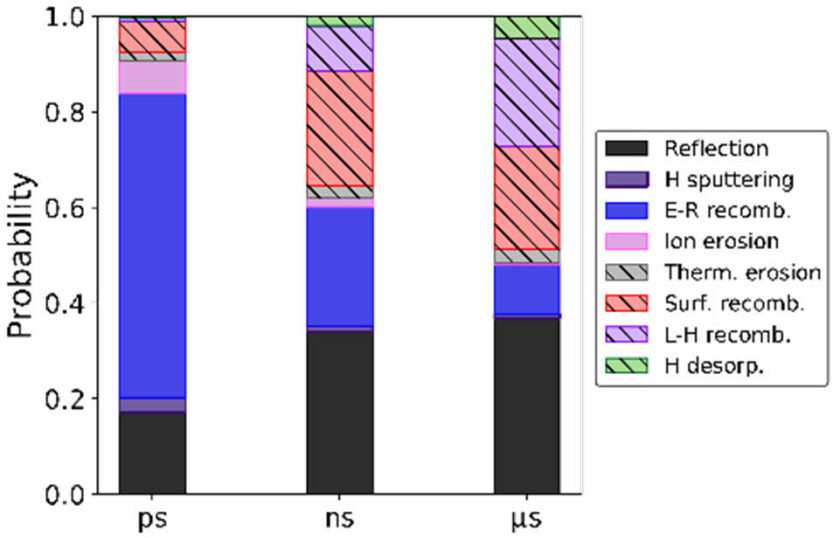
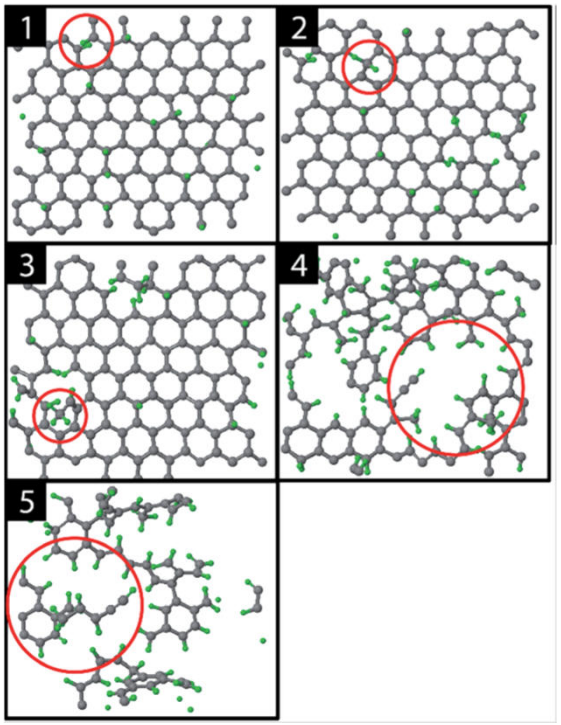


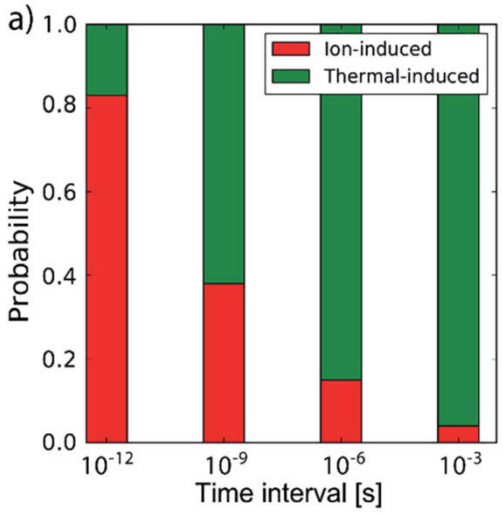


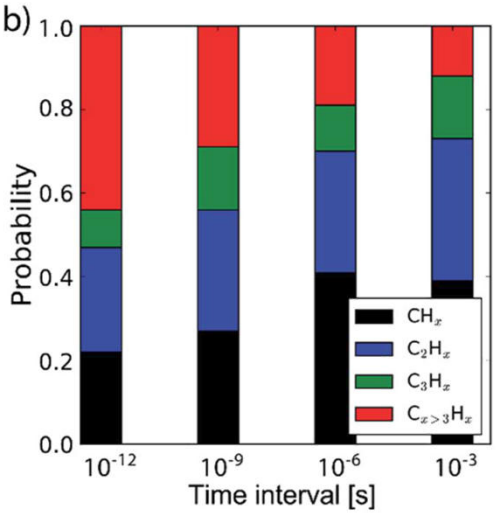
Experimentally relevant regimes in CVHD

→ different interaction mechanisms

CARBON NANOSTRUCTURES: GRAPHITE ETCHING





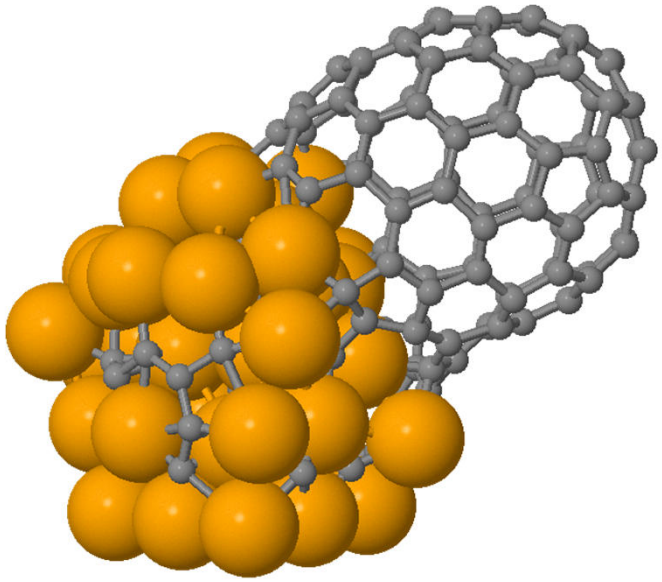


Experimentally relevant regimes in CVHD

→ different interaction mechanisms

→ different surface evolution and etched species

CNT GROWTH



250 µs time scale

Application of CVHD to CNT growth works…

…but not always

→ Many processes not included in CV

→ We haven’t identified all relevant processes yet

WRAPPING UP

CONCLUSIONS

In molecular simulations, accounting for long time scales is not only useful, **it is necessary**

Our method is **generically applicable** to any reactive system, if a suitable CV can be found

CVHD allows to better understand fundamental dynamic processes, e.g., in deposition of materials, **under realistic conditions**

We are always open to **collaborate**, in particular to combine simulations with experiments

ACKNOWLEDGEMENTS

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fwo

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CNT growth

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graphite etching

THANK YOU FOR YOUR ATTENTION