Molecular growth and aerosol dynamic in some dusty/sooty discharges

- LSPM group (HC discharges : particle formation and film deposition)

F. Silva[1], G. Lombardi[1], F. Mohasseb, A. Michau[1], X. Bonnin[1], X. Duten, F. Benedic, K. Hassouni, J. Achard and A. Gicquel[1]

- PIIM group (carbon particle formation)

C. Arnas

- PICM group (Si-H discharge and Si-H particles formation)

H. Vach and N. Ning

- Minnessota group (coupled discharge-aerosol dynamic in Si/H plasmas)

S. L. Girshick

Journées du Réseau Plasmas Froids : 17-21 octobre 2016

Outline

Objective : to give an **illustration** of the work performed on dusty plasma modeling in the non-equilibrium discharge plasmas (laboratory plasmas) community

→ **Plasma physicist point of view**

→ **non exhaustive**

→ **Try to show different aspects that need to be considered**

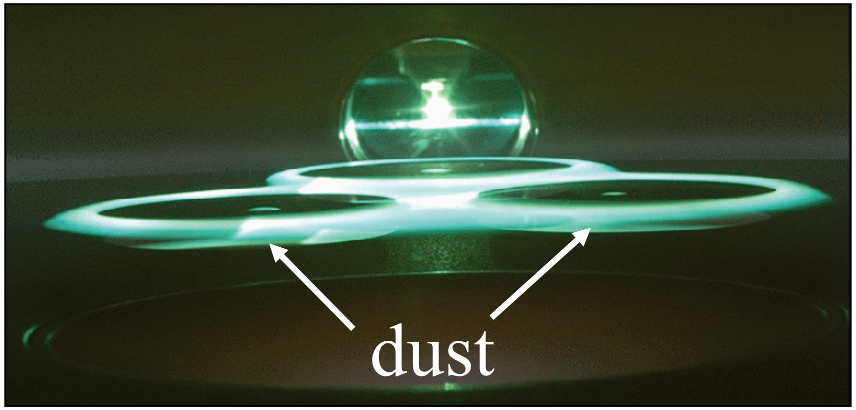
Research on dusty laboratory plasmas exhibits :

- **First phase : investigation of dusty plasmas as complex media and the effect of dust on the plasma equilibrium**
- **Second phase : dust formation in discharge plasmas and dusty plasma effect**

Motivation for the investigation of dust particle formation in laboratory plasma

In the beginning (late 80's, early 90's) : Particle issues in IC's manufacturing (50% of reject)

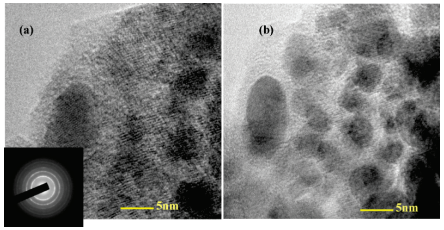
Merlino and Goree. Physics Today(2004)

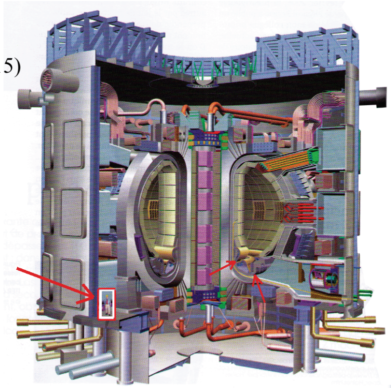


Particle formation in RIE and PECVD devices using capacitively coupled Rf discharge ➔ **Most of the effort devoted to 13.56 MHz CCP discharges**

http://www-cadarache.cea.fr/fr/activites/fusion/

Liu et al. Int. J. Nanomat., Nanotech and nanomed (2015)

