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Dust charging and dust-surface interaction in the laboratory

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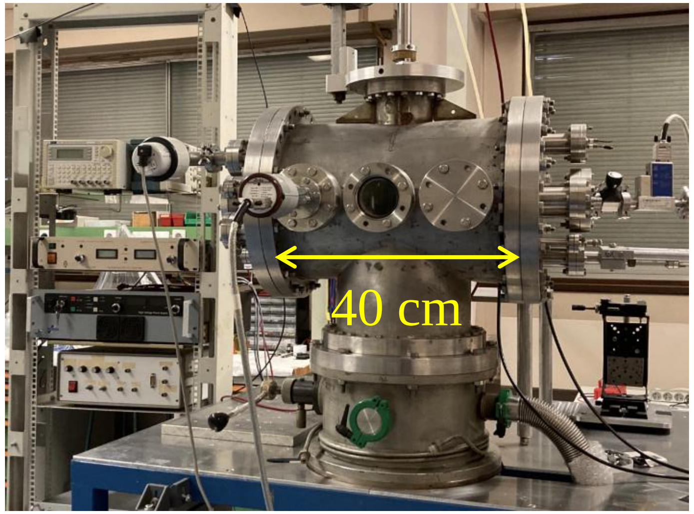
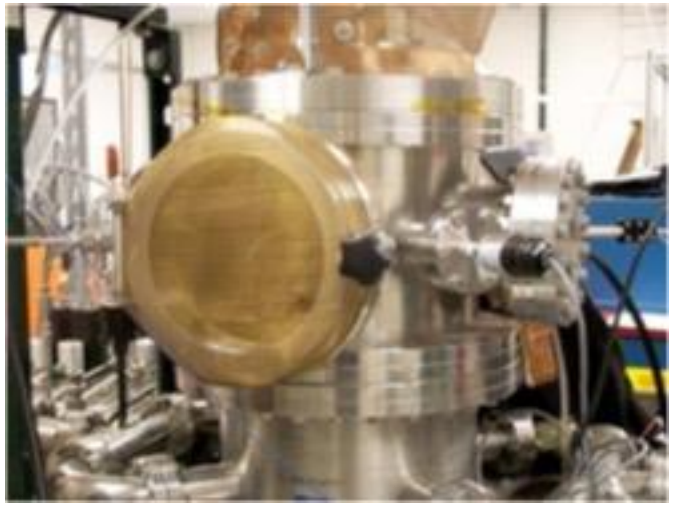
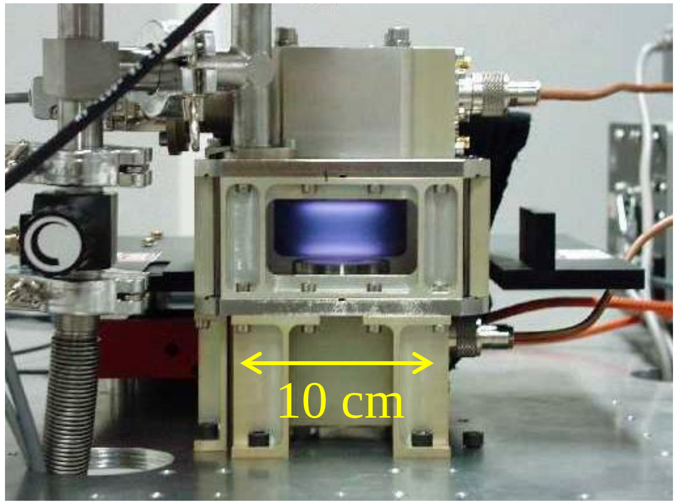
Workshop on Dust Charging and Beam-Dust Interaction in Particle Accelerators, CERN (13-15 June 2023)

Discharge chambers for dust-nanoparticle production





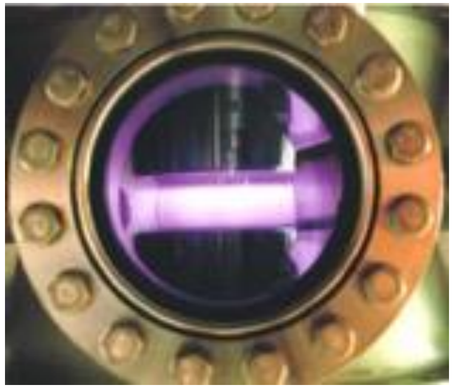


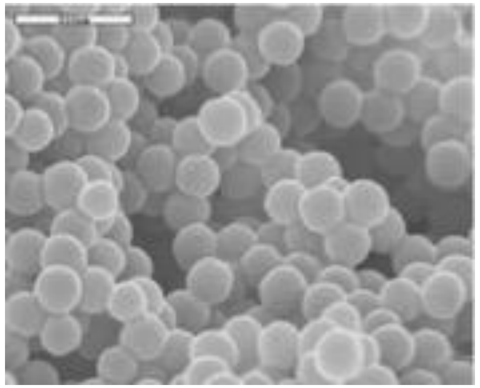
Base vacuum: from 10^{-5} Pa to 10^{-4} Pa

Plasmas (gas): 10 - 100 Pa

Discharges between electrodes in reactive gases

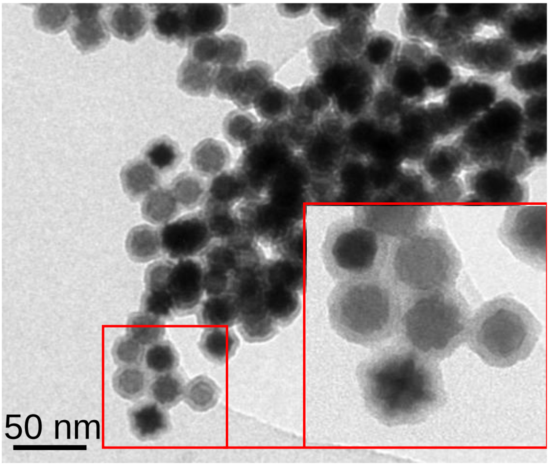
98% Ar plasmas mixed with 2% methane





carbonaceous
nanoparticles
$\simeq$ 200 nm

Ar plasma with sputtered atoms



W nanoparticles
$\simeq$ 25 nm

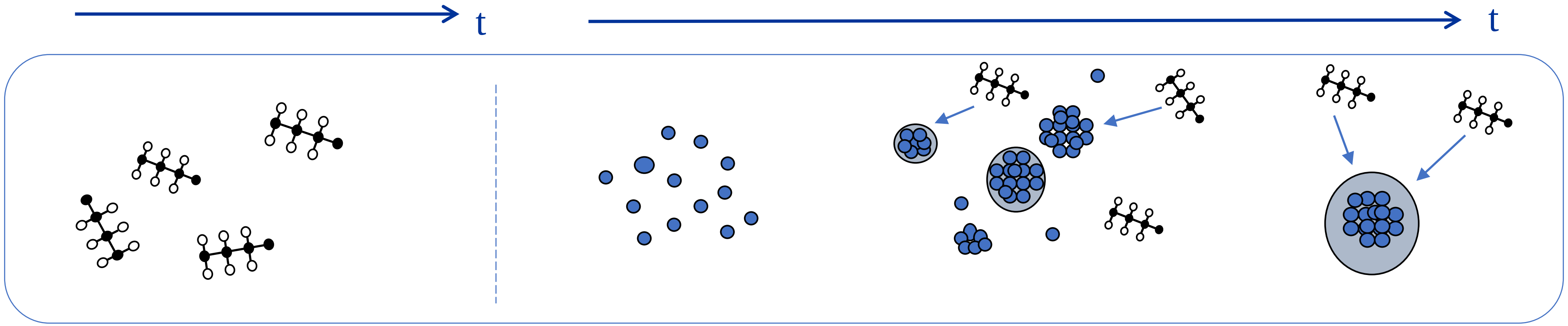
Outline

Nanoparticles produced from cathode sputtering in DC discharges

- Size evolution, density, internal structure (indication on growth mechanisms)
- Modification of the discharge parameters during negative charging
- Modeling of charging mechanisms
- Transport inside the plasma

