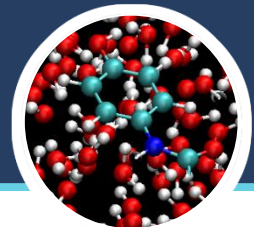


Reactive molecular dynamics simulations of plasma treatment of emerging pollutants in water

Pascal Brault

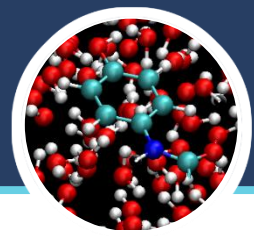
GREMI, UMR7344 CNRS Université d'Orléans, Orléans, France



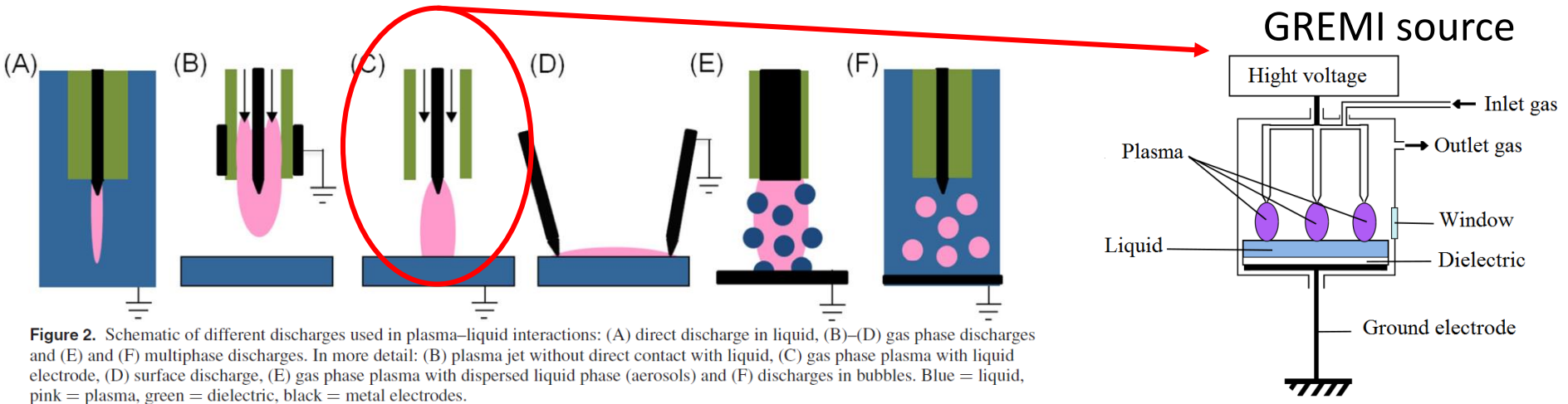


Outline

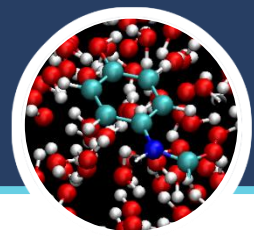
- Plasma- liquid interactions
- Reactive Molecular dynamics principles
- First attempts of paracetamol active oxydation
- Conclusions & perspectives



