

Plasmas froids à pression atmosphérique pour les procédés de production, coating et charge de nanoparticules

13^{ème} journées d'échange du réseau plasmas froids
Octobre 2016

Jidenko N. et Borra J-P,



Laboratoire de Physique des Gaz et des Plasmas
Décharges Electriques et Aérosols

Tél. : 01.69.15.36.78, nicolas.jidenko@u-psud.fr



Comprendre le monde,
construire l'avenir*

université
PARIS-SACLAY

1- Décharges à pression atmosphérique

2- Production de nanomatériaux par plasma

a- Intérêt des procédés aérosol

b- Interaction plasma-surface: vaporisation & nucléation

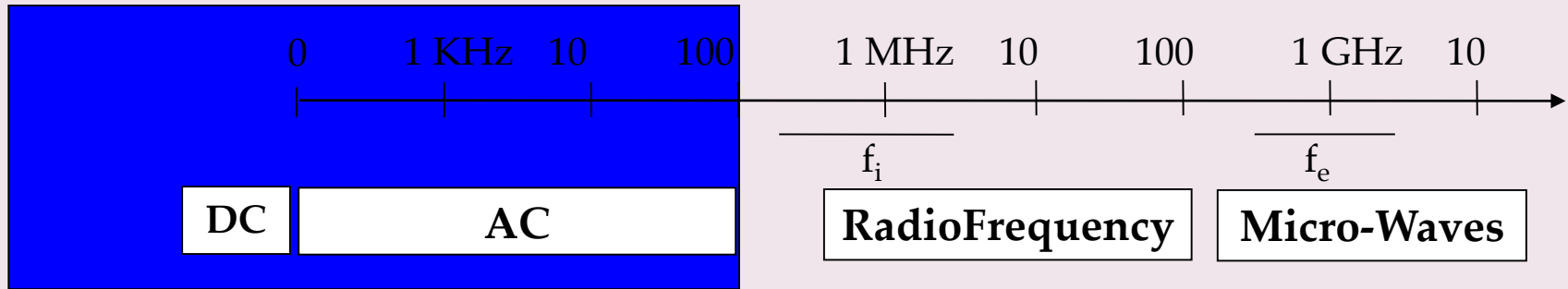
c- Coatings en post-DBD

3- Charge des nanoparticules en post-plasma

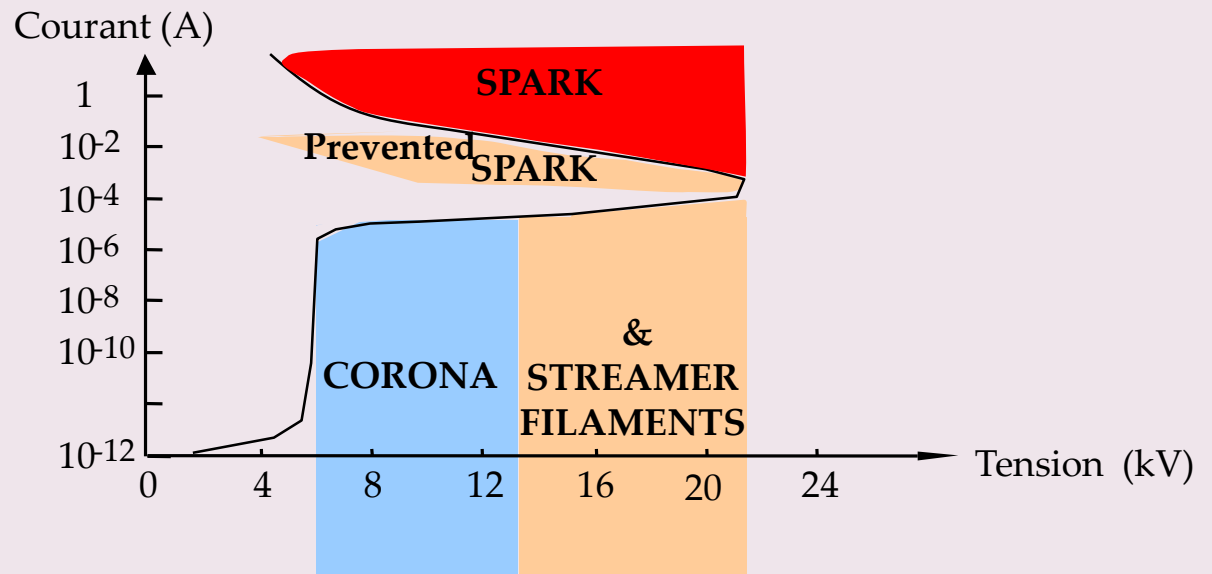
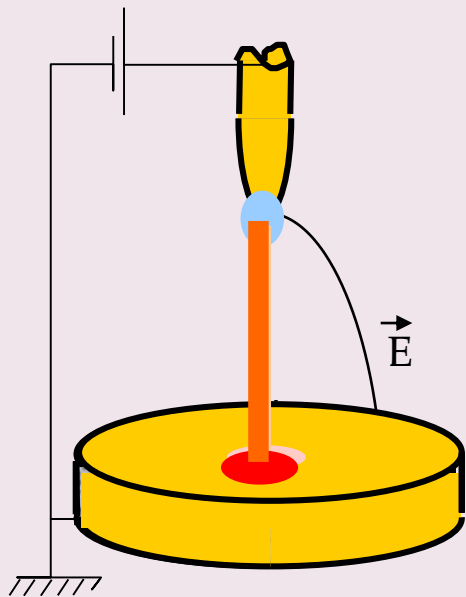
a- Mécanismes et lois de charge

b- Problématique métrologique nano (taille, concentration)

1- Décharges à pression atmosphérique (DEA)



- DC**
- Corona (*corona +/-, Trichel-, glow + streamer & arc entravé*)
 - Voltage below sparking voltage
 - RC circuit limiting the spark current & energy
 - Micro-Hollow-Cathode
- AC**
- Dielectric Barrier Discharges (DBD)
 - Insulator in the discharge gap
 - Pulsed Discharges,
 - Polarisat° shorter than streamer-to-spark transition ($\sim \mu\text{s}$ at AP)
 - Plasma jet



PRODUCTION d'ION
for Aerosol CHARGING

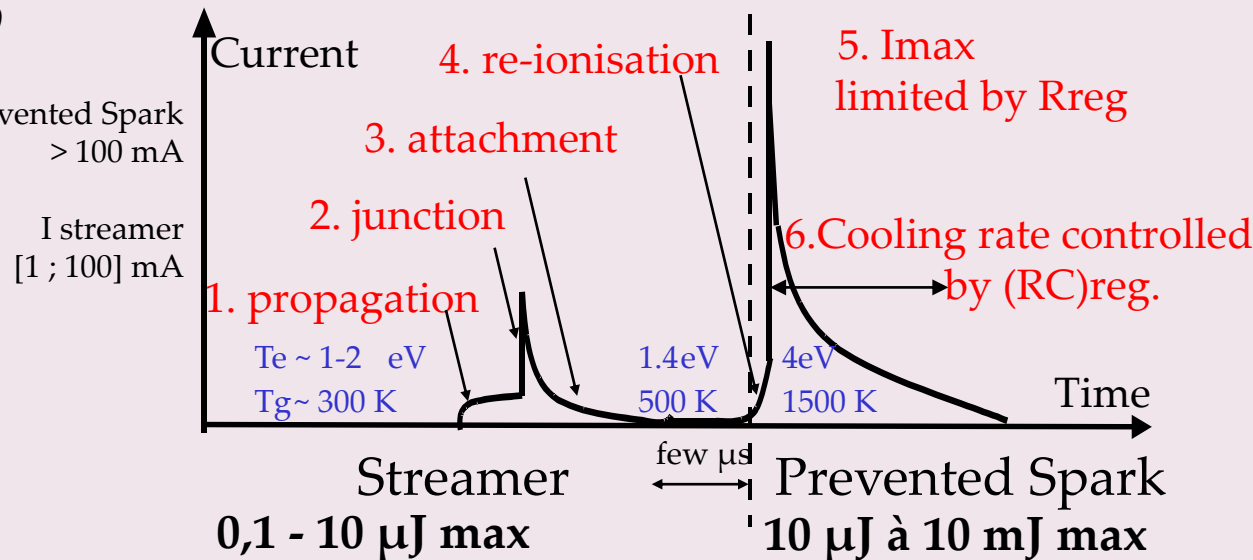
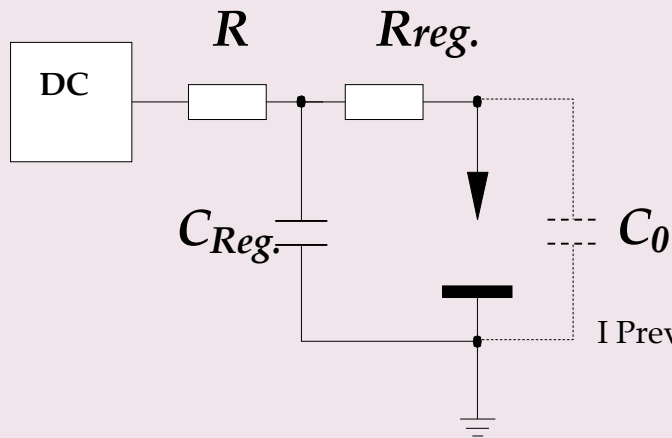
REACTIVE SPECIES and
VAPOR PRODUCTION

Versus $V \rightarrow \neq$ regimes with discharge current \sim flux of charges, collisions freq. and T_{gas}
 $I < \text{mA}$, nt-PLASMAS \rightarrow ionisation & chemical activation rather than heating

- Corona \rightarrow Aerosol charging & processing

- Streamer ($< 100 \mu\text{J}$) & Prevented Spark ($< 10 \text{mJ}$) Filaments - surface interaction
 with energy densities in the spot $>$ fluency threshold of any material (10^3J/m^2)

\Leftrightarrow surface vaporisation \rightarrow Physical nucleation



with tuneable

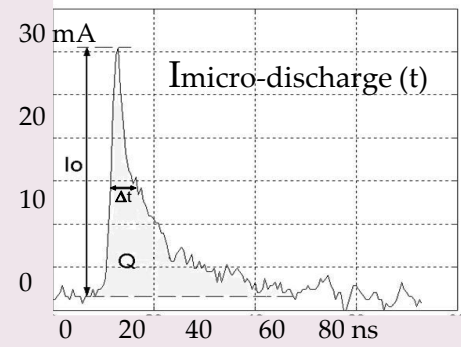
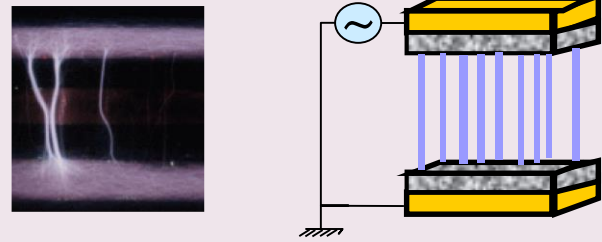
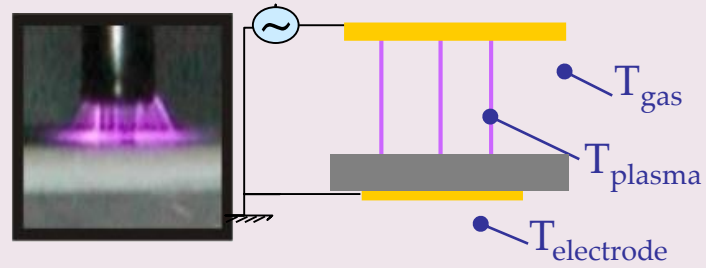
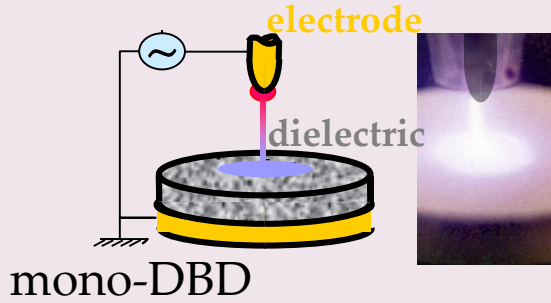
- Energy/charge per filament versus $C_{regulation}$.
- T_{surf} max and T_{gas} profiles versus I_{max} ($R_{regulation}$)
- Cooling rate versus $R.C_{regulation}$

→ Energy densities in the spot of interaction between plasma & surface are higher than fluency threshold of any material ⇔ vaporisation of surfaces

... suitable for aerosol production studies

Polarisation of dielectric surface

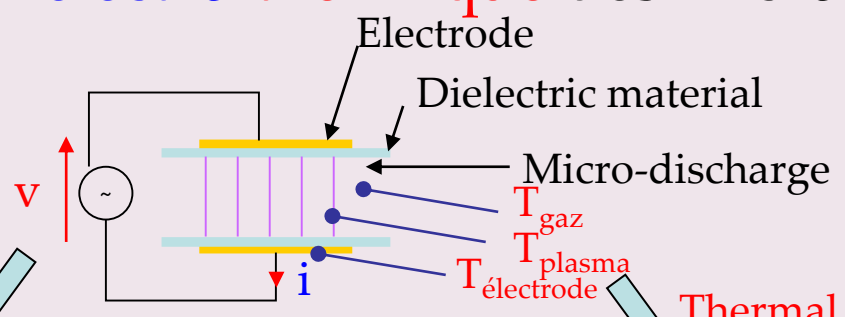
- No spark by decreasing E/N for the 1/2 T
- Requires AC field
- E/N Reinforcement from one 1/2 T to next one



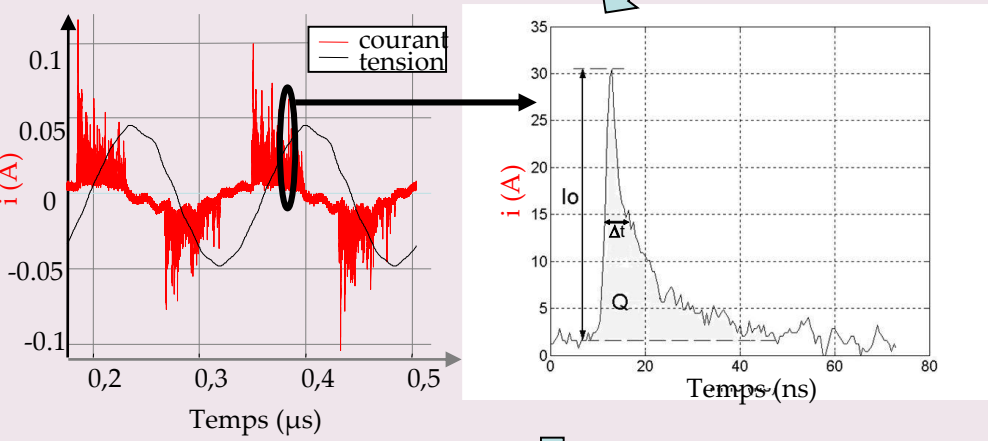
- 1- Lower energy per filament / DC (0.1 to few $\mu\text{J}/\text{fil.}$)
- 2- Constant properties of filaments \forall the voltage and frequency (1 -100 kHz)
- 3- Tuneable energy (0.1-10 μJ) and T_{gas} profiles with d , ϵ_r and gas nature
 → controlled vapour production and transport

... suitable for aerosol production studies and processes

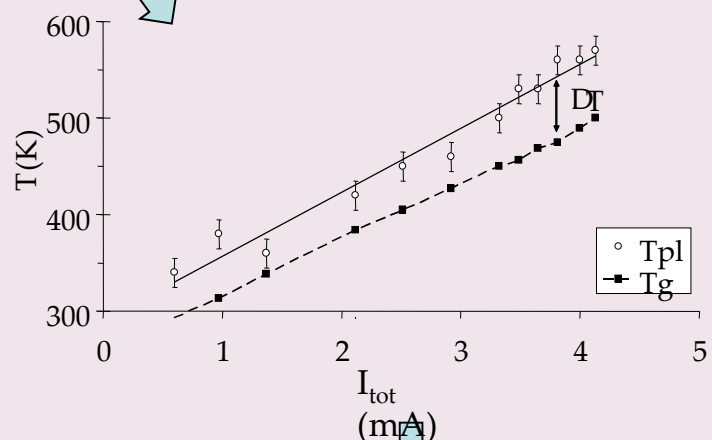
Caractérisation électro-thermique des micro-décharges



