Molecular dynamics simulations of nanoparticle growth … and beyond

Pascal Brault

GREMI, UMR7344 CNRS Université d'Orléans,

Orléans, France

pascal.brault@univ-orleans.fr

http://www.univ-orleans.fr/gremi/pascal-brault

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Outline

- Practical MD simulations
- Supported nanoparticle growth
- Free nanoparticle growth in a Gas Agregation Source
- Hydrocarbon plasma soot growth
- MD simulations of plasma processing as a whole
- Conclusions/Future works

Practical Molecular Dynamics simulation

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

and

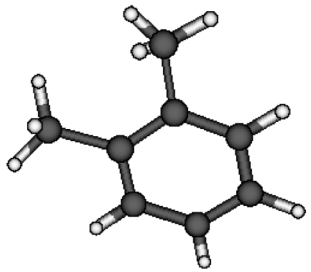
$$\vec{F}_i = -\vec{\nabla}_{ri} U\left(\vec{r}_1, \vec{r}_2, \vec{r}_3, \cdots, \vec{r}_N\right)$$

- ✓ **Calculate all trajectories of a set of atoms, molecules, ...**
  via the Newton equation of motion
  → Suitable for processes at nanoscale (up to 10^9 atoms)

- ✓ **A rigourous approach requires the use of robust interaction potentials and initial conditions (positions, velocities) preferably matching experimental conditions**
  → appropriate velocity distribution functions can be derived from experimental conditions.

- ✓ **Proper energy dissipation:**
  - **Energy release during bond formation : deposition, bond formation/breaking**
  - **Annealing**

  → via friction term(s), thermostat(s)



Practical Molecular Dynamics simulation

Relevance/significance of MD Simulations

Flux :

Exp. 1 $10^{15} cm^{-2} s^{-1}$ = 10 species / nm^2 / s - MD 1 specie /10x10 nm^2 / 2 ps

Prohibit long time diffusion, except if including specific strategies (fbMC, CVHD, hyperdynamics, …)

Pressure/simulation box size

Solid density : Pt 65 nm^{-3} → Can be treated. Diffusion coefficients can be calculated without additional approximation(s)

Liquid density: water 33 nm^{-3}

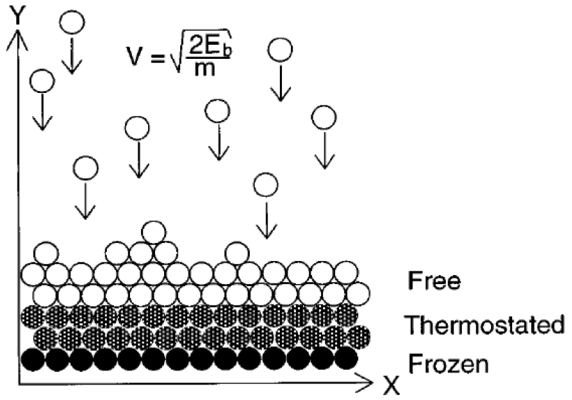
Gas density : 1 atm = 2.4 10^{-2} nm^{-3} → Not enough species in box of size d at pressure P

Solution: relevant parameter = Collision number $\propto$ P.d

→ ↑P ↓d should work.

Thermal relaxation

- Choose a relevant specie release time: i.e. greater than thermalisation time
- Choose a relevant thermostat (region i.e. what should be thermostated) within this relevant time
- For interactions with surface, one can guess that only the substrate should be thermostated



Practical Molecular Dynamics simulation: Interactions potentials

Metals : Embedded Atom Method (EAM)

⇒ energy of a solid is a unique functional of the electron density.

⇒ uses the concept of electron (charge) density to describe metallic bonding:

⇒ each atom contributes through a spherical, exponentially-decaying field of electron charge, centered at its nucleus, to the overall charge density of the system.

⇒ Binding of atoms is modelled as embedding these atoms in this "pool" of charge, where the energy gained by embedding an atom at location r is some function of the local density.

⇒ The total energy thus writes:

$$E_{pot} = \sum_{i=1}^{N} E_i = \frac{1}{2}\sum_{i=1}^{N}\sum_{i,j,i\neq j}^{N}\phi_{ij}(r_{ij}) + \sum_{i=1}^{N} F_i(\rho_i) \qquad \rho = \sum_{j,j\neq 1}^{N} f_i(r_{ij}) \qquad f(r) = \frac{f_e \exp\left[-\beta\left(\frac{r}{r_e}-1\right)\right]}{1+\left(\frac{r}{r_e}-\lambda\right)^{20}}$$

With pairwise function:

$$\phi(r) = \frac{A\exp\left[-\alpha\left(\frac{r}{r_e}-1\right)\right]}{1+\left(\frac{r}{r_e}-\kappa\right)^{20}} - \frac{B\exp\left[-\beta\left(\frac{r}{r_e}-1\right)\right]}{1+\left(\frac{r}{r_e}-\lambda\right)^{20}}$$

and mixing rule:

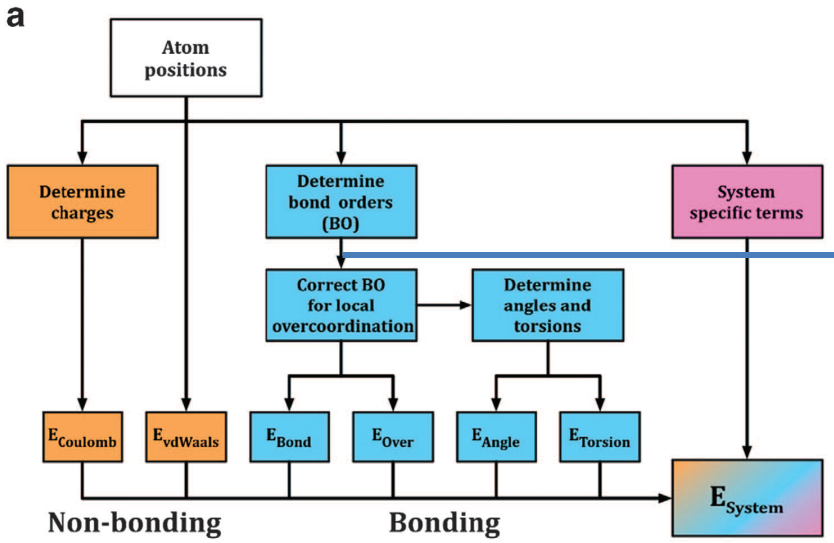
$$\phi^{ab}(r) = \frac{1}{2}\left[\frac{f^b(r)}{f^a(r)}\phi^{aa}(r) + \frac{f^a(r)}{f^b(r)}\phi^{bb}(r)\right]$$

S.M. Foiles, M.I. Baskes Contributions of the embedded-atom method to materials science and engineering, MRS Bulletin, 37 (2012) 485-491.
X. W. Zhou et al, Misfit-energy-increasing dislocations in vapor-deposited CoFe/NiFe multilayers, Phys. Rev. B 69 (2004) 144113

Practical Molecular Dynamics simulation: Interactions potentials

ReaxFF allows for computationally efficient simulation of materials under realistic conditions, *i.e.* bond breaking and formation with accurate chemical energies. It also includes variable partial charges.

