



# Molecular Dynamics simulations for low temperature plasma processes

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# Outline

## ■ Practical MD simulations

- Basics
- Relevance/Significance
- Which species, which phenomena
- (Interaction Potentials)

## ■ Plasma processing and MD

- Processes: electric fields effects, vibrational excitation, electrical breakdown, etching, deposition
- Applications: Nanoparticle growth, hydrocarbon plasmas, wastewater plasma treatment

## ■ Next step as conclusion



# Practical Molecular Dynamics (MD) simulations: Basics

- ✓ Calculate all trajectories of a set of atoms, ions, molecules, ... via the Newton equation of motion

$$\vec{F}_i = m_i \vec{a}_i = m_i \frac{d\vec{v}_i}{dt} = m_i \frac{d^2 \vec{r}_i}{dt^2}$$

and

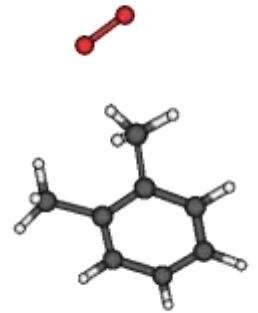
$$\vec{F}_i = -\vec{\nabla}_{\vec{r}_i} \mathbf{U}(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_N)$$

- Suitable for processes at nanoscale (up to  $10^9$  atoms)
- ✓ A rigorous approach requires the use of robust interaction potentials (many-body, reactive, variable charge) if comparison with experiments is looked for.
  - If necessary running DFT, i.e. electronic calculations
  - *ab-initio* or *first-principles* MD and/or Machine Learning methods



# Practical MD simulations: Basics

- ✓ and initial conditions (positions, velocities) preferably matching experimental conditions → appropriate kinetic energy or velocity distribution functions can be obtained/deduced from experiments (MS, laser spectroscopy, etc) or plasma-kinetic models.
- ✓ Proper energy dissipation:
  - Energy release during bond formation : deposition, bond formation/breaking
  - Annealing→ via friction term(s), thermostat(s)





# Practical MD simulations: Relevance/significance

## Flux

Exp  $\rightarrow 1 \cdot 10^{15} \text{cm}^{-2} \text{s}^{-1} = 10 \text{nm}^{-2} \text{s}^{-1}$  while MD  $\rightarrow \approx 10 \text{nm}^{-2} \text{ps}^{-1}$

Prohibits long time diffusion, except if including specific strategies (fbMC, CVHD, hyperdynamics, temperature accelerated dynamics ...)

## Pressure/simulation box size

- Solid density : Pt  $65 \text{nm}^{-3}$   $\rightarrow$  Statistical quantities can be calculated with enough precision for a  $10^3 \text{nm}^3$  box
- Liquid density: water  $33 \text{nm}^{-3}$
- Gas or plasma density :  $1 \text{atm} = 2.4 \cdot 10^{-2} \text{nm}^{-3}$ 
  - $\rightarrow$  Not enough species in box of size  $d$  at pressure  $P$
  - Solution: relevant parameter = Collision number  $\propto P \cdot d$
  - $\rightarrow \uparrow P \downarrow d$  should work.

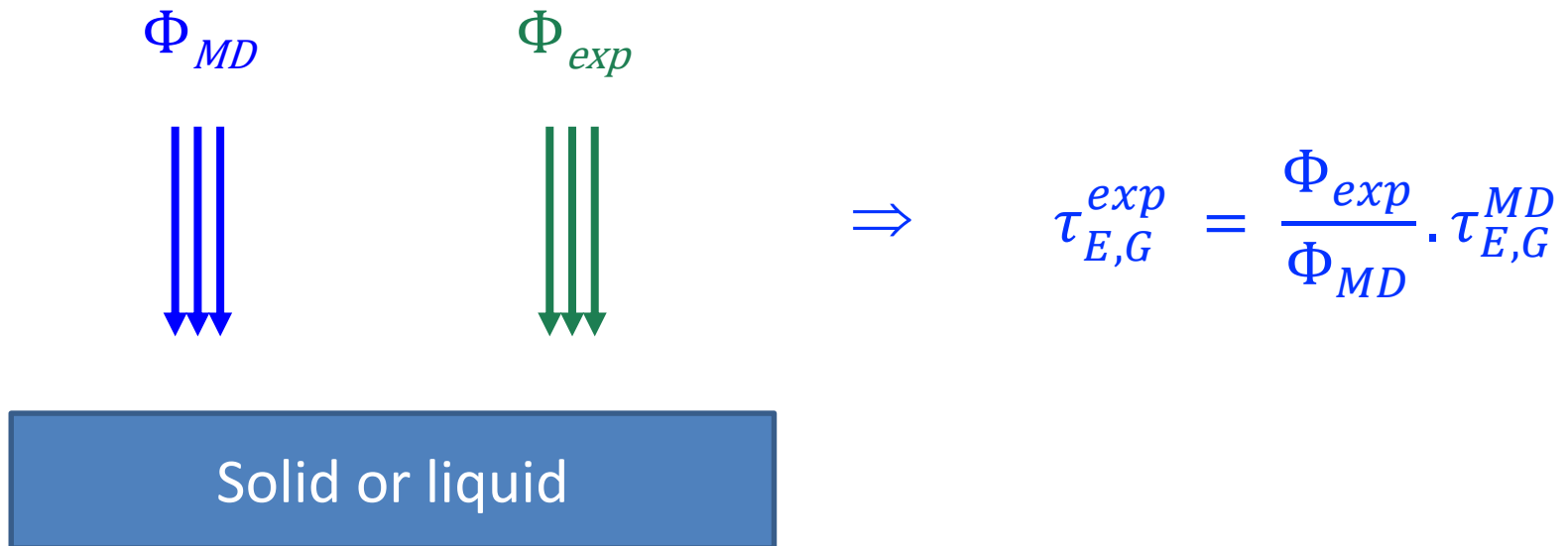
$$P_{exp} d_{exp} = P_{sim} d_{sim} \text{ thus } N_{sim} = \frac{P_{exp}}{k_B T_g} \cdot S_{sim} \cdot d_{exp}$$



# Practical MD simulations: Relevance/significance

## ■ Plasma surface interactions (solid/liquid)

- Density differences → high MD fluxes → significance of resulting deposition/etching rates
- Solution: Growth or etching probability provided energy dissipation through the condensed medium is properly addressed → scaling with experimental flux





# Practical MD simulations: Which species, which phenomena

Plasma feature	Possible?	Example
electric field	yes	CNT growth
atoms and hyperthermal species	yes	Si-NW oxidation, sputter deposition
radicals	yes	a-C:H growth
ions	yes	sputtering
electronically excited states	yes	etching
vibrationally excited states	yes	Dissociative chemisorption
photons	implicit	Polymer degradation
electrons	Yes (eFF, e-reaxFF)	Electrical breakdown, e <sup>-</sup> attachment

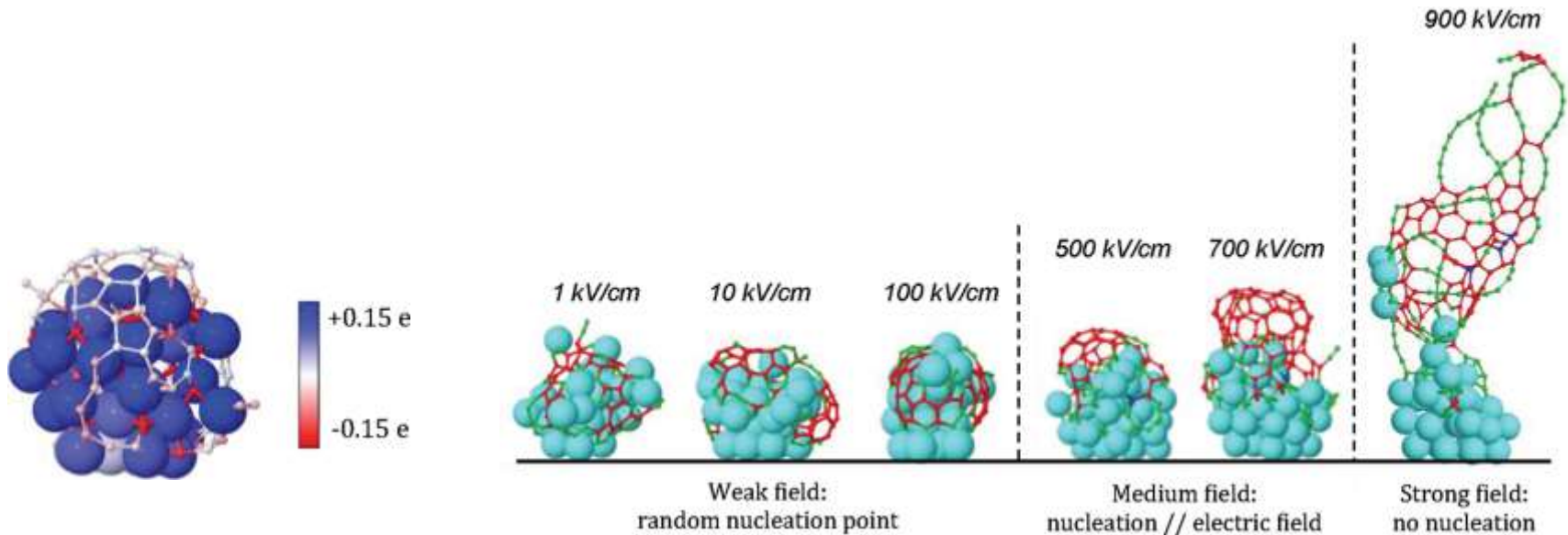
E. Neyts, P. Brault, *Molecular dynamics simulations for plasma surface interactions*, Plasma Processes and Polymers 14 (2017) 1600145

D. B. Graves, P. Brault, *Molecular dynamics for low temperature plasma-surface interaction studies*, J. Phys. D 42 (2009) 194011



# Plasma processing & MD: Electric field effects

- **Effect of the electric field** on the nanotube growth from a sputtered carbon vapor
- Use of the reactive and variable charge reaxFF forcefield allows us to calculate partial charge and thus action of external electric field can be monitored.