Plasma - liquid interactions

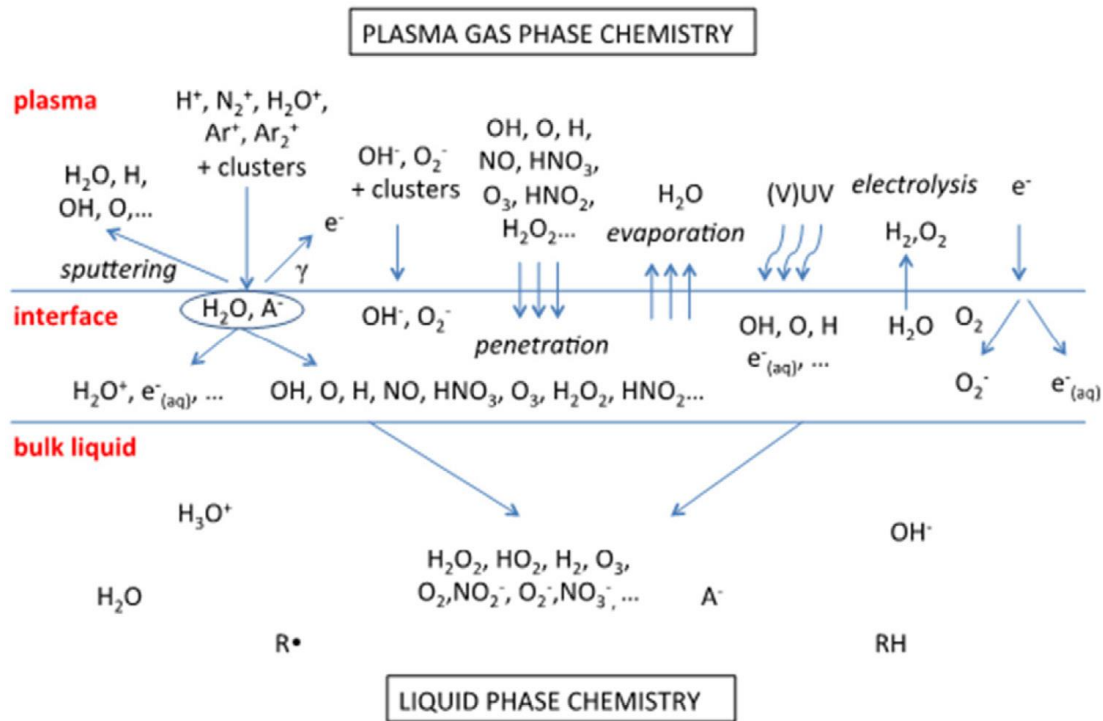


Y Baloul, et al, Paracetamol degradation in aqueous solution by non-thermal plasma. *Eur. Phys. J. Appl. Phys.* 79 (2017) 30802
 Y. Baloul, et al, Preliminary study of a non-thermal plasma for the degradation of the paracetamol residue in water, *International Journal of Plasma Environmental Science & Technology*, 10 (2016) 102



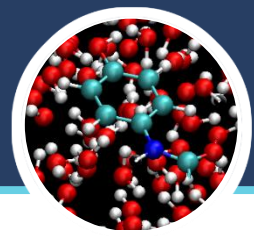
Plasma - liquid interactions

- Sketch of air atmospheric plasma on a liquid



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

P J Bruggeman et al 2016 Plasma-liquid interactions: a review and roadmap Plasma Sources Sci. Technol. 25 053002

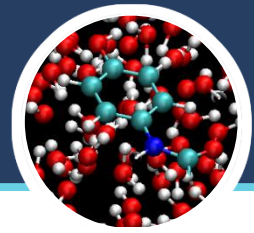


Plasma - liquid interactions

Table 1. Typical plasma properties for four often used discharges: pulsed direct discharge in liquid, DC air glow discharge with a water electrode, pulsed plasma jet (non-touching) and filamentary dielectric barrier discharge (DBD).

	Direct liquid discharge [17, 21]	DC air glow discharge [50, 52, 57–59]	Pulsed jet (non-touching) [60, 61]	Filamentary DBD (single filament) [62]
Medium/gas	Water	Humid air	He–Ar	Air
Plasma generation time	1–10 s μ s	Continuous	10–100 ns	1–10 ns
Electron density (m^{-3})	10^{24} – 10^{26}	10^{18} – 10^{19}	10^{19} – 10^{20}	10^{19} – 10^{21}
Pressure (bar)	10^4 (peak)	1	1	1
Gas temperature (K)	1000–7000	2000–3000	300–400	300–400
Ionization degree	1 – 10^{-3}	10^{-5} – 10^{-7}	10^{-5} – 10^{-6}	10^{-5} – 10^{-6}
Energy/power	1 J per pulse	5–100 W	<10 μ J per pulse	<10 μ J per pulse
Power density	$\leq 10^{15}$ W m^{-3}	$\sim 10^6$ W m^{-3}	< 10^{12} W m^{-3}	< 10^{12} W m^{-3}
Current	~ 1 A	5–100 mA	2–10 mA peak	<100 mA
Electron temperature (eV)	1 (close to LTE)	1–2	1–2	2–3
Electric field (kV cm^{-1})	$\sim 10^3$	1 (in positive column)	1–10	10–100
Ion density at interface (m^{-3})	10^{24}	10^{18} – 10^{19}	$\leq 10^{16}$	10^{20} – 10^{21}
UV ($\text{m}^{-2}\text{s}^{-1}$)	Broadband UV emission	Strong UV (NO(A-X), OH(A-X), N ₂ (C-B))	5×10^{22}	5×10^{23}
Radical density (e.g. $\bullet\text{OH}$ and $\text{O}\bullet$) m^{-3} s	$\sim 10^{24}$	10^{21} – 10^{23}	10^{19} – 10^{21}	10^{20} – 10^{21}
Reactive species flux ($\text{m}^{-2} \text{s}^{-1}$)	Extremely large gradients	10^{23} – 10^{25}	5×10^{21} – 5×10^{23}	5×10^{22} – 5×10^{23}
Flow effects	Shockwaves	Thermal convection	Forced flow	Convective