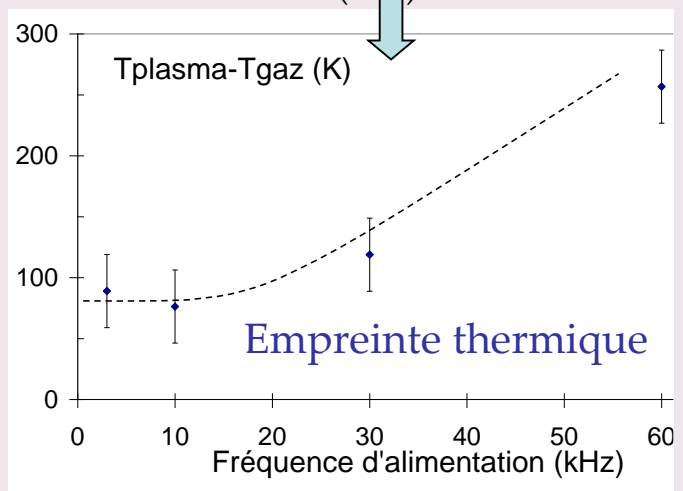
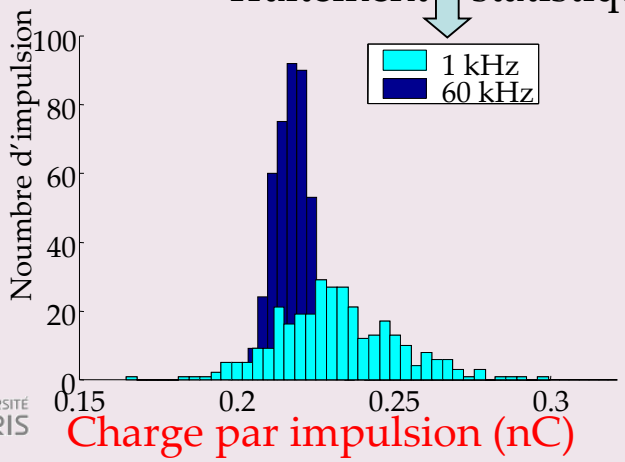
Electrical measurements



Thermal measurements



Traitement statistique



2- Production de nano-matériaux par plasma

- a- Intérêts des procédés aérosol
- b- Interaction plasma-surface
vaporisation & nucléation
- c- Coatings en post-DBD

= nanoparticules aux propriétés exacerbées par la taille si $\sigma_{dp} < 1.2$

Intérêts des procédés aérosols pour les nanotechnologies

→ Efficace : opérations successives simples et rapides

→ Pas de sous-produits liquide à retraiter

→ Forte valeur ajoutée des nanoparticules contrôlées en :

- taille,

- composition,

- morphologie

- surface spécifique

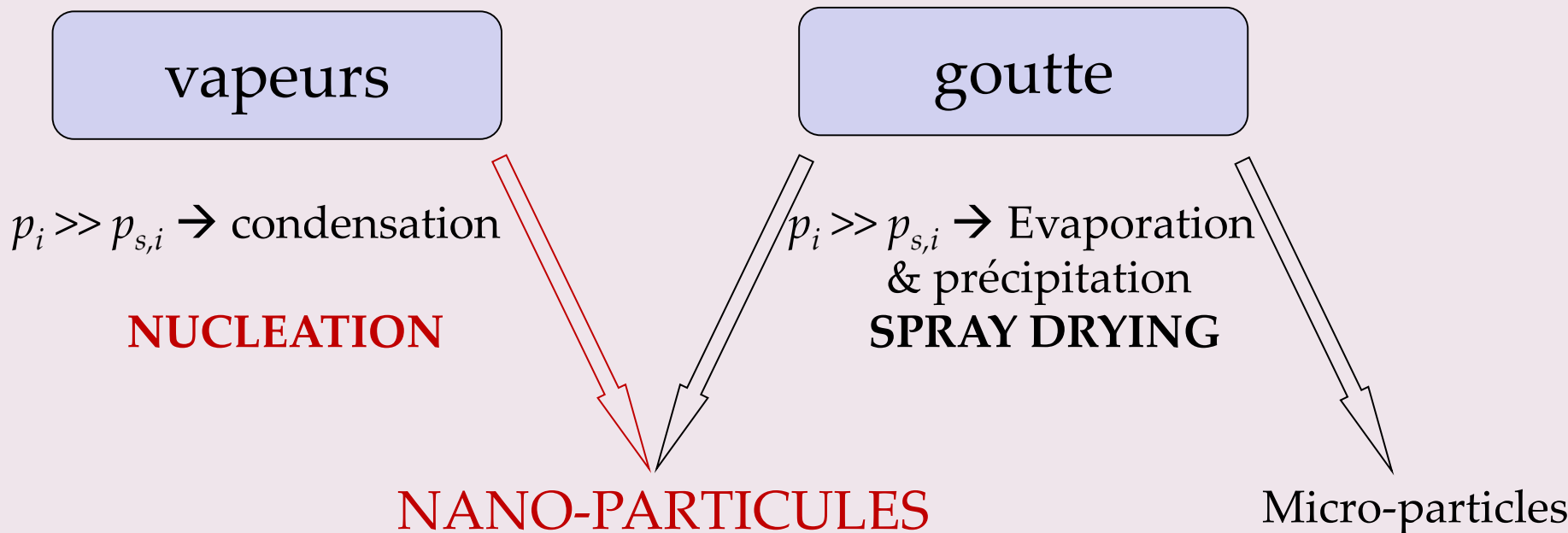


de nanoparticules primaires

des agglomérats

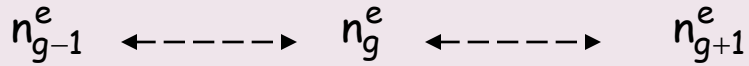
.... et possibilité d'obtenir des phases métastables par refroidissement rapide

→ Procédés de post-production simples (suspension, composites, coatings)

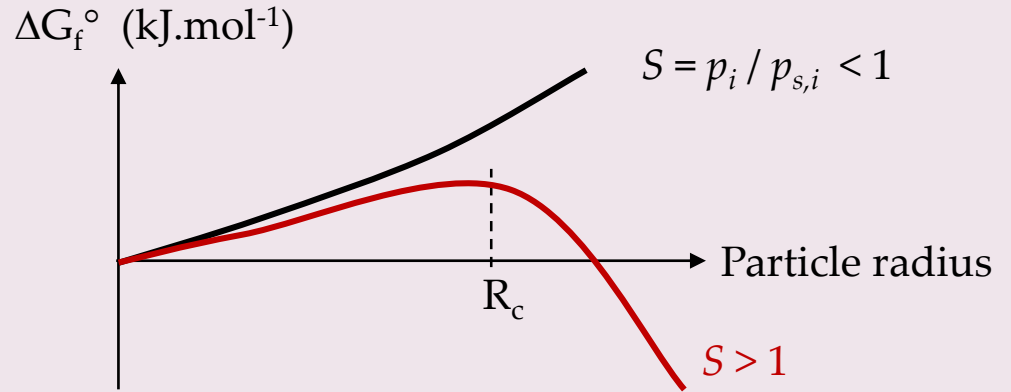


\rightarrow NUCLEATION = “all or nothing” process

Energie de formation



$$\Delta G_f^\circ \text{ et } R_c \sim f(p_{s,i})$$



Approche cinétique → Fréquence de nucléation J (particules s⁻¹.cm⁻³), en assumant que les agrégats avec $R > R_{critique}$ sont formés de façon irréversible (i.e. $\Delta G < 0$, if $p_i \gg p_s$).

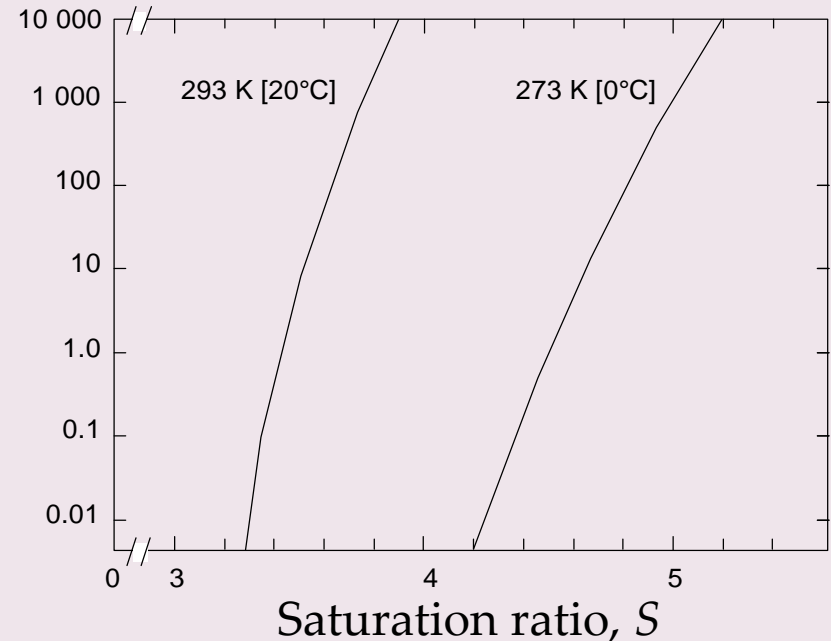
$$J \sim A \cdot \text{Exp}(-\Delta G_f^\circ / kT)$$

$$J(\text{part.s}^{-1}.\text{cm}^{-3}) \sim A' \cdot \text{Exp}(S)$$

NUCLEATION

= processus "tout ou rien"

→ Forte concentration de particules



REACTIVE NUCLEATION

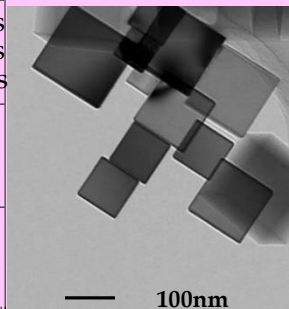
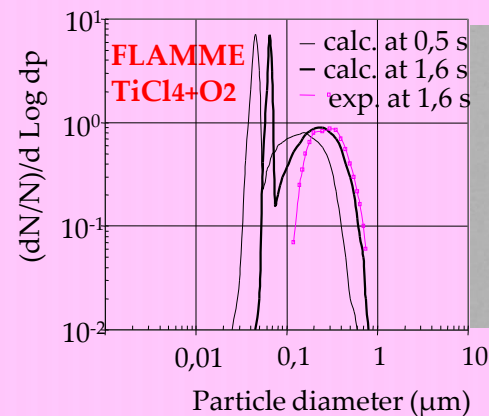
Gaseous reactants → **condensable products by chemical reactions**

- Photo-reactions
 - Natural sunlight oxidation (blue haze from terpens, smog from ozone and VOC),
 - Laser (Carbides and Nitrides from CH₄ and N₂)
- Ox/red. Pyrolysis of gaseous, liquid or suspensions precursor
 - HAP from VOC
 - MO_x from :- Metalorganic precursors (e.g. SiO_x from TEOS, HMDSO or Silane / MO₂ from MCl₄ or M(Acetate)₄ / MO from MCl₂ or M(Ac)₂ ...)
 - Metal (e.g. with Mg → MgO)
- Sol-gel reactions (M-OR + H₂O → M-OH → MO_x)
- Polymerisation from monomers,
 - ... by lasers, furnaces, flames and **plasmas**

e.g. : Flame metal combustion

μm-Mg part, H₂/Ar/O₂+Shield Ar (7/1/2 +3 lpm)

→ **Cubic or terraced particles**



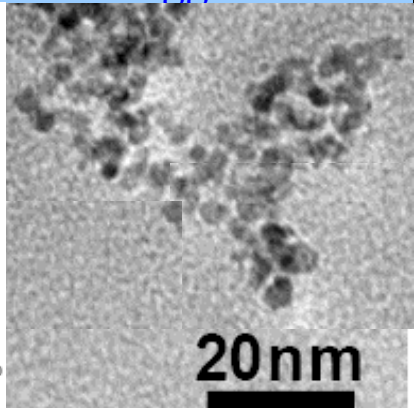
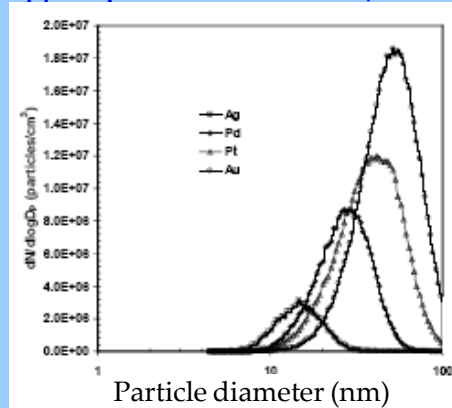
(Korean Patent, Choi et al, 2005)

PHYSICAL NUCLEATION

Cooling decreases the P_{saturation} & increases S = P_i/P_{sat}.

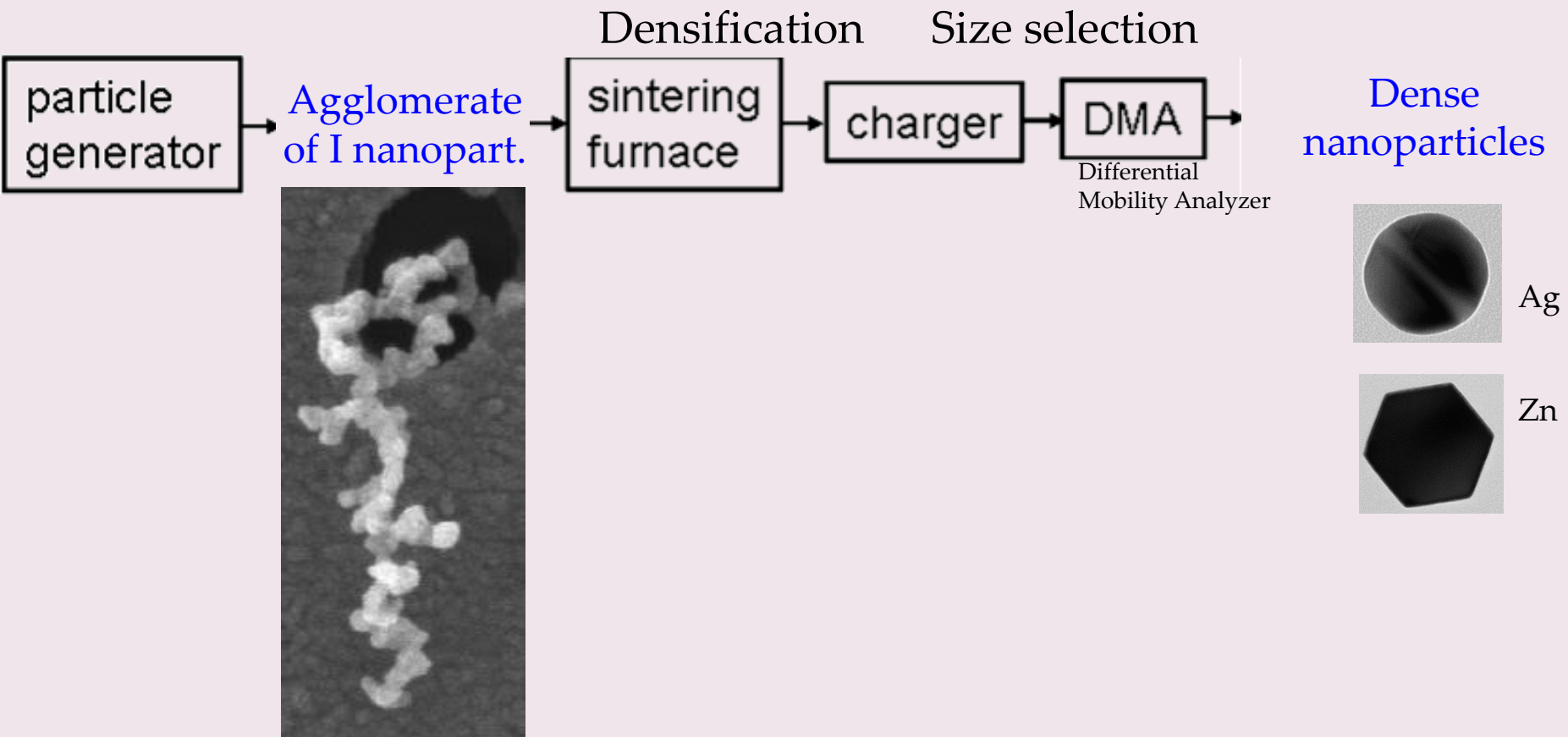
- Adiabatic expansion (champagne or venturi nozzles)
- Evaporation-condensation methods
 - Hot wires
 - Hot walls reactors (Furnace)
 - Laser ablation
 - **Plasma filaments**