Neyts, E. C.; van Duin, A. C. T.; Bogaerts, A. Insights in the Plasma-Assisted Growth of Carbon Nanotubes through Atomic Scale Simulations: Effect of Electric Field. *J. Am. Chem. Soc.* 2012, 134, 1256–1260

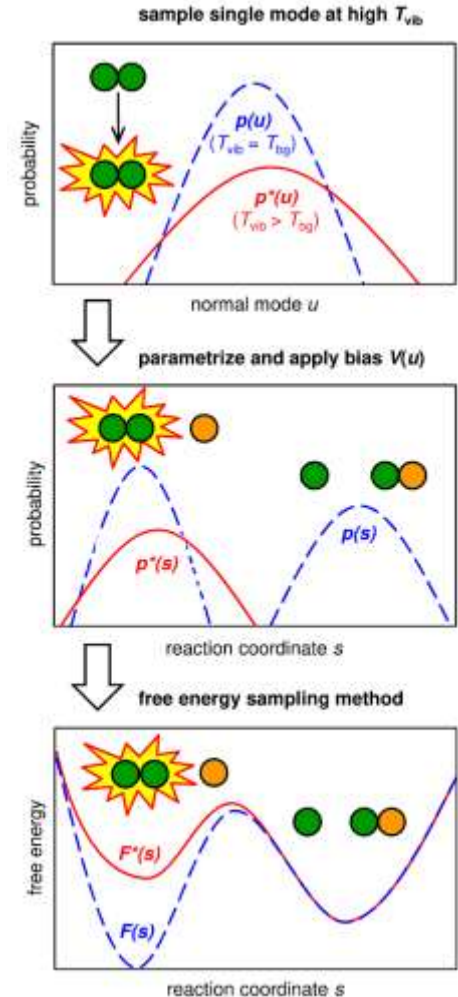




# Plasma processing & MD: Effect of vibrationally excited states

- (Amazing) idea → apply a bias potential to the vibrational energy accordingly to the probability distribution at the excited temperature  $T_{\text{vib}}$ . To model systems in which most modes are in equilibrium with each other at a background temperature ( $T_{\text{bg}}$ , say 300K for example), while certain selected modes have a (higher) vibrationally excited temperature ( $T_{\text{vib}}$ )
- Probability distribution  $p(\mathbf{R})$  of any system in configuration space  $\mathbf{R}$  at temperature  $T$  and potential energy  $U(\mathbf{R})$  follows the Boltzmann distribution, used for each 2 temperatures
- Probability distribution along a reaction coordinate  $s$  can be related to the free energy surface (FES)  $F(s)$  along this coordinate

$$p(\mathbf{R}) \propto e^{-\beta U(\mathbf{R})} \text{ and } F(s) = -\frac{1}{\beta} \ln p(s) + C$$





# Plasma processing & MD: Effect of vibrationally excited states

## ■ H<sub>2</sub> dissociation on Ni

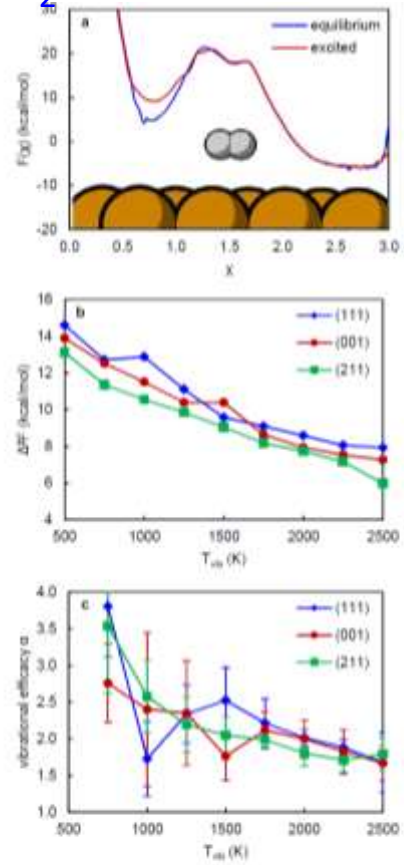


Figure 1. H<sub>2</sub> dissociation on nickel surfaces at T<sub>bg</sub> = 500 K. (a) Effect of vibrational excitation on the free energy surface F(x) of dissociative adsorption on the Ni(111) surface (inset): comparing thermal equilibrium (T<sub>vib</sub> = 500 K) with T<sub>vib</sub> = 1500 K. (b) Apparent free energy barrier ΔF\* and (c) vibrational efficacy α as a function of T<sub>vib</sub> for the different facets. Lines are drawn to guide the eye.

## ■ CH<sub>4</sub> dissociation on Ni

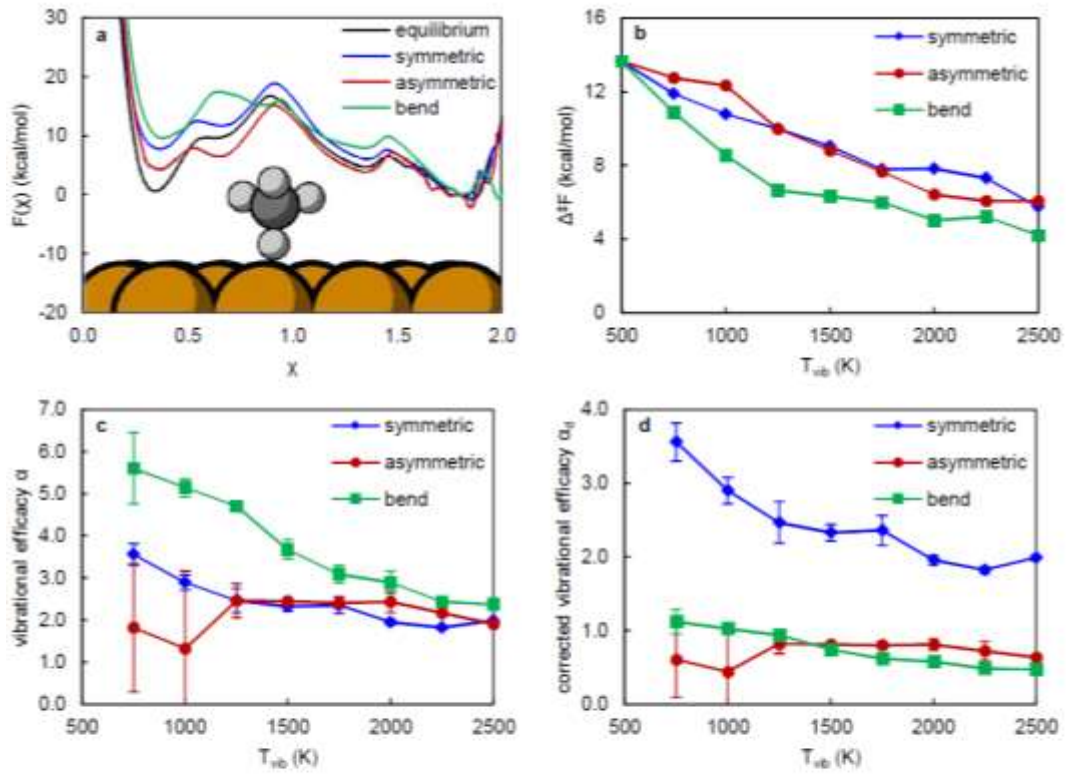


Figure 2. CH<sub>4</sub> dissociation on the Ni(111) surface at T<sub>bg</sub> = 500 K. (a) Effect of vibrational excitation of different classes of CH<sub>4</sub> vibrational on the free energy surface F(x) of dissociative adsorption (inset): comparing thermal equilibrium (T<sub>vib</sub> = 500 K) with T<sub>vib</sub> = 1500 K. (b) Apparent free energy barrier ΔF\*. (c) Vibrational efficacy α as a function of T<sub>vib</sub> for the different modes. (d) Vibrational efficacy α<sub>d</sub> taking into account degeneracy. Lines are drawn to guide the eye.

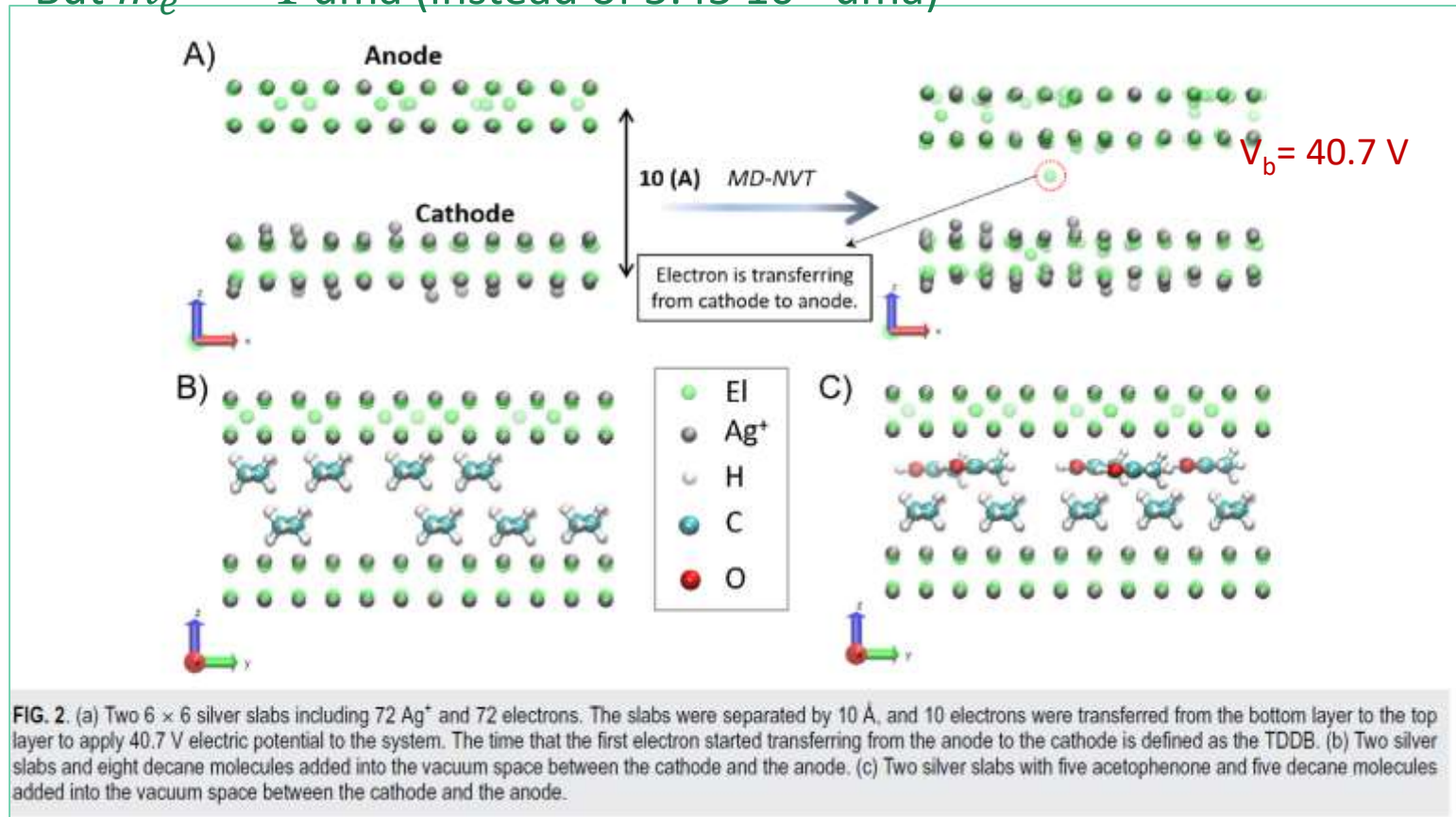
K. Bal and E. Neyts, Quantifying the impact of vibrational nonequilibrium in plasma catalysis: Insights from a molecular dynamics model of dissociative chemisorption J. Phys. D: Appl. Phys. 54 (2021) 394004