Standard model of formation

Molecular (ion, neutral) precursors **Nanoparticles**



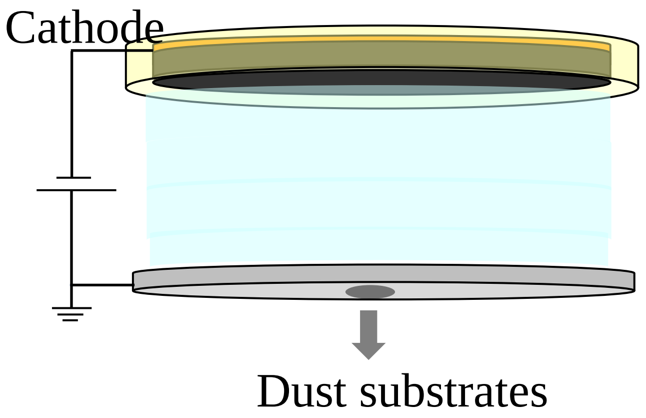
Specific collisions/reactions (complex plasma chemistry)

Nucleation
(nuclei of 1-4 nm)

Agglomeration

Molecular sticking

Nanoparticle growth in sputtering DC discharges

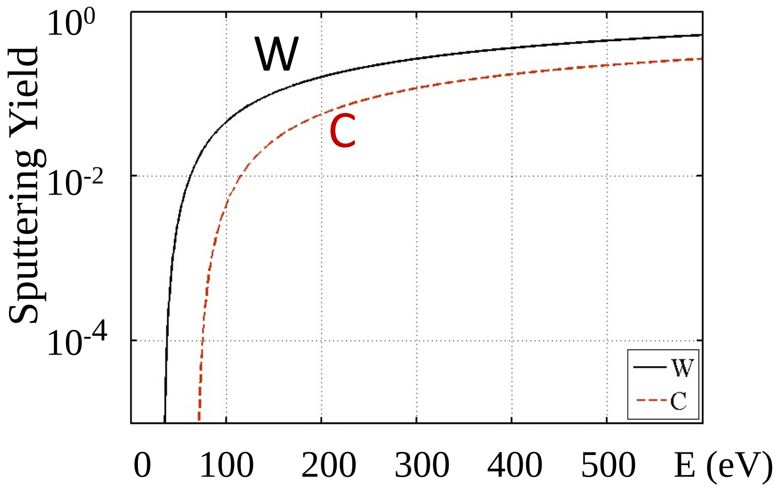


- Ar (30-60 Pa)
- Ar^+ accelerated in the cathode sheath

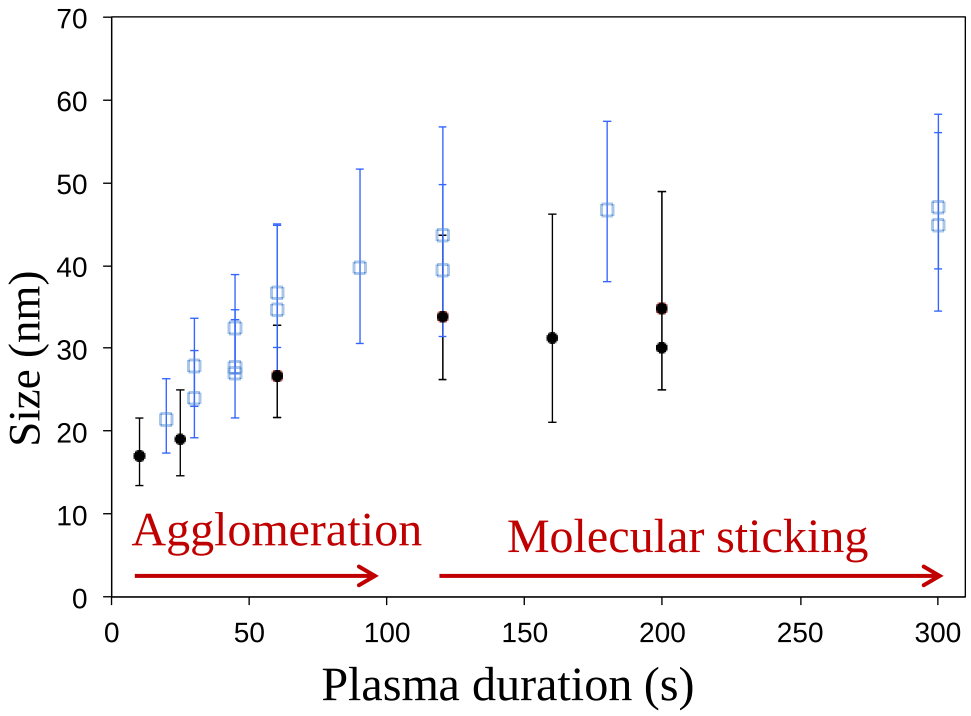
Substrate holder

Cathode sputtering with energetic Ar^+

- sputtering threshold (Ar/C) ~ 70 eV
- sputtering threshold (Ar/W) ~ 34 eV



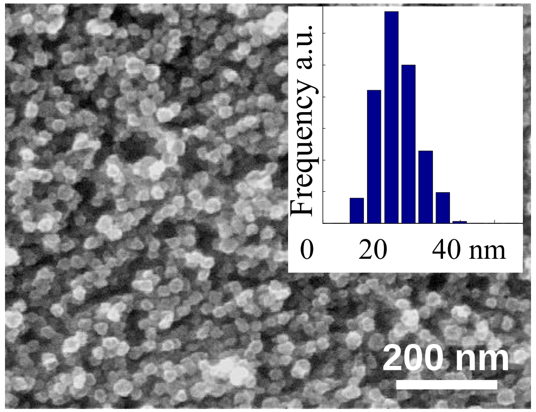
Size increase vs plasma duration



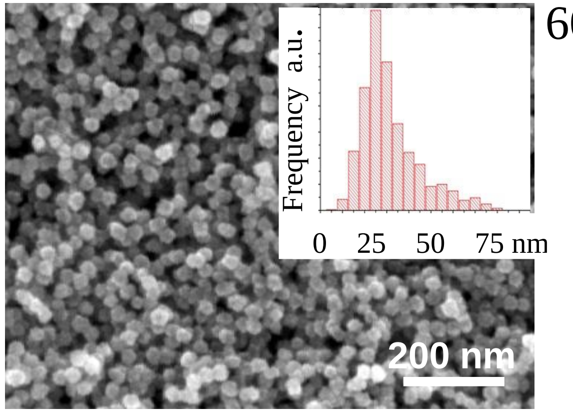
Carbon nanoparticles

Tungsten nanoparticles

45 s



60 s



SEM images

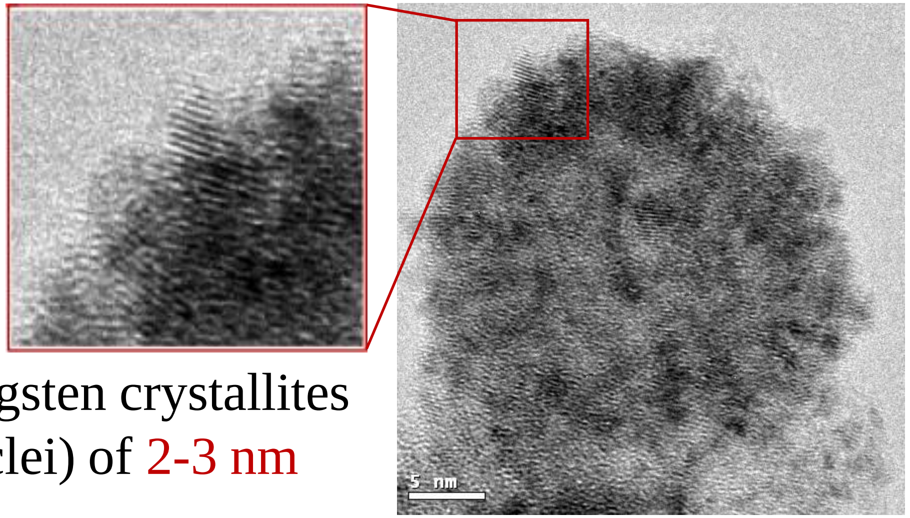
Flux of sputtered atoms:

$\Gamma_C \sim \Gamma_W \sim 10^{18}\ m^{-2}s^{-1}$

Growth by agglomeration and deposition

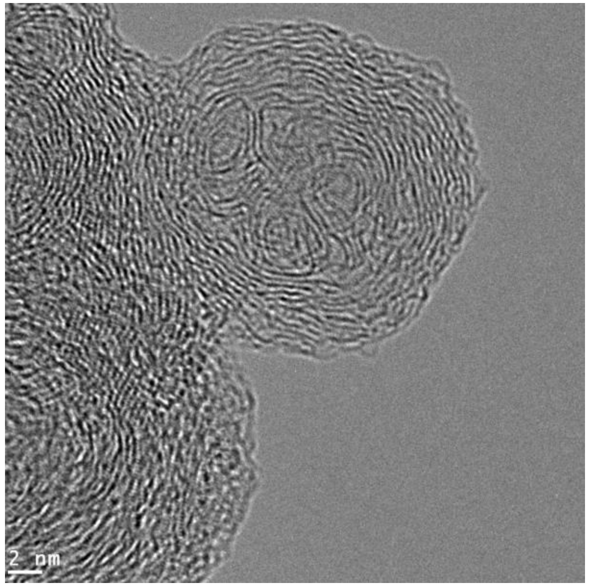
TEM-HR image

60 s



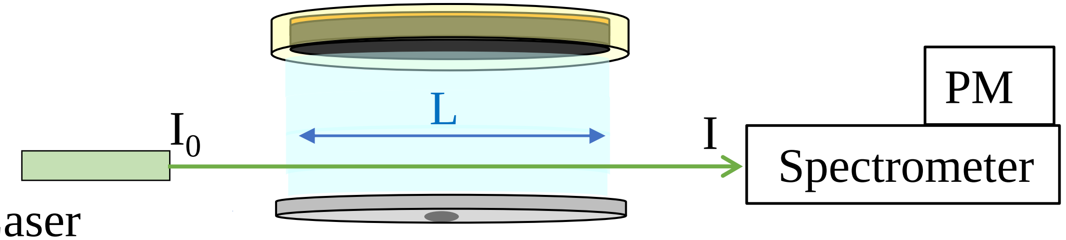
Tungsten crystallites (nuclei) of 2-3 nm

Tungsten nanoparticle ~ 28 nm



Carbon nanoparticle ~ 25 nm
Nuclei of ~ 3 nm
Carbon sticking around

Nanoparticle density



Laser

0.53 µm

Beer-Lambert law: $I/I_0 = \exp(-\pi a^2 C_{ext} n_d L)$

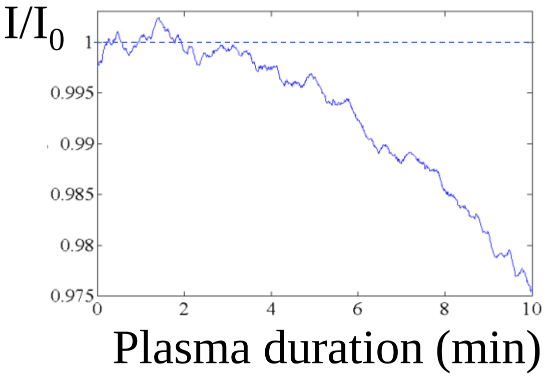
Extinction coeficient: $C_{ext} = C_{abs} + C_{scat}$ and $x = 2\pi a/\lambda_0 < 0.3$

$$C_{abs} = 4x\,\mathrm{Im}\left(\frac{m^2-1}{m^2+2}\right) \quad C_{scat} = \frac{8}{3}x^4\left|\frac{m^2-1}{m^2+2}\right|^2$$

m = complex refractive index of **carbon nanoparticle**

m = 1.3 + i 0.08

Carbon nanoparticles:



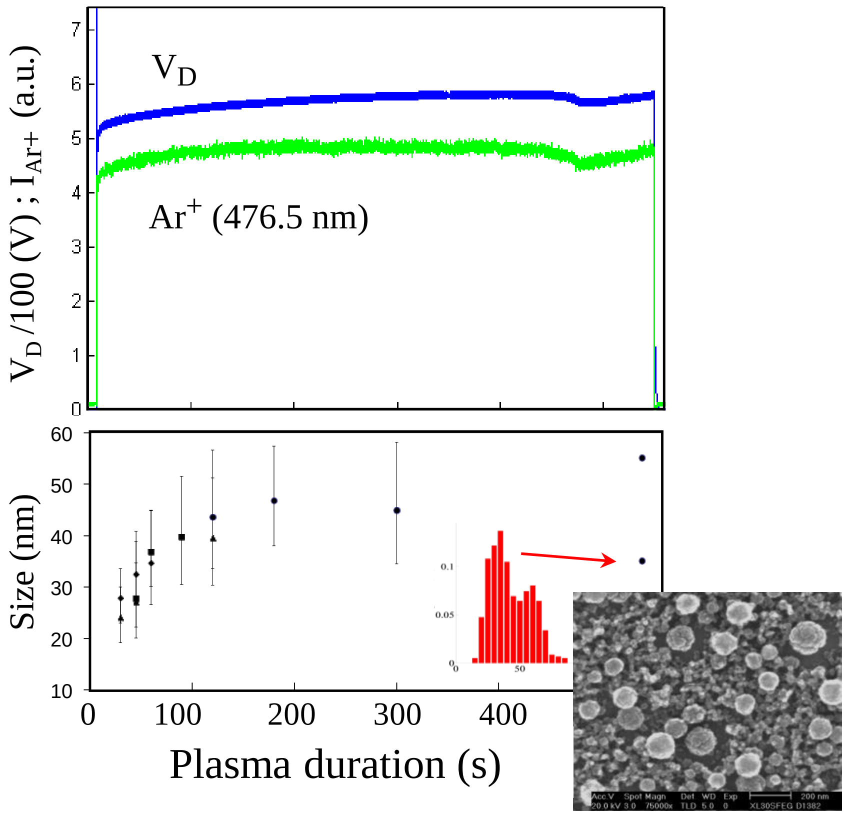
$2a \sim 55$ nm

t = 600 s

$n_{NP} \sim 2\ 10^8\ cm^{-3}$

Nanoparticle-plasma coupling

Charging of **carbon nanoparticles**
to the detriment of discharge/plasma



Three discharges parameters : P_{Ar} = 60 Pa, I_d = 70 mA,

V_d : self-regulated parameter (control the ionization)

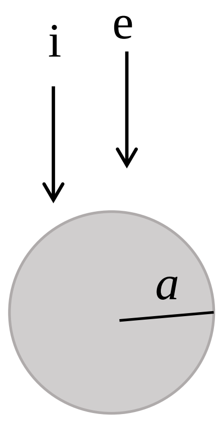
No sputtering: P_{Ar} , I_d , V_d are cte

With sputtering and NPs production:

- Compensation of the electron loss by the increase of V_d
- decrease of V_d due to the loss of a part of NPs on the anode
- Increase again due to the appearance of a new NP generation

Charge of an isolated spherical dust particle

Maxwellian e⁻ and ions: $T_e < 5$ eV and $T_e >> T_i \sim T_g$

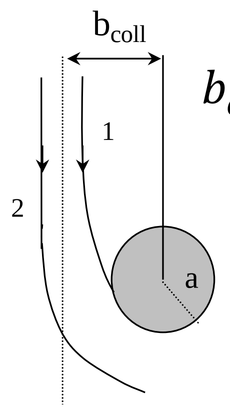


Dust charge (vacuum approximation): $Q = C\varphi \approx 4\pi\varepsilon_0 a\varphi = Ze$

Looking for φ, the floating potential : $J_i(\varphi) - J_e(\varphi) = 0$

higher mobility of e⁻ : $\varphi < 0$

Orbital Motion Limited model (**OML**):



$b_{coll}^2 = a^2(1 - \frac{e\varphi}{k_B T_i})$

Ion current : $I_i = \frac{1}{4}\pi a^2 e n_0 \mathrm{v_i}(1 - \frac{e\varphi}{k_B T_i})$

$$\exp(\frac{e\varphi}{k_B T_e}) = \left(\frac{T_i m_e}{T_e m_i}\right)^{\frac{1}{2}} (1 - \frac{e\varphi}{k_B T_i})$$