Due to the chemistry, ReaxFF has a complicated potential energy function: $E_{system} = E_{bond} + E_{over} + E_{angle} + E_{tors} + E_{vdWaals} + E_{Coulomb} + E_{Specific}$



Overview of the ReaxFF total energy components

$$BO_{ij} = BO_{ij}^{\sigma} + BO_{ij}^{\pi} + BO_{ij}^{\pi\pi}$$
$$= \exp\left[p_{bo1}\left(\frac{r_{ij}}{r_o^{\sigma}}\right)^{p_{bo2}}\right] + \exp\left[p_{bo3}\left(\frac{r_{ij}}{r_o^{\pi}}\right)^{p_{bo4}}\right]$$
$$+ \exp\left[p_{bo5}\left(\frac{r_{ij}}{r_o^{\pi\pi}}\right)^{p_{bo6}}\right]$$

Correct Bond Order ⇒ Correct description of reaction energy barriers

TP Senftle et al, *The ReaxFF reactive force-field: development, applications and future directions*, npj Computational Materials 2, (2016) 15011

Supported Pt_2PdAu nanocatalyst growth on porous carbon: Pt, Pd, Au co-deposition

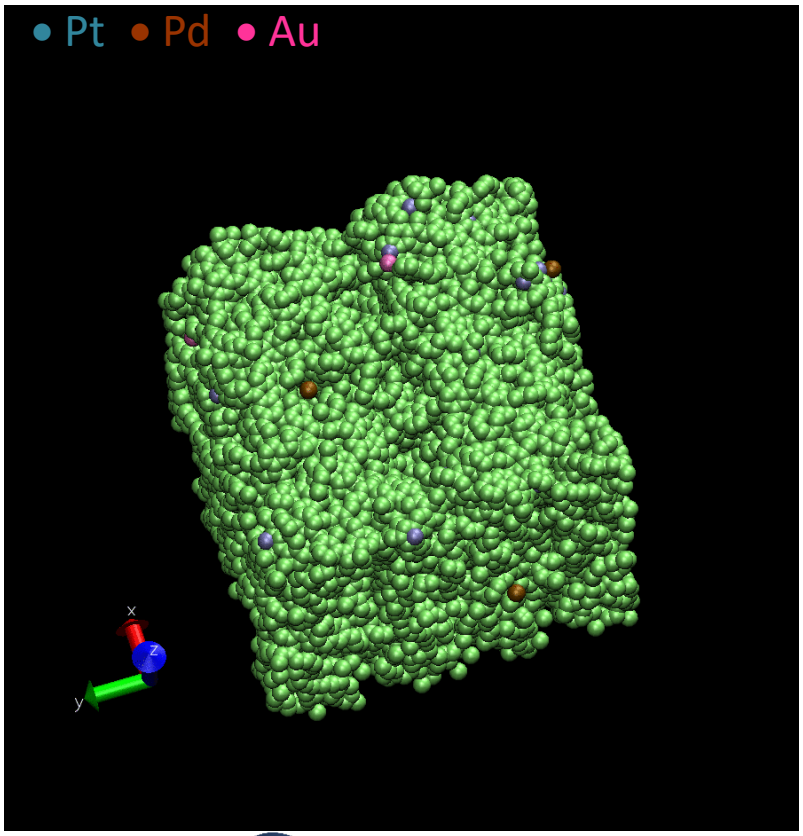
Potentials used in the system:

Pt-Pd-Au: EAM potentials

C – C: Tersoff potential -> thermostat

Metal – C: LJ potential (Steele)

Model porous carbon from TEM measurements



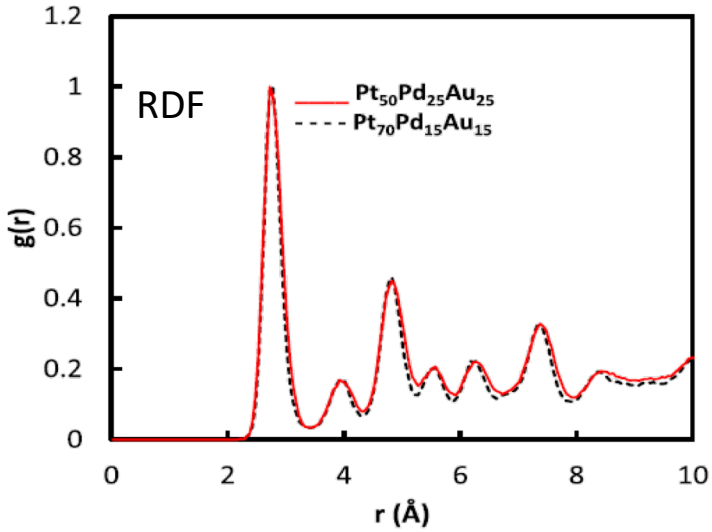


Table 1 – EAM and average experimental surface energies of the low index faces of Pt, Pd, Au in Jm^{-2} [40].

	Pt	Pd	Au
(111)	1.44	1.22	0.79
(100)	1.65	1.37	0.92
(110)	1.75	1.49	0.98
Experimental, face averaged	2.49	2.00	1.5

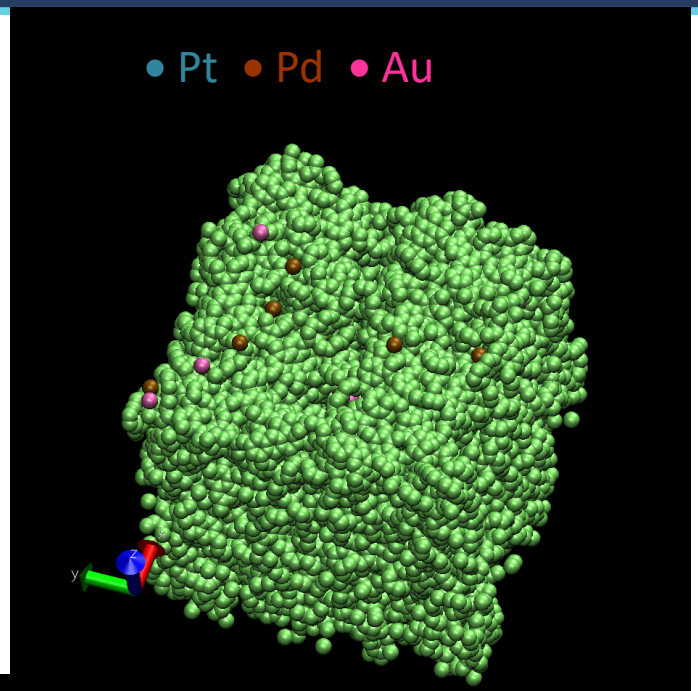
- Gold surface segregation

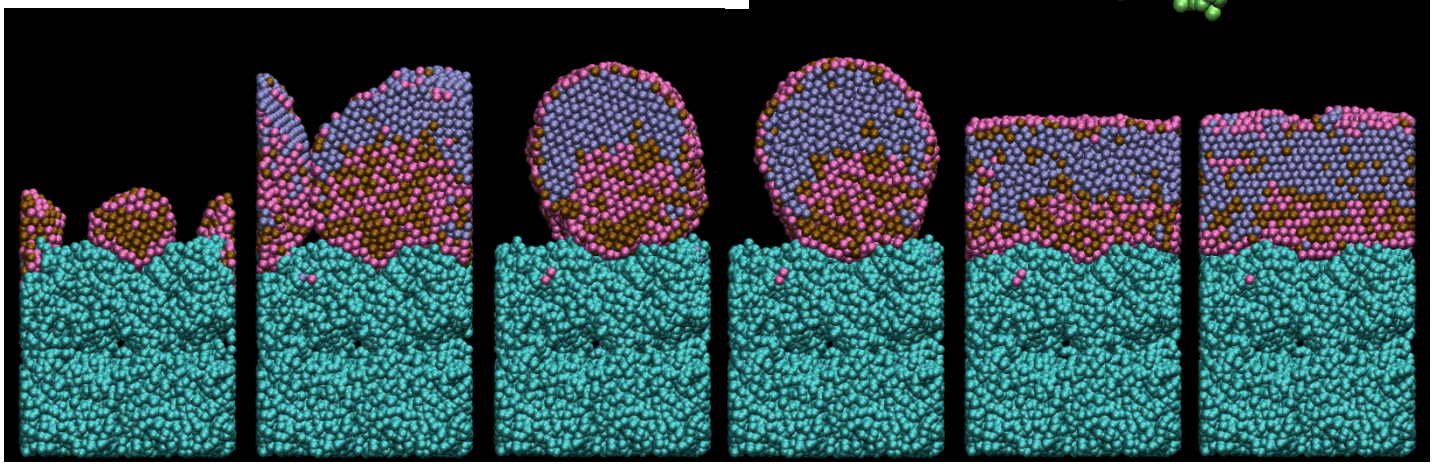
P. Brault, Molecular dynamics simulations of ternary PtxPdyAuz fuel cell nanocatalyst growth, International Journal of Hydrogen Energy 41 (2016) 22589-22597