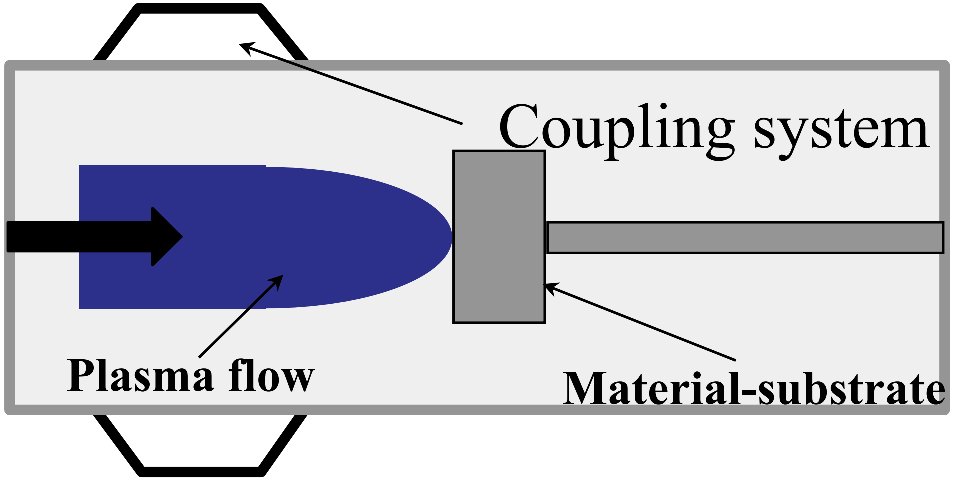




Today we have a large number of motivations ::

- nanotechnology,
- nanocomposite materials,
- ITER project

Laboratory discharge plasmas

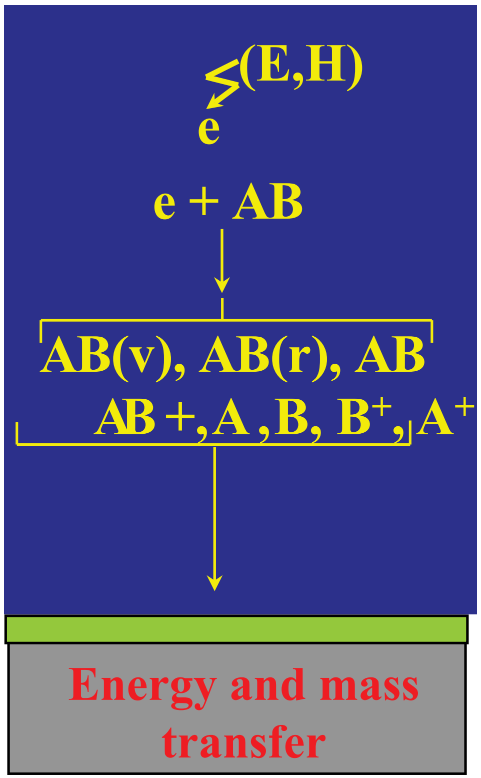


Discharge conditions :
- Pressure : 0.1-10^5 Pa
- Input-Power : 1 – few 10^3 W
- τ_s : 10^{-3}-qqs sec
-$Pe_n < 10$, $Re_{gaz} < 100$
-Power density : 10^{-3}-10^3 W/cm^3

Some orders of magnitude :

* $n_e = 10^8$-10^{12} cm^{-3} (<10^{-2} and more often <10^{-5})
* $<\varepsilon_e> = 1$-10 eV
* $T_g = 300 - 6000$ K
* 'T_v' = 1000 - 5000 K (molecular gases)

Phenomenological description of typical laboratory plasma system



Plasma-wave interaction

Electron heating

Electron-heavy species collisions

Energy transfer, ionisation, etc

Collisions between heavy species

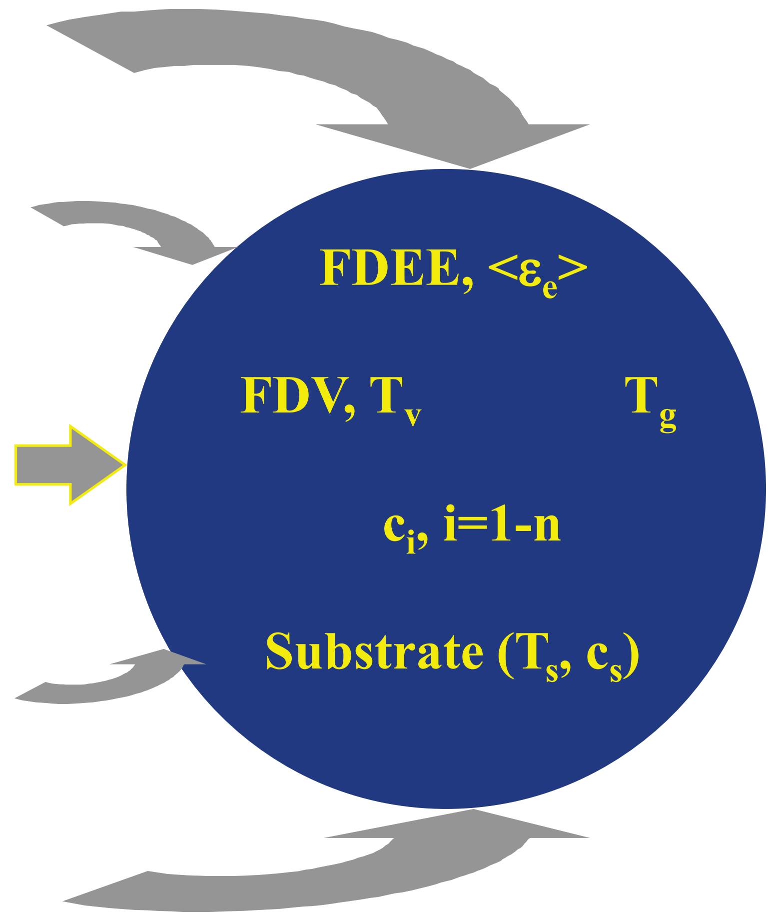
Energy transfer, chemistry, clustering, nucleation