eg : Spark → mono/bi-metallic agglom. Part



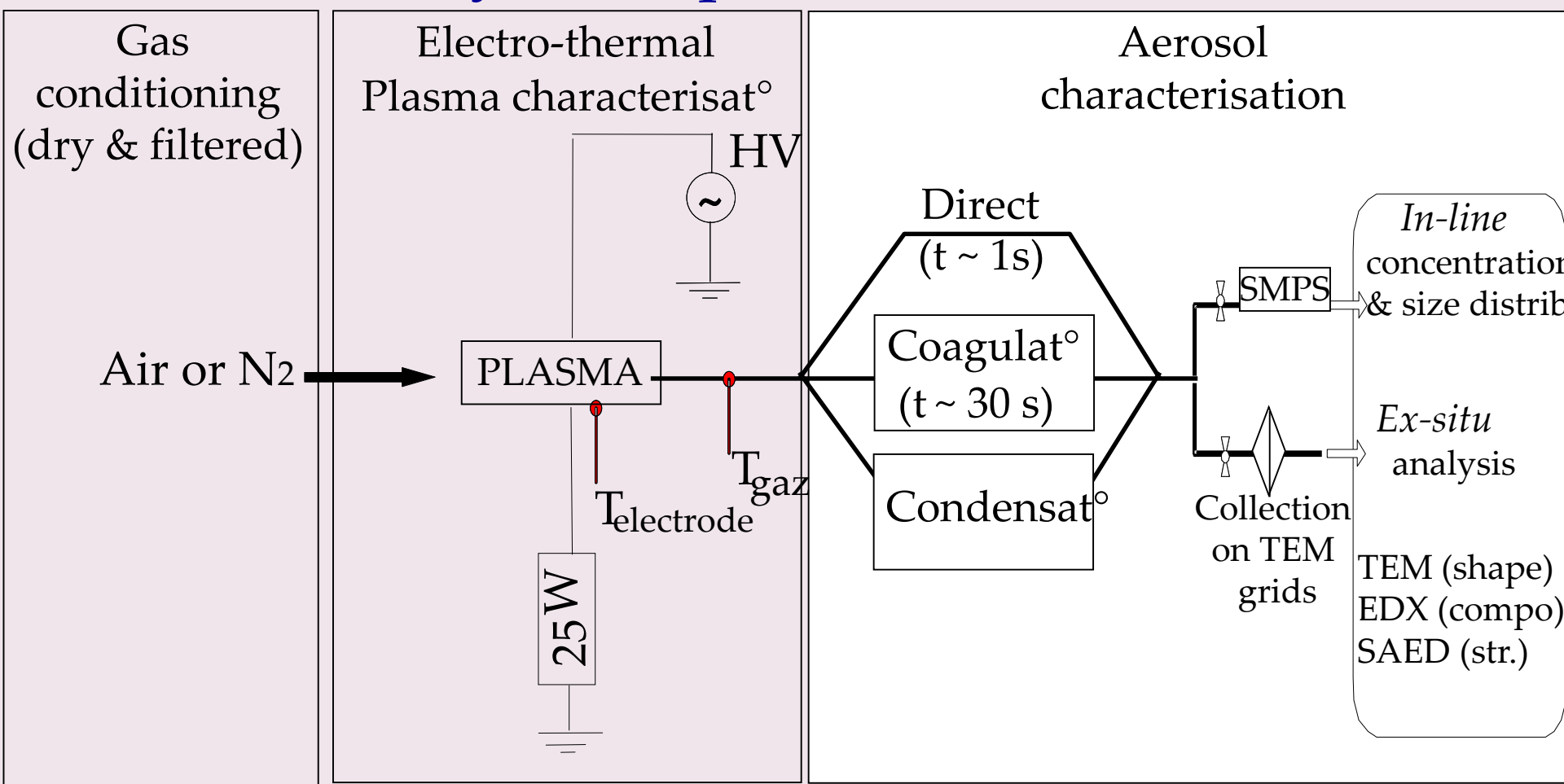
Jeong Hoon Byeon, Jae Hong Park, and Jungho Hwang, JAS 2008

Problème = COAGULATION post-nucléation



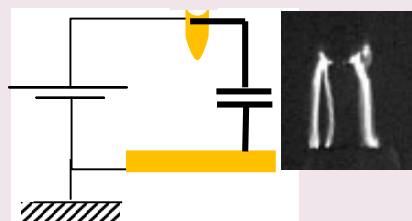
Comment éviter ces étapes successives ?

2b- Interaction plasma-surface vaporisation & nucléation

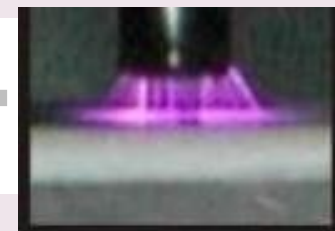
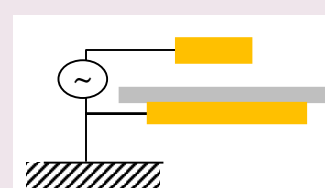


1- Partial detection of part < 10 nm with DMA \rightarrow TEM for size distributions on primary nano & N_p and DMA size dist. on larger A produced by post-discharge coagulation/condensation

2- Losses and coagulation to be quantified for N_p and d_p evaluation from downstream meas^t.



electrode
dielectric

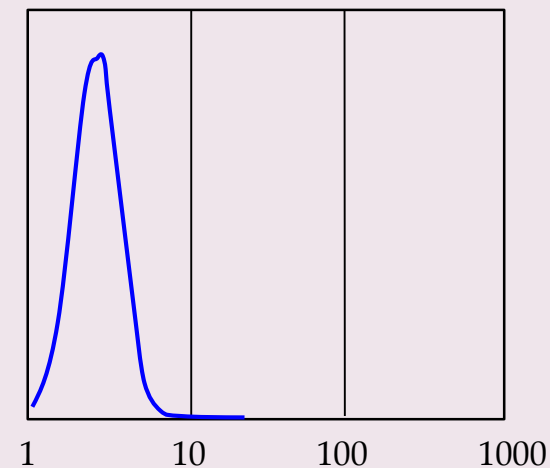
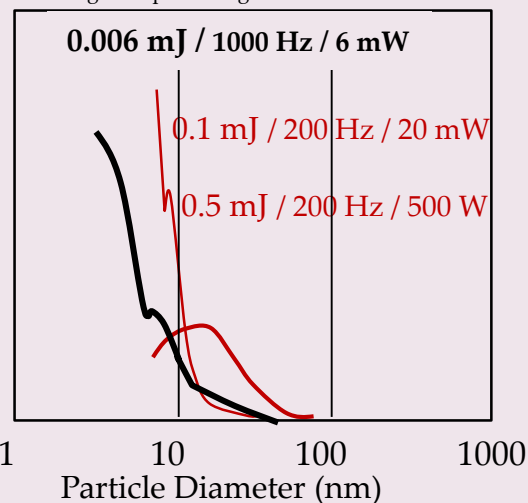
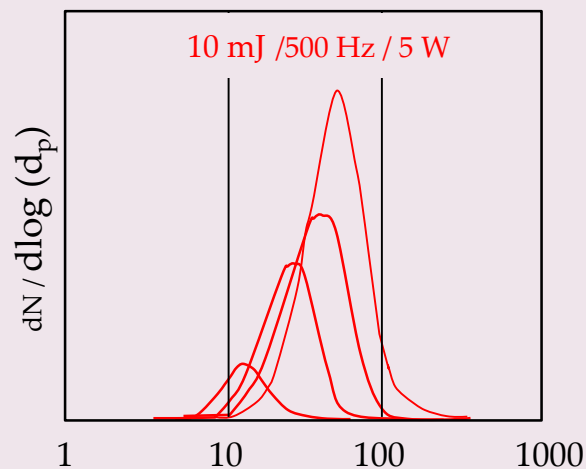


DC SPARK ($E_{fil.} > 10 \text{ mJ}$)

DC PREVENTED SPARK ($< 10 \text{ mJ}$)
& STREAMER ($5\text{-}10 \mu\text{J}$)

AC MICRO-DISCHARGES ($< 10 \mu\text{J}$)
in Dielectric Barrier Discharges

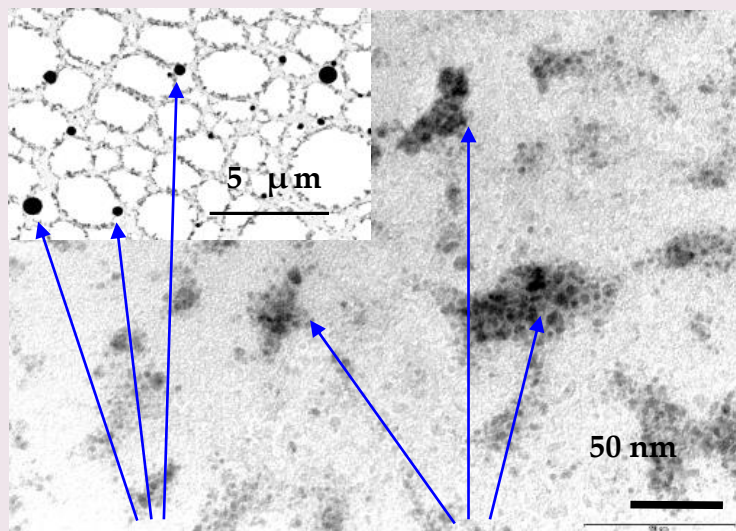
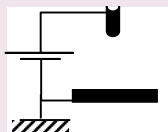
(8mm Rh point-Cu plane, N2 at 6 lpm,
 $C_{reg} = 120 \text{ pF}$ et $R_{reg} = 10^5 \text{ Ohm}$)



L'énergie par filament et les propriétés du matériau
→ flux de vapeur → taille et concentration des particules

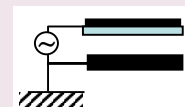
→ nucleation of vapors and nano-droplets ejection

PREVENTED SPARK
(< 10 mJ)

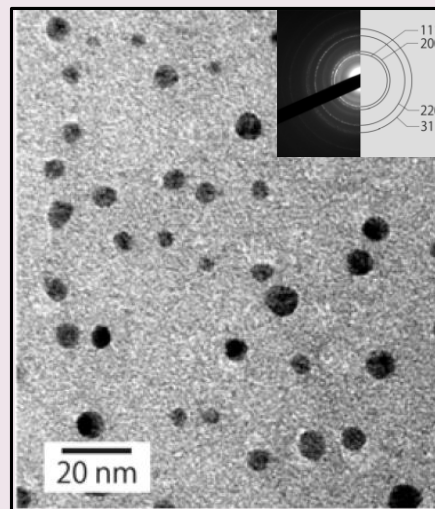


10-100 nm Solidified
NANO-DROPLETS

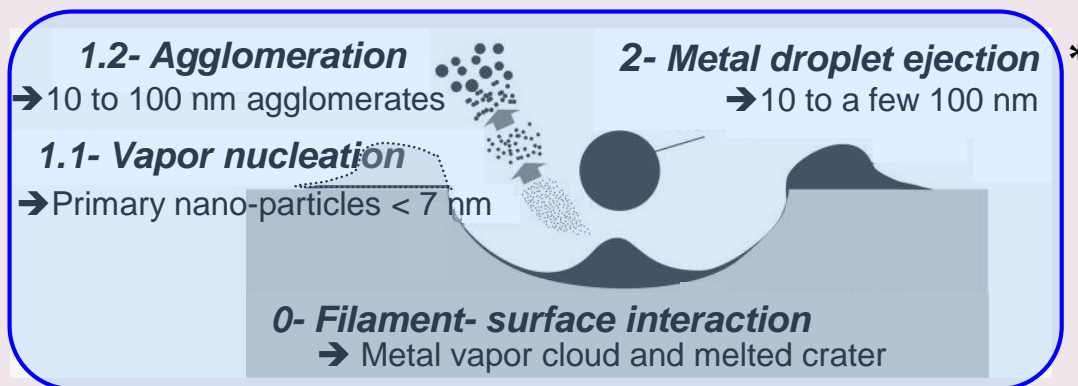
& 10-100 nm
AGGLOMERATES



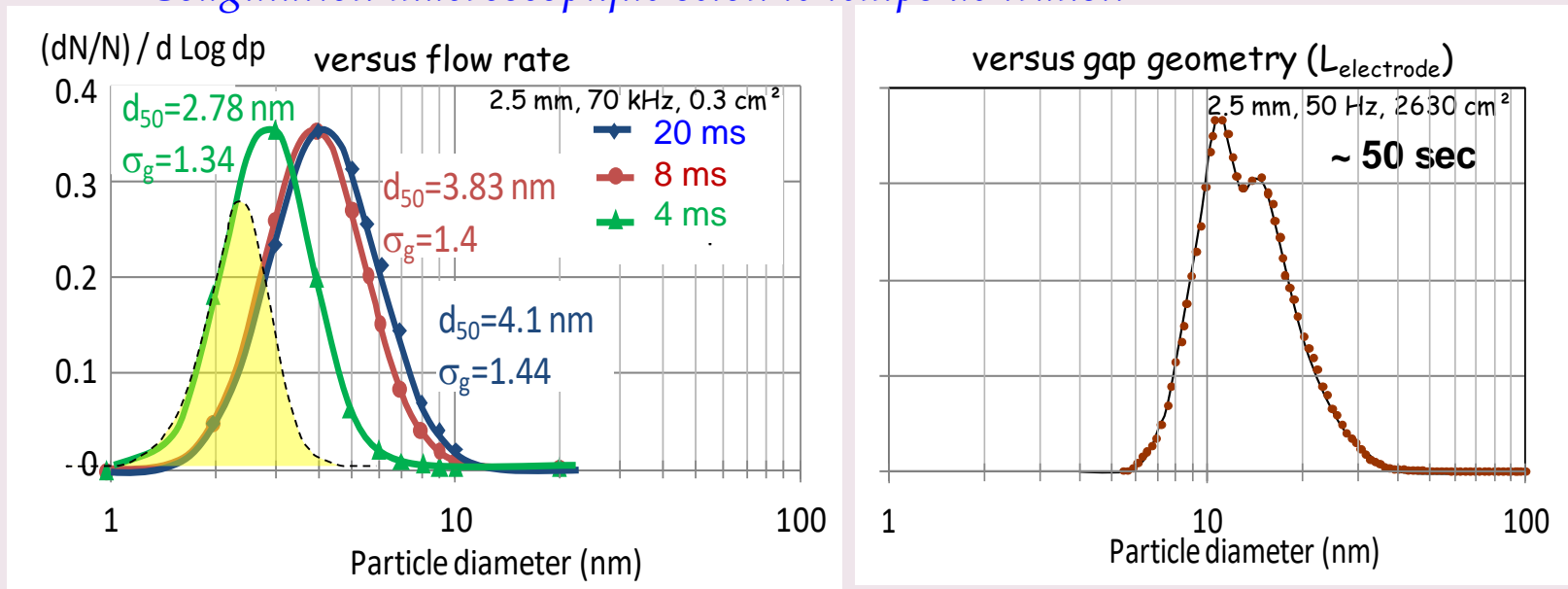
MICRO-DISCHARGES
in DBD (< 10 μJ)