Supported Pt_2PdAu nanocatalyst growth on porous carbon: Sequential PdAu deposition followed by Pt deposition

→ $AuPd@Pt_2$ core@shell

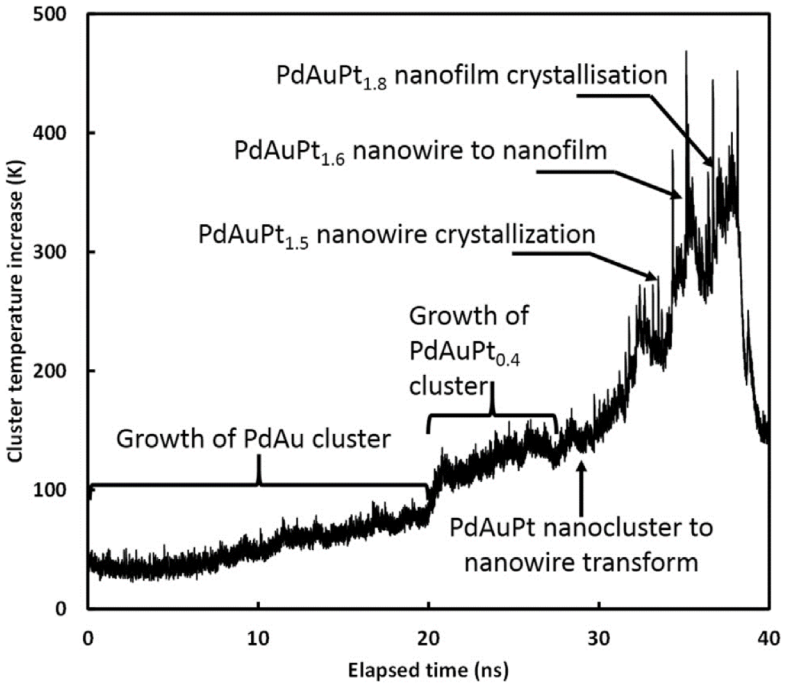
But always Au segregation towards surface!

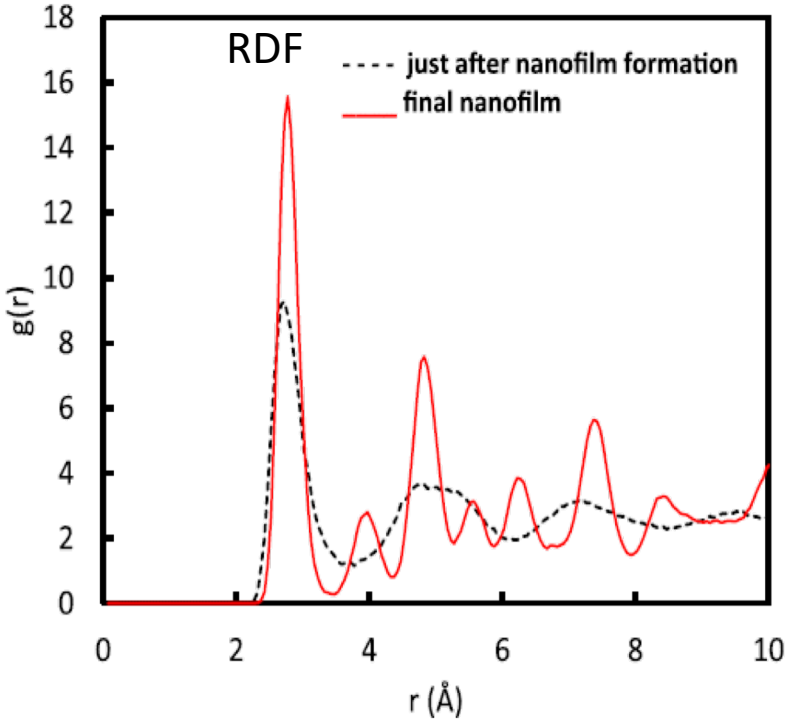




Molecular dynamics simulation of sputtering plasma catalysts growth: Supported Pt_2PdAu nanocatalyst growth on porous carbon

Correlations between cluster temperature evolution and morphology transform in the course of deposition of core-shell $PdAu@Pt_2$ nanocatalyst

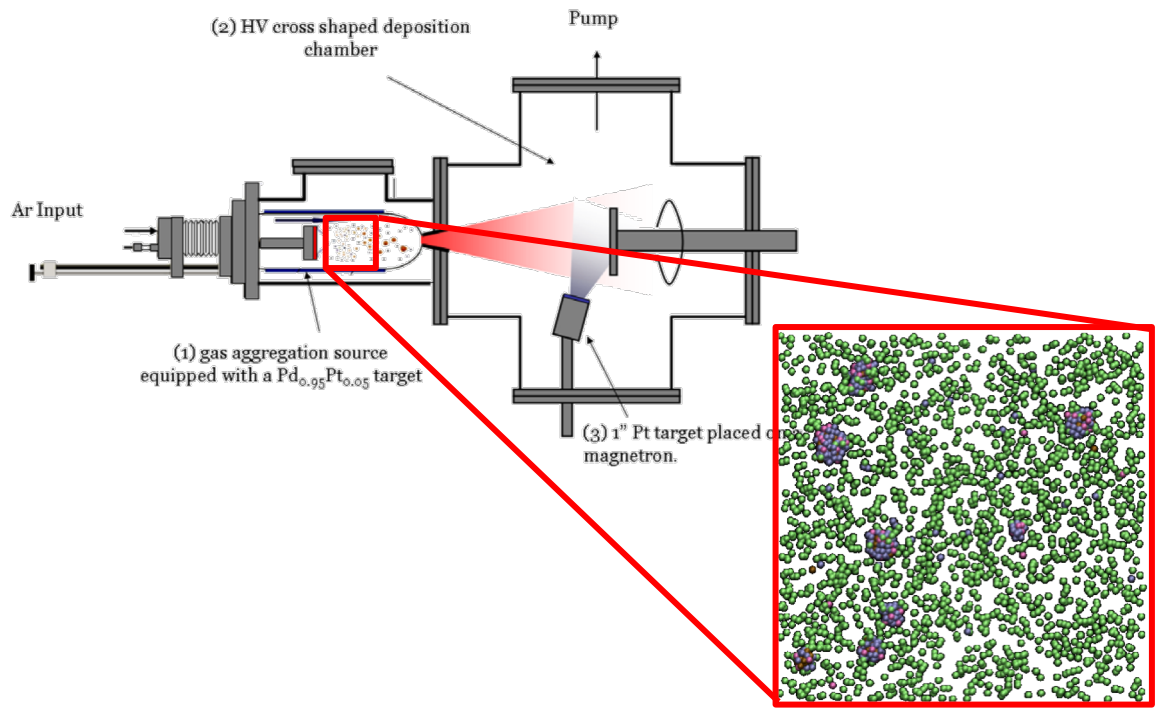




- L. Xie, P. Brault, C. Coutanceau, A. Caillard, J. Berndt, E. Neyts Appl. Cat. B, 62 (2015) 21 – 26
- P. Brault, et al, International Journal of Hydrogen Energy 41 (2016) 22589-22597
- E. Neyts, P. Brault, Plasma Processes and Polymers 14 (2017) 1600145 - FP7 FCH-JU SMARTCat project #325327

Free nanoparticle growth in a Gas Agregation Source

Gas agregation source: simulation principles



Matching experimental and simulation conditions

- Metal vapor density in the aggregation chamber

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

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

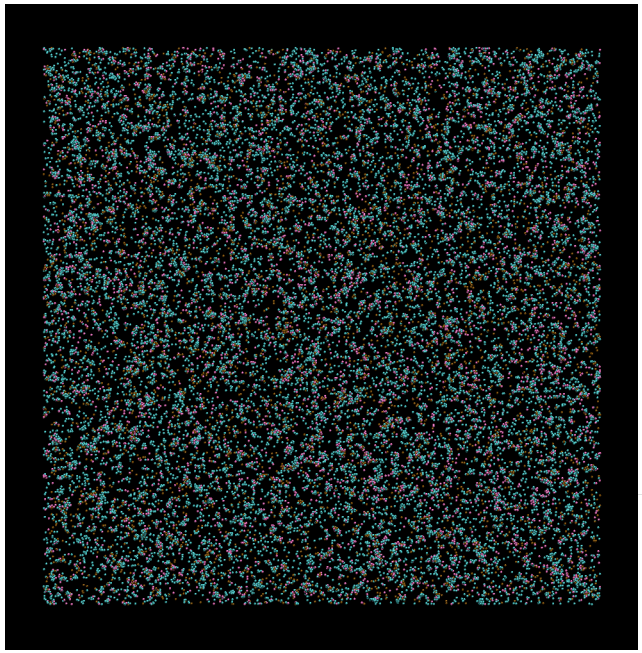
- Collision number identical in experiments and in simulation