Self consistent field structure and charged particle transport : Drift, Diffusion, convection

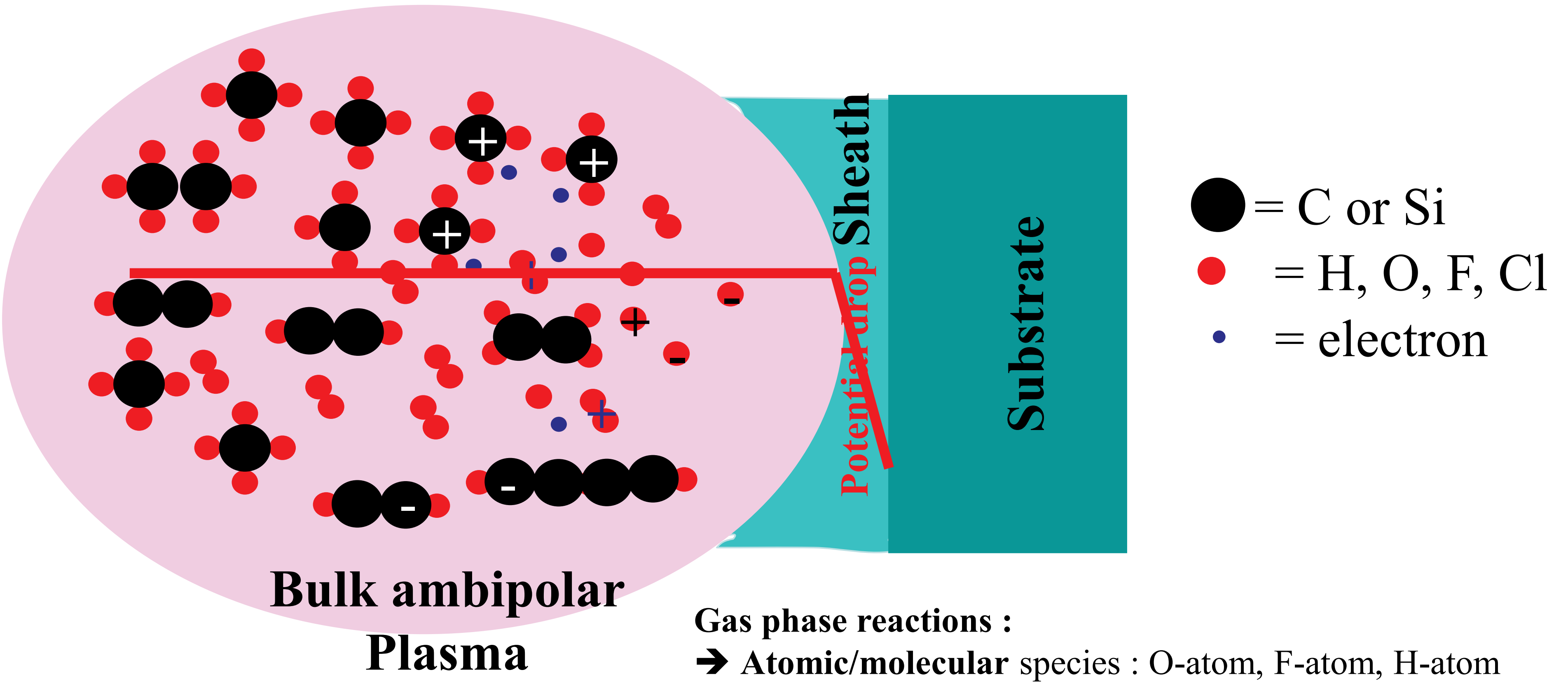
Energy and mass transport

plasma/surface Interaction

Energy and mass transfer



Gas phase generated species in laboratory plasmas

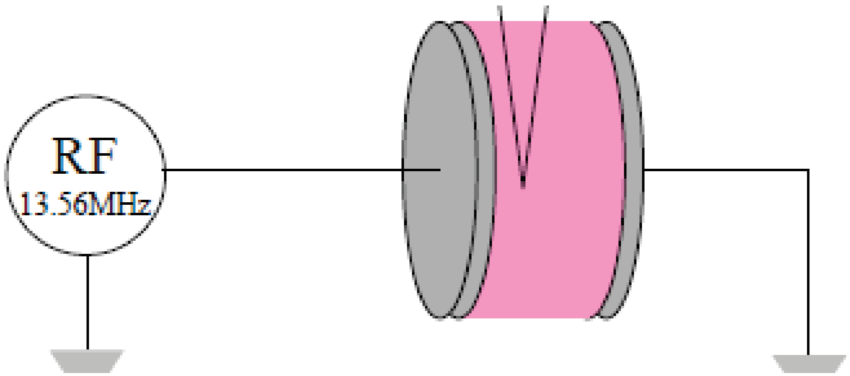


Gas phase reactions :

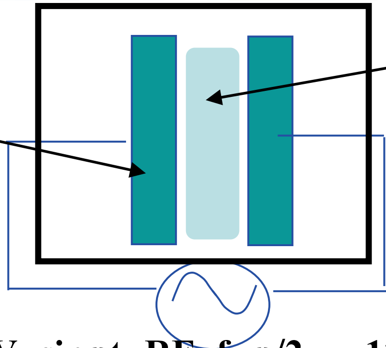
- ➔ **Atomic/molecular** species : O-atom, F-atom, H-atom
- ➔ Radicals : CH_3, CF_3, SiH_2, SiH, SiH_3
- ➔ Positive ions : CH_5^{+}, SiH_5^{+}, H_2^{+}, H_3^{+}, H^{+}, O_4^{+}, etc.
- ➔ Negative ions : H^{-}, O^{-}
- ➔ Large molecular structures : $S_nH_m^{-}$, $C_nH_m^{-}$, etc.
- ➔ Nucleation and growth of solid particles

The mostly used discharge system for the investigation of laboratory dusty plasma

The parallel plate capacitively coupled radiofrequency discharges (13.56 MHz) (interest for the microelectronic industry)



Peculiarity of CCP RF discharges (13.56 MHz)



$V=V_0 \sin\omega t$- RF- $f=\omega/2\pi$ = 13.56 MHz

p=0.1-1 torr, T_g=300 K,
Power=0.1-10 W

$\lambda_{Debye} \approx 1$ cm $\approx d_{syst}$

$\lambda_{RF} \approx 20$ m >> d_{syst}