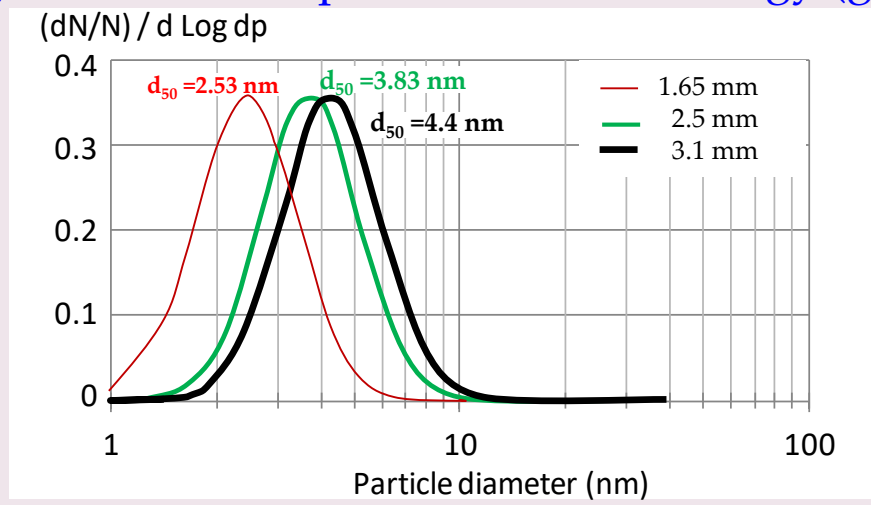
unagglomerated
NUCLEATED part. I < 7 nm



Coagulation macroscopique selon le temps de transit



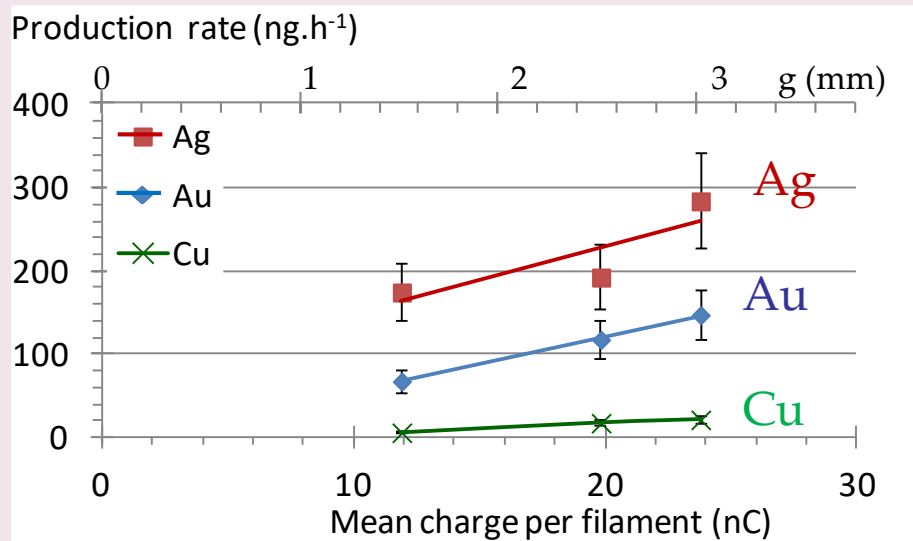
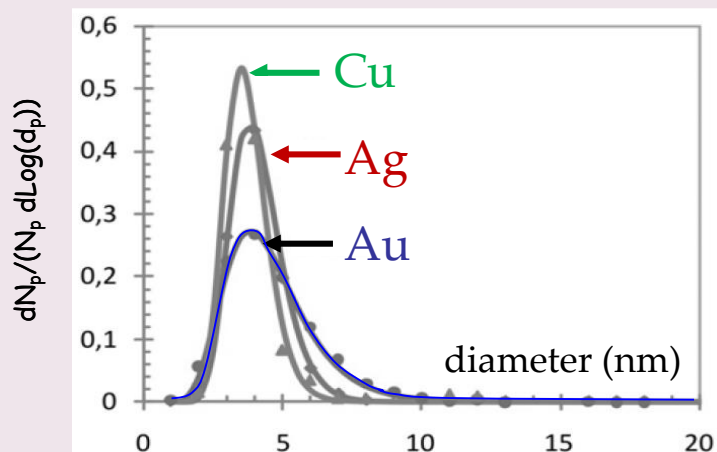
Local coagulation versus plasma filament energy (gap length)



Borra et al. (2015) Vaporization of bulk metals into single-digit nanoparticles by dielectric barrier discharges JAS, 79

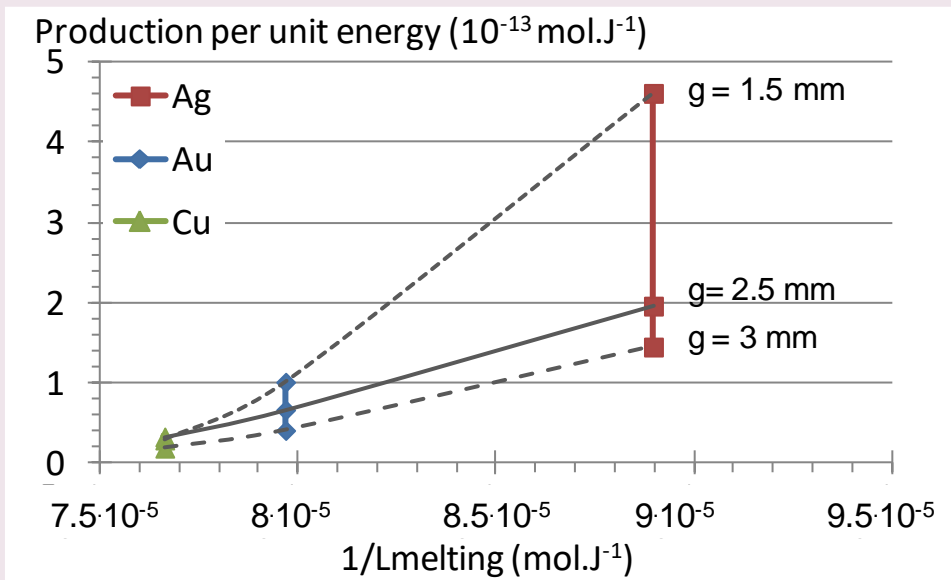
Coagulation en 2 étapes contrôlées par $E_{fil.}$ et le temps de transit pour la production de nanoparticule < 10 nm

At constant flow and energy per fil. 30 μ J



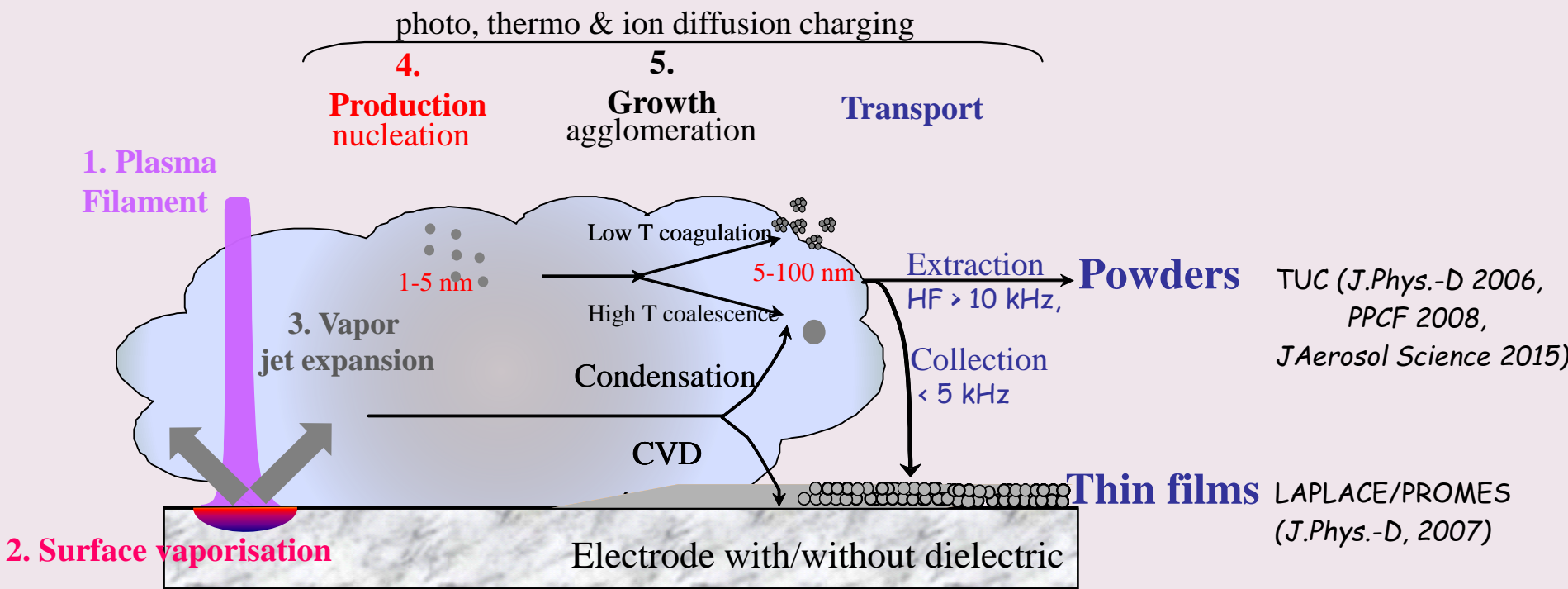
\rightarrow small $\Delta d_p \propto \Delta(\text{vapor flux})^{1/3}$

..... with vapor flux = $f(p_s, 1/DH_{\text{melting}})$,



\rightarrow Energy yield decreases at increasing vapor flux

Interest of AP-Plasmas for NUCLEATION



Nucleation in the vapors jet produced by each filament and subsequent growth by coagulation

Plasma filaments with tuneable E prevent from coagulation
 → controlled size nano-particles
 with size-dependant properties

2c- Coatings post-DBD

Condensation hétérogène

- (i) Nano formées par DBD → générateur de nano étalon
- (ii) Précurseur gazeux → stabilisation de catalyseur

Dépôt de couches minces

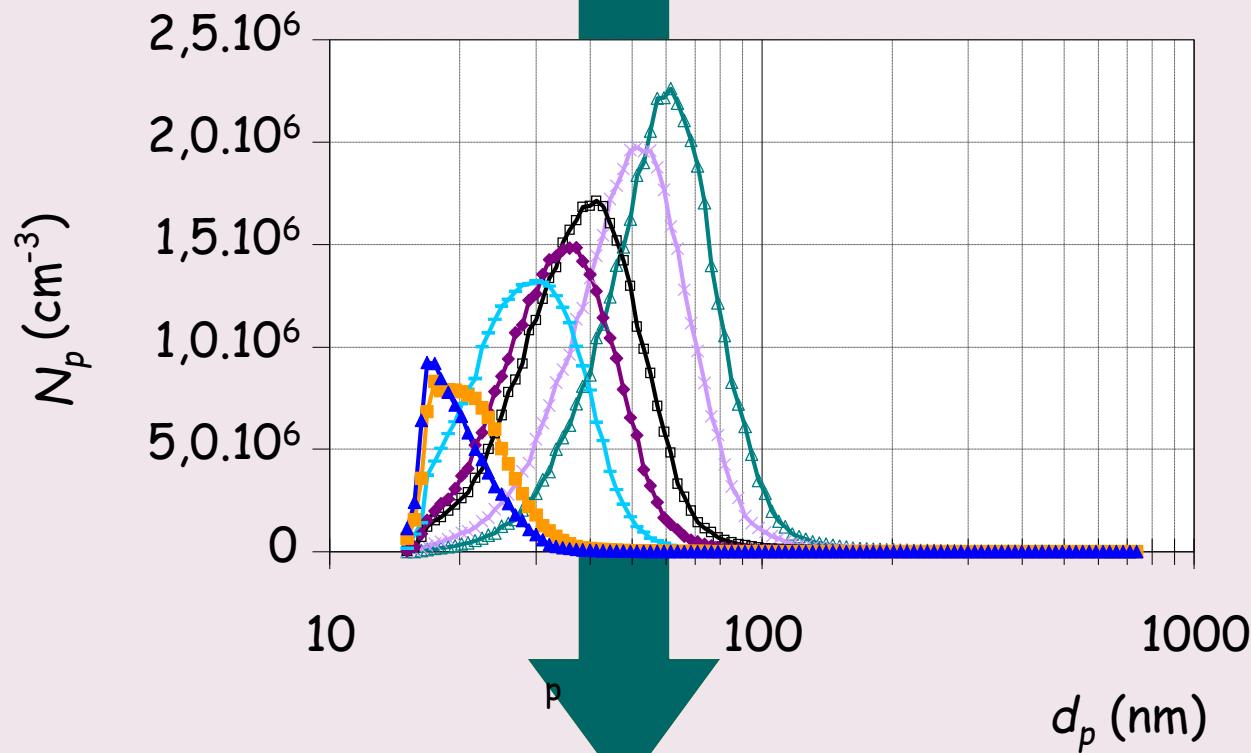
- (iii) *Fonctionnalisation de surface en post-DBD*

Growth by condensation in postDBD

N_I = concentration of primary particles produced by homogeneous nucleation in DBD (0.5 mm , 7 kV, 70 kHz, in N_2)