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

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

Free $Pt_3Me(Au)$ (Me = Ni, Cu) nanocatalyst growth



Tricks :

NVE ensemble for Pt, Ni and Au

NVT ensemble for Ar : surrounding gas is the thermostat

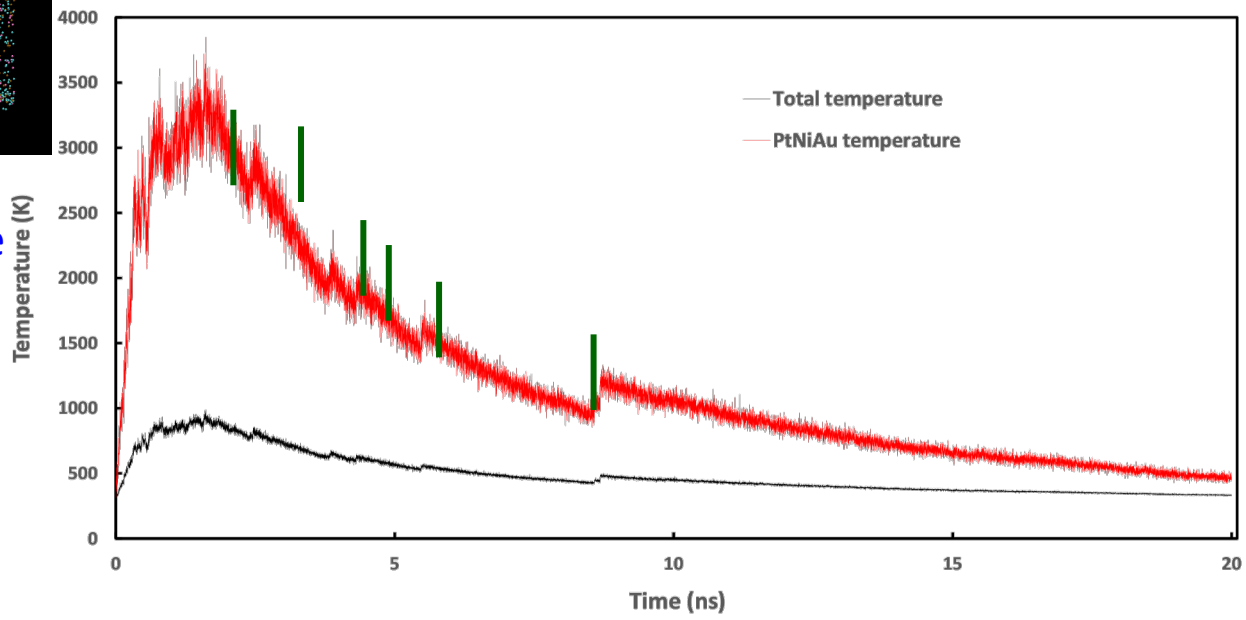
Ratio of N_{Ar} to N_{metal} estimated from experiments: depends on discharge current, Ar pressure, …

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

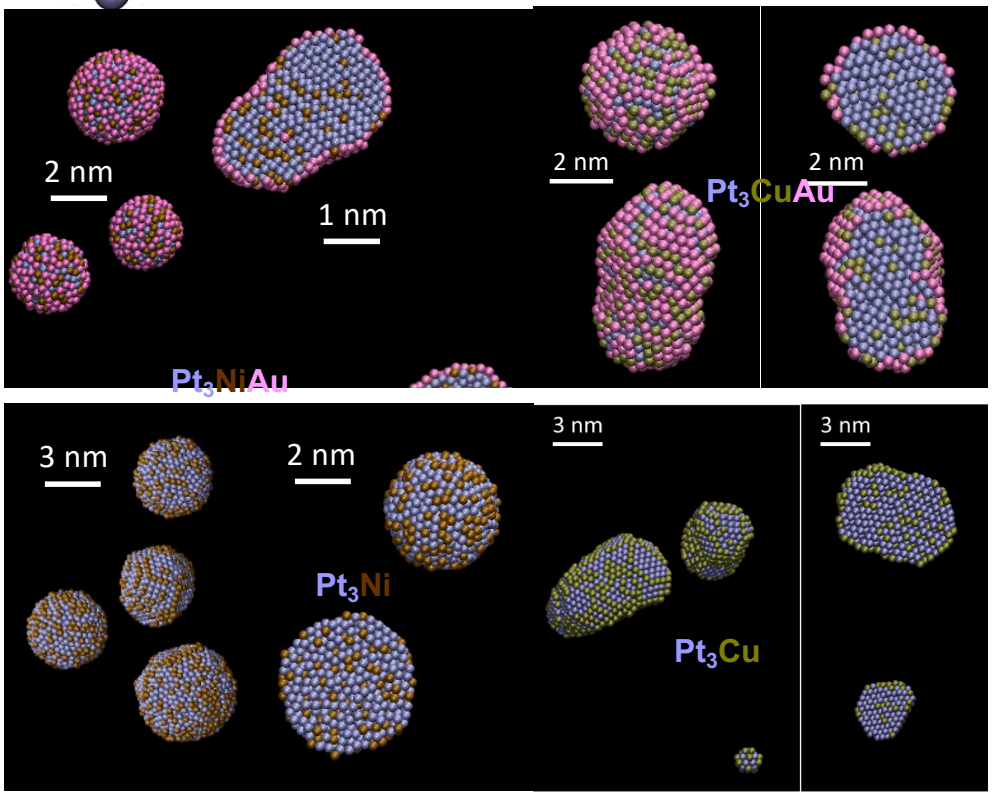
Box size 64x64x64 nm^3; dt = 1 fs, 4. 10^7 timesteps

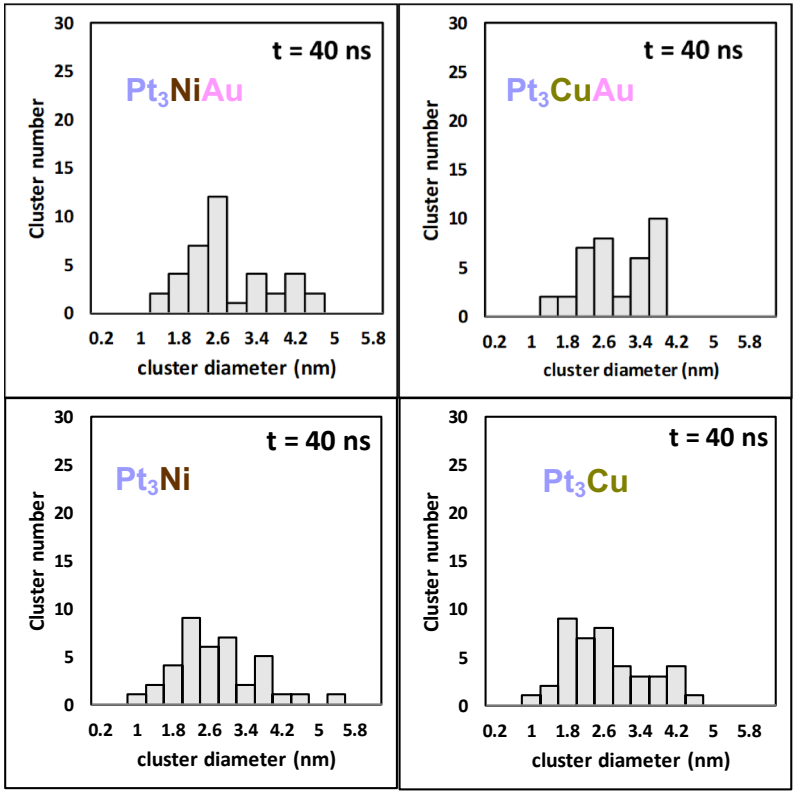
Temperature evolution of the vapor and of the metal vapor and then of clusters the