From Boltzman law:

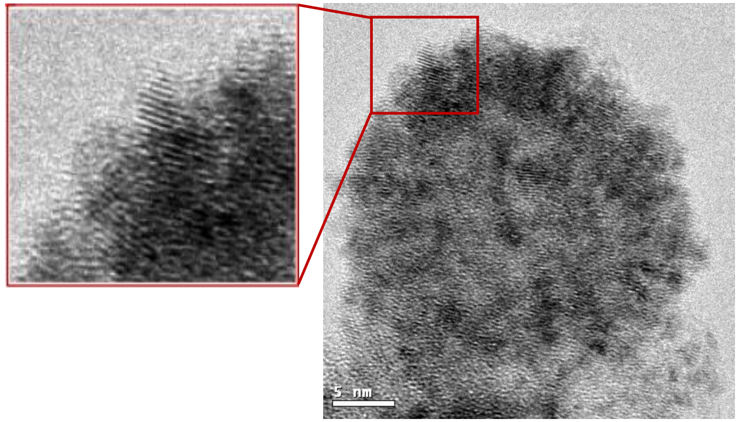
Electron current : $I_e = -\frac{1}{4}\pi a^2 e n_0 \mathrm{v_e} \exp(\frac{e\varphi}{k_B T_e})$

Charge during the agglomeration phase

For T_e = 2 eV , T_i = 0.04 eV

OML --> φ = - 4.3 eV

a ~ 2-3 nm: Z ~ 6e⁻ - 9e⁻



a = 14 nm: Z ~ 42 e⁻

- OML cannot explain agglomeration (Coulomb repulsion)
- Consider **charge fluctuations** --> nuclei can be briefly neutrals, positively charged

Charge distribution (T. Matsoukas *et al*, J. Appl. Phys.,1995)

- n_q : fraction of nanoparticles carrying the charge q

$$\frac{\partial n_q}{\partial t} = I_i(q-1)n_{q-1} + I_e(q+1)n_{q+1} - [I_e(q) + I_i(q)]n_q$$

- Transformed to a partial differentiel equation:

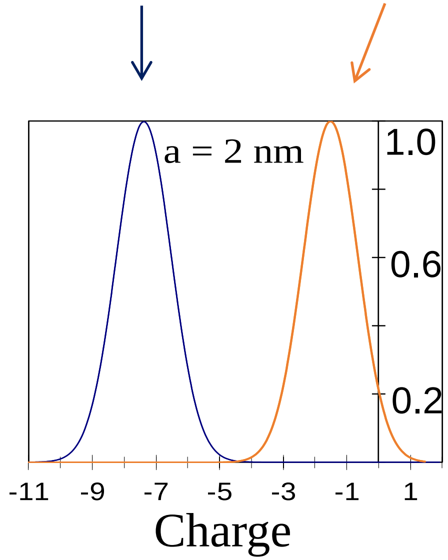
$$\frac{\partial n}{\partial t} = - \frac{\partial (I_i - I_e)n}{\partial q} + \frac{1}{2}\frac{\partial^2 (I_i + I_e)n}{\partial q^2}$$

Charge during the agglomeration phase

Gaussian charge distribution: $n(q) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(q-\bar{q})2}{2\sigma^2}\right)$

Average charge: $\bar{q} = k\,\frac{4\pi\varepsilon_0 a T_e}{e^2}\,\mathrm{Ln}\left[\frac{n_i}{n_e}\left(\frac{m_e\,T_e}{m_i\,T_i}\right)^{1/2}\right]$

$\frac{n_i}{n_e} = 1$ $\frac{n_i}{n_e} = 10$



- $\bar{q} \sim 7e$ when n_i / $n_e = 1$
- $\bar{q} \sim 2e$ when n_i / $n_e = 10$

Explains the nanoparticle growth by agglomeration **of nuclei at the condition of n_e depletion**

→ charging to the detriment of plasma electrons

T. Matsoukas *et al* , J. Appl. Phys. 77, 1995

Modelling of the growth and charge evolution

3 coupled numerical modules*: argon DC discharge – molecular ions formation – NP evolution

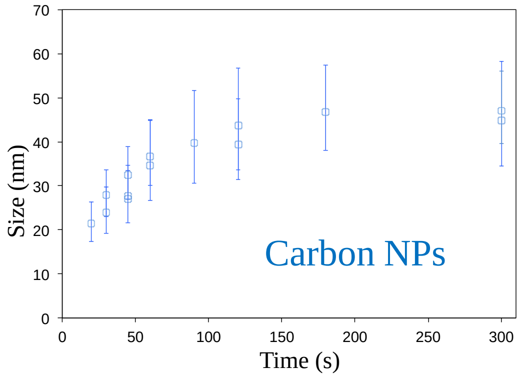
1D sectional model: size distribution divided into bins or sections along the plasma

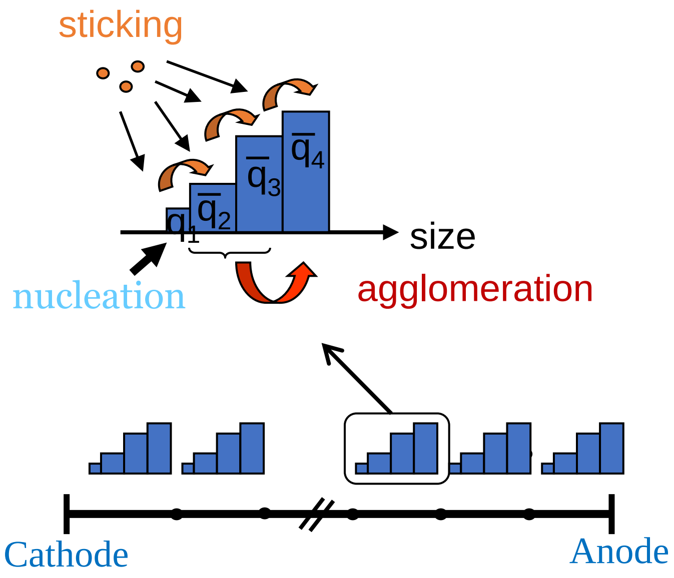
In each section: sizes 1-100 nm

100 continuity eq for the total volume density

+ 100 eq for the average chargeTapez une équation ici.

- Nucleation
- Transport
- Growth by sticking
- Growth by agglomeration





NP volume balance in each section

$$\frac{\partial V_l}{\partial t} = \frac{\partial V_l}{\partial t}_{aggl} + \frac{\partial V_l}{\partial t}_{stick} + S_{nuc} - \nabla F_l$$

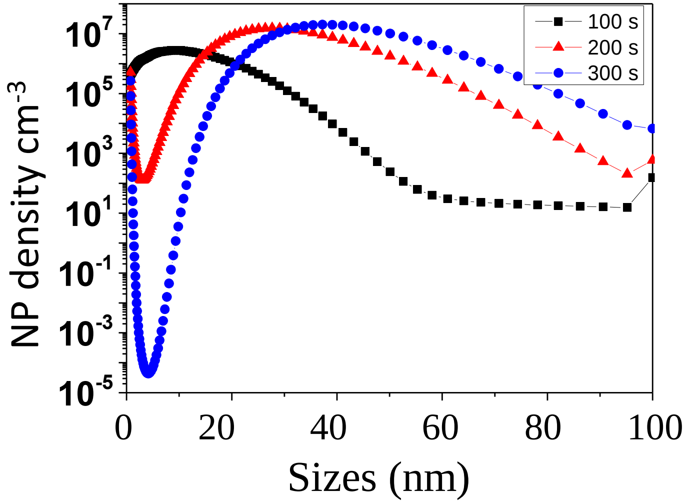
Averaged NP charge of each section:

$$\frac{\partial q_l}{\partial t} = -\frac{\vec{\nabla}(q_l \vec{F_l})}{V_l} + \left(I_{e\text{- }slow} + I_{e\text{- }fast} + I_i\right).S_l + S^q{}_{nuc} + S^q{}_{aggl} + S^q{}_{sticking}$$

Gaussian charge distribution : smallest NPs can be neutral or > 0

*A. Michau, K. Hassouni et al, *Plasma Chem. Plasma Process.* ***32*** *(2012); J. Appl. Phys.* ***121*** *(2017)*