Water density $3.3 \times 10^{28} \text{ m}^{-3}$



Molecular dynamics simulations

- ✓ 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)

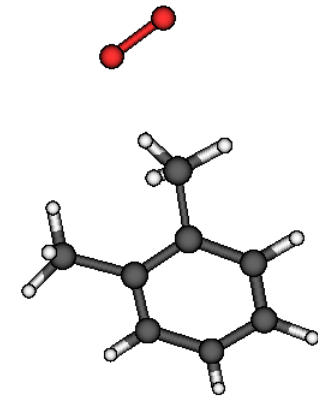
$$\vec{F}_i = m_i \vec{a}_i = m_i \frac{d\vec{v}_i}{dt} = m_i \frac{d^2 \vec{r}_i}{dt^2}$$

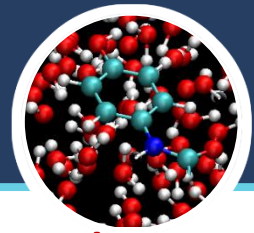
and

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

- ✓ A rigorous 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)





Molecular dynamics simulations

Relevance/significance of MD Simulations

Flux :

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

Prohibit long time diffusion, except if including specific strategies

Pressure/simulation box size

Solid density : Pt 65 nm^{-3}

Liquid density: water 33 nm^{-3}

→ Can be treated. Diffusion coefficients can be calculated without additional approximation(s)

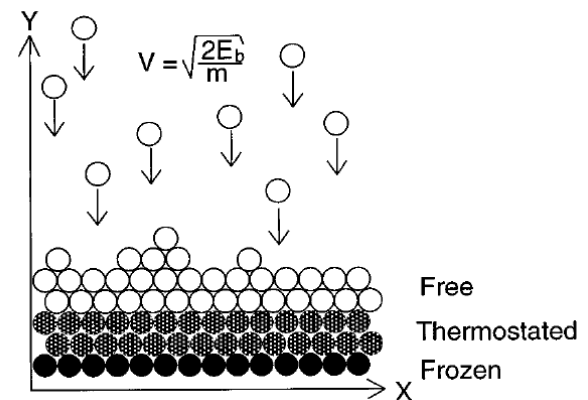
Gas density : $1 \text{ atm} = 2.4 \cdot 10^{-2} \text{ nm}^{-3}$ → Not enough species in box of size d at pressure P

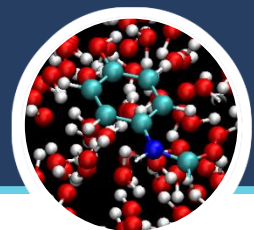
Solution: relevant parameter = Collision number $\propto P \cdot d$

→ ↑ 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



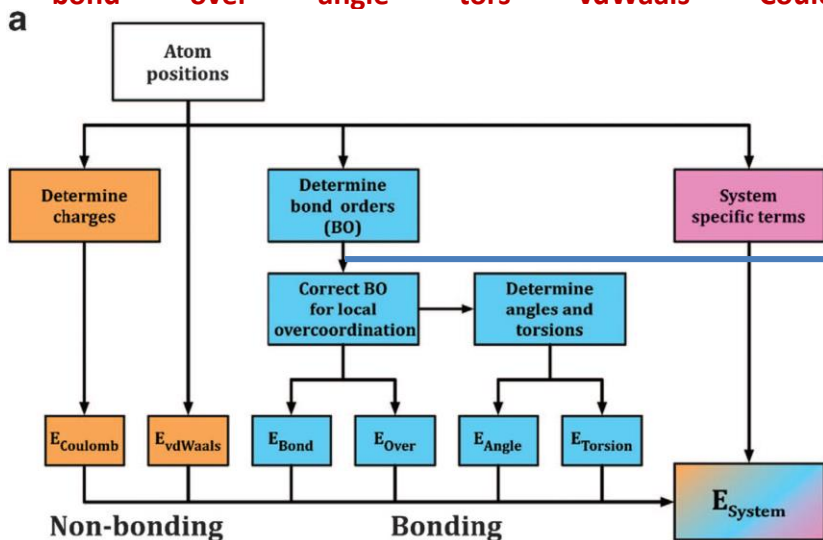


Molecular dynamics simulations: Interactions potentials

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: $E_{\text{system}} =$

$$E_{\text{bond}} + E_{\text{over}} + E_{\text{angle}} + E_{\text{tors}} + E_{\text{vdWals}} + E_{\text{Coulomb}} + E_{\text{Specific}}$$