N_v = vapour density, controlled by the temperature of an external source

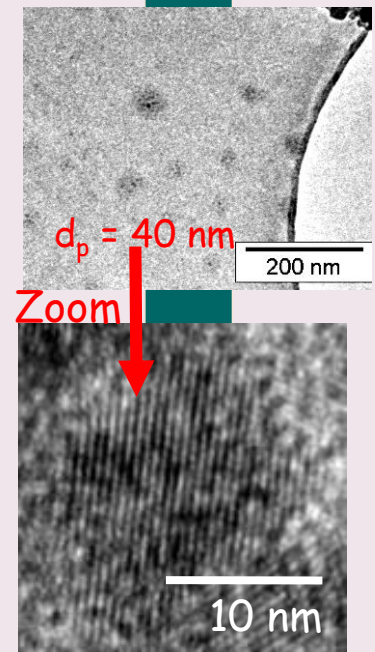
Increase of N_v at constant N_I



Unimodal aerosol

d_p controlled from 15 to 100 nm by N_v/N_I

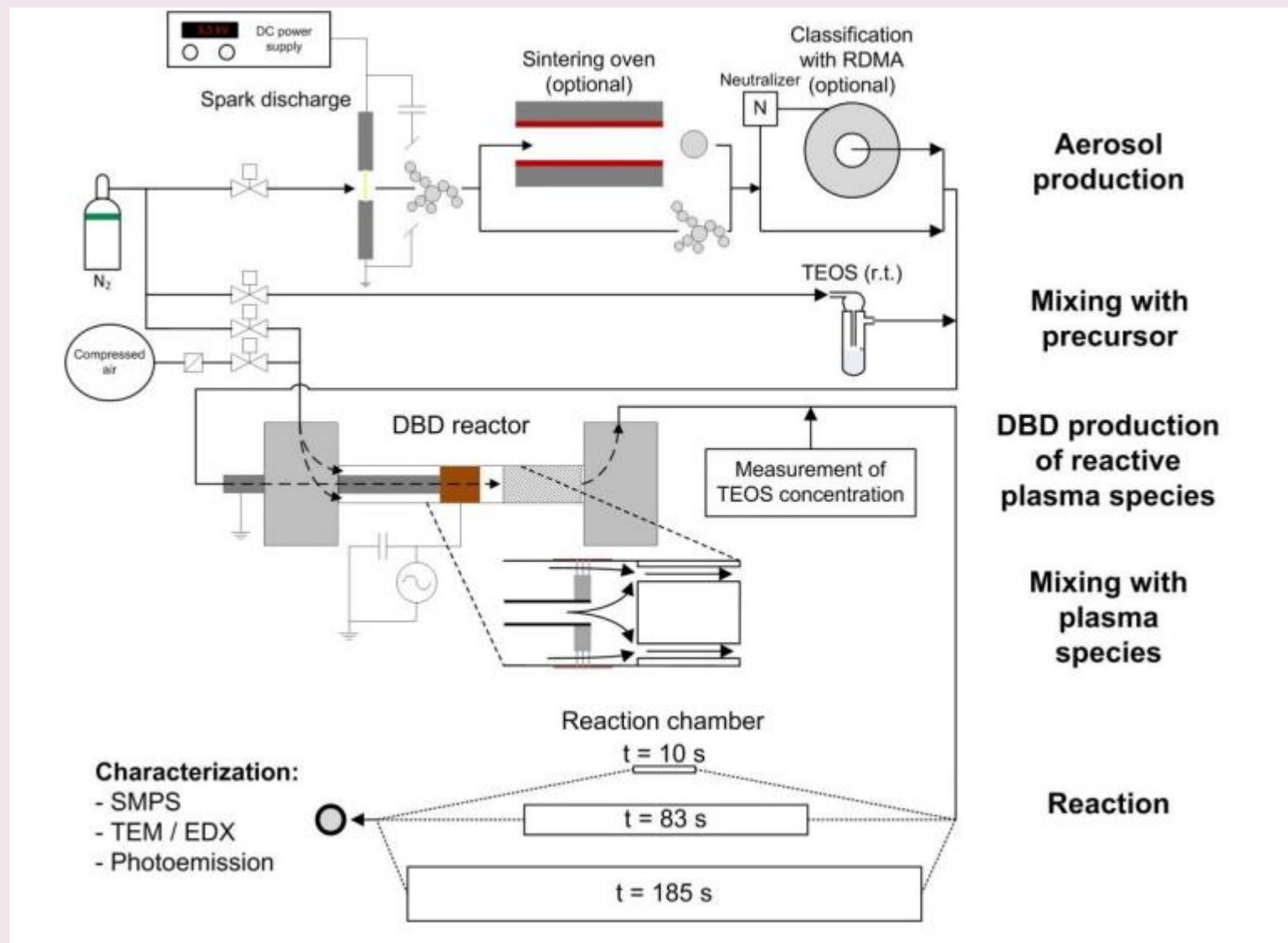
TEM pictures



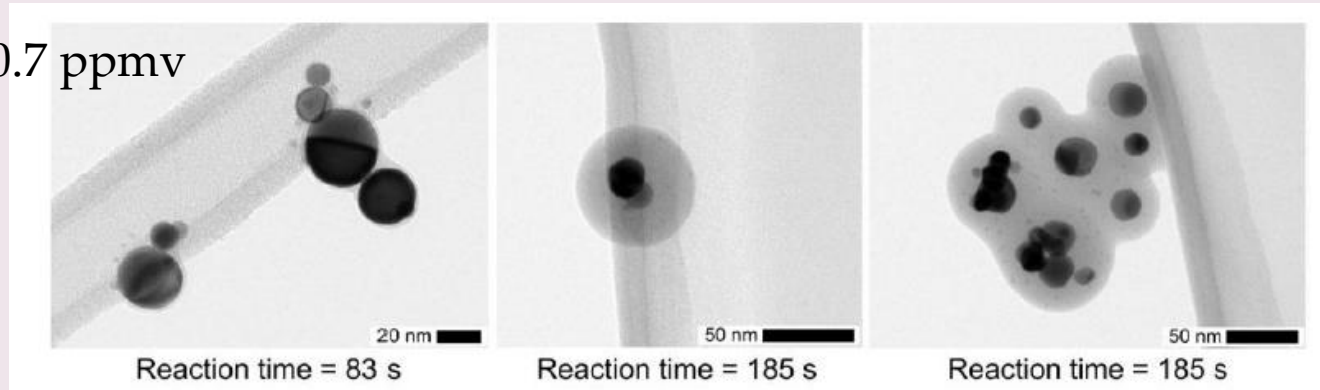
Condensation on crystallised primary part.

(ii) Condensation hétérogène en post-DBD

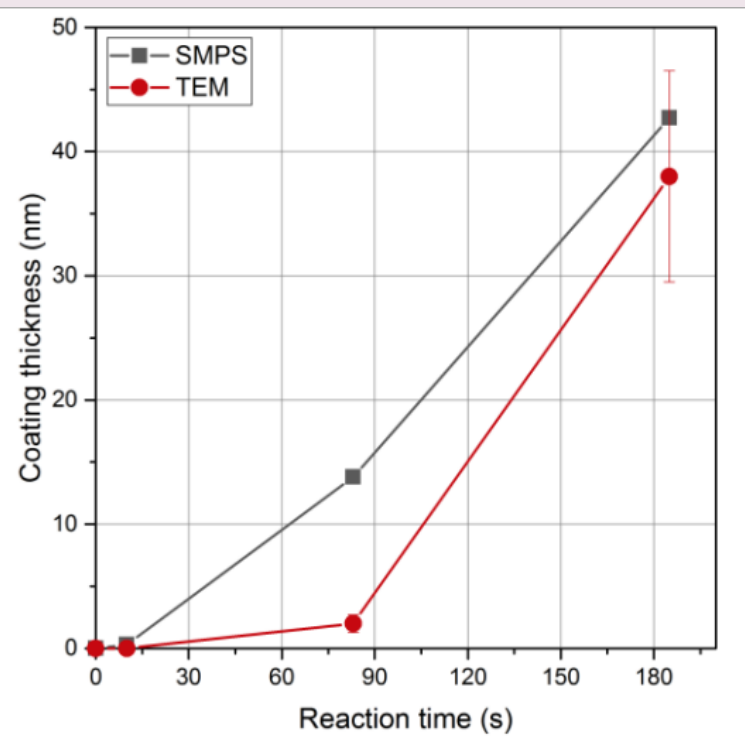
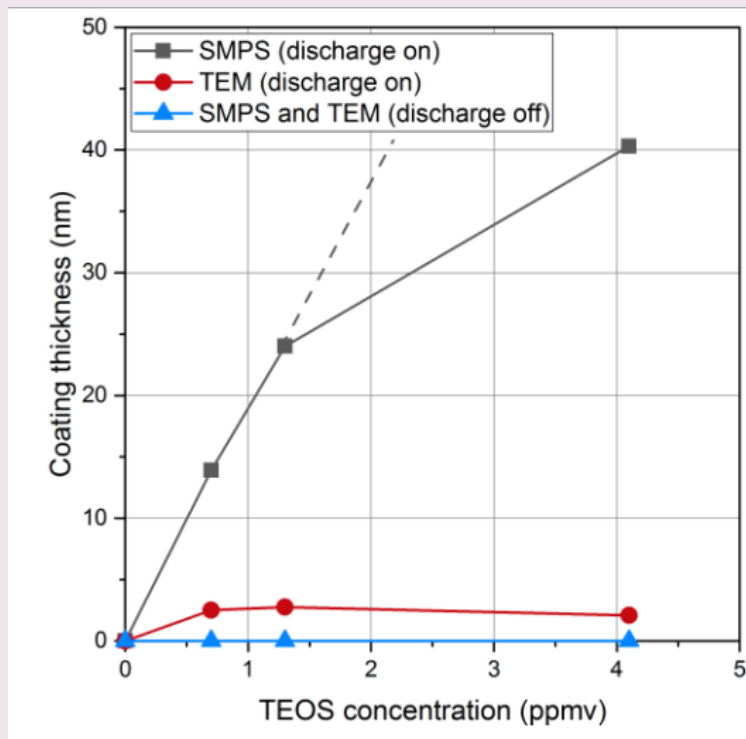
*Enrobage de nano-particules catalytiques
pour la stabilisation thermique*

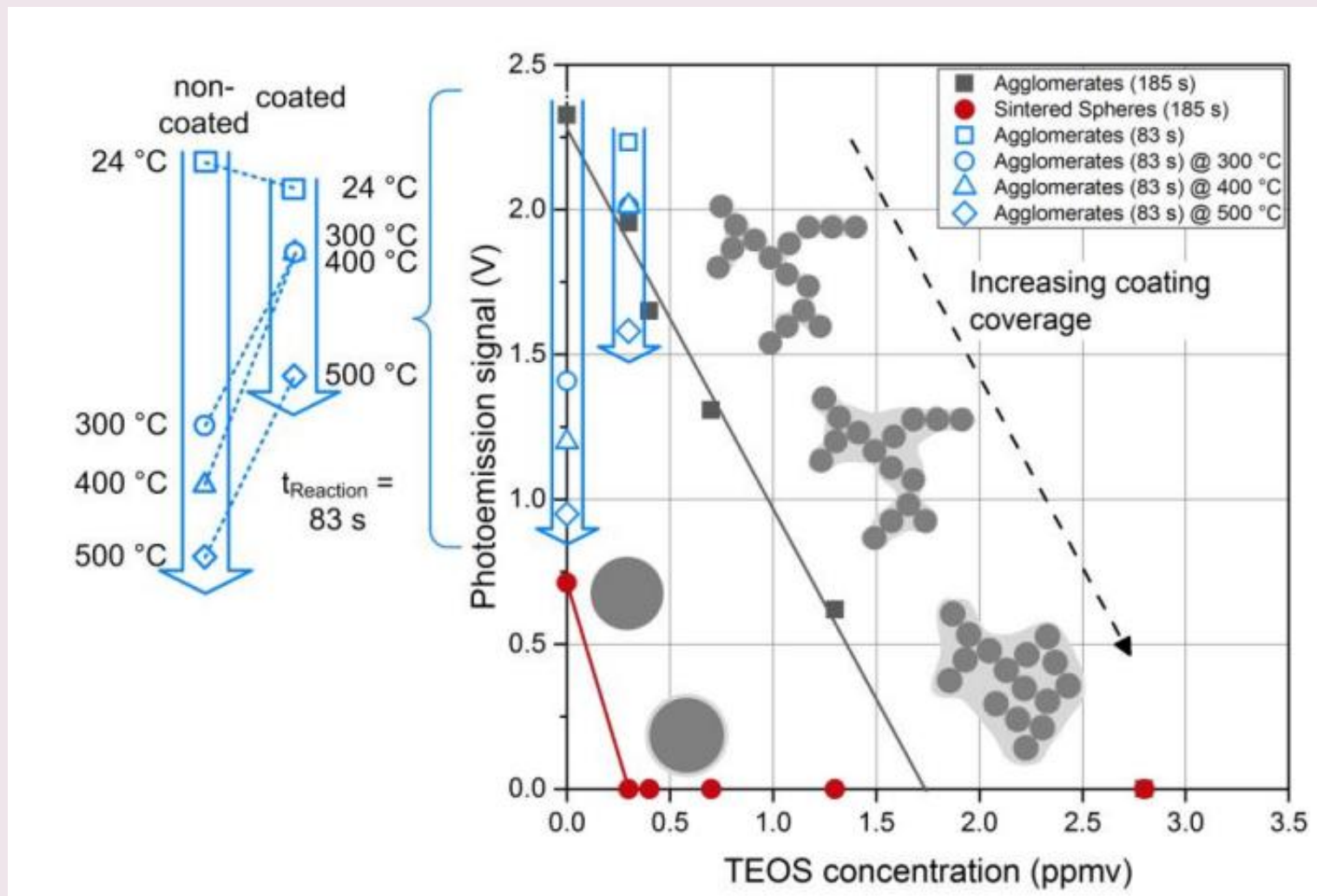


[TEOS] = 0.7 ppmv



Time → coating thickness

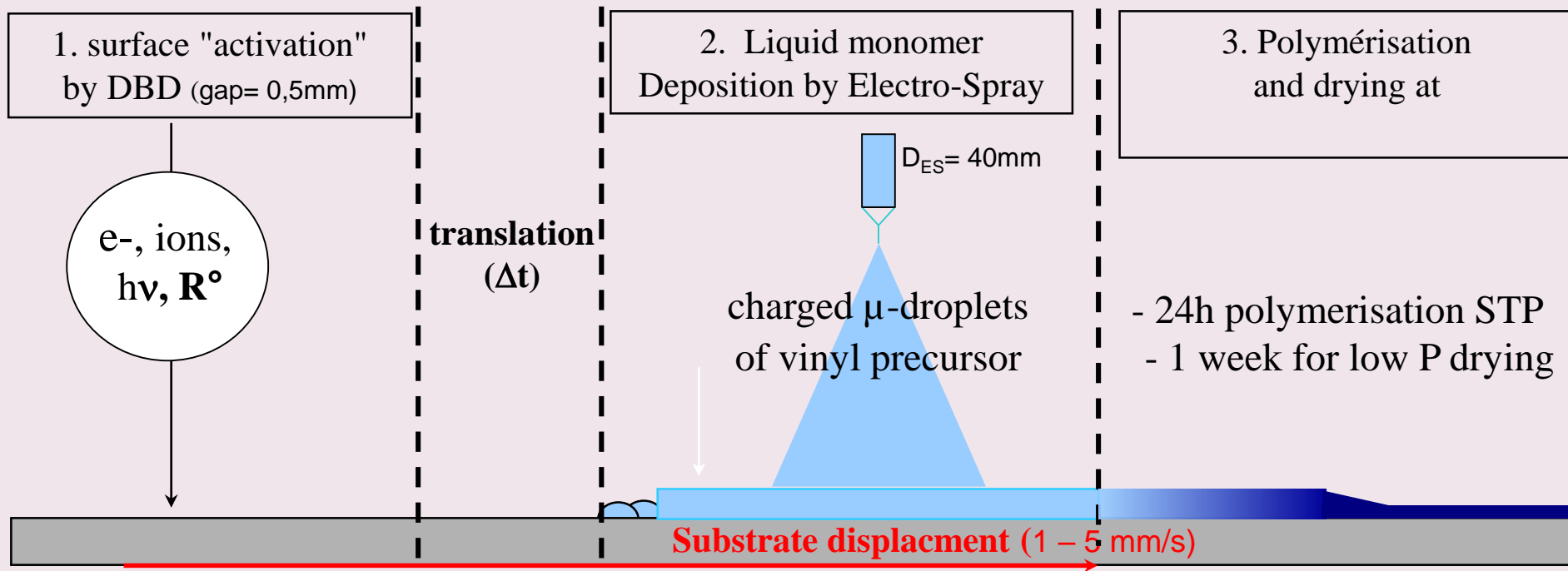




Partial coating of Pt agglomerates stabilises the aggregates

*(iii) Fonctionnalisation de surface
par dépôt de couche mince
en post-DBD*

PRINCIPLE of post-DBD polymerisation



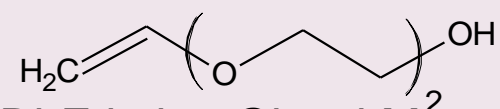
- 24h polymerisation STP
- 1 week for low P drying

R°/m^2

dR°/dt

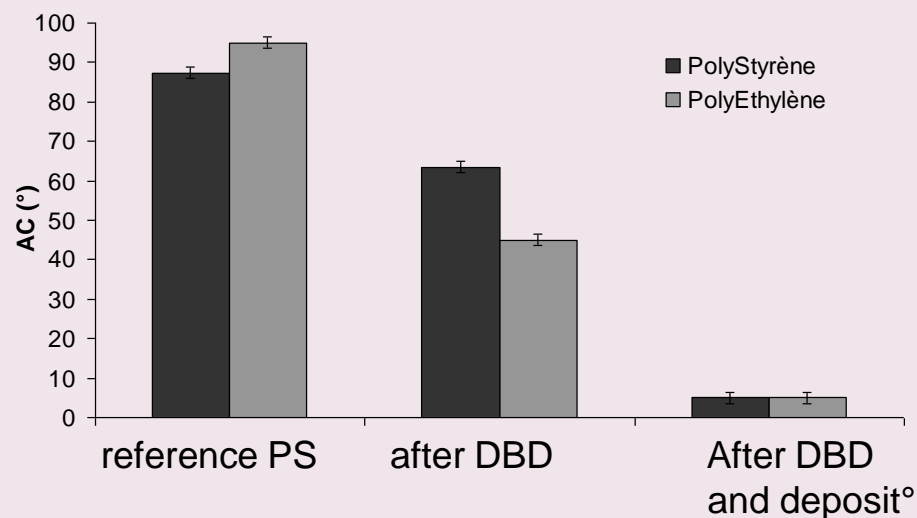
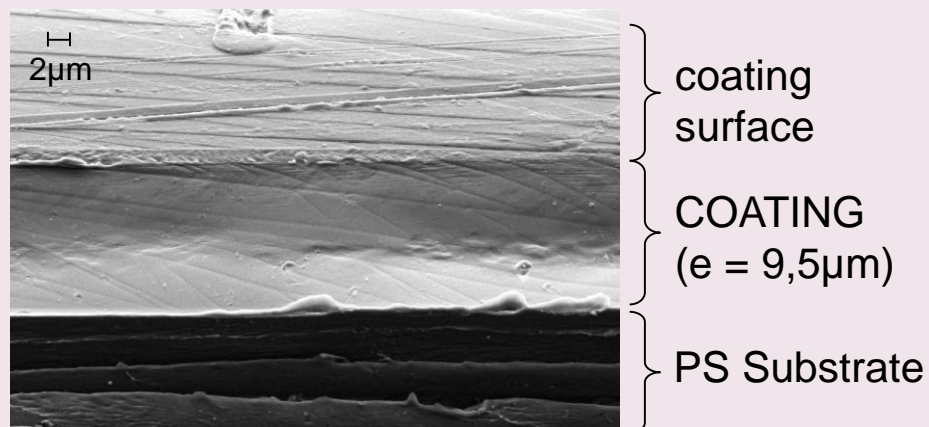
$[M]/[R^\circ]$

Competition
Evap./Polym.