→cluster growth and coalescence : breaks in the plot (green vertical sticks)



Free $Pt_3Me(Au)$ (Me = Ni, Cu) nanocatalyst growth





- Au segregation towards cluster surface
- CuAu surface alloy for Pt_3CuAu → better efficiency for Oxygen Reduction Reaction
- $Pt_3Cu(Au)$ more well crystallized

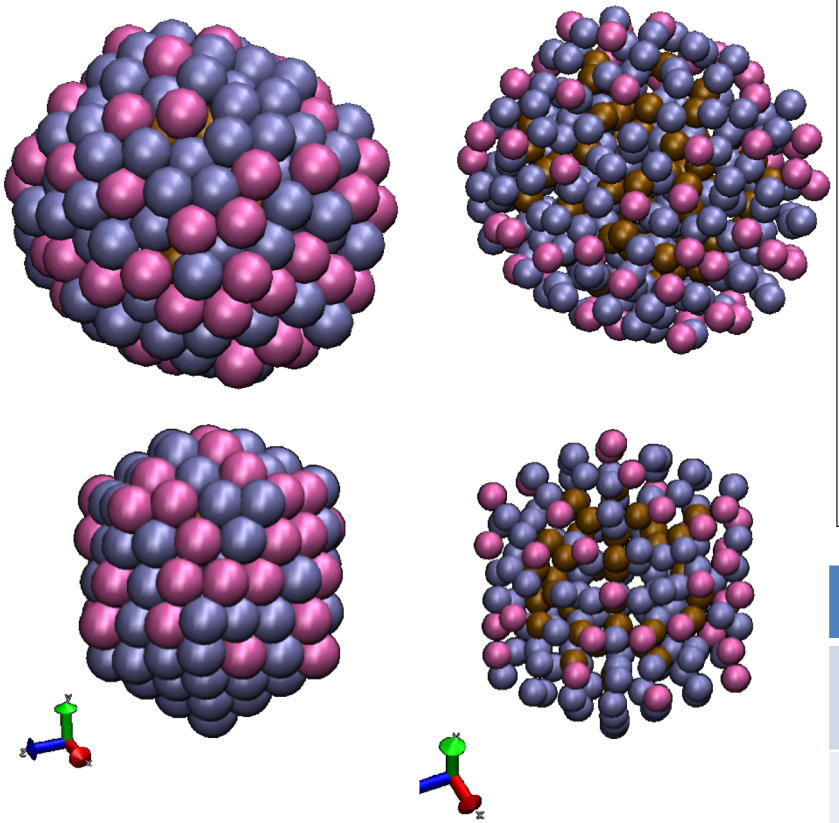
P. Brault, et al, Pt_3MeAu (Me = Ni, Cu) fuel cell nanocatalyst growth, shapes and efficiency: A molecular dynamics simulation approach, J. Phys. Chem. C 123 (2019) 29656 – 29664

Free $Pt_3Me(Au)$ (Me = Ni, Cu) nanocatalyst growth

Cluster 1 (318 at.) : cuboctahedron ?

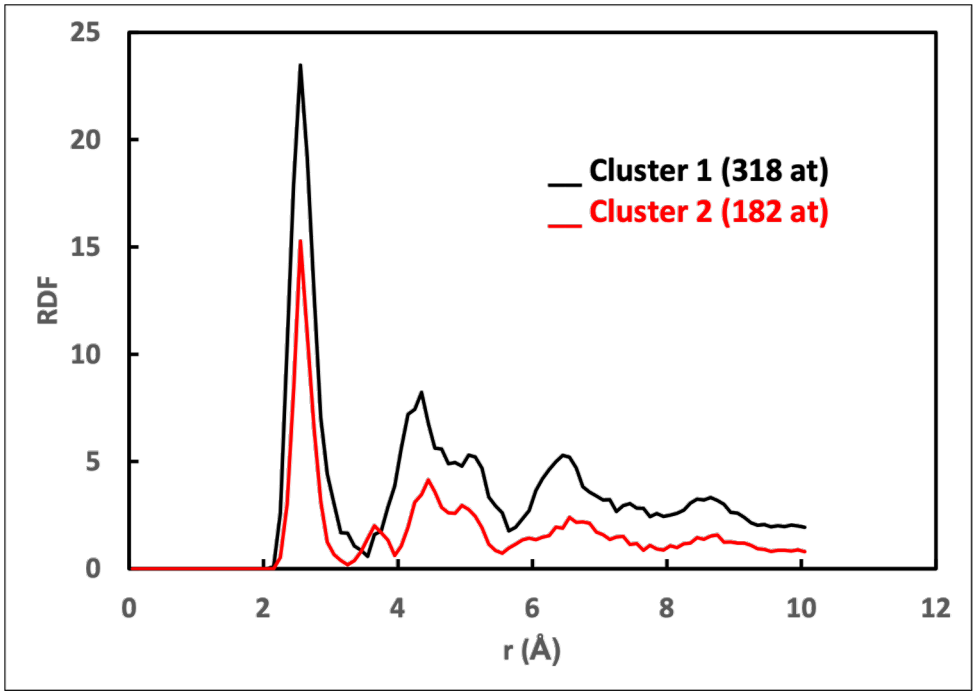
$Pt_{189}Ni_{62}Au_{67} \approx Pt_3NiAu$

• Pt; • Ni; • Au



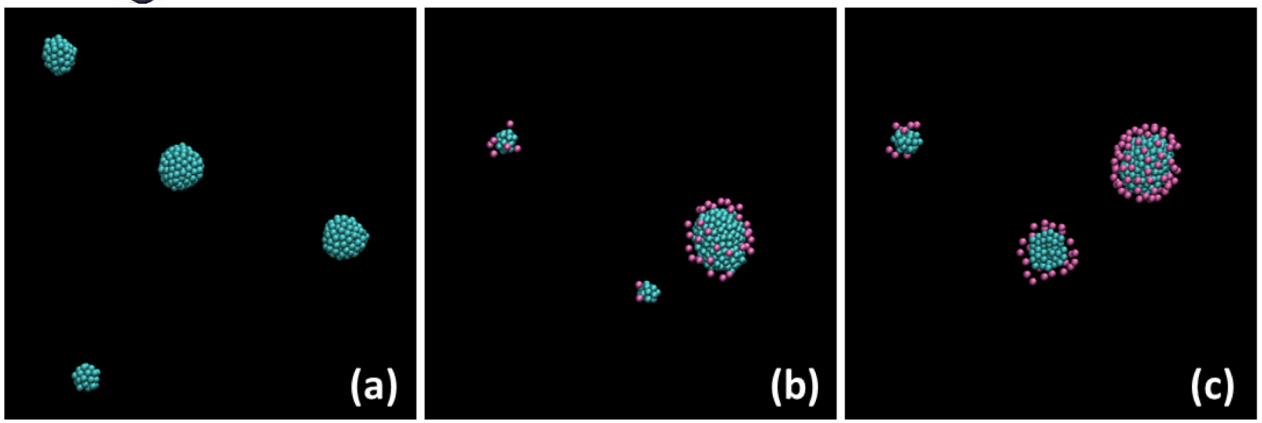
Cluster 2 (182 at.) : icosahedron ?