# Plasma processing & MD: Electrical breakdown

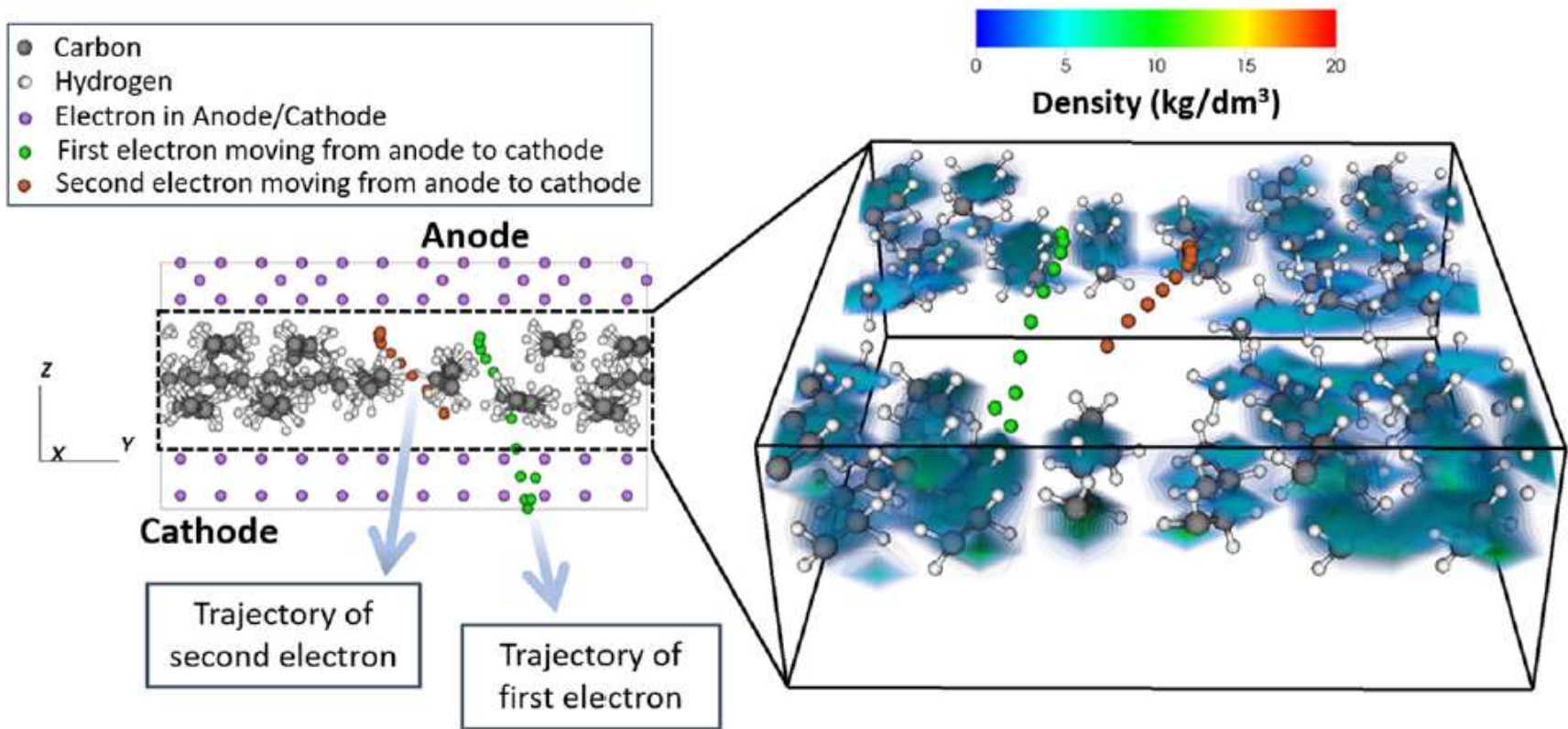
- Explicitly including electrons in MD simulations:
- The first attempt to « describe » a low pressure plasma breakdown using MD
- But  $m_{e^-} = 1 \text{ uma}$  (instead of  $5.45 \cdot 10^{-4} \text{ uma}$ )



D. K. Ganeshan, W. H. H. Woodward, J. Moore, and A. C. T. van Duin, Atomistic-scale insight into the polyethylene electrical breakdown: An eReaxFF molecular dynamics study. *J. Chem. Phys.* **154**, 024904 (2021)



# Plasma processing & MD: Electrical breakdown



- Contour of the system density between the cathode and the anode
- Trajectories of the first two electrons transferring from the anode to cathode, indicating that electrons travel through the voids during the electrical breakdown.

D. K. Ganeshan, W. H. H. Woodward, J. Moore, and A. C. T. van Duin, Atomistic-scale insight into the polyethylene electrical breakdown: An eReaxFF molecular dynamics study, *J. Chem. Phys.* **154**, 024904 (2021)



# Plasma processing & MD: Etching

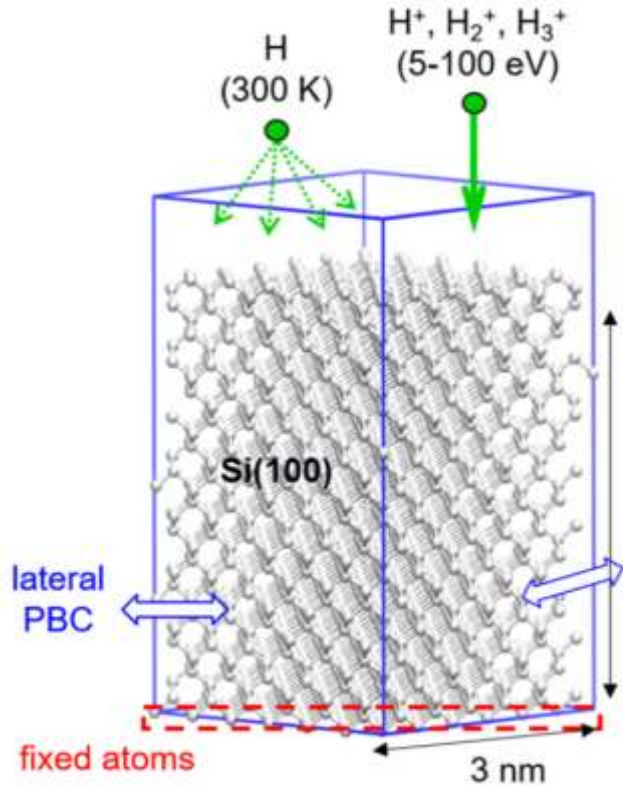
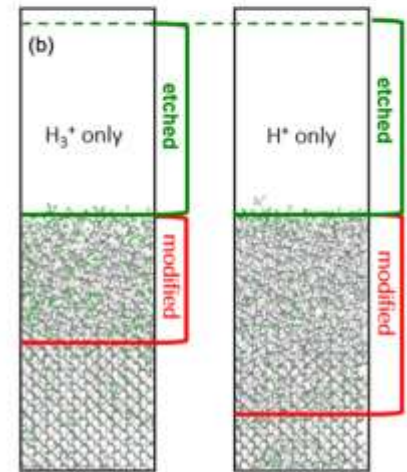
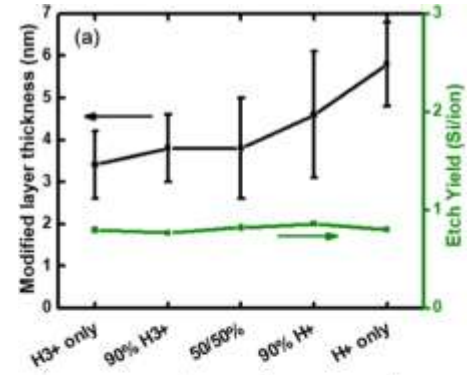
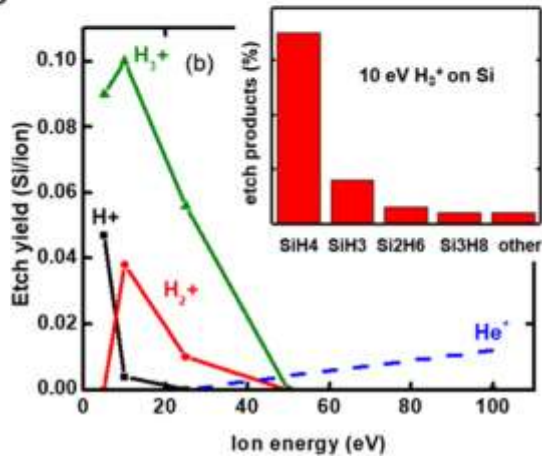
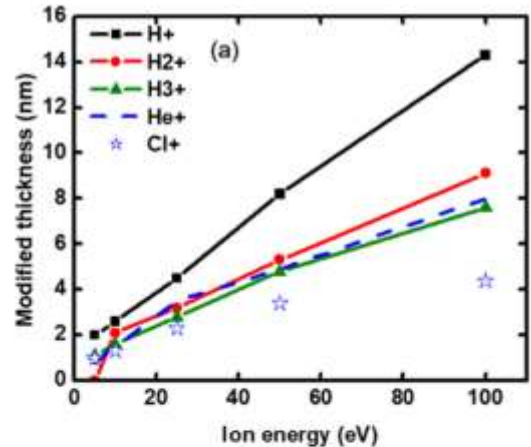
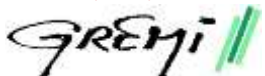


Figure 1. Initial (100) e-Si simulation cell used in the MD calculations.