1 We take into account the charge separation (the non neutral region – sheath- are wide)

2 No wave-length effect :
Quasi-static field assumption

3 Drift-diffusion flux

$\omega_{p-i} << \omega << \omega_{p-e}$

- OK for electrons
- Not valid for ions => Use of the effective field concept

$$\frac{\partial \vec{E}^s_{eff}}{\partial t} = -\nu_m (\vec{E}^s_{eff} - \vec{E})$$

Typical modeling approach for RF discharges

Discharge module

Poisson equation:

$$\left(\varepsilon_0 / e\right)\Delta V = n_e - \sum_{ions} z_i n_i$$

$$\frac{\partial \vec{E}^s_{eff}}{\partial t} = -\nu_m (\vec{E}^s_{eff} - \vec{E})$$

Species continuity equations:

$$\frac{\partial n_s}{\partial t} = -\nabla\left(\vec{\phi}_s\right) + S_s$$

Electron energy transport equation:

$$\frac{\partial (n_e \varepsilon_e)}{\partial t} = -\nabla\vec{\phi}_\varepsilon - q_e.\vec{\phi}_e \bullet \vec{E} - S_\varepsilon$$

Time integration during several periods

Time averaged e-neutral collision rates

Neutral Module

Stationnary solution

Continuity equations for neutrals

$$\frac{\partial n_s}{\partial t} = -\nabla \times \left(n_s \vec{u}_s\right) + W_s = 0$$

