Nanometer structuration effects in water radioysis : Confinment and nanoparticles.

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1 – Water radiolysis

Radiolysis: -molecular bond breaking by ionizing radiations → radical formation.

-present along nuclear fuel cycle, radiotherapy.

-pure water radiolysis well studied: reference results.

Confinment & NP:

-composite medium – dose distribution – transent effects

-nanometric size, specific aspects associated to existence of interface

iacts on chemical yields

Goal: -to propose and check explanation scenarios for observed phenomenons

-to identify the key parameters governing these phenomenons

-to establish a link between these parameters and the observables (chemical yields = G)

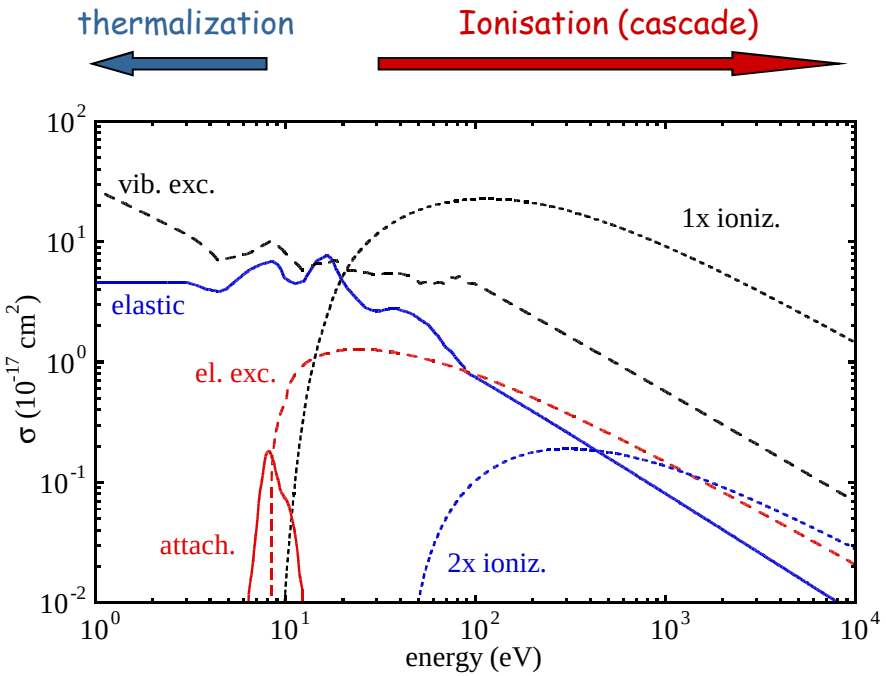
Simulation:

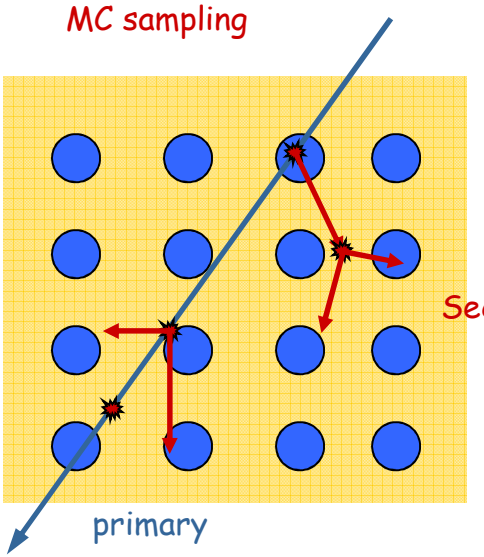
-physical stage = MC from cross section

-physical-chemical stage = branching ratios

-chemical stage = KMC from diffusion constants and reaction rates

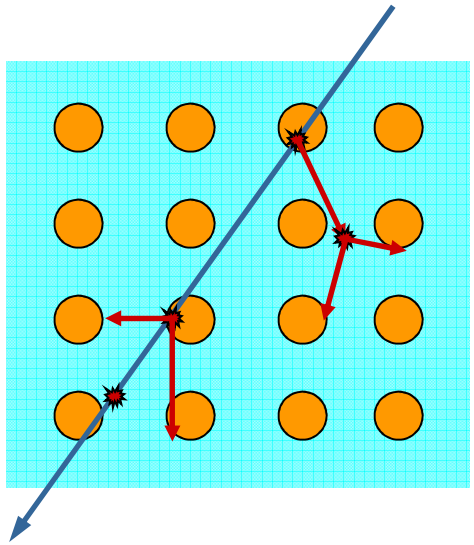
2 – physical stage simulation





Model of water confined in a porous medium (silica)

Model of NP (silica) embedded in liquid water



Composite medium geometry:
array of cylinders or spheres: radius, concentration

Typically a high energy electron induces an electron cascade.