M = Di-Ethylen Glycol Mono Vinyl ETHER
or M = Acrylic Acid

SUBSTRATE = PS/PE



Thin Coatings
(from few nm to 100 µm)

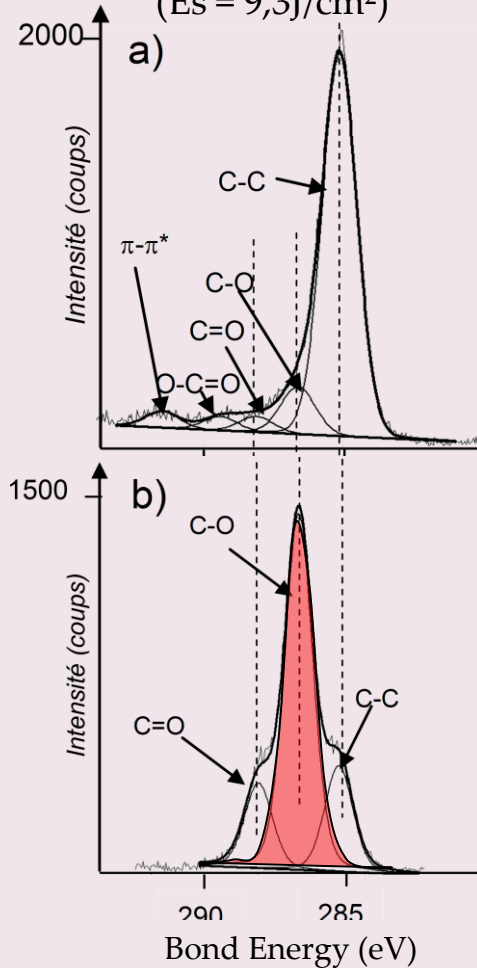
hydrophilic COATINGS
(∀ substrate)

M. Tatoulian, Gallino E, Jafari R, Arefi F, Tatoulian L, Borra J-P, Lewis F, Mantovani D, Plasma and Electro spray deposition for biocompatibility of stents, *Materials Science Forum*. **539-543**, 529-534

Analyses chimiques

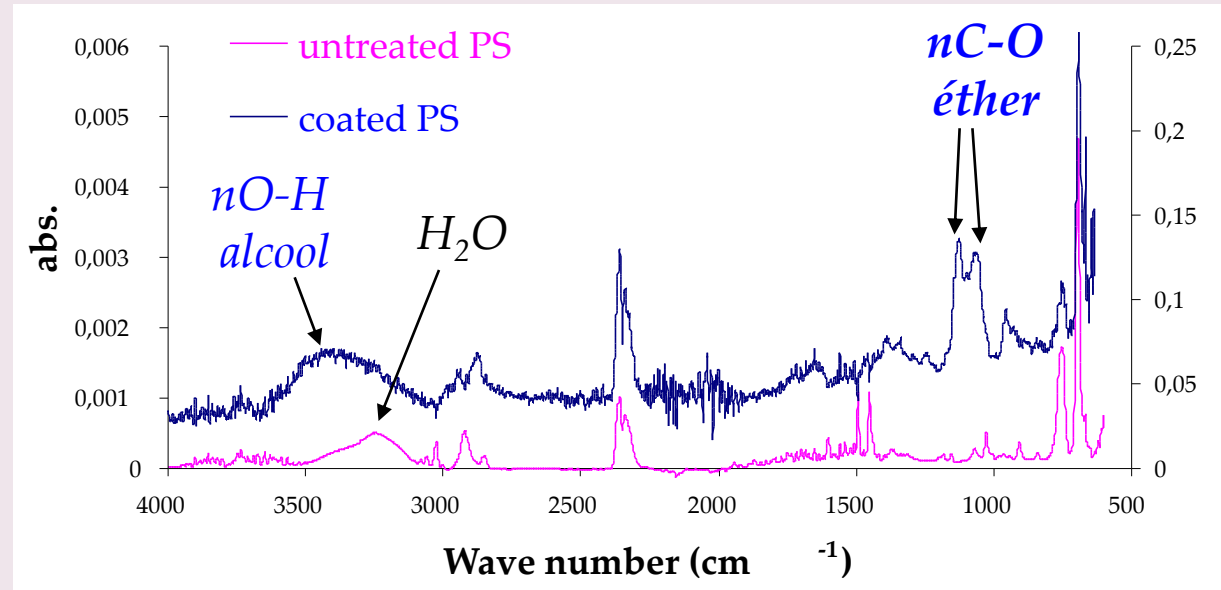
XPS

PS post-DBD
($E_s = 9,3 \text{ J/cm}^2$)

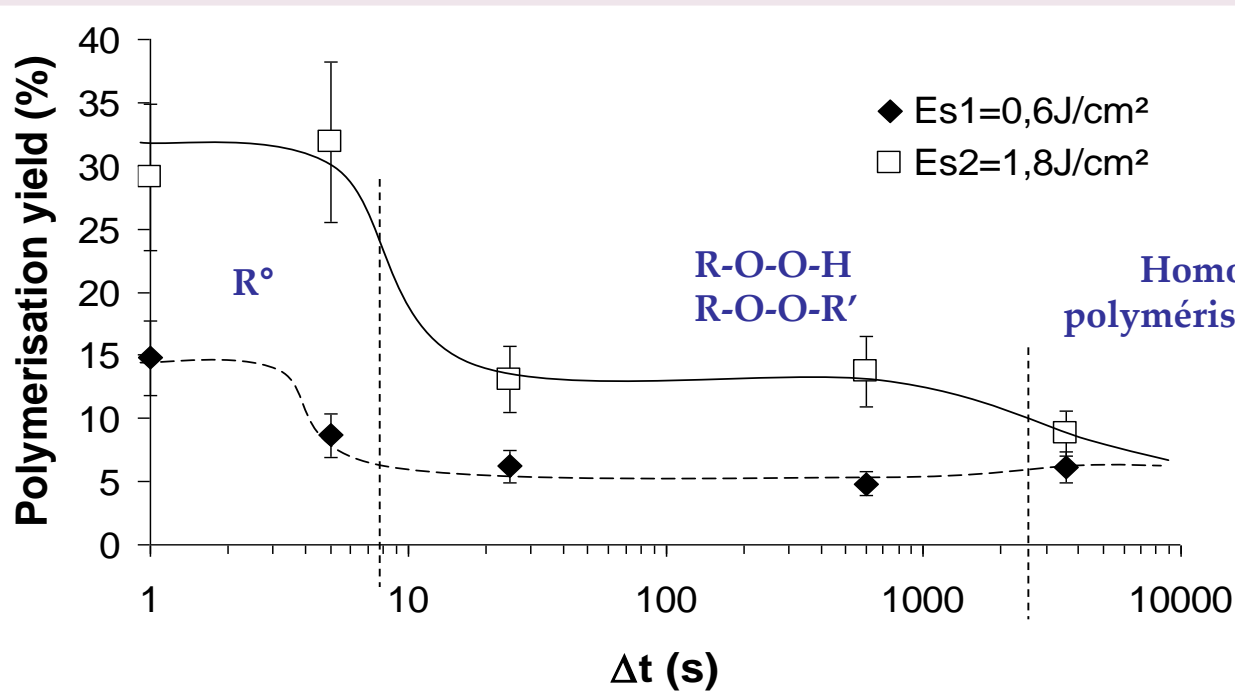


coated PS

FTIR-ATR



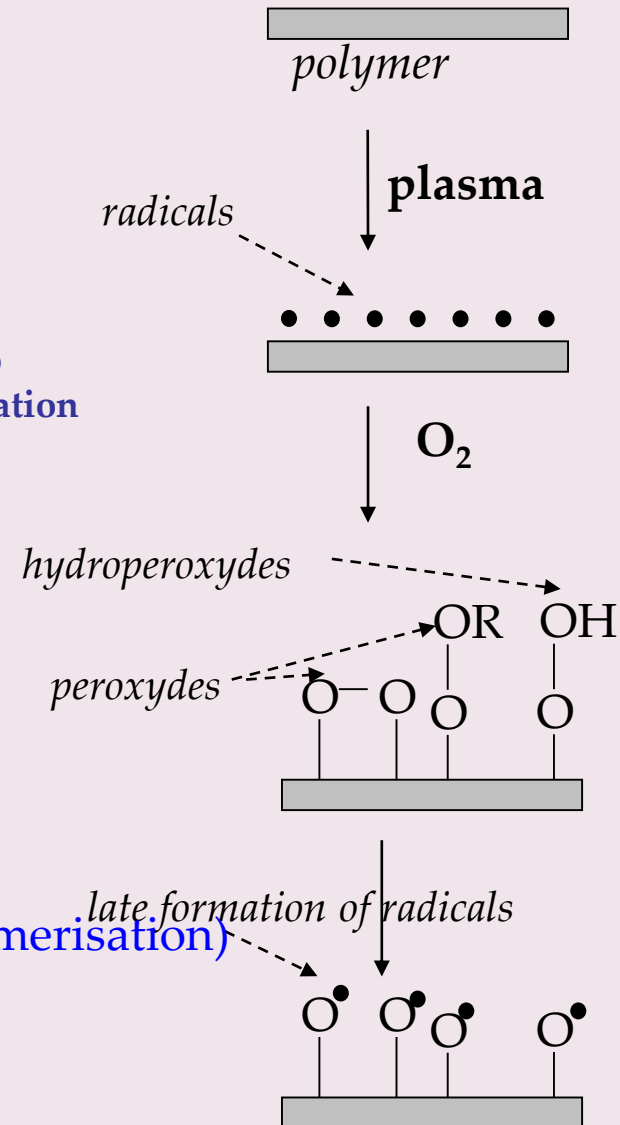
- Disappearance of $p\text{-}p^*$ → Coated PS > 5nm
- 60% of C-O/C1s → high retention of the monomer functionality



shorter $\Delta t \Rightarrow$ higher polymerisation yields

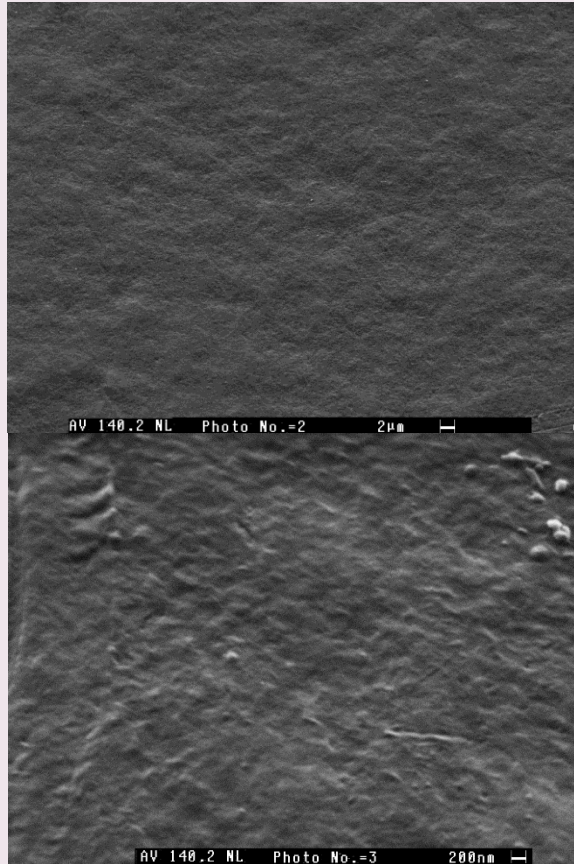
3 yield ranges(Δt) \rightarrow H: $\Delta t \rightarrow$ species triggering polymerisation

- $\Delta t <$ few sec.. \Rightarrow Radicals
- few sec. $< \Delta t <$ tens of min \Rightarrow Peroxyde / Hydroperoxyde
- $\Delta t >$ tens of min \Rightarrow Homo (self) polymérisation



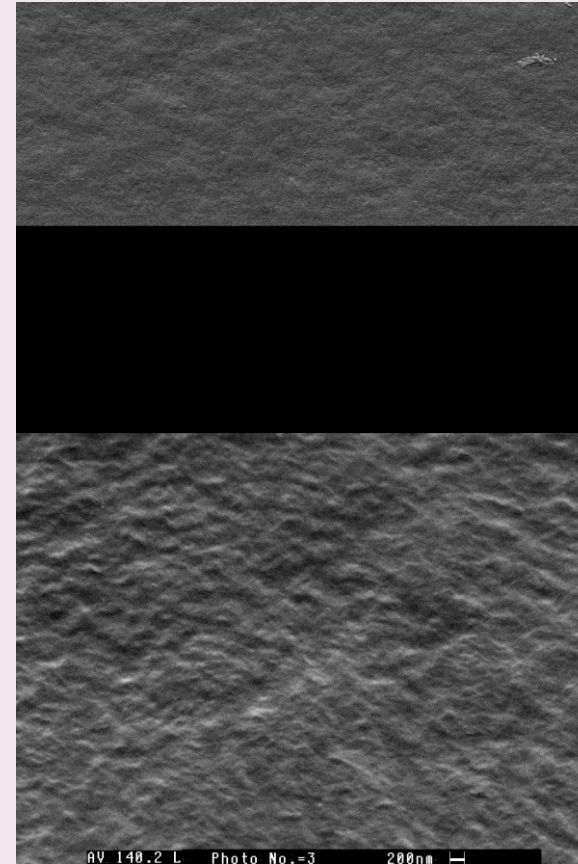
Before

($E_s=1,8\text{J}/\text{cm}^2$, $\Delta t=1\text{s}$, $m_s=95\mu\text{g}/\text{cm}^2$)



after WASHING

(12h immersed in water)



Stabilité du coating malgré lavage

3- Charge des nanoparticules en post-décharge

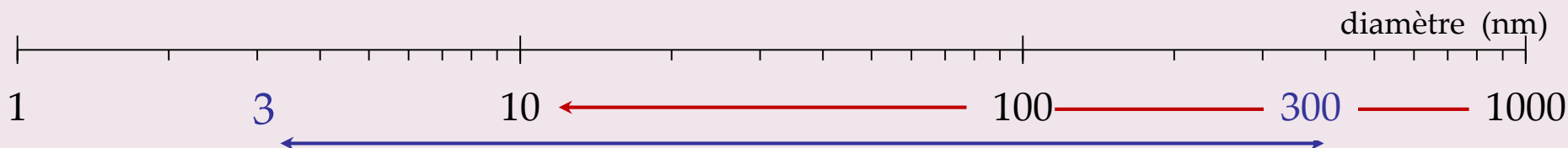
- a- Mécanismes et lois de charge
- b- Problématique métrologique nano (taille, concentration)

- Interaction molécules-particules (solide et/ou liquide)

Nombre de Knudsen: $K_n = \frac{2 \cdot \lambda_m}{d_p}$

$K_n < 10$ Moléculaire $K_n \sim 1$ Intermédiaire $0,1 > K_n$ Continu

d_p : diamètre de la particule
 λ_m : libre parcours moyen
 66 nm à PA, 20 °C



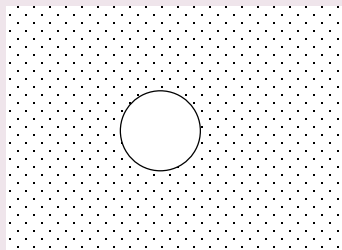
- Interaction ion-particules

Dans un plasma $\frac{\lambda_{ion}}{\lambda_{Debye}}$ $\ll 1 \rightarrow$ Gaine collisionnelle