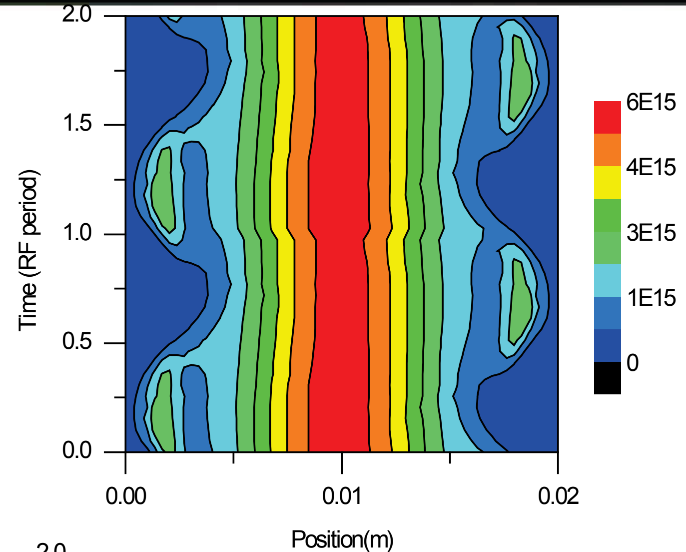
New gas composition

TABLE 1. Reaction model used to describe the chemistry of small molecular species in H_2/SiH_4 RF discharges.

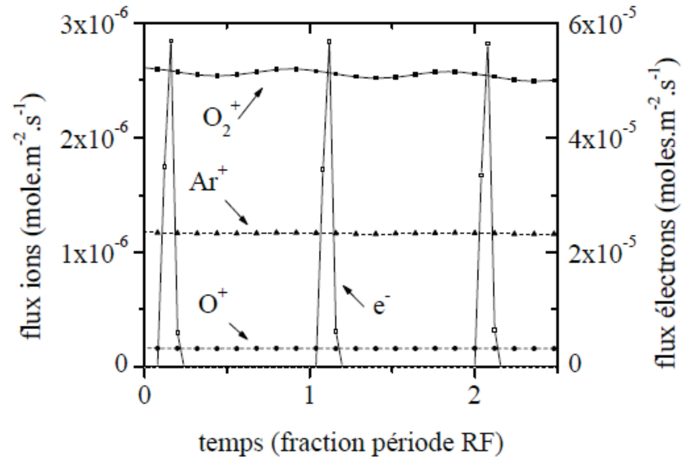
Reaction	Reference	Reaction	Reference
$e^- + H_2(v{=}0) \rightarrow e^- + H_2(v{=}1)$	(R1) [3]	$H_2^+ + H \rightarrow H^+ + H_2$	(R25) [4]
$e^- + H_2(v{=}0) \rightarrow e^- + H_2(v{=}2)$	(R2) [3]	$H_2 + H_2^+ \rightarrow H_3 + H$	(R26) [4]
$e^- + H_2(v{=}0) \rightarrow e^- + H_2(v{=}3)$	(R3) [3]	$H + H^- \rightarrow e^- + 2H$	(R27) [4]
$e^- + H_2(v{=}0) \rightarrow e^- + H_2(v{=}4)$	(R4) [3]	$H + H^- \rightarrow e^- + H_2$	(R28) [4]
$e^- + H_2(v{=}0) \rightarrow e^- + H_2(v{=}5)$	(R5) [3]	$H^+ + H_2 \rightarrow H_2^+ + H$	(R29) [4]
$e^- + H_2 \rightarrow 2e^- + H_2^+$	(R6) [3]	$H^+ + H^- \rightarrow 2H$	(R30) [4]
$e^- + H_2 \rightarrow e^- + 2H$	(R7) [3, 5]	$H^+ + 2H_2 \rightarrow H_3^+ + H_2$	(R31) [4]
$e^- + H \rightarrow 2e^- + H^+$	(R8) [6]	$H^- + H_2^+ \rightarrow H_2 + H$	(R32) [4]
$e^- + H_3^+ \rightarrow 3H$	(R9) [7]	$H^- + H_3^+ \rightarrow 2H_2$	(R33) [4]
$e^- + H_3^+ \rightarrow H + H_2$	(R10) [7]	$SiH_3^- + SiH_2^+ \rightarrow SiH_3 + SiH_2$	(R34) [8, 9]
$e^- + H_3^+ \rightarrow e^- + H^+ + 2H$	(R11) [6]	$SiH_3^- + H_2^+ \rightarrow SiH_3 + H_2$	(R35) [8, 9]
$e^- + H_2(v{=}4) \rightarrow H^- + H$	(R12) [5, 10]	$e^- + SiH_4 \rightarrow SiH_2^- + H_2$	(R36) [8, 9]
$e^- + H_2(v{=}5) \rightarrow H^- + H$	(R13) [5, 10]	$e^- + SiH_4 \rightarrow SiH_3^+ + H + 2e^-$	(R37) [8, 9]
$e^- + H_2(v{=}6) \rightarrow H^- + H$	(R14) [5, 10]	$SiH_3^- + H_3^+ \rightarrow SiH_3 + H_2 + H$	(R38) [8, 9]
$e^- + H_2(v{=}7) \rightarrow H^- + H$	(R15) [5, 10]	$SiH_3^- + H^+ \rightarrow SiH_3 + H$	(R39) [8, 9]
$e^- + H_2^+ \rightarrow e^- + H^+ + H$	(R16) [6]	$SiH_3^- + SiH_3^+ \rightarrow SiH_3 + SiH_3$	(R40) [8, 9]
$e^- + H_2^+ \rightarrow 2H$	(R17) [6]	$SiH_2^- + SiH_2^+ \rightarrow SiH_2 + SiH_2$	(R41) [8, 9]
$e^- + H^- \rightarrow 2e^- + H$	(R18) [6]	$SiH_2^- + H_2^+ \rightarrow SiH_2 + H_2$	(R42) [8, 9]
$e^- + SiH_4 \rightarrow 2e^- + SiH_2^+ + 2H$	(R19) [8, 9]	$SiH_2^- + H_3^+ \rightarrow SiH_2 + H_2 + H$	(R43) [8, 9]
$e^- + SiH_4 \rightarrow e^- + SiH_3 + H$	(R20) [8, 9]	$SiH_2^- + H^+ \rightarrow SiH_2 + H$	(R44) [8, 9]
$e^- + SiH_4 \rightarrow e^- + SiH_2 + 2H$	(R21) [8, 9]	$SiH_2^- + SiH_3^+ \rightarrow SiH_2 + SiH_3$	(R45) [8, 9]
$e^- + SiH_4 \rightarrow e^- + SiH_4(v{=}1)$	(R22) [8, 9]	$H + SiH_4 \rightarrow SiH_3 + H_2$	(R46) [8, 9]
$e^- + SiH_4 \rightarrow e^- + SiH_4(v{=}2)$	(R23) [8, 9]	$H_2 + SiH_2 \rightarrow SiH_4$	(R47) [8, 9]
$e^- + SiH_4 \rightarrow SiH_3^- + H$	(R24) [8, 9]		