MC sampling of electron cascade:
ionization, elec. Excitation, elec. Attachment,
vib. Excitation, elastic scattering.

Electrons followed until thermalisation in both medium.

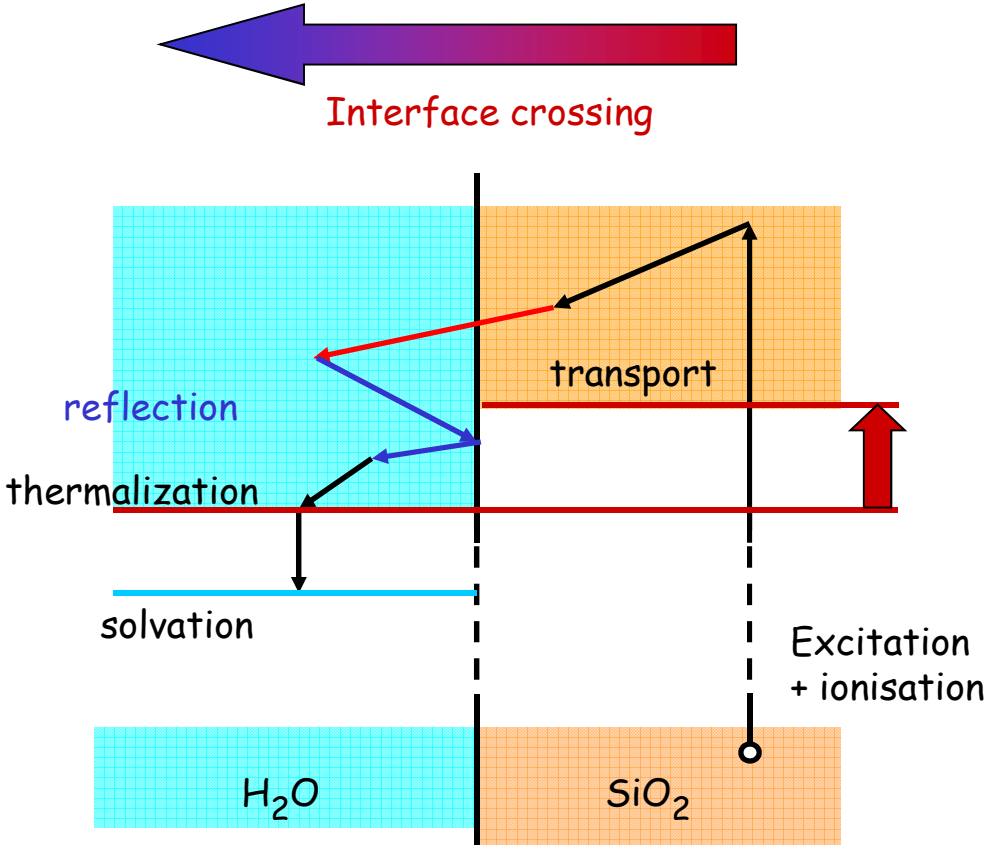
3 – Some aspects of confinement in porous silica

Critical parameter: beside the nature of the material,

relative position of conduction bands is of paramount importance.

relative electronic affinities as well.

For nanometric object: diffusion length of low-energy electron is comparable to object size