up to 15 nm





# Plasma processing & MD: Deposition

## ■ Copper deposition

(a) Thermal evaporation

(b) dc magnetron deposition

(c) HiPIMS deposition with a mixture of copper neutrals and ions

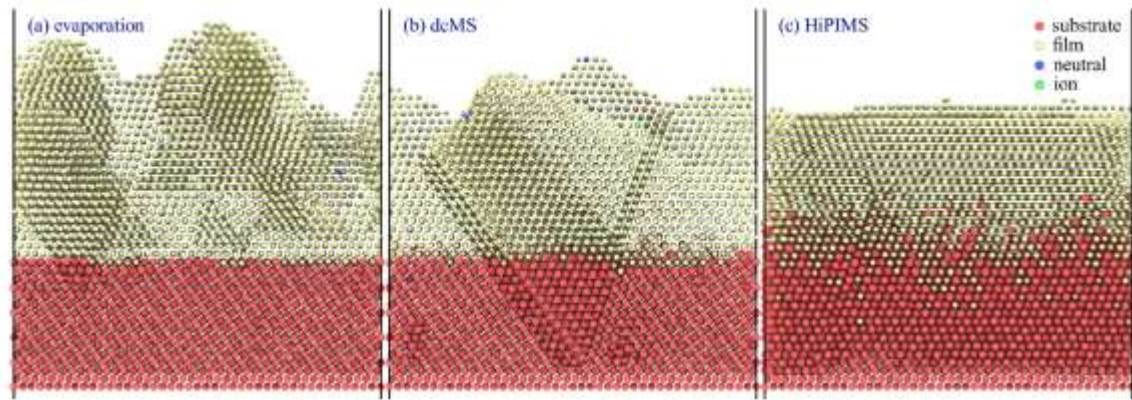


FIG. 1. Illustration of interface mixing using (a) thermal evaporation, (b) dcMS and (c) HiPIMS after 2.5 ns deposition. The red, green, blue and yellow are indicating substrate, neutral, ions and film atoms.

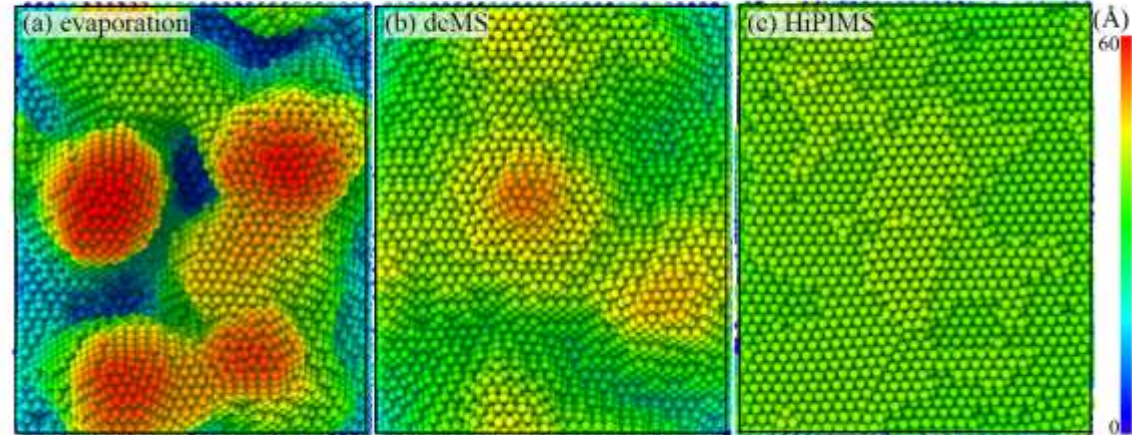
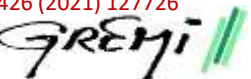


FIG. 2. The surface topology obtained using (a) thermal evaporation (b) dcMS and (b) HiPIMS deposition with similar deposition time and energy distribution. The deep blue indicates substrate surface and red denotes thickness higher than 6 nm.

M Kateb, H. Hajihoseini, JT Gudmundsson, S. Ingvarsson, Role of ionization fraction on the surface roughness, density, and interface mixing of the films deposited by thermal evaporation, dc magnetron sputtering, and HiPIMS: An atomistic simulation, *Journal of Vacuum Science & Technology A* 37, 031306 (2019)

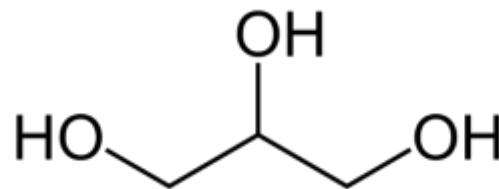
M Kateb, JT Gudmundsson, P Brault, A Manolescu, S. Ingvarsson, On the role of ion potential energy in low energy HiPIMS deposition: An atomistic simulation *Surface & Coatings Technology* 426 (2021) 127726





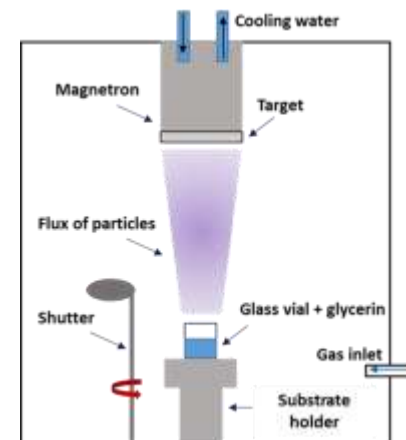
# Plasma processing & MD: Nanoparticle growth

## Sputtered nanoparticle growth on/in liquid: Pt on glycerol



- Glycerol box :  $7 \times 7 \times 50 \text{ nm}^3$   $1.26 \text{ g.cm}^{-3}$ .
- 400 Pt atoms released every 0.2 ps (80 ps deposition) + further 80 ps wo deposition
- Glycecol = thermostat 100 fs damping time.
- Simulate Pt sputtering at 1 and 9 Pa (target-substrate  $d = 12 \text{ cm}$ )  
→  $\langle E_{\text{Pt}} \rangle = 2.0$  and  $0.039 \text{ eV}$  respectively

*Potentials used in the system:*  
reaxFF (\*) for all elements.

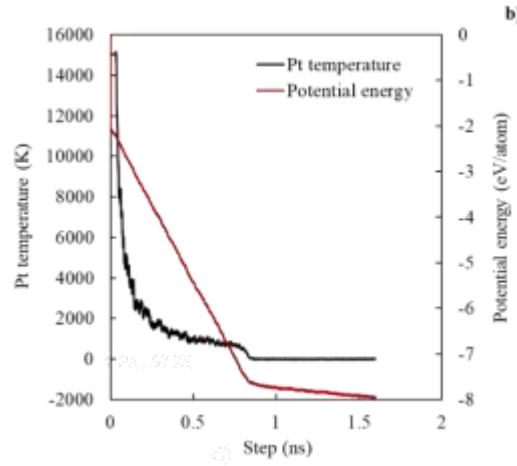
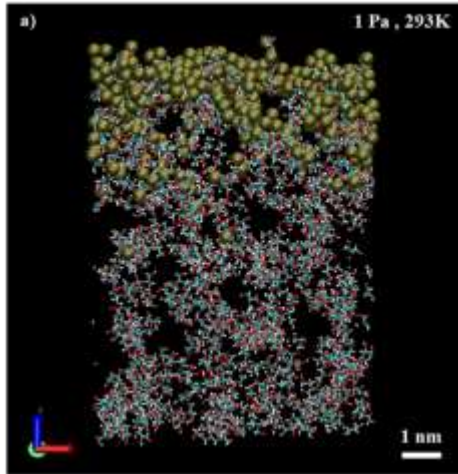


(\*)Shin, Y. K.; Gai, L.; Raman, S.; Van Duin, A. C. T. Development of a ReaxFF Reactive Force Field for the Pt-Ni Alloy Catalyst. *J. Phys. Chem. A* 2016, 120 (41), 8044–8055.  
<https://doi.org/10.1021/acs.jpca.6b06770>.



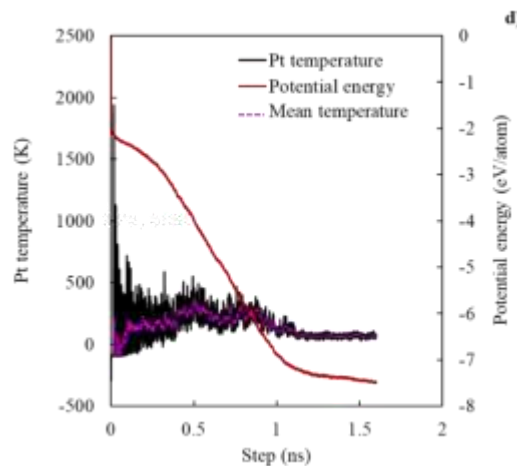
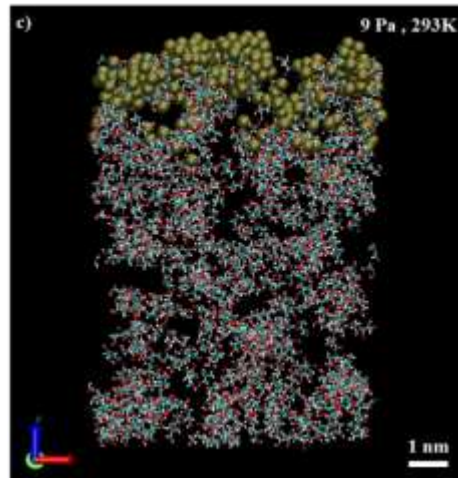
# Plasma processing & MD: Nanoparticle growth

## Sputtered nanoparticle growth on/in liquid: Pt on glycerol



■ Fast PE decrease → fast bonding at 1 Pa i.e.  $\langle E_{pt} \rangle = 2$  eV

■ At 9 Pa temperature → low frequency oscillations → NP growth



■ Consistent with experiments.