Dans un gaz $K_{ni} = \frac{2 \cdot \lambda_{ion}}{d_p}$ $\lambda_{ion} \sim 15$ nm à PA, 20 °C

Charge par diffusion

$\tau_{\text{diffusion charging}} \sim \text{ms}$



$\forall d_p$ et unique mec. pour $d_p < 100 \text{ nm}$

$$q_p(t) = \left(\frac{2\pi\epsilon_0 \cdot d_p \cdot k_B \cdot T}{e^2} \right) \cdot \ln \left(1 + \frac{e^2 \cdot c_i \cdot d_p \cdot N_i \cdot t}{8\pi\epsilon_0 \cdot k_B \cdot T} \right)$$

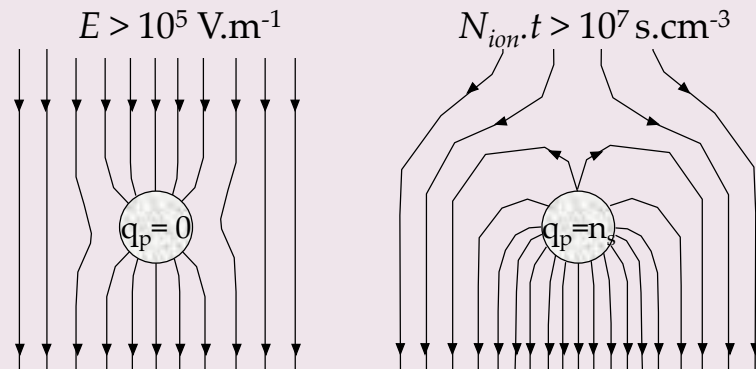
(White 1951)

Paramètres ioniques: $\mu_i, c_i, m_i, \lambda_i, D_i$

Paramètres aérosols: N_p et d_p

Paramètres de mélange: $\langle N_i \cdot t \rangle, E$

Charge par champ



Négligeable pour $d_p < 100 \text{ nm}$

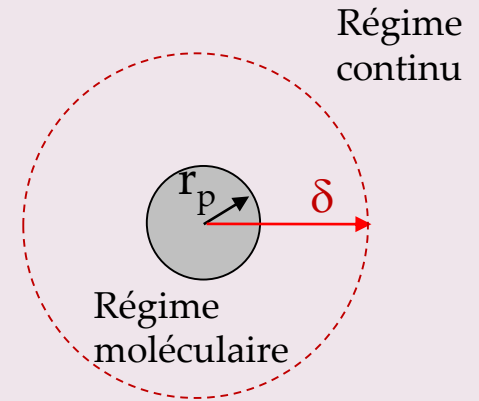
$$q_p(t) = q_s \cdot \frac{e \cdot \mu_i \cdot N_i \cdot t}{1 + e \cdot \mu_i \cdot N_i \cdot t}$$

$$q_s = \frac{3\epsilon_r + 1}{\epsilon_r + 2} \cdot \frac{4\pi\epsilon_0 \cdot d_p^2 \cdot E}{e}$$

(Pauthenier 1932)

Flux d'ions sur un aérosol (Fuchs 1963)

$$j = \frac{\pi \gamma \bar{v}_i \delta^2 \cdot N_i \exp\left(-\frac{\varphi(\delta)}{k.T}\right)}{1 + \exp\left(-\frac{\varphi(\delta)}{k.T}\right) \frac{\gamma \cdot \bar{v}_i \cdot \delta^2}{4D_i} \int_{r_p}^{\infty} \frac{1}{r^2} \exp\left(-\frac{\varphi(r)}{k.T}\right) dr} = \frac{dq_p}{dt}$$

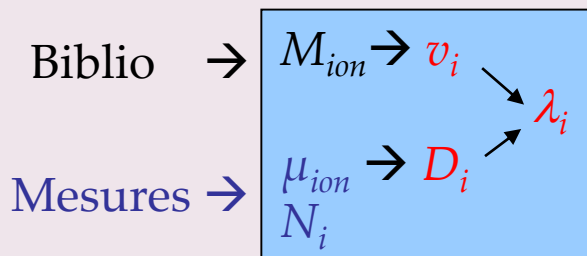


Energie d'interaction ion-particule

$$\varphi(r) = \int_r^{\infty} F dr = \frac{e^2}{4\pi\epsilon_0} \cdot \left[\frac{n_p}{r} - \frac{\epsilon_r - 1}{\epsilon_r + 1} \cdot \frac{r_p^3}{2r^2(r^2 - r_p^2)} \right]$$

Sphère limite

$$\delta = \frac{r_p^3}{\lambda_i^2} \left[\frac{\left(1 + \frac{\lambda_i}{r_p}\right)^5}{5} - \frac{\left(1 + \frac{\lambda_i^2}{r_p^2}\right) \left(1 + \frac{\lambda_i}{r_p}\right)^3}{3} + \frac{2}{15} \left(1 + \frac{\lambda_i^2}{r_p^2}\right)^{5/2} \right]$$

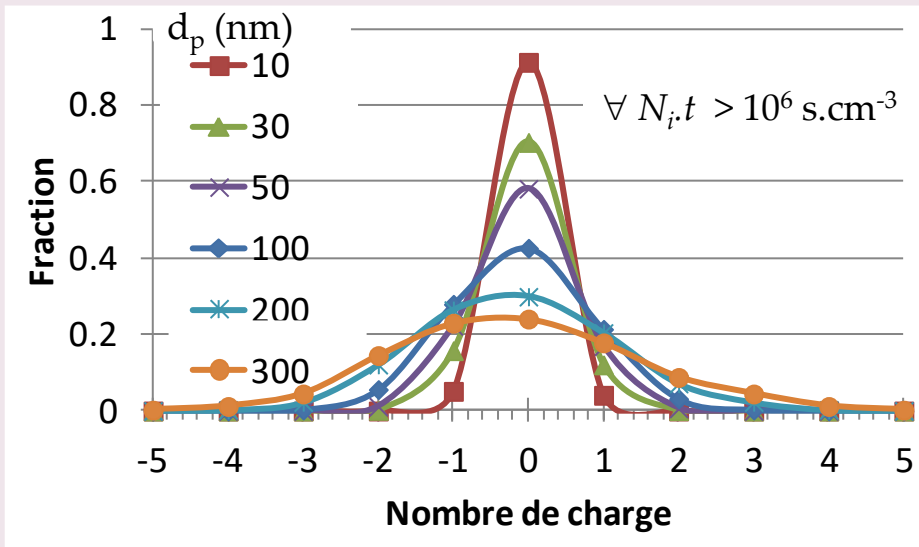


- LOI de CHARGE valide en UNIPOLAIRE $\langle q_p \rangle = f(N_i \cdot t)$ et $\propto dp$
en BIPOLAIRE $\langle q_p \rangle \propto \ln \left(\frac{N_i^+ \cdot Z_i^+}{N_i^- \cdot Z_i^-} \right)$

Charge par diffusion uni- & bi-polaire :

paramètres aérosol (d_p , ε , forme, q_p°) et de mélange ($N_i \cdot t$)

Bipolaire (Kr⁸⁵ ou AC DBD)

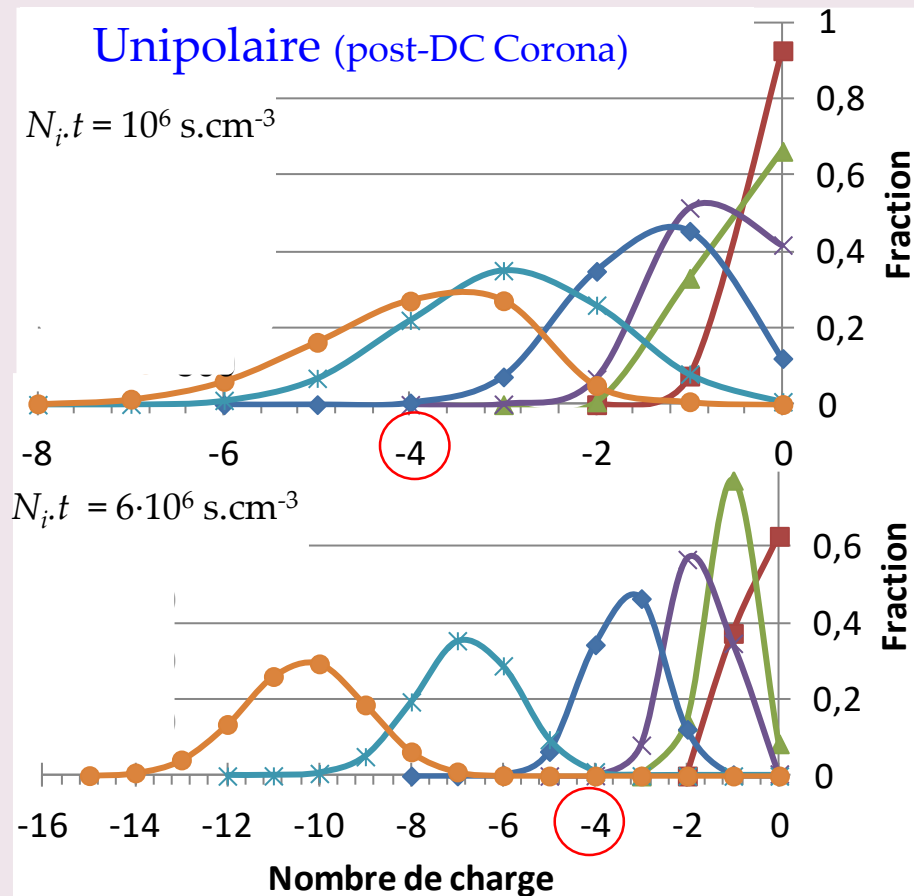


- F° neutre dominante $\forall d_p < 100 \text{ nm}$

- pour $d_p < 10 \text{ nm}$, f° chargée < %
 → représentativité mesure = ?

- Perte électrostat faibles MAIS RADIOACTIF
 → Alternative LPGP Décharge bipolaire AC DBD

Unipolaire (post-DC Corona)



- F° neutre NULLE pour $d_p > 30 \text{ nm} - 200 \text{ nm}$ vs $N_i \cdot t$

- pour $d_p < 10 \text{ nm}$: $N_i \cdot t = 6 \cdot 10^6 \text{ s.cm}^{-3}$, f° chargée > 30 %
 → Meilleure représentativité et abaissement du seuil de détection en N_p et/ou en d_p qu'en bipolaire

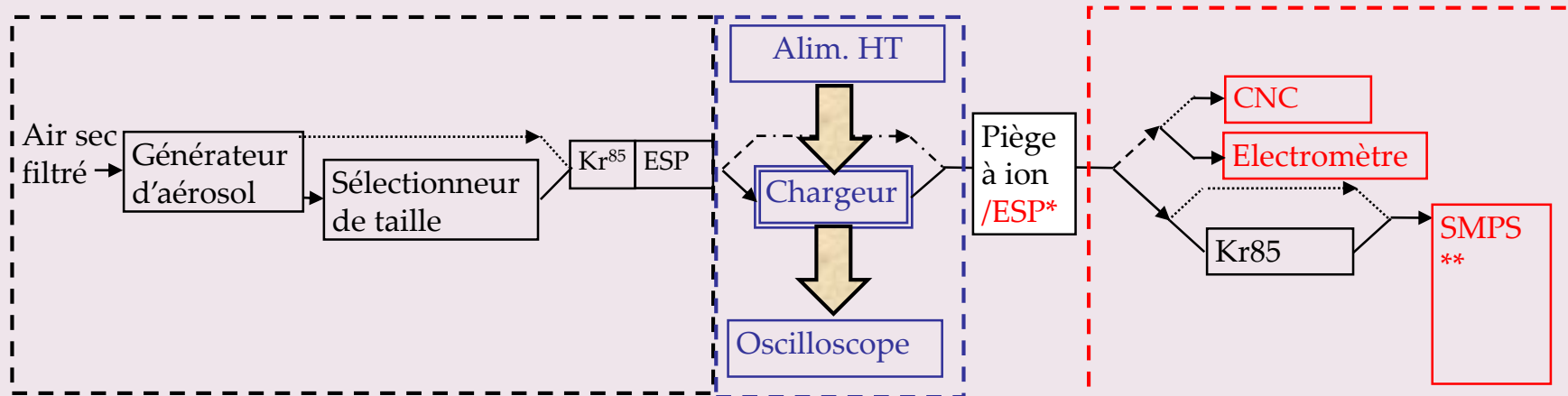
- mais $\forall d_p$, fort $N_i \cdot t \Leftrightarrow$ pertes électrostat (t , mélange)

Caractérisation de chargeurs pour la granulométrie (Distribution de charge en sortie et pertes)

PRODUCTION D'AÉROSOLS MONODISPERSÉS CHARGES OU NEUTRES

CHARGEUR PLASMA

MESURES AÉROSOL



Débit: 0,3-10 L.min⁻¹ Générateurs
 Four 10- 70 nm
 Nébuliseur 70-200 nm
 Sinclair-La Mer 300-900 nm

Alimentation HT AC/DC
 Tension: 1-20 kV

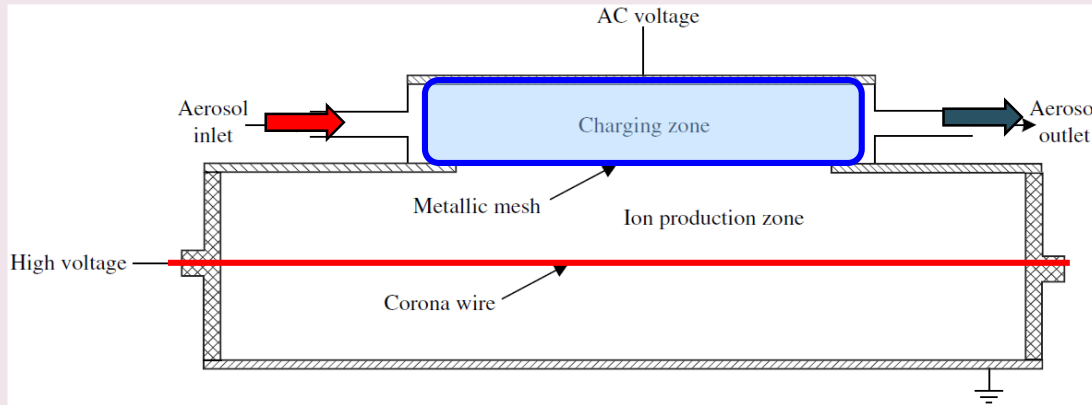
Mesures plasma
 Courant instantané (A)

- Pénétration (diff°, électrostat.)
- Charge moyenne ($I_p/Q.N_p$)
- * Fractions neutre
- ** → dN/dq ou dN/dd_p

CHARGEURS par DIFFUSION en POST-CORONA pour la granulométrie : principe & conditions de mélange ion-particule

1) Extraction électrostatique → dilution réduite

HEWITT 1957 et autres (Liu 1967, Kruijs 2001, Biskos 2004, Marquard 2006).