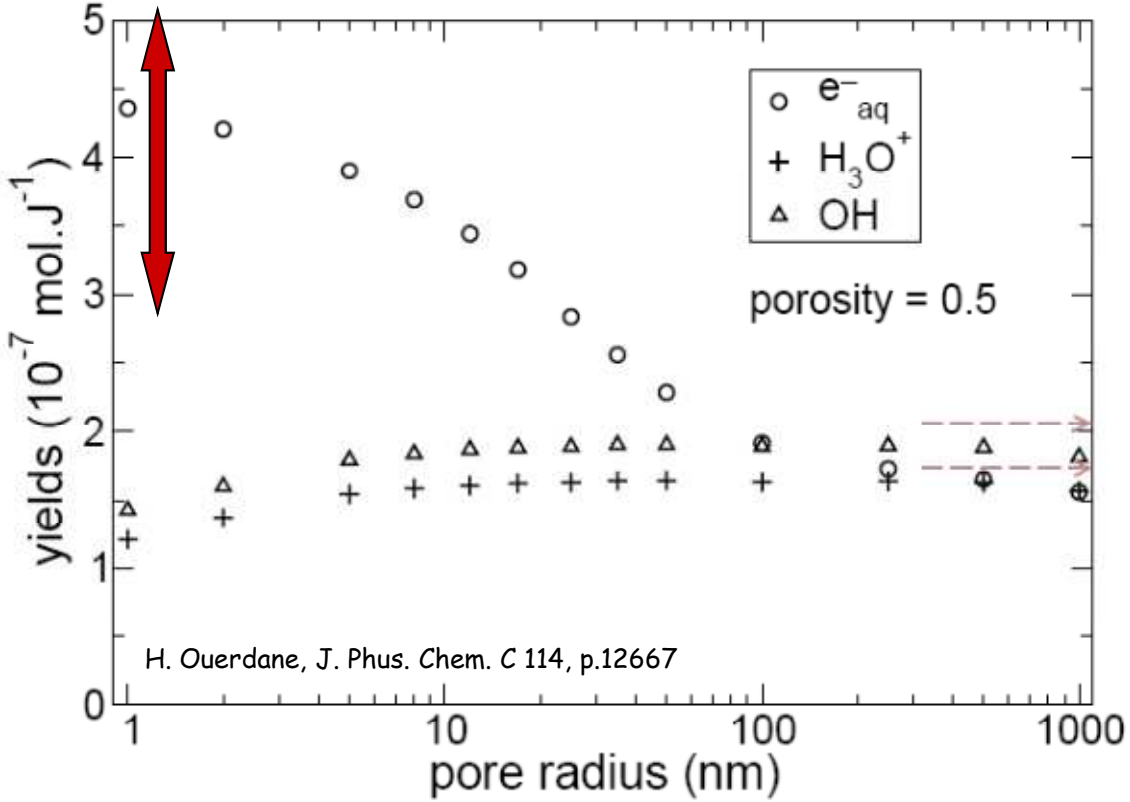


Exciton and hole migration much slower than electron transport in silica: typically 10nm / 1 μs

= reach the interface much later.

3a – confined radiolysis : physico-chemistry

3D map of chemical species:
~few ps time scale
e_{aq}^-, H_3O^+, OH, H, O(3P), O*, H_2, OH^-



Normalisation:

$$y = \frac{\text{N species}}{\text{total deposited energy}}$$

$$y_W = \frac{\text{N species}}{\text{Energy deposited in water}}$$

$y_W = f_W\, y$

f_W = IMFP ratio or relative absorption

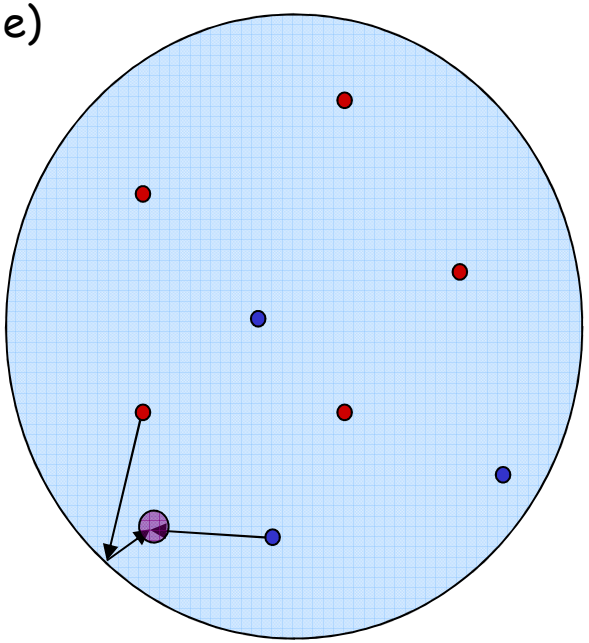
Inverse geometry: silica NP with Radius = 3–10 nm : good agreement of simulation with experiment.