■ Greater sizes and longer times are required for more detailed discussion

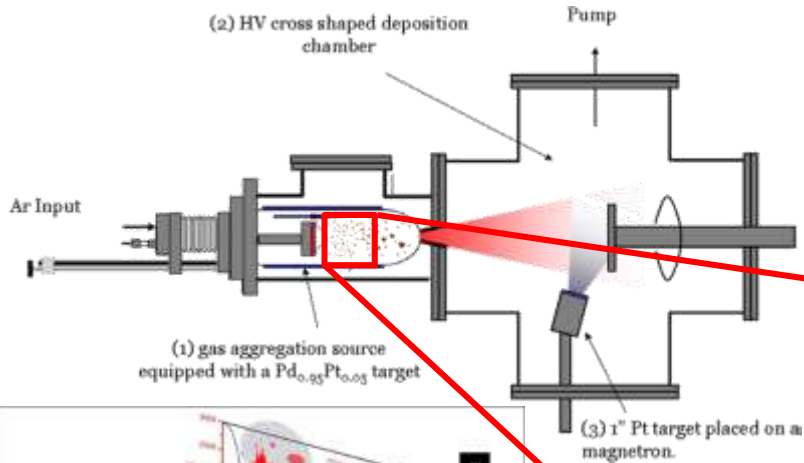
V. Orozco-Montes, A. Caillard, P. Brault, W. Chamorro-Coral, J. Bigarre, A. Sauldubois, P. Andreazza, S. Cuynet, S. Baranton, and C. Coutanceau, Synthesis of Platinum Nanoparticles by Plasma Sputtering onto Glycerol: Effect of Argon Pressure on Their Physicochemical Properties, J. Phys. Chem. C 125 (2021) 3169–3179





# Plasma processing & MD: Nanoparticle growth

## Free Pt<sub>3</sub>NiAu nanoparticle growth in a Gas Aggregation Source



Matching experimental and simulation conditions



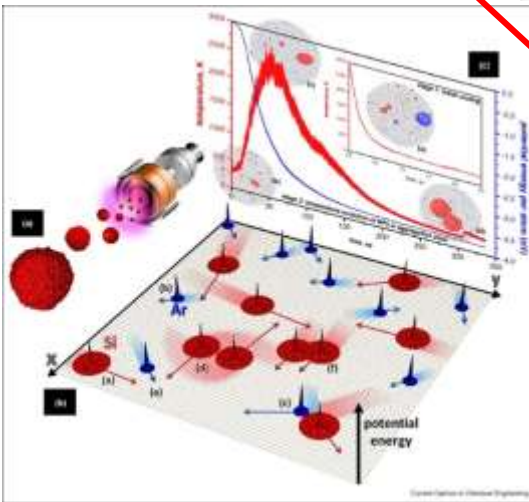
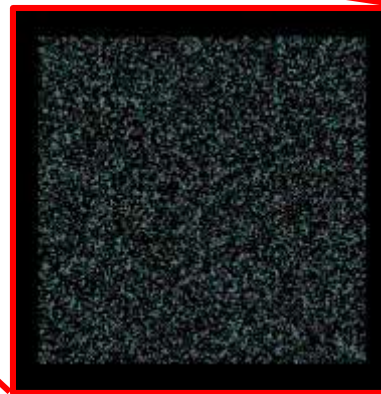
- Metal vapor density in the aggregation chamber

$$N_M = (Y_{Ar} I / q) / (\Phi(Ar) \cdot P_{at} / P_{Ar})$$

→ will give the proper ratio of  $N_M / N_{Ar}$  in the simulation box

- Collision number identical in experiments and in simulation

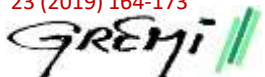
$$i.e. P_{exp} \cdot d_{exp} = P_{sim} \cdot d_{sim}$$



$$N_{Ar} = 128000; N_{Pt} = 19200; N_{Ni} = 6400; N_{Au} = 6400$$

$$\text{Box size } 64 \times 64 \times 64 \text{ nm}^3; dt = 1 \text{ fs}, 4 \cdot 10^7 \text{ timesteps}$$

A. Caillard et al, PdPt catalyst synthesized using a gas aggregation source and magnetron sputtering for fuel cell electrodes, J. Phys. D: Appl. Phys. 48 (2015) 475302  
 E Quesnel et al Modeling metallic nanoparticle synthesis in a magnetron-based nanocluster source by gas condensation of a sputtered vapor, J. Appl. Phys. 107 (2010) 054309  
 P. Brault, et al, Pt<sub>3</sub>MeAu (Me = Ni, Cu) fuel cell nanocatalyst growth, shapes and efficiency: A molecular dynamics simulation approach, J. Phys. Chem. C 123 (2019) 29656 – 29664  
 P. Grammatikopoulos, Atomistic modeling of the nucleation and growth of pure and hybrid nanoparticles by cluster beam deposition, Current Opinion in Chemical Engineering 23 (2019) 164-173

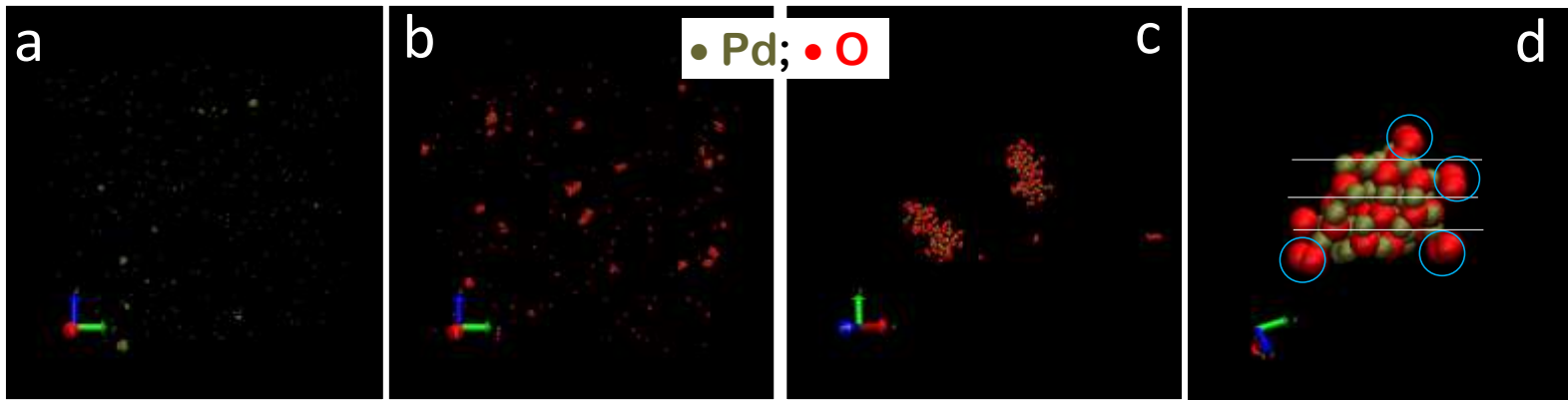




# Plasma processing & MD: Nanoparticle growth

## Reactive free PdO nanocatalyst growth

ReaxFF reactive variable charge potentials for Pd sputtering in Ar-O<sub>2</sub> gas mixture

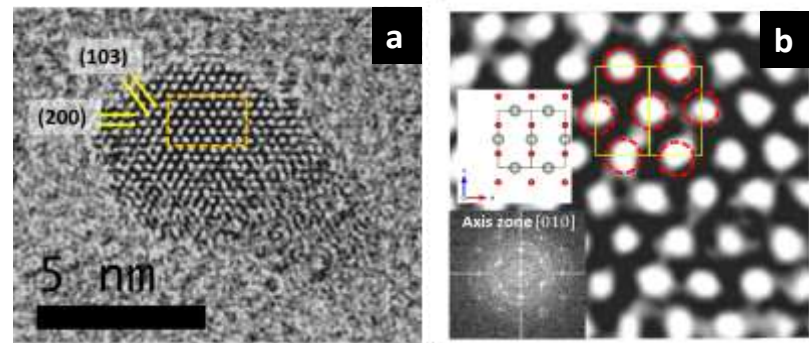


Snapshot of (a-b) the overall Pd and PdO clusters at 25 ns simulation time (c-d) of the detailed PdO clusters.

First results: O addition -> no more free Pd, more PdO than Pd clusters

Ratio of  $N_{Ar}$  to  $N_{metal}$  estimated from experiments = 40 here;  
 $N_{Ar} = 20000$ ;  $N_{Pd} = 500$ ;  $N_{O} = 1000$ ; Box size : 40 x 40 x 40 nm<sup>3</sup> Integration time 0.25 fs → 1. 10<sup>8</sup> iterations

■ GAS Experiments, W. Chamorro-Coral et al



ReaxFF Potential: T. Senftle et al, J. Chem Phys 139 (2013) 044109

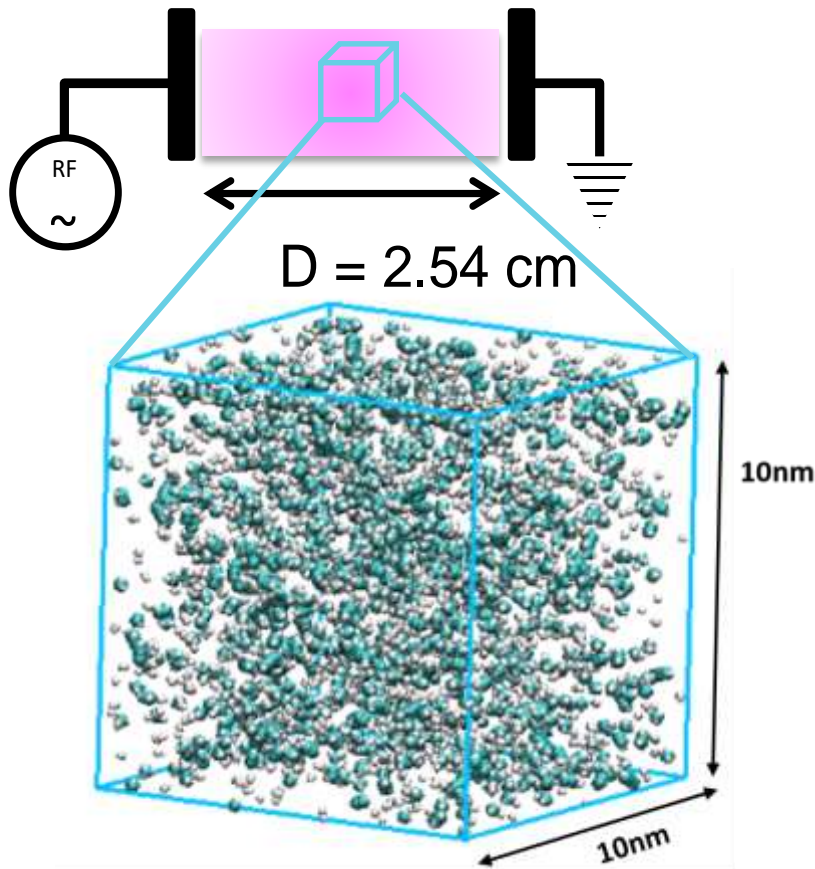
P. Brault et al. , Frontiers in Chemical Science and Engineering Frontiers of Chemical Science and Engineering 13 (2019) 324 – 329

W. Chamorro-Coral et al, Plasma Processes and Polymers 16 (2019) e1900006



# Plasma processing & MD: Hydrocarbon plasmas

- Initial conditions issued from 1D fluid model of Ar/4% CH<sub>4</sub>  
→ RF plasma,  $P = 70 \text{ Pa}$ ,  $V_b = 100 \text{ V}$  (\*)