Size evolution during the charging mechanism

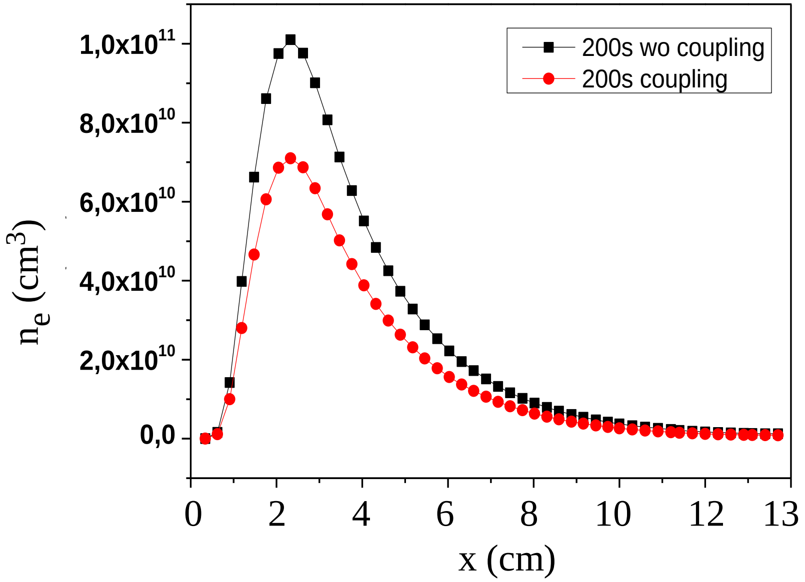


At x ~ 2 cm from the cathode
(position of electric field reversal)

Agglomeration can only occur between

nuclei (neutral, positively charged)

and big nanoparticles (negatively charged)



Red curve:

n_e calculated self-consistenly through the coupling of the 3 numerical modules: coupling of negative molecular ions, negatively charged nanoparticles and n_e

Outline

Nanoparticles produced from cathode sputtering in DC discharges

- ❑ Size evolution, internal structure (indications on formation), density
- ❑ Modification of the discharge parameters at large density
- ❑ Modeling of charging mechanisms (agglomeration)
- ⇨ ❑ Transport inside the plasma

Applied forces on an isolated spherical nanoparticle

- *Electric force* : F_e = ZeE (E = - ∇V_p where Vp: plasma potential)

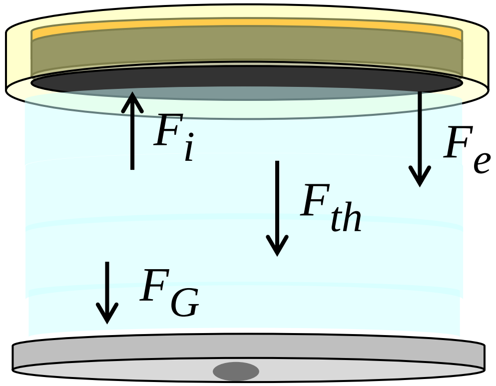
- *Ion drag force* : $F_i = 2/3\pi a^2 n_0 m_{ar} v_i u_i \left(1 - \frac{\rho_0}{2a} + \frac{\rho_0^2}{4a^2}\Lambda\right)$

$$\rho_0 = \frac{Ze^2}{m_i v_{th}^2}$$: Coulomb radius

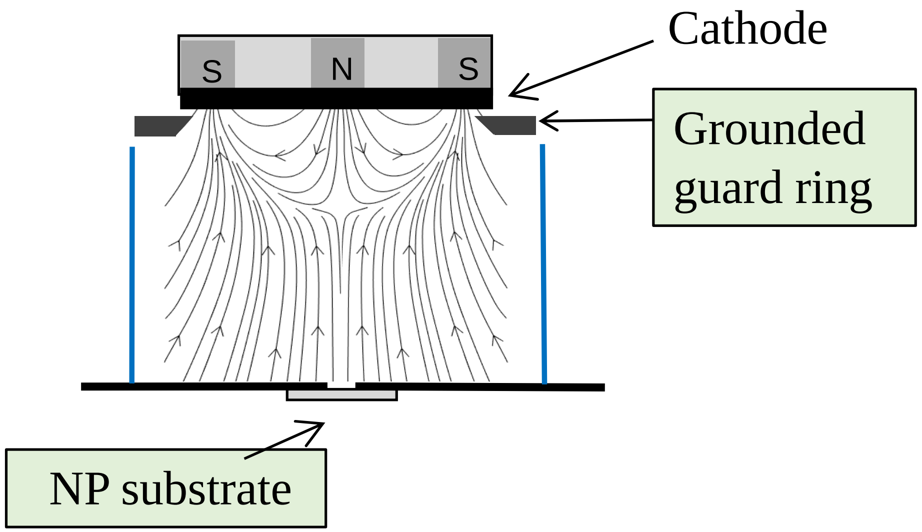
Λ : Coulomb logarithm

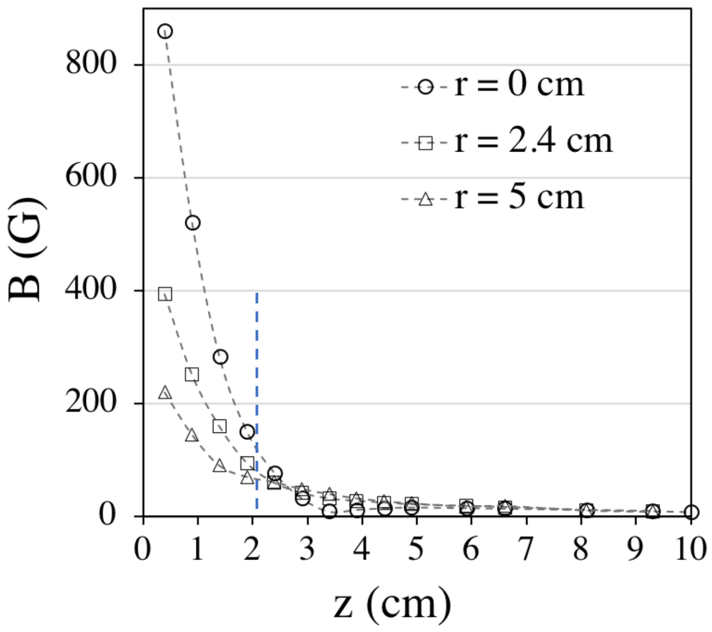
- *Thermophoretic force* : $F_{th} = -\frac{32}{15}\frac{a^2}{v_{th}} k_{th} \nabla T_{ar}$

- *Gravity*: $F_G = 4/3\pi a^3 \rho g$ (negligible)



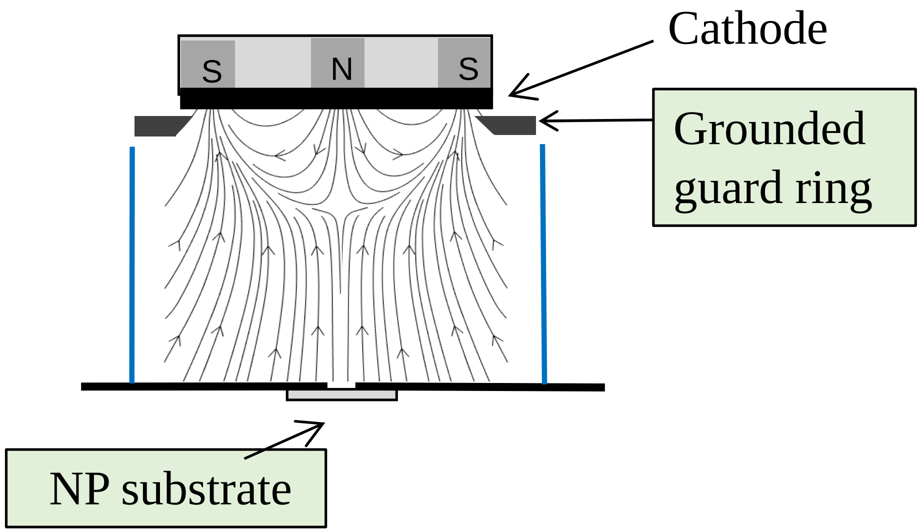
Sputtering DC magnetron discharges





- Tungstène cathode (sputtering)
- P_{ar} = 30 Pa, I_d = 0.3 A (V_d ~ 200 V)