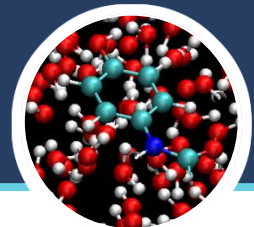


$$\begin{aligned}
 BO_{ij} &= BO_{ij}^{\sigma} + BO_{ij}^{\pi} + BO_{ij}^{\pi\pi} \\
 &= \exp \left[p_{\text{bo}1} \left(\frac{r_{ij}}{r_o^{\sigma}} \right)^{p_{\text{bo}2}} \right] + \exp \left[p_{\text{bo}3} \left(\frac{r_{ij}}{r_o^{\pi}} \right)^{p_{\text{bo}4}} \right] \\
 &\quad + \exp \left[p_{\text{bo}5} \left(\frac{r_{ij}}{r_o^{\pi\pi}} \right)^{p_{\text{bo}6}} \right]
 \end{aligned}$$

Correct Bond Order \Rightarrow Correct description of reaction energy barriers

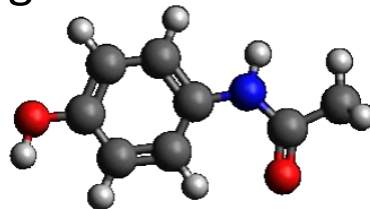
Overview of the ReaxFF total energy components

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

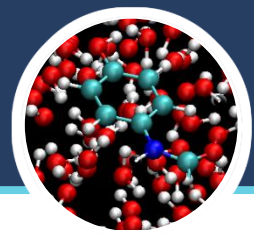


Paracetamol plasma active oxidation

- Paracetamol is a common and (well) studied drug pollutant present in water resulting from human intake → good candidate for developing a new simulation methodology

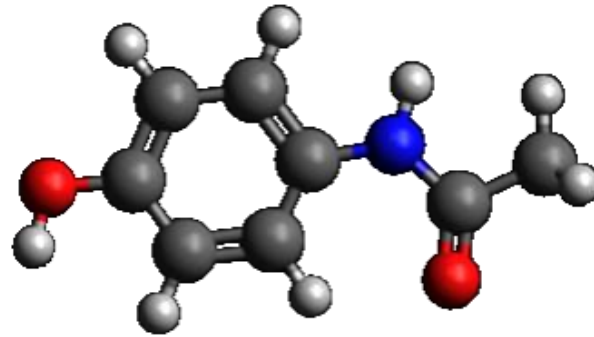


- Goal of a reactive MD
 - Identifying reaction pathways
 - To provide with the oxidation by-products and identifying possible toxic ones
 - In turn, to deduce the most appropriate oxidation process
 - More generally providing an insight of plasma – liquid interactions in developing an appropriate methodology
- Requirements
 - To parametrize and/or to use (already available) reactive force fields (e.g. ReaxFF, AIREBO, ...)
 - Ultimately include electron force fields for including electron processes in MD (available forcefields : e-reaxFF, eFF or in a new one)

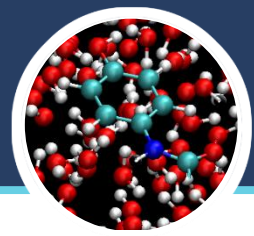


Paracetamol plasma active oxidation

Preliminary results on paracetamol



- Oxidation at temperature 2500 K → insight in the kinetics
 - MD oxidation using O_2 , OH, O_3
 - Intermediate and final products



Paracetamol plasma active oxidation Oxidation at 2500 K

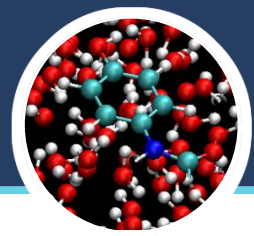
■ Simulation box

- $2.5 \times 2.5 \times 2.5 \text{ nm}^3$: 1 paracetamol + 100 active molecules \rightarrow O₂, OH or O₃
- Time step : 0.1 fs, $2 \cdot 10^8$ iterations $T_{\text{calc}} = 20 \text{ ns}$