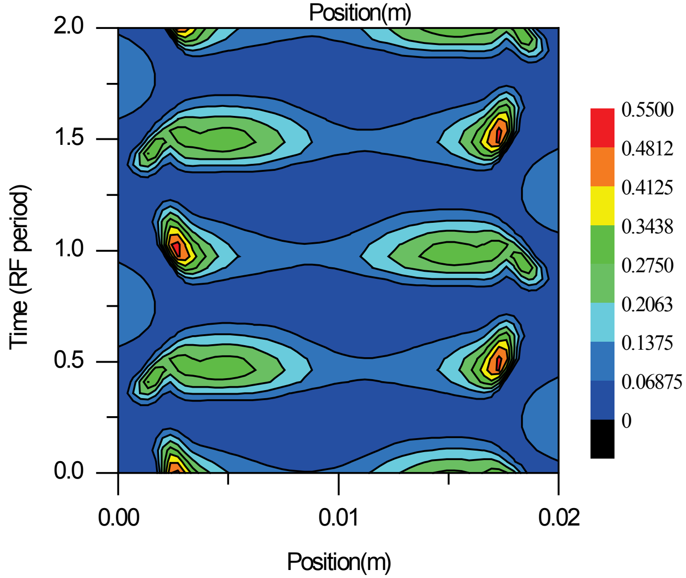
Dynamic of charged species (O_2/Ar plasmas)

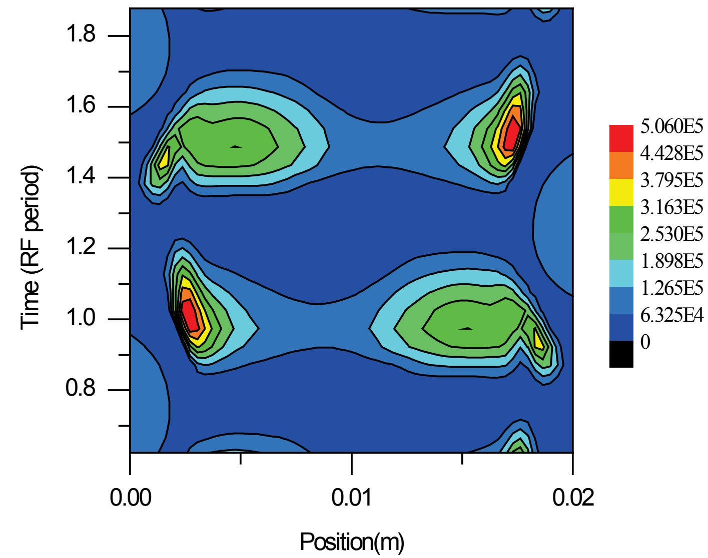
Electron density, electron and ion currents, power deposition and electron temperature