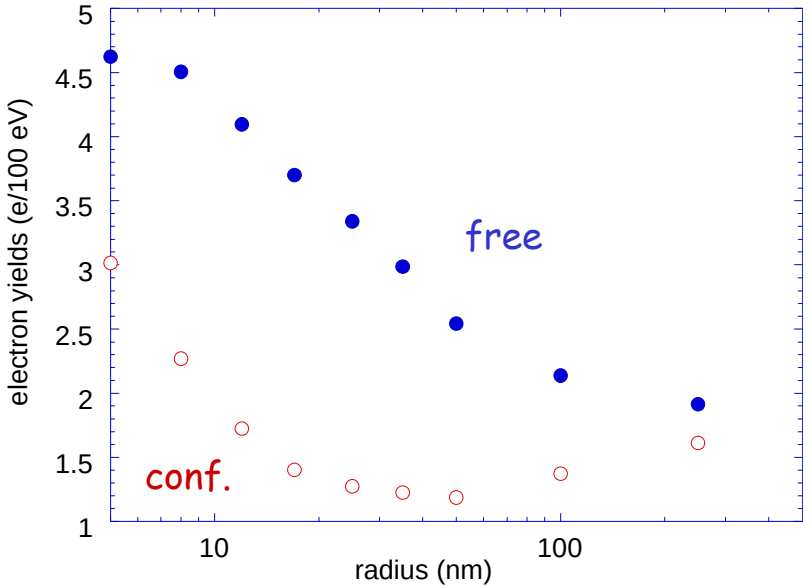
3b – confined radiolysis : chemistry (~ few μs time scale)

Simulation of chemical diffusion-reaction evolution : KMC

- confinment effect: ideal case = less réactions / faster

→ modification of the yields: Y(OH); Y (H_2); Y(H_2O_2)





confined = reflection at the surface only

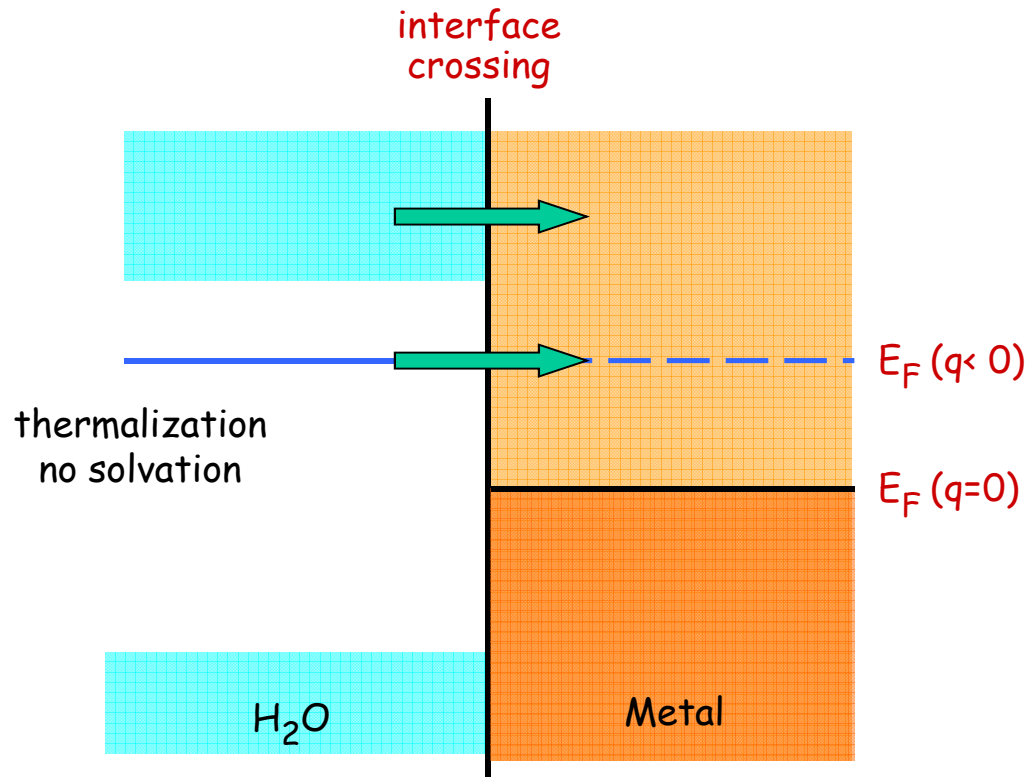
free = same initial distribution – no surface

- However, specific reaction at interface: reaction rates ???