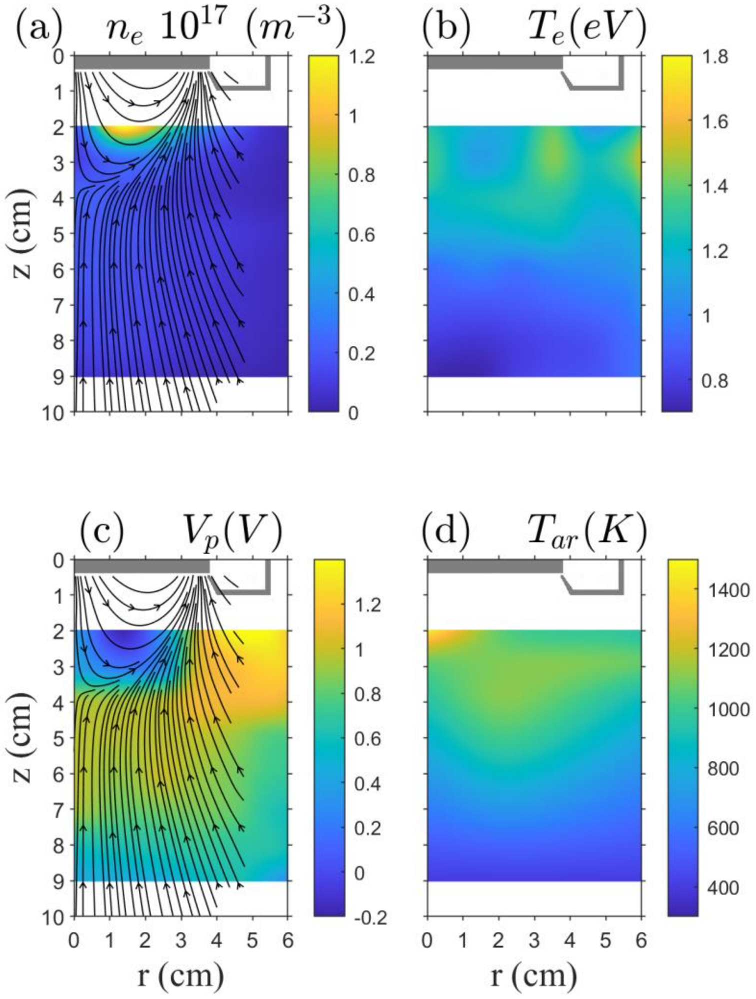
W nanoparticles produced in magnetron discharges



- Tungstène cathode (sputtering)
- P_{ar} = 30 Pa, I_d = 0.3 A (V_d ~ 200 V)

(10 successive plasmas of 200s)

2D plasma parameters measurements



n_e, T_e, V_P : Langmuir probe measurements

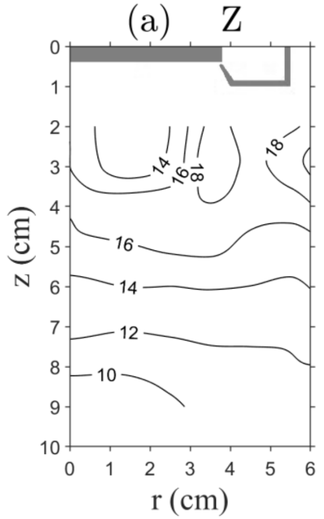
T_{ar}: measurement byLIF

- n_e : maximum inside magnetic arches
- T_e : inverse variation of n_e
- V_P : increase inside magnetic arches

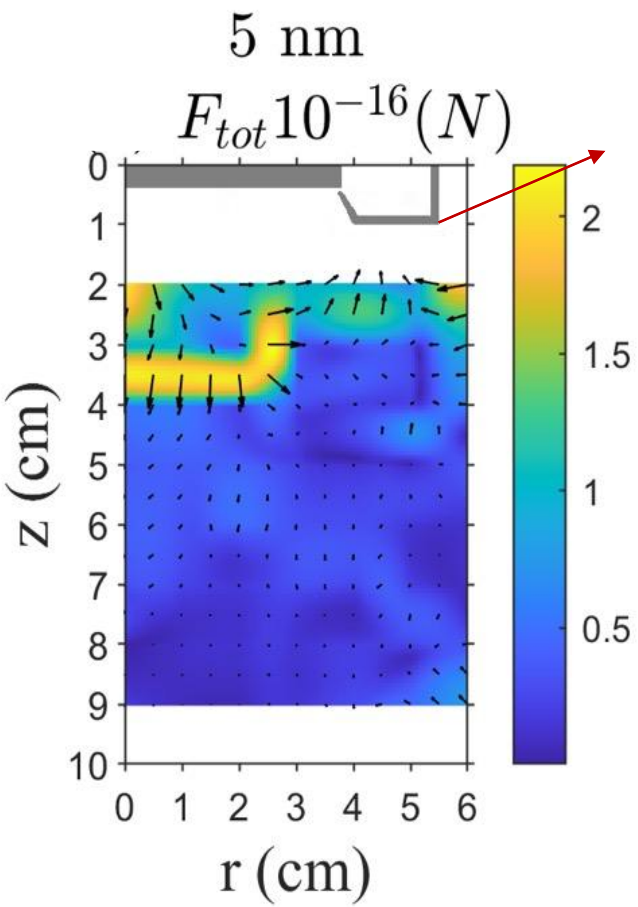
  max after the last magnetic arch
- T_{ar} : Ar heating due to collisions

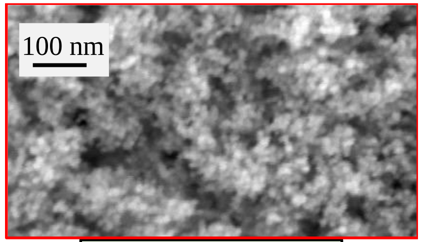
  with sputtered atoms of <E> ~ 12 eV

OML model; *a* = 5 nm



Force balance





Guard ring

a ~ 5 nm

$$F_e + F_{th} + F_i = 0$$

negligible

Upper part:

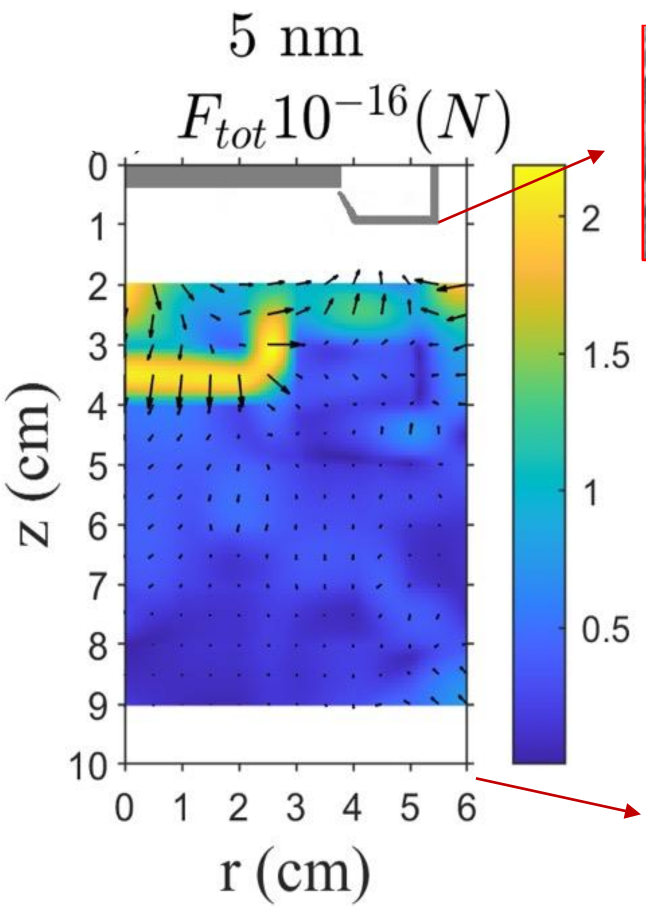
F_e and F_{th} : same range of values

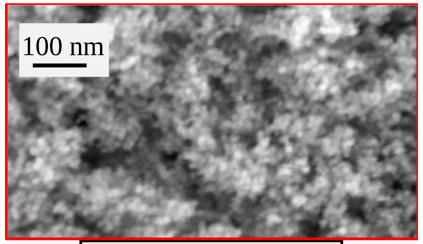
- nanoparticles under the guard ring are pushed to the the guard ring
- near the axis: pushed outside magnetic arches and downwards