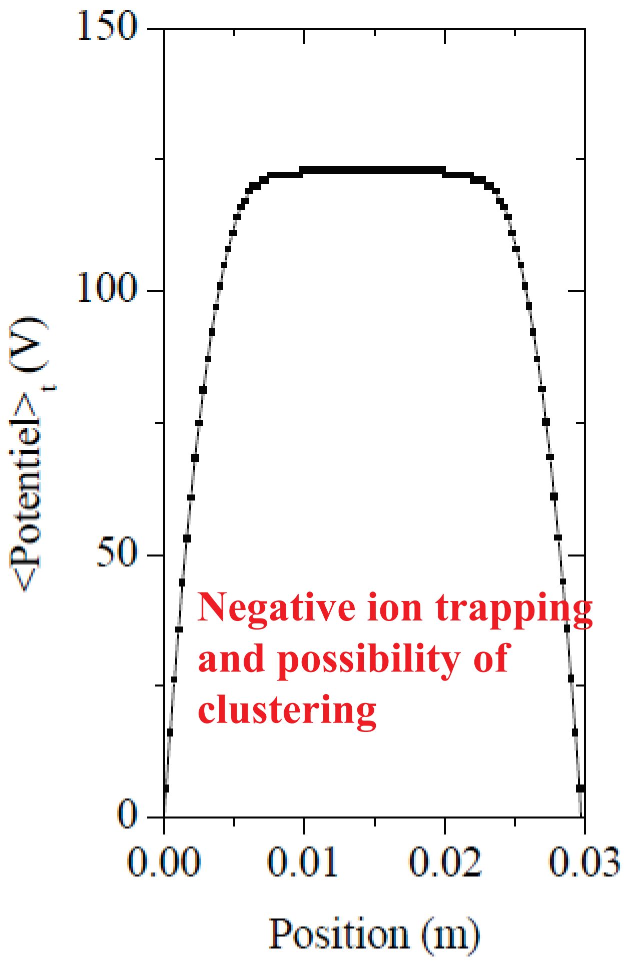
A simple model : oscillating electron cloud