$e_{aq}^- + \text{-SiOH} \rightarrow SiO^- + H^\circ$; …

$H^+ + \text{-SiOH} \rightarrow SiO^\circ + H^+$; $SiO^\circ + H_2O \rightarrow$??

4-perspectives: metallic NP



In metal NP, electronic affinity (Fermi level) dpends on charge. Thermalized and Solvated elect. subject to thermodynamic equilibration.

Very different from SiO2 and more generally from wide band gap insulators.

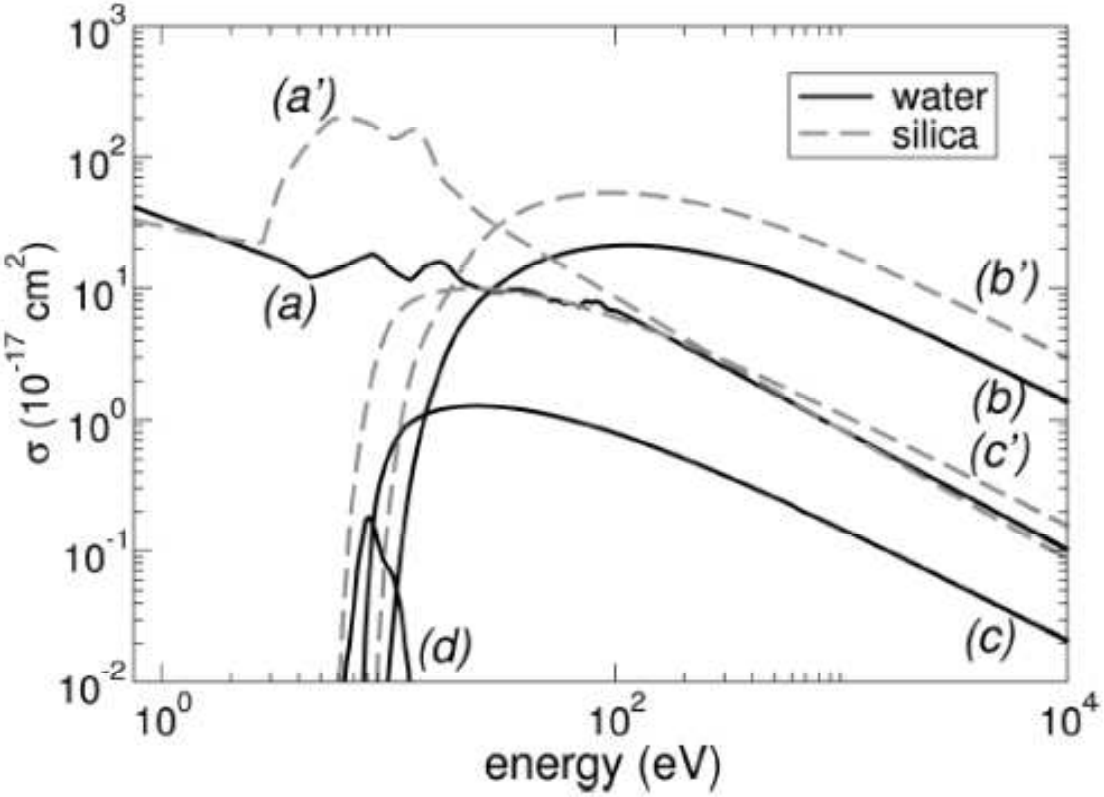
Usually low concentration of NP

Complete KMC simulation : a lot of work remains to be done…

-specific interface reaction : reaction rates ?

$e_{aq}^- + NP(q) \rightarrow NP(q-1)$; $OH + NP(q) \rightarrow OH^-$; $H^+ + NP(q) \rightarrow H + H2O$; etc …

- specific chemical aspects of NP : catalytic effects ?


water
silica
(a')
(a)
(b')
(b)
(c')
(c)
(d)
σ (10^-17 cm^2)
energy (eV)
10^3
10^2
10^1
10^0
10^-1
10^-2
10^0
10^2
10^4