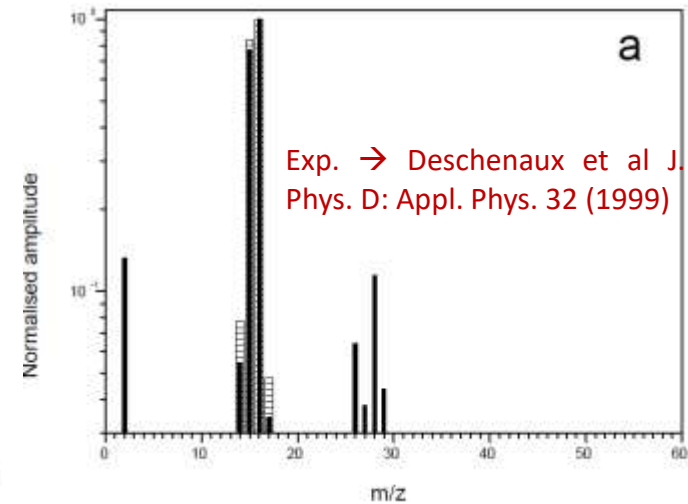
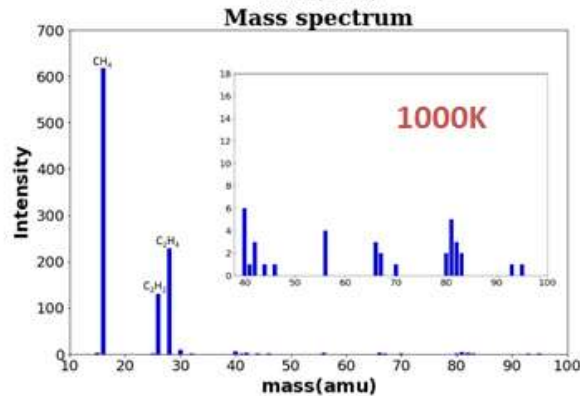
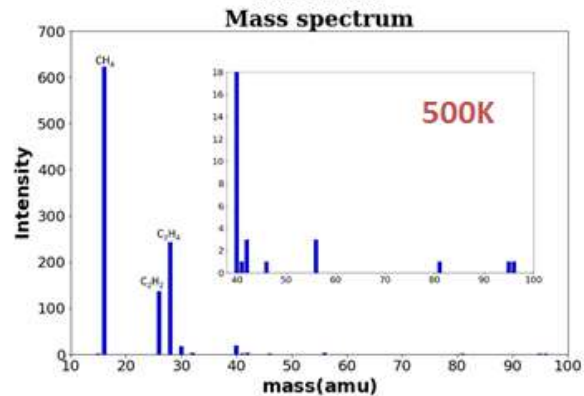
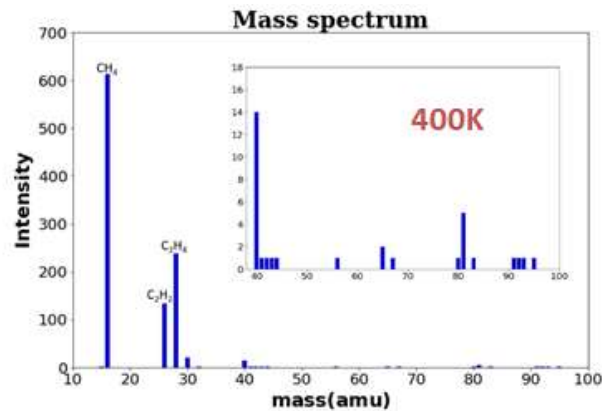
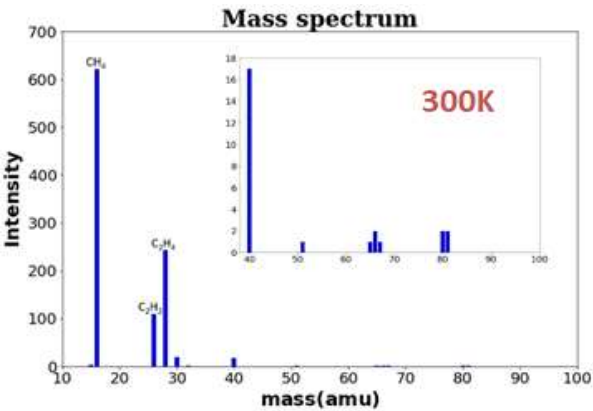
Neutral species	Molar ratio	Molecule number in sim box
CH <sub>4</sub>	$1.4 \cdot 10^{-2}$	630
H <sub>2</sub>	$3.2 \cdot 10^{-2}$	1440
C <sub>2</sub> H <sub>4</sub>	$5.3 \cdot 10^{-3}$	243
C <sub>2</sub> H	$3.2 \cdot 10^{-3}$	144
C <sub>2</sub> H <sub>2</sub>	$2.7 \cdot 10^{-3}$	122
CH <sub>3</sub>	$2.3 \cdot 10^{-3}$	104

(\*) G. Têtard et al, Discharge dynamics, plasma kinetics and gas flow effect in argon-acetylene discharges, PSST 30 (2021) 105015

S. Prasanna et al, Self-consistent simulation studies on effect of methane concentration on microwave assisted H<sub>2</sub>-CH<sub>4</sub> plasma at low pressure, Plasma Sources Sci. Technol. 26 (2017) 097001



# Plasma processing & MD: Hydrocarbon plasmas

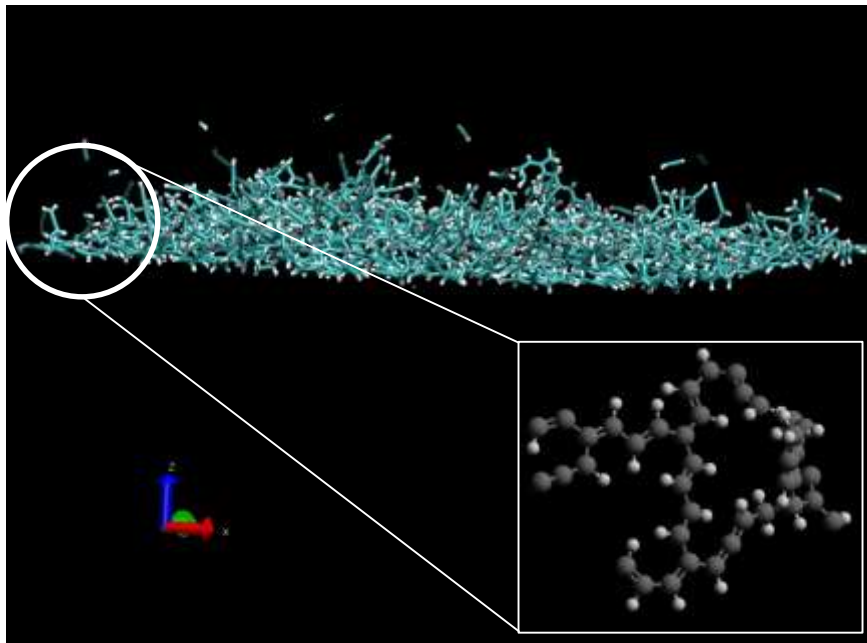


- The species  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ , are the more abundant.
- Higher mass  $\text{C}_n\text{H}_m$ ,  $n > 3$  have been identified. Among them aromatic compounds are growing above  $t = 500\text{K}$

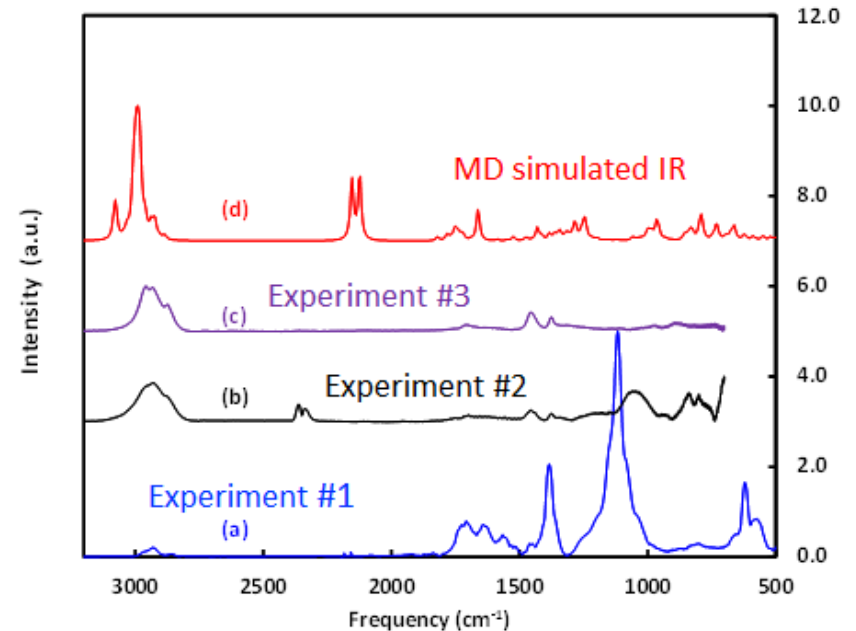


# Plasma processing & MD: Hydrocarbon plasmas

## ■ Pure acetylene plasma deposition



Experiment	C <sub>2</sub> H <sub>2</sub> flow (sccm)	Pressure (mbar)	Support electrode
#1	10	0.01	grounded
#2	10	0.2	powered
#3	10	0.2	grounded