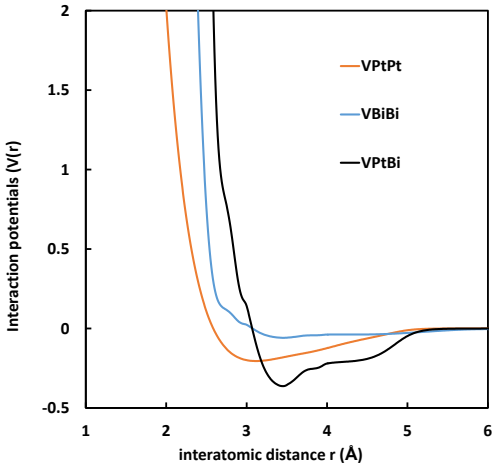
$Pt_{111}Ni_{38}Au_{33}$



	1st NN	2nd NN	3rd NN
Theoretical (fcc) 0.6Pt+0.2Ni+0.2Au	2.738 Å	3.872 Å	4.74 Å
Cluster 1	2.55 Å	(3.75 Å)	4.35 Å
Cluster 2	2.55 Å	3.65 Å	4.45 Å

Pt_xBi_y nanocatalyst growth





Snapshot of the final clusters at 20 ns. Argon atoms (4000) are not represented for clarity. $n_{Pt} + n_{Bi} = 500$. (a) Pt alone (b) Pt_9Bi_1 (c) Pt_8Bi_2. Box size 16x16x16 nm^3

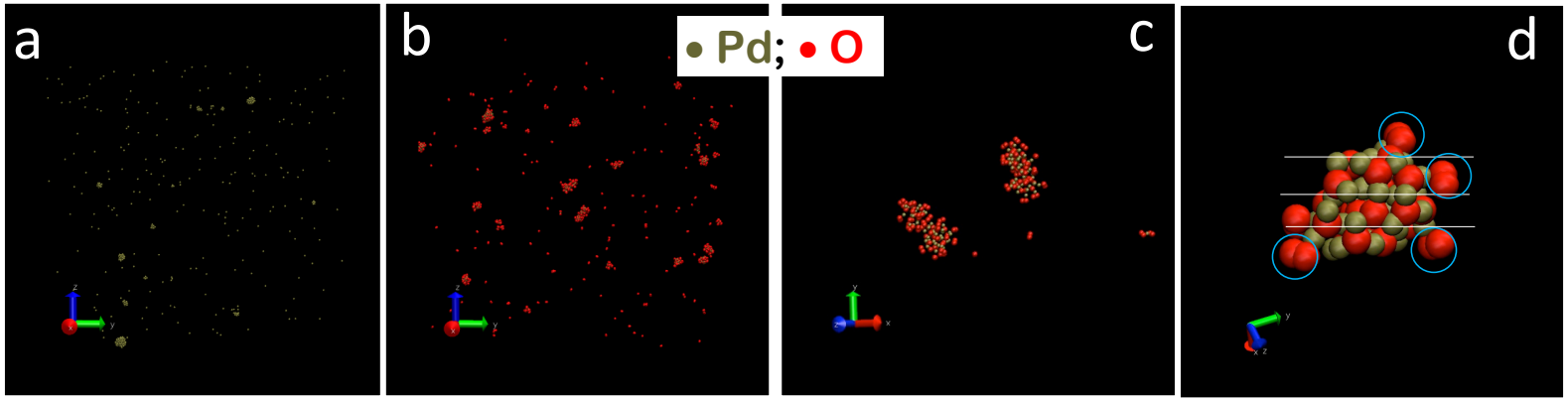
Plots of the pair part of the EAM interaction potentials: $V_{PtPt}(r)$, $V_{BiBi}(r)$, $V_{PtBi}(r)$.

- Cluster atomic arrangements are typical of a crystalline structure of the Pt cores, with numbers of 1st nearest neighbors between 10 and 12 (i.e. consistent with fcc arrangement)
- Bi composition < 20% leads to cluster surfaces with both Pt and Bi, allowing catalytic activity enhancement.
- Pt/Bi atomic composition is not only globally preserved, but is also verified for each cluster

B.S.R. Kouamé et al, Insights on the unique electro-catalytic behavior of PtBi/C materials, Electrochimica Acta 329 (2020) 135161

Reactive free PdO nanocatalyst growth

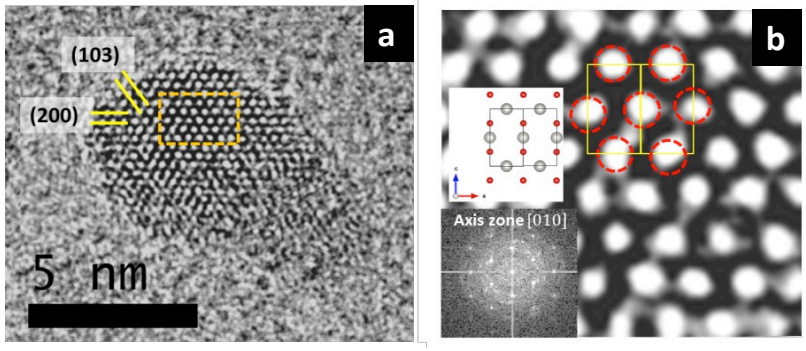
ReaxFF reactive variable charge potentials for Pd sputtering in Ar-O_2 gas mixture



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^3 Integration time 0.25 fs → 1. 10^8 iterations

- GAS Experiments, W. Chamorro-Coral et al



Potential ReaxFF : 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

Hydrocarbon plasma and soots

µwave plasma H_2/10% CH_4
Initial conditions for MD simulations
from 0D model (*)

	1450 K	1650 K	1950K
H_2 (*)	1000	1000	1000
H	7	30	100
CH_4	200	100	100
$\bullet CH_3$	2	5	7
C_2H_4	50	20	3
C_2H_2	400	500	600

(*) au lieu de 10000
Suffisant pour thermostat

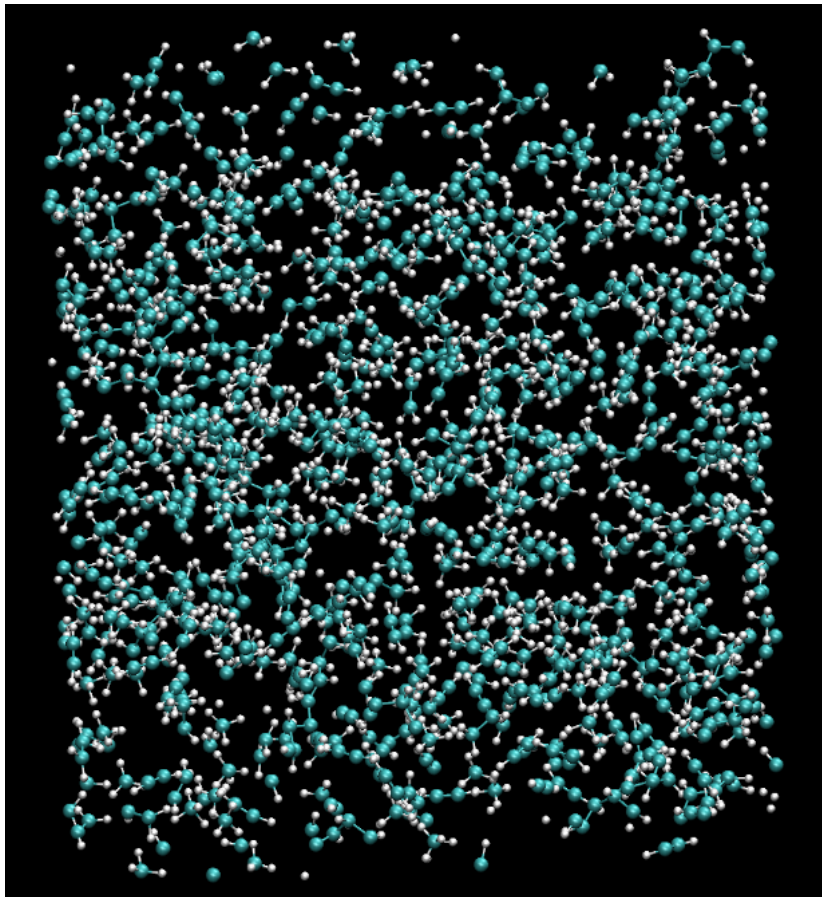
→ Reactions can freely occur

→ Bond formation energy is transported to walls by H_2 buffer gas, as in experiment (96% of molecules are H_2). H atoms from H_2 are thermostated.