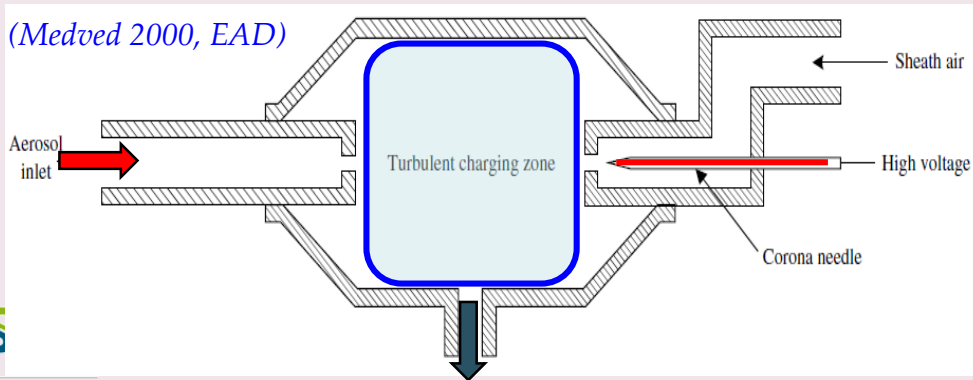


Laminaire et $N_i(r,z)$ eqs homogène
 $\langle N_i \cdot t \rangle \Rightarrow q_p(d_p)$
 mais tps long (> sec.) → pertes
 pour aérosol concentré $> 10^6 \text{ cm}^{-3}$ & stable
 (Biskos 2004, FAST)

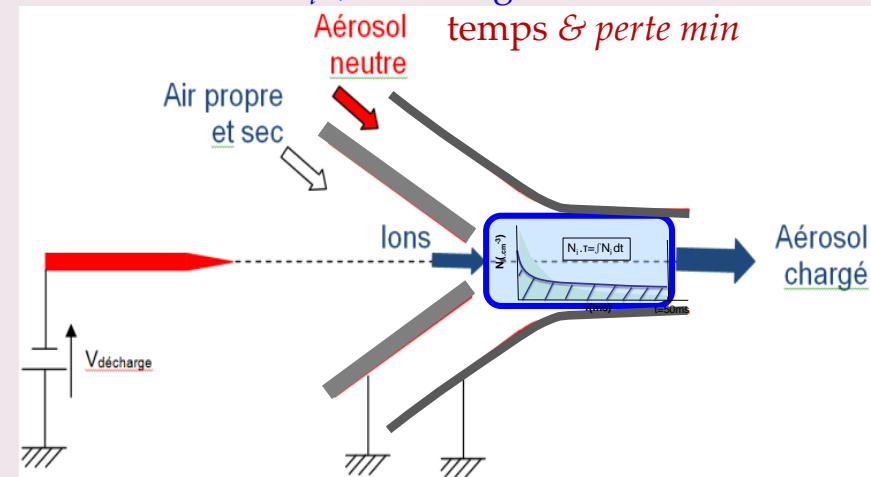
2) Extraction électro-hydro-dynamique ⇒ Dilution de l'aérosol

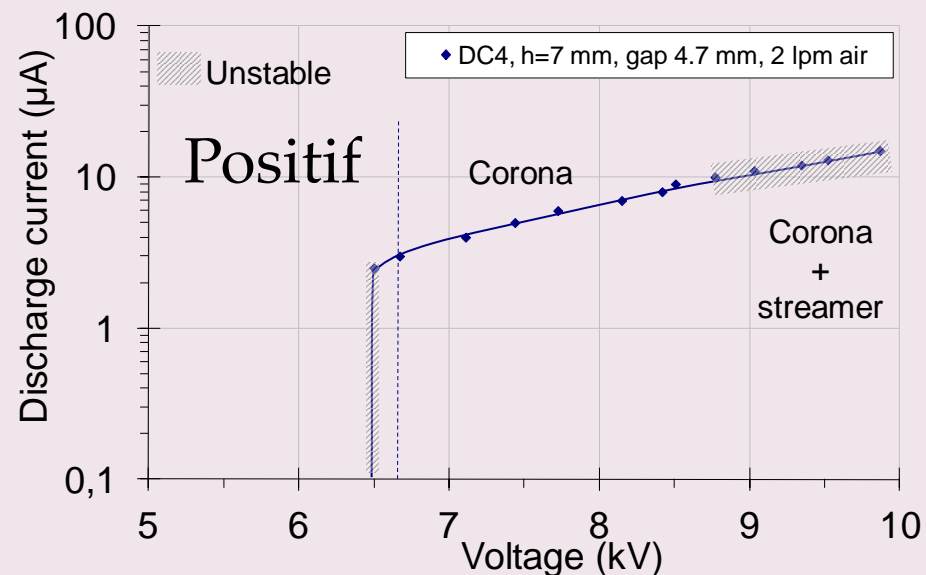
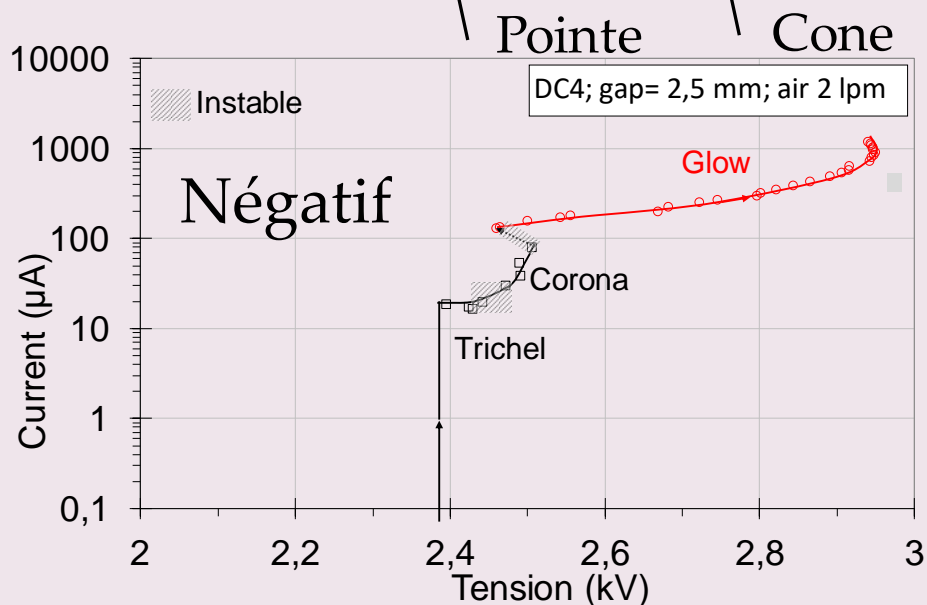
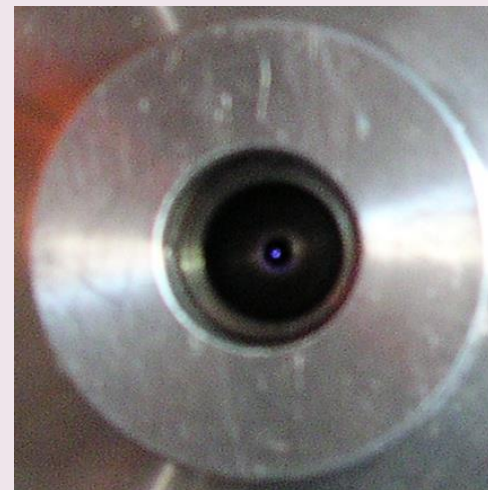
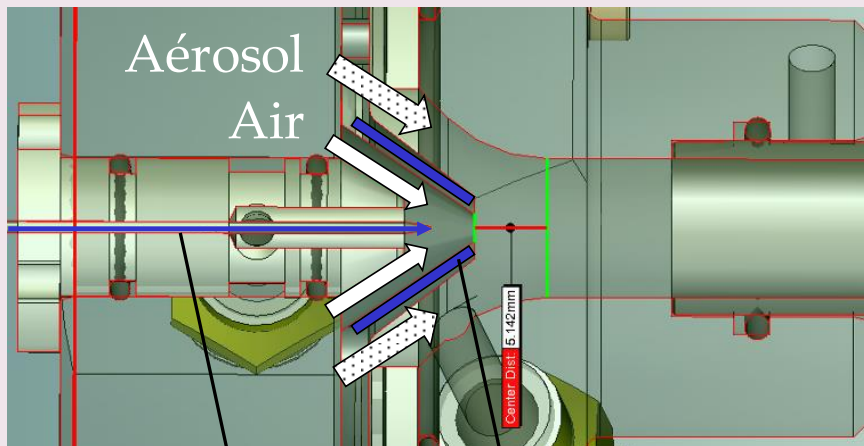
WILSON CTR 1899 et autres (White 1951, Whitby 1961, Liu et Pui 1977, Piu 1988, Yun 1997, LPGP 1998, Medved 2000, Alonso 2000-2008, Park 2007, Intra 2009, Alonso 2010...)

Mélange turbulent
 → $\langle N_i \cdot t \rangle$ et $q_p(d_p)$



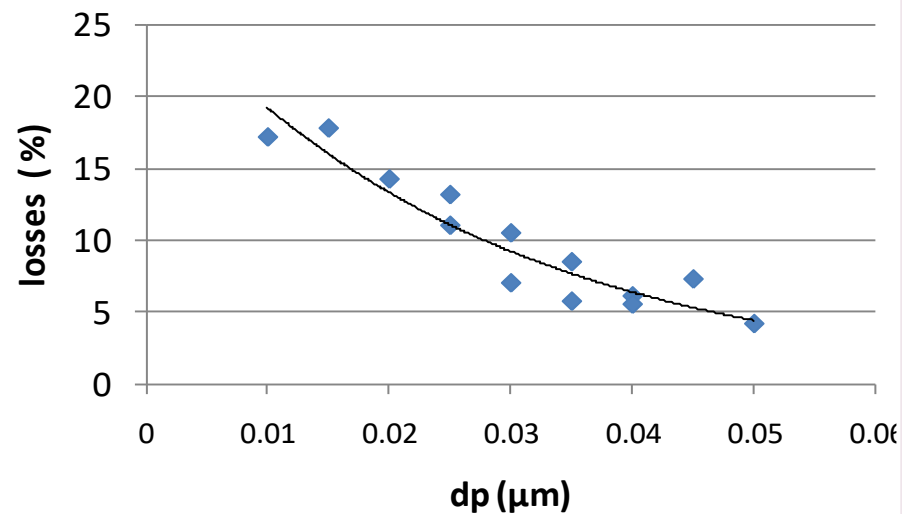
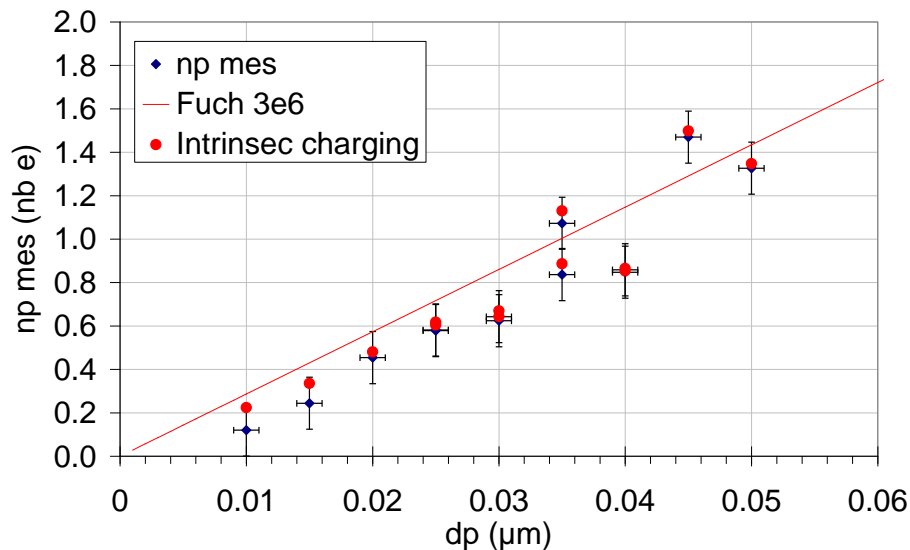
→ Laminaire et $N_i(r,z)$ hétérogène (LPGP 2008)





➤ 4 régimes de décharge utiles pour la production d'ions

$$I_d = -40 \mu\text{A}, Q_{ion} = Q_{aerosol} = 2 \text{ L}\cdot\text{min}^{-1}, N_p \sim 10^5 \text{ cm}^{-3}$$

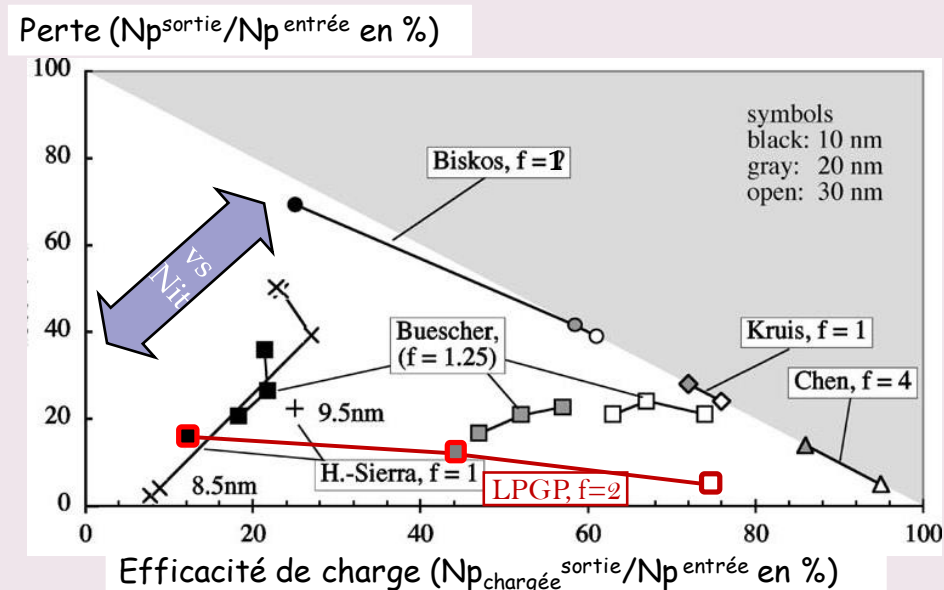


Pertes d'aérosol max pour les aerosols les plus mobiles (20 % for 10 nm, 10^5 cm^{-3})

- Augmenter l'efficacité de charge → augmenter les pertes
- Stratégie LPGP = chargeur à perte minimum

Comparaison des chargeurs pour les « nano » par diffusion d'ions unipolaires en post-décharge

	Extraction EHD		Electrostatique
	LPGP 2007	Medved-Chen 2000	Biskos 2004
Polarité	-	+	+
Mélange	Laminaire	Turbulent	Laminaire
N_i (cm ⁻³) Profil de Ni	10 ¹⁰ - 10 ⁵ HETEROGENE	10 ⁷ ~ HOMOGENE	10 ⁶ -5.10 ⁷ HOMOGENE
t (sec.)	0.05	0.2-2	0.2-10
$N_i \cdot t$ (sec.cm ⁻³)	10 ⁶ - 5.10 ⁷		
Dilution	1.1 - 2		1-2



➤ Efficacité de charge parmi les meilleurs chargeurs à pertes minimum

Intérêts des procédés aerosol basés sur les plasmas pour les nanomat.

1- Nucléation et croissance contrôlées par les paramètres plasma, hydro. et thermiques avec une large gamme d'énergie des décharges filamenteuses

→ *distribution en taille resserrée de particules inférieures à 10 nm...*

en contrôlant : **taille** des I (Flux de vapeur) & agglomération
composition (MO_x, M, Si, C, Polym,...)
structure à partir des gradient de température
pureté

... pour obtenir des propriétés dépendantes de la taille

- Générateur de nano-aérosol calibré $d_p \sim [5 ; 100]$ nm
- Post-DBD coating pour nanoparticules enrobées (e.g. Pt enrobées de SiO₂) & pour films bio-compatibles

2- Charge "nano" bipolaire → unipolaire depuis 2000

Contraintes → à pertes limitées pour le processing post production
 les diagnostics en taille et concentration

- Chargeur "nano" unipolaire à pertes limitées → **métrologie nano-aérosol**

Thank you for your attention & to co-workers

Physics and Chemistry of nt-Plasmas : Alice et Max Goldman, Emmanuel Marode, Gildas Hartman, Robert Haug, Françoise Massines, Pierre Atten, Djamel Djermoune, Emmanuel Odic, Emilie Bourgeois

Aerosols Science : Denis Boulaud, Manuel Alonso, Alfred Weber

Aerosol Processes : Brian Scarlett, Alfonso Ganan-Calvo, Jan Marijnissen, André Roos, Rob Hartmann, Mashida Massachi

TEM, EDX and SAED analysis : Christophe Dutouquet, Olivier Aguerre, Frederique Prima, Jun Hou, Peggy Knopse

Process Engineering : Jacques Amouroux, Michael Tatoulian