■ Preliminary results

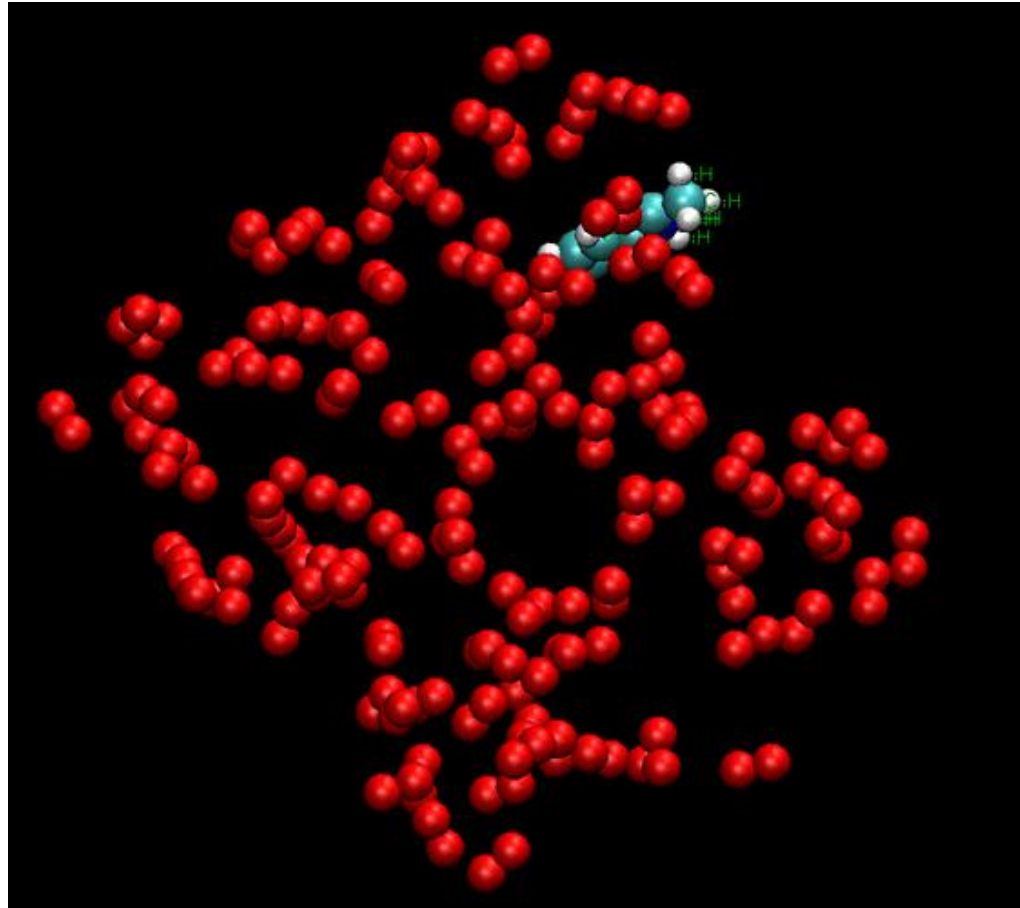
- O₂ and OH lead to same final products.
- But with OH, reactions occur faster than with O₂ and at lower temperature.
- O₃ leads to deeper oxidation very quickly, even at room temperature

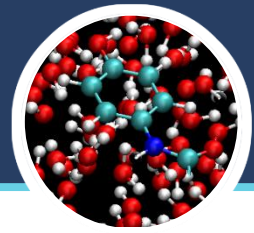
	O ₂	OH	O ₃
Final products	NC ₄ O 4 H ₂ O 1 OH 4 CO n O ₂	NC ₅ O 3 CO 1 HO ₂ 8 H ₂ O nH ₂ O + n/2 O ₂	NO C ₂ O 6 CO 1 HO ₂ 4 H ₂ O n O ₂



Paracetamol plasma active oxidation Oxidation at 2500 K

- Paracetamol oxidation with O₂





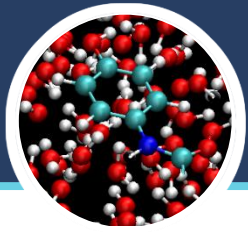
Conclusions & perspectives

■ Conclusions

- Reactive MD is able to describe advanced oxidation
- No activity (OH) if only water, active radicals and electric field at 300K

■ Perspectives

- Simulation should mimic convection and continuous uptake of active species in water
- To include interface with plasma phase above the liquid with plasma species (e-reaxFF ?) and UV-light effect.



Thank you for your attention