S. Prasanna, A. Michau, C. Rond, K.Hassouni, A Gicquel, Plasma Sources Sci. Technol. 26 (2017) 097001

P Brault, C Rond, unpublished

Hydrocarbon plasma and soots



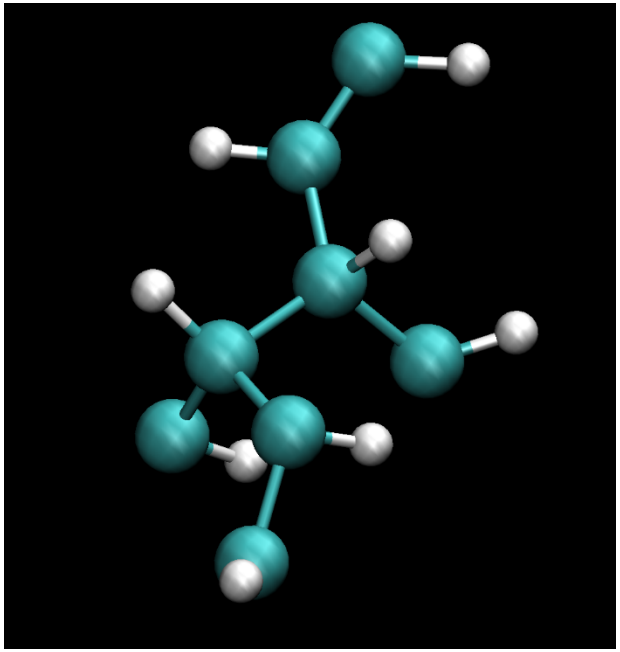
1450 K

- ReaxFF potential
- NVT for H_2 → thermostat
- NVE for other species
- 4 x 4 x 4 nm^3
- dt = 0.25 fs; 10^7 timesteps
- 300h on 8 core Intel Xeon

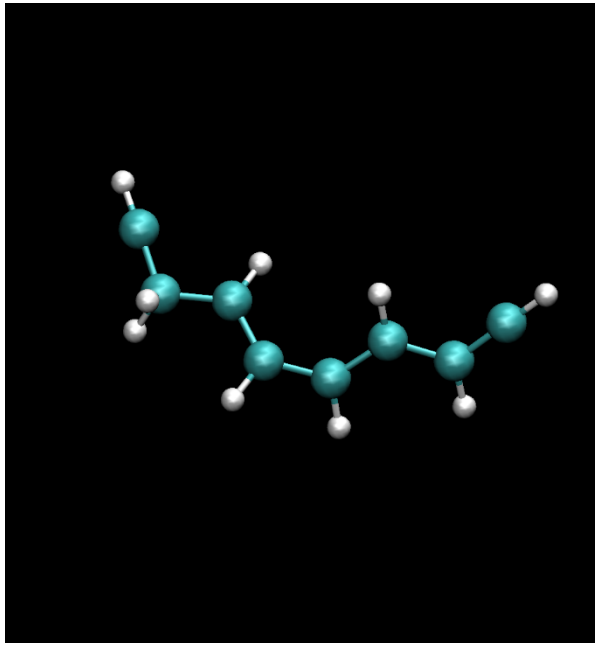
Hydrocarbon plasma and soots

1450 K

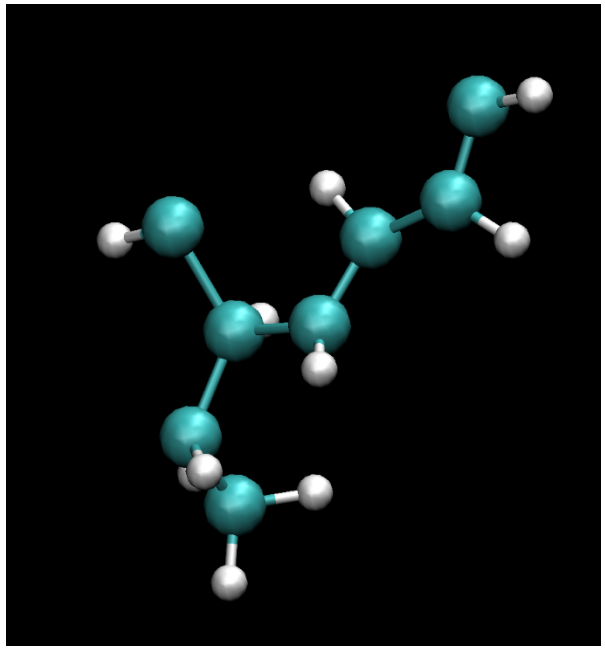
- Negatively charged ions



#2603
q = -0.45



#2004
q = -0.2



#3088
q = -0.25

Hydrocarbon plasma and soots

1450 K

	H2	H	CH4	CH3	C2H4	C2H2						
initial molar fraction	94%	0.07%	2.00%	0.02%	0.50%	4.00%						
# initial molecules SB	1000	7	200	2	50	400						
	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12
initial #molecules	202	450	0	0	0	0	0	0	0	0	0	0
final #molecules	201	330	6	15	4	9	1	5	1	1	1	1
initial #Cx	202	900	0	0	0	0	0	0	0	0	0	0
final #Cx	201	660	18	60	20	54	7	40	9	10	11	12
final fraction Cx	18.24%	59.89%	1.63%	5.44%	1.81%	4.90%	0.64%	3.63%	0.82%	0.91%	1.00%	1.09%

Hydrocarbon plasma and soots

1650 K

	H2	H	CH4	CH3	C2H4	C2H2						
initial molar fraction	94.00%	0.30%	1.00%	0.05%	0.20%	5.00%						
# initial molecules SB	1000	30	100	5	20	500						
	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12
initial #molecules	105	520	0	0	0	0	0	0	0	0	0	0
final #molecules	114	380	13	19	4	15	0	3	0	1	0	1
initial #Cx	105	1040	0	0	0	0	0	0	0	0	0	0
final #Cx	114	760	39	76	20	90	0	24	0	10	0	12
final fraction Cx	9.96%	66.38%	3.41%	6.64%	1.75%	7.86%	0.00%	2.10%	0.00%	0.87%	0.00%	1.05%

Hydrocarbon plasma and soots

1950 K

	H2	H	CH4	CH3	C2H4	C2H2						
initial molar fraction	93.00%	1.00%	0.30%	0.07%	0.03%	6.00%						
# initial molecules SB	1000	100	100	7	3	600						
	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12
initial #molecules	107	603	0	0	0	0	0	0	0	0	0	0
final #molecules	121	415	18	40	3	13	0	2	1	0	0	0
initial #Cx	107	1206	0	0	0	0	0	0	0	0	0	0
final #Cx	121	830	54	160	15	78	0	16	9	0	0	0
final fraction Cx	9.43%	64.69%	4.21%	12.47%	1.17%	6.08%	0.00%	1.25%	0.70%	0.00%	0.00%	0.00%

MD simulations of plasma processing as a whole

1/ recovering/scaling experimental conditions

Hypothesis : Collision number are the same in experiments and simulations so, $P_{exp}d_{exp} = P_{sim}d_{sim}$ thus $N_{sim} = \frac{P_{exp}}{k_B T_g} \cdot S_{sim} \cdot d_{exp}$ and if r_{cut} is the largest cutoff radius : $d_{sim} > \frac{N_{sim}}{S_{sim}} \cdot {r_{cut}}^3$

(S_{sim} is the chosen smallest area of the simulation box)