Lower part:

- F_{th} is dominant: pushed down

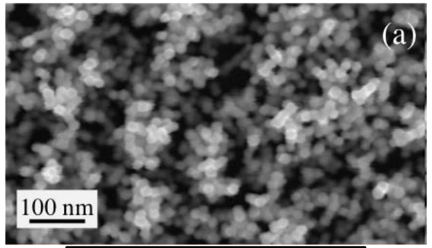
Force balance





Guard ring

a ~ 5 nm



NP substrate

a ~ 15 nm

$$F_e + F_{th} + F_i = 0$$

negligible

Upper part:

F_e and F_{th} : same range of values

- nanoparticles under the guard ring are pushed to the the guard ring
- near the axis: pushed outside magnetic arches and downwards

Lower part:

- F_{th} is dominant: pushed down

⇩

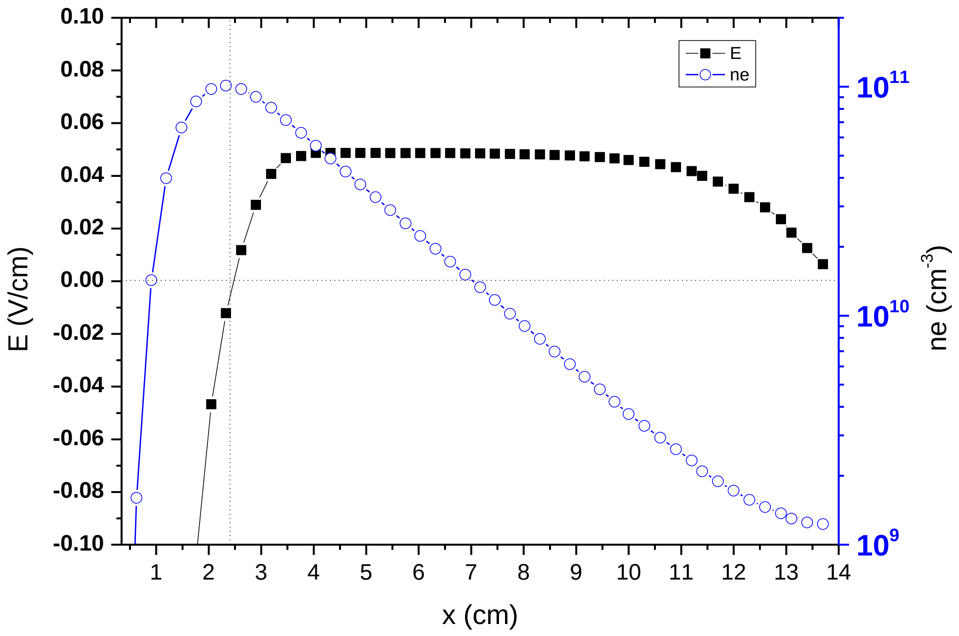
When NPs are transported down they have more "space, time" to grow than NPs near the guard ring

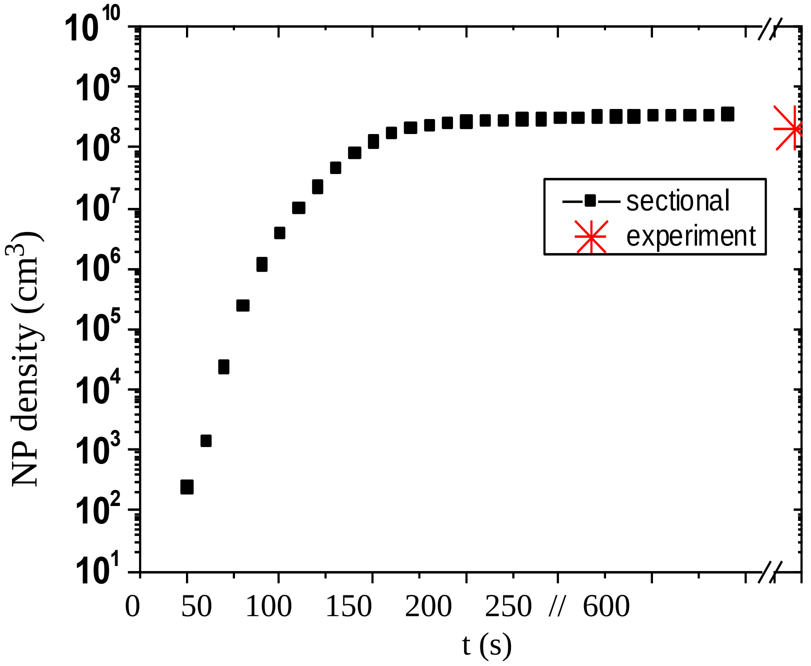
Summary

Nanoparticles produced from cathode sputtering in DC discharges

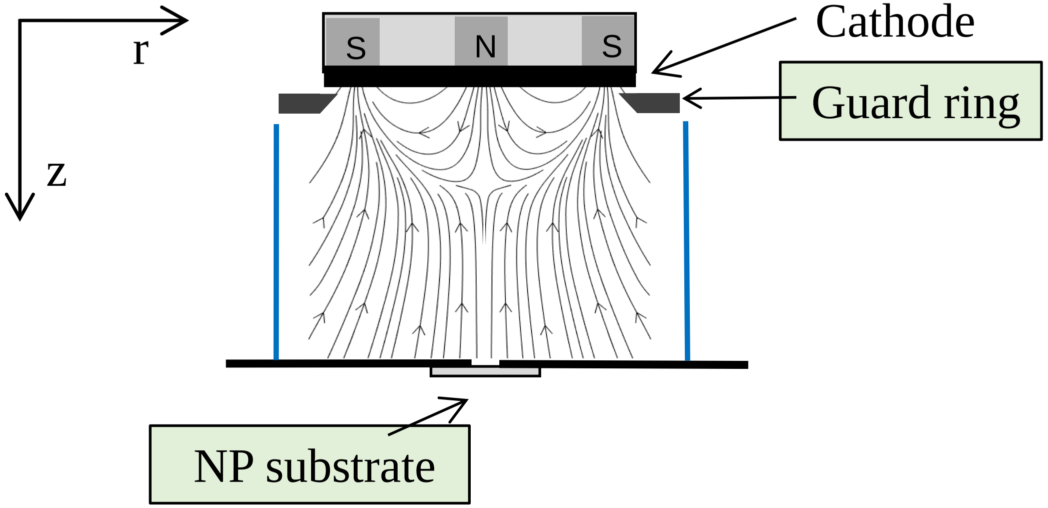
- Size evolution, density, internal structure (growth by agglomeration, sticking)
- Modification of the discharge parameters due to their negative charge
- Various modeling of charging mechanisms (+ fluctuations) and growth
- Applied forces for their transport in the plasma

Additional slides





NP density reaches ~ 10^8 cm^{-3}
also found experimentally



- <u>Cylindrical Langmuir probe</u>

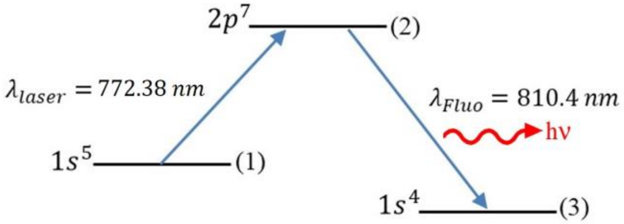
  $r_{LP} << r_{larmor}$ for z > 2 cm and probe ⊥ B