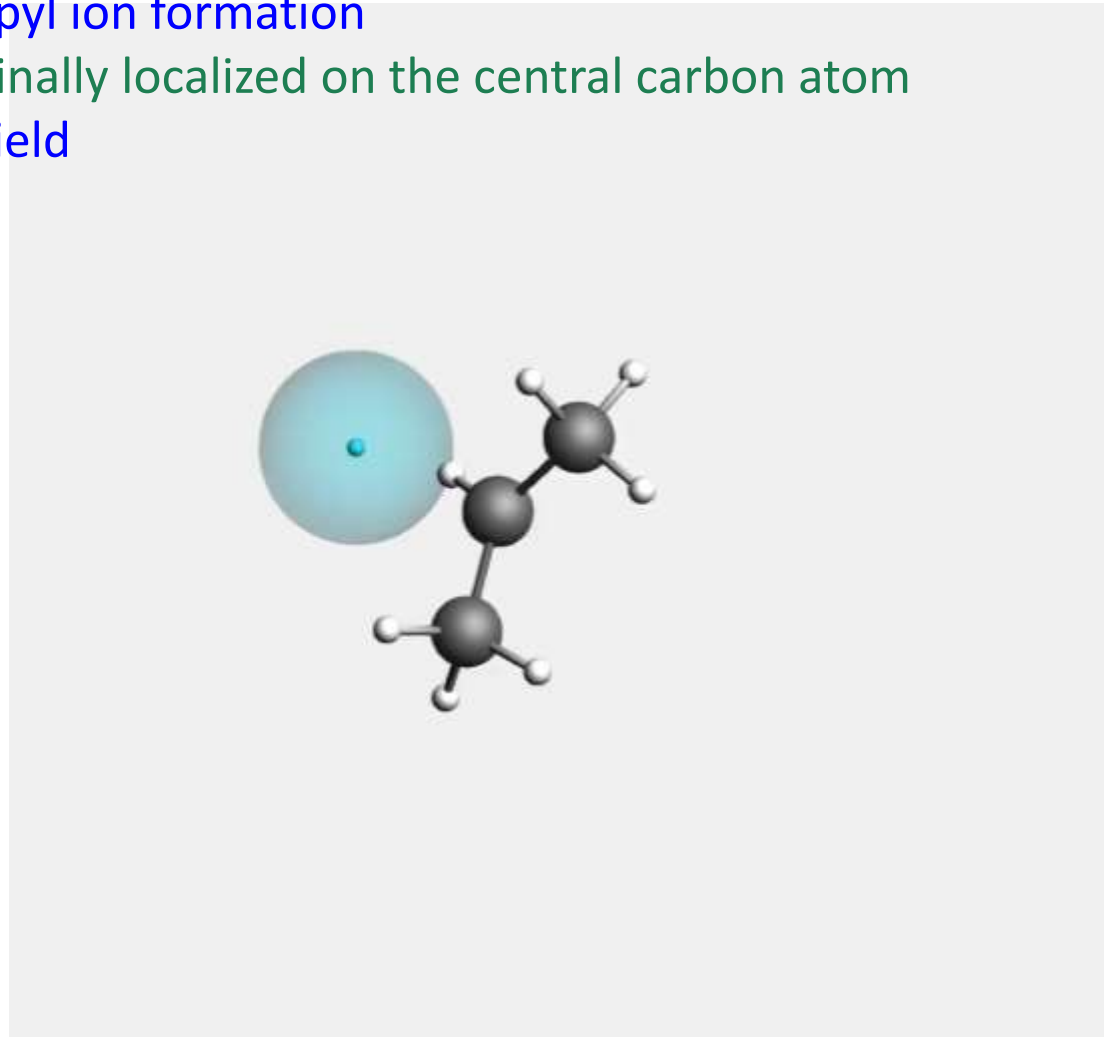
## ■ Close comparison with experiments requires consistent initial conditions

P. Brault, M. Ji, D. Sciacqua, F. Poncin-Epaillard, J. Berndt, Eva Kovacevic, Insight into acetylene plasma deposition using molecular dynamics simulations, Plasma Processes and Polymers 19 (2021) <https://onlinelibrary.wiley.com/doi/full/10.1002/ppap.202100103>



# Plasma processing & MD: electron attachment

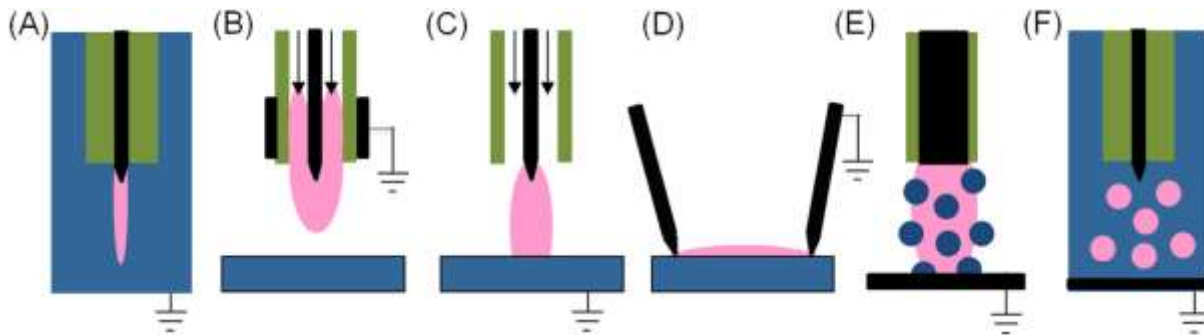
- Negative isopropyl ion formation
- the electron is finally localized on the central carbon atom
- e-reaxFF force field



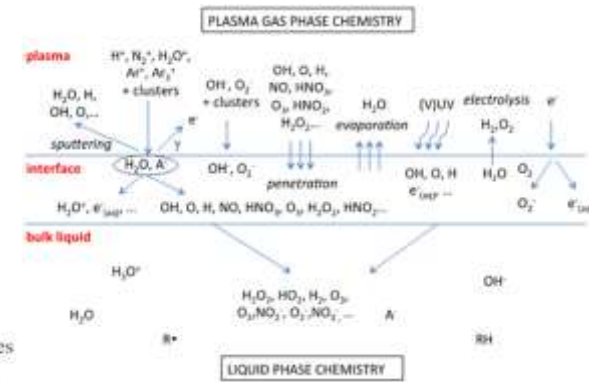


# Plasma processing & MD: Wastewater treatment

- Within the scope of plasma-liquid interactions



**Figure 2.** Schematic of different discharges used in plasma-liquid interactions: (A) direct discharge in liquid, (B)–(D) gas phase discharges and (E) and (F) multiphase discharges. In more detail: (B) plasma jet without direct contact with liquid, (C) gas-phase plasma with liquid electrode, (D) surface discharge, (E) gas phase plasma with dispersed liquid phase (aerosols) and (F) discharges in bubbles. Blue = liquid, pink = plasma, green = dielectric, black = metal electrodes.



- Non Thermal Plasma at Atmospheric Pressure (NTPA) is creating oxidizing species (RONS) expected to interact with organic pollutant in water

- Efficiently degrade the parent molecule to non-toxic products
- Optimize (plasma) process: requires knowledge of oxidation chemistry in water : reactants, reaction products, pathways and selectivity
  - ➔ molecular simulations ?

Samukawa S et al, The 2012 plasma roadmap, J. Phys. D: Appl. Phys. 45 (2012) 253001

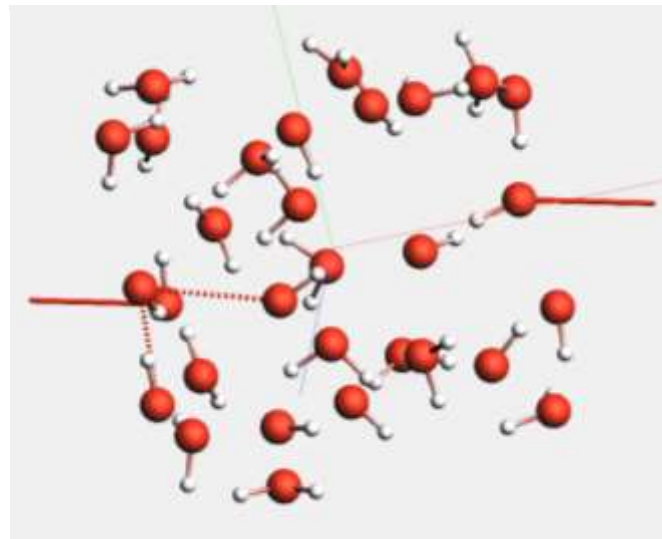
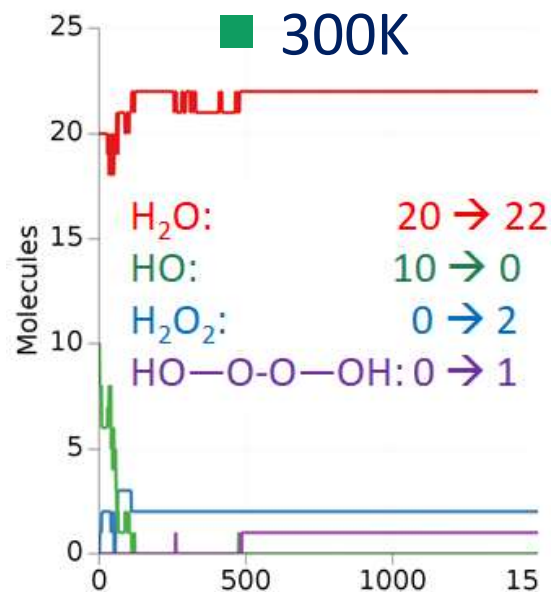
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M Magureanu et al, A review on non-thermal plasma treatment of water contaminated with antibiotics, J Haz. Mat. 417 (2021) 125481

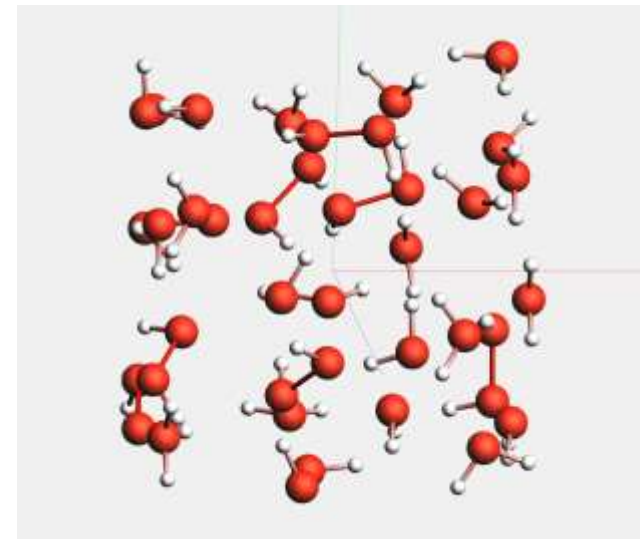


# Plasma processing & MD: Wastewater treatment

- ab-initio MD: calculating interaction potentials on the fly.
- Major drawback: Computer time (very) expensive
- Effect of reactive species (so-called RONS), generated by the plasma in air, on the liquid



■ 10 HO + 20 H<sub>2</sub>O  
→ HO quickly reacts



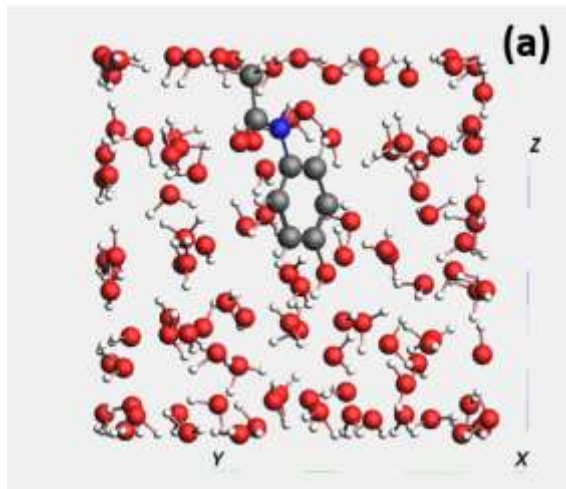
■ 5 H<sub>2</sub>O<sub>2</sub> + 20 H<sub>2</sub>O  
→ very stable