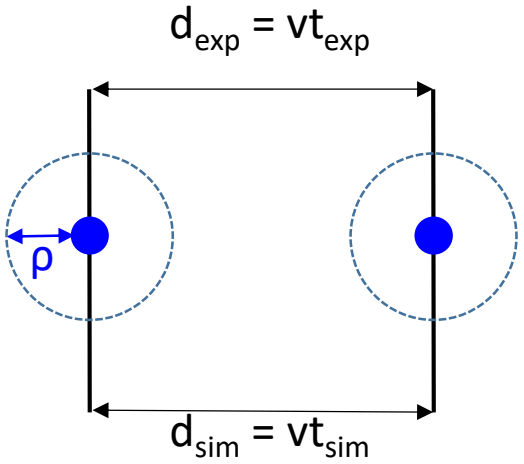
2/ experimental time recovery

Velocities are same in exp and simulations

$$v = \frac{d_{exp}}{t_{exp}} = \frac{d_{sim}}{t_{sim}}, when\ d_{exp}, d_{sim} > 2\rho$$

$$then, t_{exp} = \frac{d_{exp}}{d_{sim}} . t_{sim}, when\ d_{exp}, d_{sim} > 2\rho$$

$$or, t_{exp} = t_{sim}, when\ d_{exp}, d_{sim} \leq 2\rho$$



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

MD simulations of plasma processing as a whole

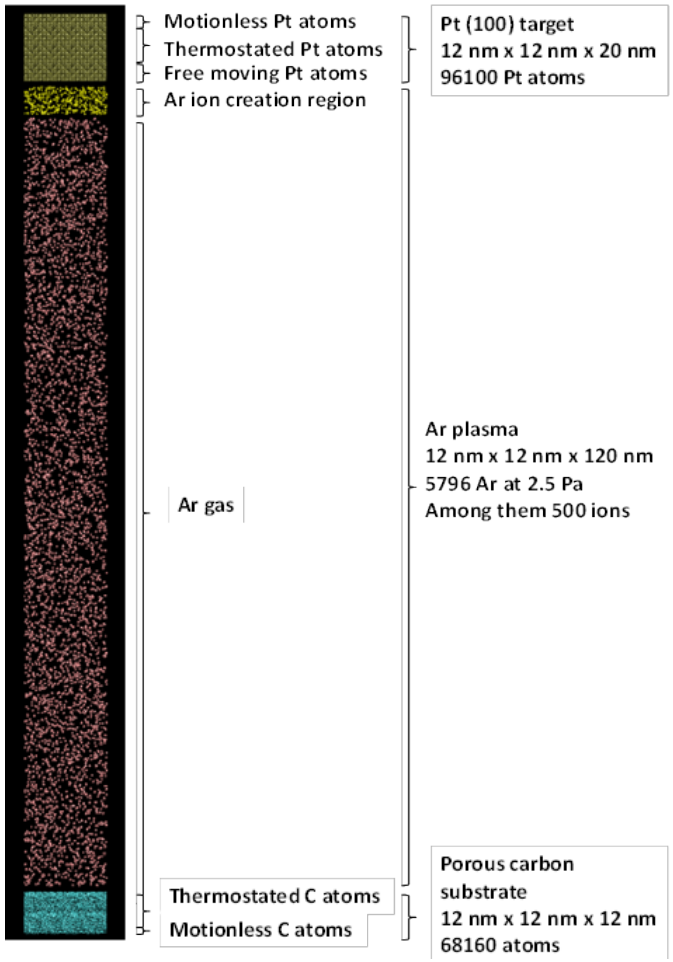
New reactive and including electron interaction potential allow targeting multiscale MD simulations of operating plasma reactor

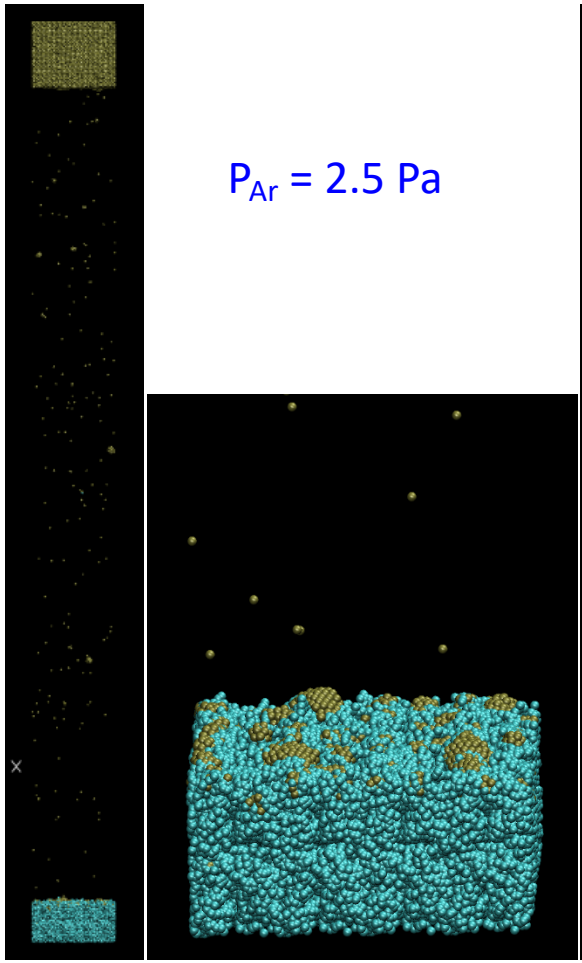
2/ combine improved force fields

Plasma factor	Possible?	Example
electric field	yes	CNT growth
atoms and hyperthermal species	yes	Si-NW oxidation
radicals	yes	a-C:H growth
ions	yes	sputtering
electronically excited states	yes	etching
vibrationally excited states	yes / no (reaxFF)	/
photons	implicit	(polymer degradation)
electrons	Yes (eFF, e-reaxFF)	/

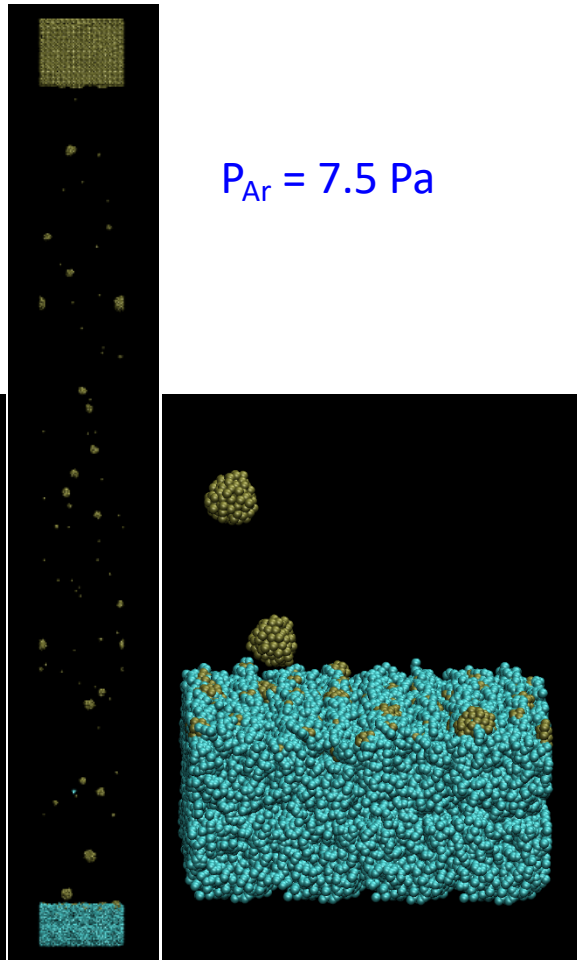
E. Neyts, P. Brault (Review article), *Molecular dynamics simulations for plasma surface interactions*, Plasma Processes and Polymers 14 (2017) 1600145

MD simulations of plasma processing as a whole
Application to nanocluster growth in plasma sputtering





P_{Ar} = 2.5 Pa



P_{Ar} = 7.5 Pa

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

Conclusions

- MD simulations of supported and free metal alloy nanoparticle provides insight of surface composition : for Pt alloy this is well correlated with experiments on catalytic performance, especially when adding Au (expected to stabilize clusters).

- Reactive MD is very powerful since availability of reactive and variable charge reaxFF potential family. Growth of free PdO clusters is well compared with GAS experiments.

- Matching experimental conditions is a condition for successful comparisons.

- Full plasma processing modelling is reachable by MD simulations provided a cutoff distance is defined for scaling down the experimental reactor size

Future works

- Nanocatalysts
  - Non Platinum Group Catalysts for fuel cell operation TiO_{2-x}, ZrO_{2-x}
  - GAS growth and reactivity → OH adsorption

- Plasma – liquid interactions
  - RONS action on Endocrine Disruptive Chemicals, Pharmaceutical residues.

- Plasma chemistry
  - Including electrons in plasma chemistry using MD

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