  (also) $v_{de}/v_{the} \leq 0.32$

  ⇓

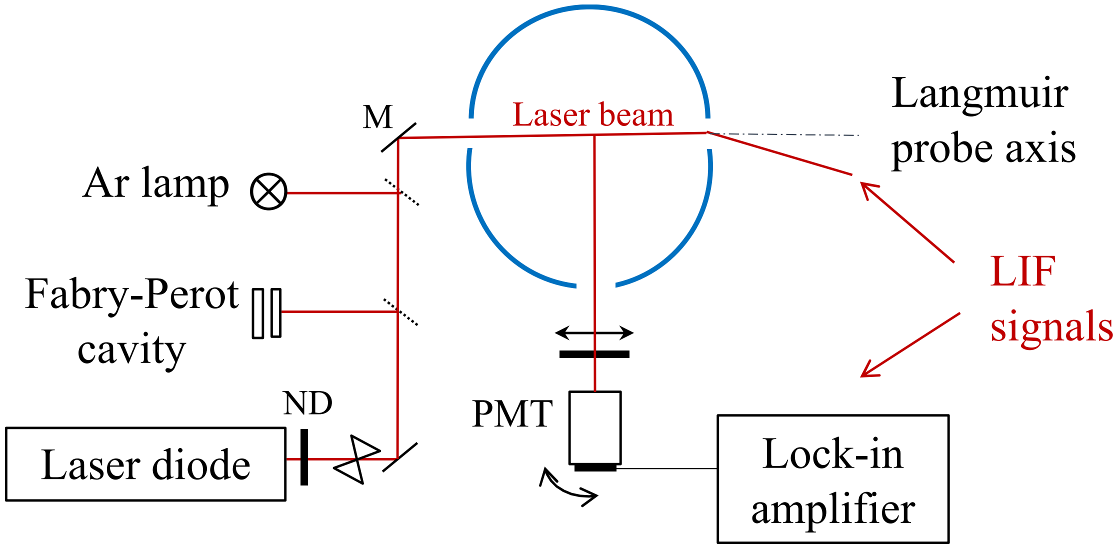
  Classical analyses of probe characteristics

- <u>Laser Induced Fluorescence</u> (tunable laser diode)

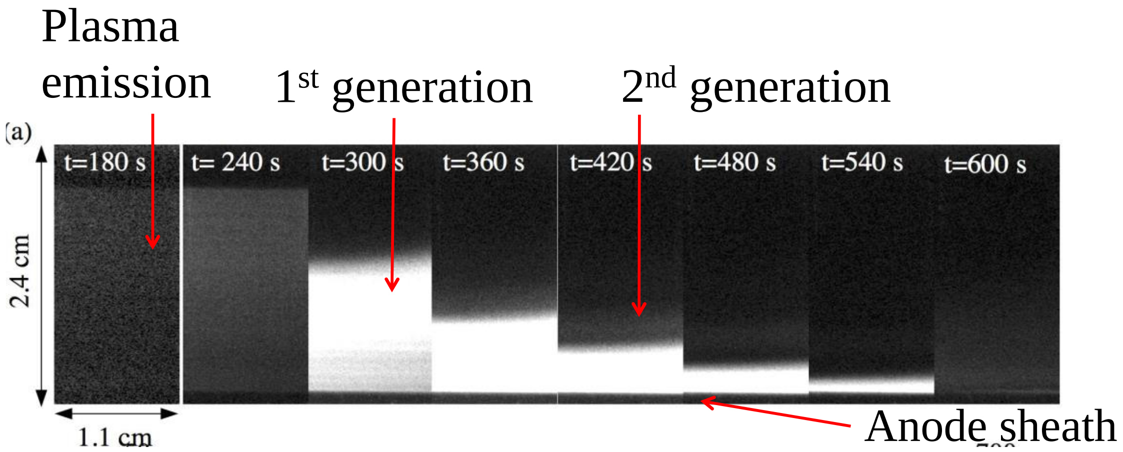


$v = c(\nu_l - \nu_0)/\nu_l$; ν_0:transition frequency of an atom at rest, ν_l: the laser frequency

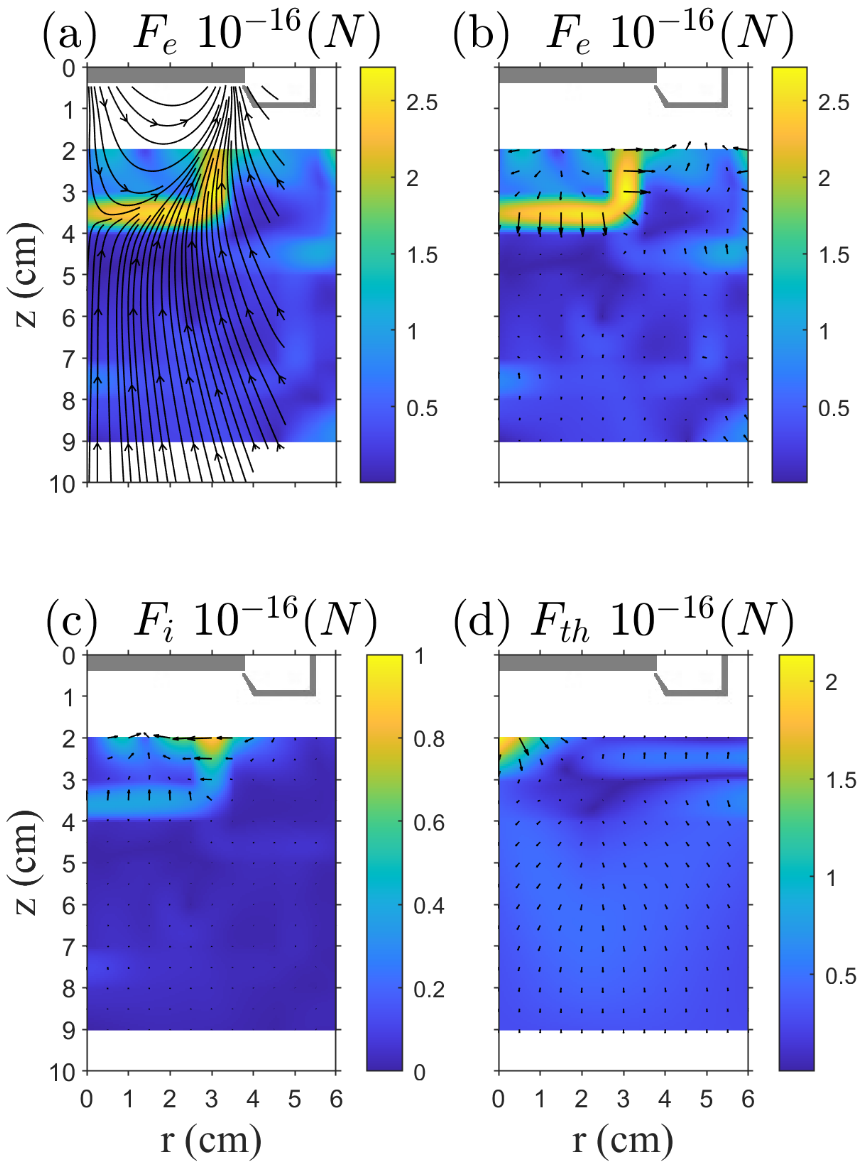
Doppler shift: $k_b T = \frac{\lambda_0^2\, M}{8\ \ln 2} \Delta\nu^2$



Laser scattering on the dust cloud during the transport of W nanoparticles towards the anode (classical DC discharges)



- V ~ 0.004 cm/s = 14.5 cm/h
- 2nd generation appears in the space freed by the 1st generation



(a) $F_e\ 10^{-16}(N)$
(b) $F_e\ 10^{-16}(N)$
(c) $F_i\ 10^{-16}(N)$
(d) $F_{th}\ 10^{-16}(N)$
z (cm)
r (cm)

- **Analogue of dust particles of ISM, planet satellites**

- **New materials, technologies:** superior properties to those of bulk materials
  - High surface area to volume ratio
  - Photo-emission wavelength decrease with the size decreases size
  - Lower melting temperature
  - Stronger materials

Applications:

- Optics: thinner displays, photophores, UV filters
- Electronics: nanodevice, single electron emission quantum dots
- Energy: hydrogen storage, improvement of solar cell efficiency
- Chemical: molecular sensor; catalyst
- Medicine: drug carriers, in-vitro imaging, cancer treatment