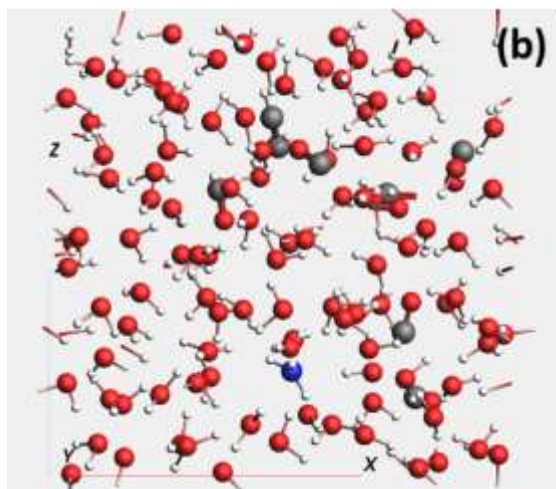


# Plasma processing & MD: Wastewater treatment

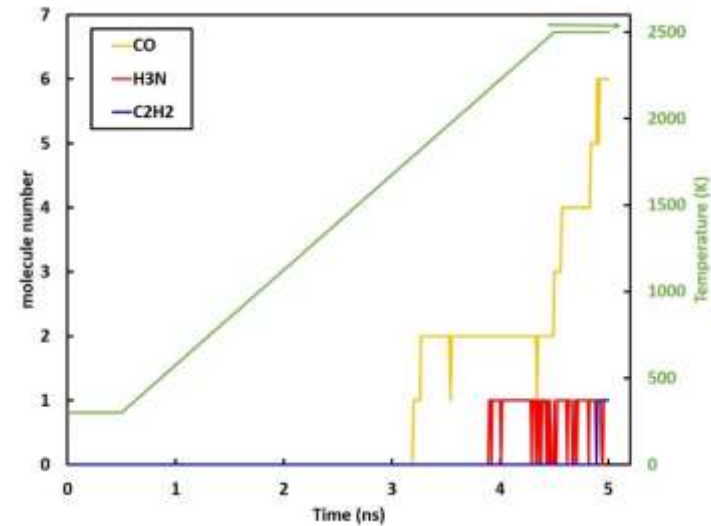
- 1<sup>st</sup> strategy: apply temperature ramp in a mixture of pollutant molecule + reactive radical + water.
- 100 H<sub>2</sub>O + 10 HO· + 1 paracetamol Exp. → 6 · 10<sup>16</sup> cm<sup>-3</sup> C<sub>6</sub>H<sub>6</sub>NO<sub>5</sub> / HO· 10<sup>18</sup> cm<sup>-3</sup>



Initial configuration



Final configuration (5 ns)



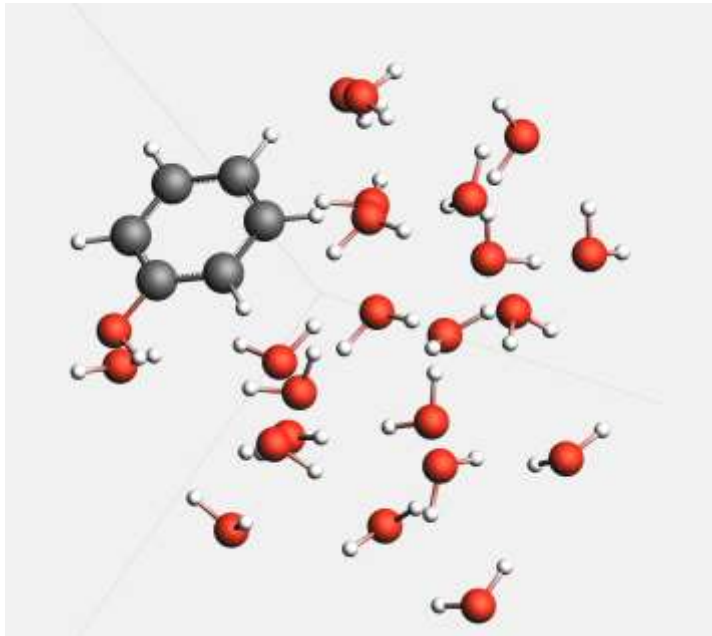
Final products:

6 CO, 1 C<sub>2</sub>H<sub>2</sub>, 1  
NH<sub>3</sub>, 103 H<sub>2</sub>O, 1 H<sub>2</sub>,  
1 H<sub>3</sub>O

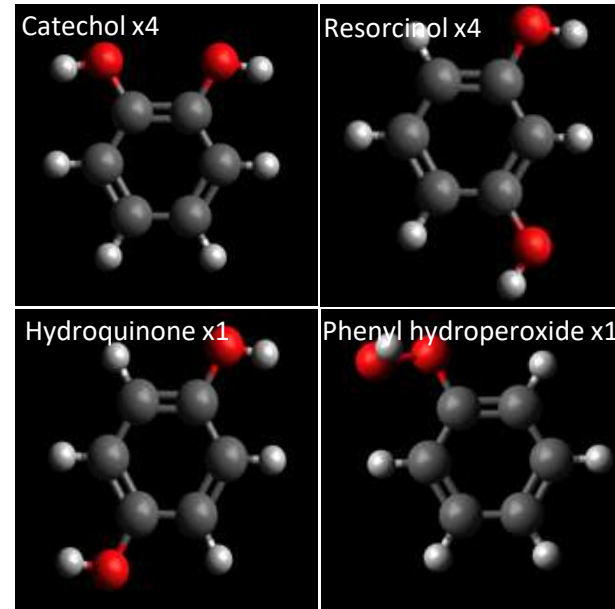


# Plasma processing & MD: Wastewater treatment

- 2<sup>nd</sup> strategy: inject periodically reactive radical in water with pollutant molecule.
- 15 H<sub>2</sub>O + 10 HO· + 1 phenol. ab-initio MD → minimal simulation box
- 10 runs with different initial conditions:
  - Different initial random positions and velocities in MB distribution (300K) of phenol and water



## ■ Intermediate products

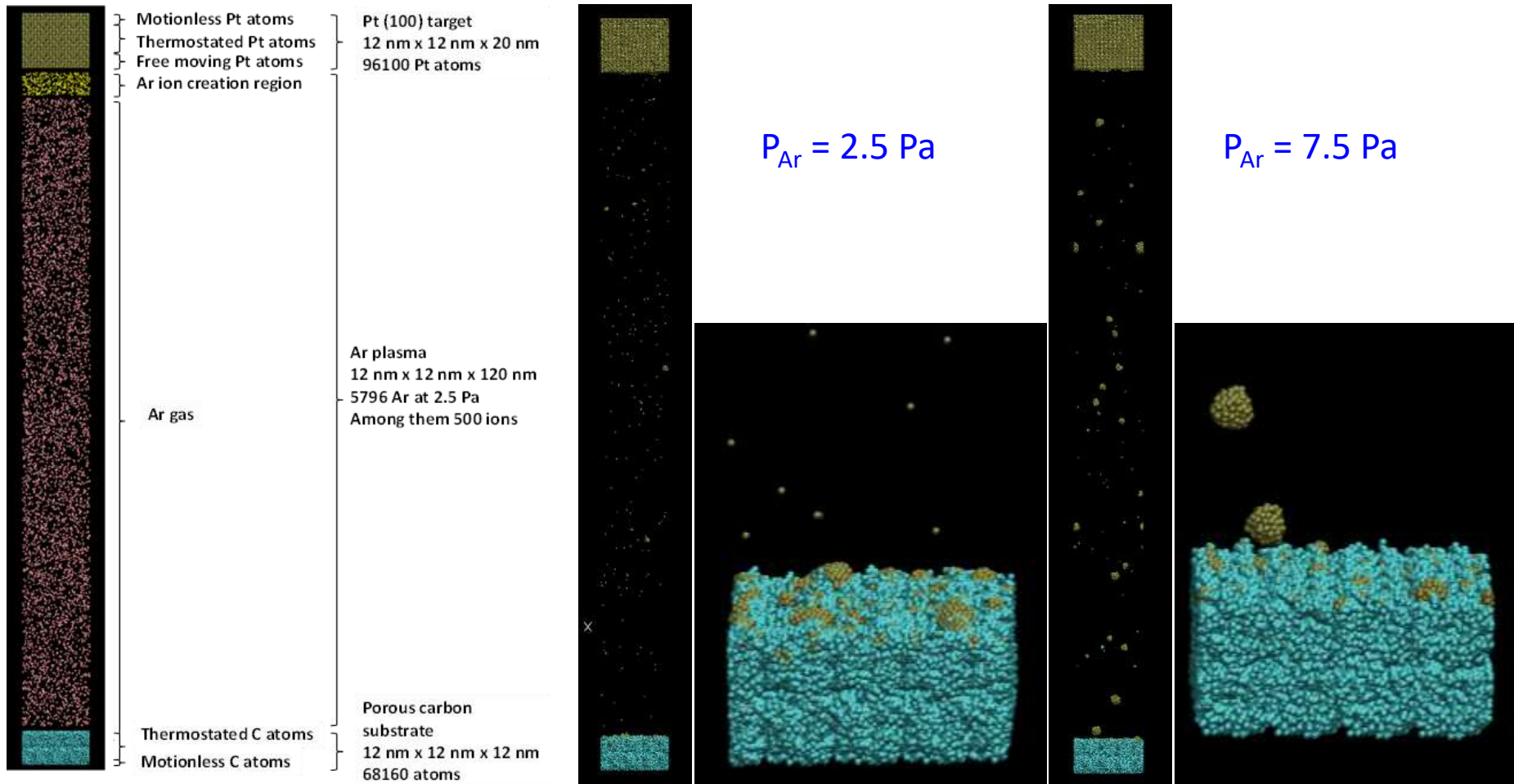


- Consistent with experiments



# Next step as Conclusion

## → MD simulations of plasma processing as a whole



P. Brault, Multiscale Molecular Dynamics Simulation of Plasma Processing: *Application to Plasma Sputtering*, Front. Phys. 6 (2018) 59

P Brault, Multiscale Molecular Dynamics Simulations of Fuel Cell Nanocatalyst Plasma Sputtering Growth and Deposition, Energies 13 (2020) 3584



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