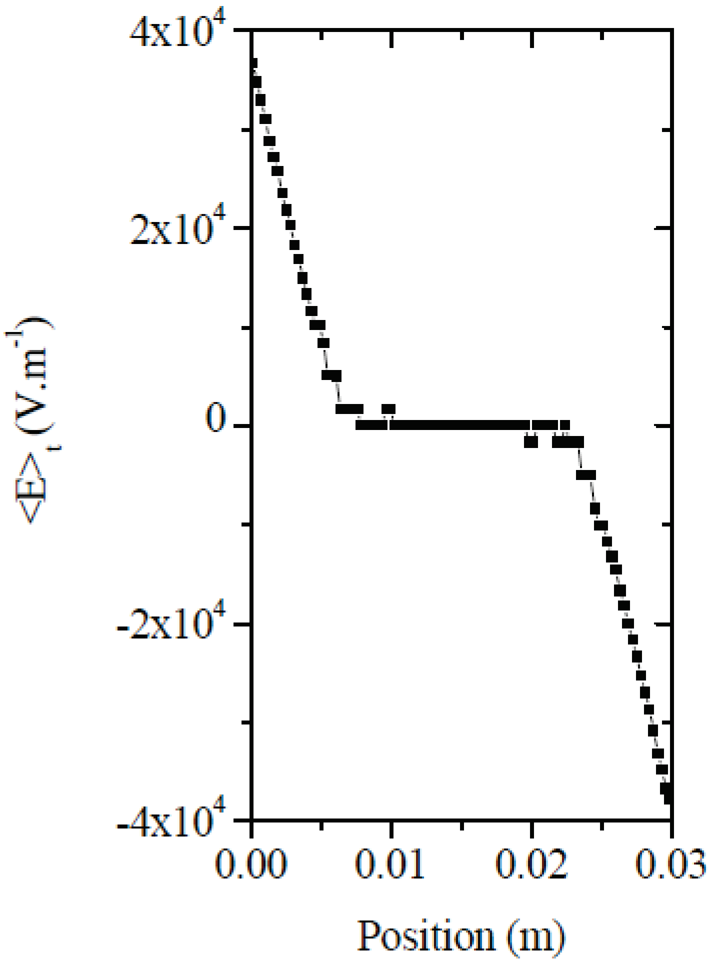






Resulting electrostatic structure

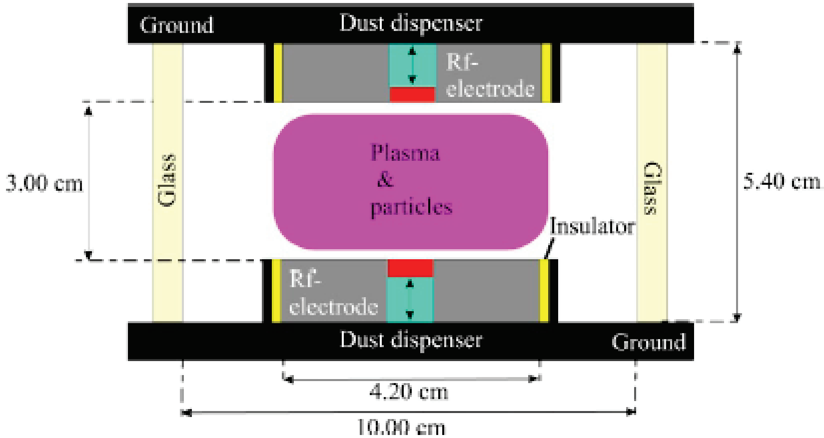




OML equilibrium (Ie+Ii=0) ➔ Particle charge negative ➔ particle trapping

1st phase investigation : investigation dust effect on the plasma equilibrium

The PKE chamber of Morfill et al., Morfill et al. PRL, 1999
Model of Akdim and Goodheer, PRE 2003
Ar, P=40 Pa, V_{RF}=70V, a=15 mm



- Particle with a given diameter are injected in the discharge
- Particle are treated as non reactive a plasma component that experiences charging and self consistent transport
- The presence of particles affect the electron/ion balance and the self-consistent field distribution

$$\frac{dn_j}{dt} + \vec{\nabla} \cdot \vec{\Gamma}_j = S_j,$$

$$\vec{\Gamma}_e = -\mu_e n_e \vec{E} - D_e \vec{\nabla} n_e$$

$$\vec{\Gamma}_i = -\mu_i n_i \overrightarrow{E_{eff,i}} - D_i \vec{\nabla} n_i$$

$$\frac{d\vec{E}_{eff,i}}{dt} = \nu_{m,i}(\vec{E} - \vec{E}_{eff,i}).$$

$$\vec{E} = -\vec{\nabla} V,$$

$$\Delta V = -\frac{e}{\epsilon_0}(n_i - n_e - Q_d n_d),$$

Electron depletion due to particle charging

Affect the self consistent field

Dust particles behavior in a discharge plasma
Forces experienced by dust particles in a plasma

- The particle density is governed by a continuity equation

$$\frac{dn_p}{dt} + \vec{\nabla}.\overrightarrow{\Gamma_p} = 0$$

$\overrightarrow{\Gamma_p}$? : Depends of the force field

Electrostatic ($\propto$a) $\vec{F}_E = q_p \vec{E}\left(1+\frac{\left(a/\lambda_d\right)^2}{3\left(1+a/\lambda_d\right)}\right)$

Magnetic (Lorentz $\propto$a) $\vec{F}_M = \frac{q_p}{c}\vec{v}_p \times \vec{B}$

Drag forces ($\propto$a^2) $\vec{F}_{n,i} = m_{n,i}\, \nu_{pn,i}(\vec{u}_{n,i} - \vec{u}_p)$

Thermophoresis ($\propto$a^2) $\vec{F}_T = -8a^2 \frac{k_b \mu_{ref}}{m_n v_T}\left(\frac{T}{T_{ref}}\right)^{0.81} \nabla T$

Gravitational force ($\propto$a^3) $\vec{F}_g = m_p\, \vec{g}$

➔ **Drift-diffusion flux for dust :** $\vec{\Gamma}_p = n_p(\vec{u}_E + \vec{u}_M + \vec{u}_g + \vec{u}_{n,i} + \vec{u}_T) - D_p \vec{\nabla} n_p$

Dust particles behavior in a discharge plasma
Forces experienced by dust particles in a plasma

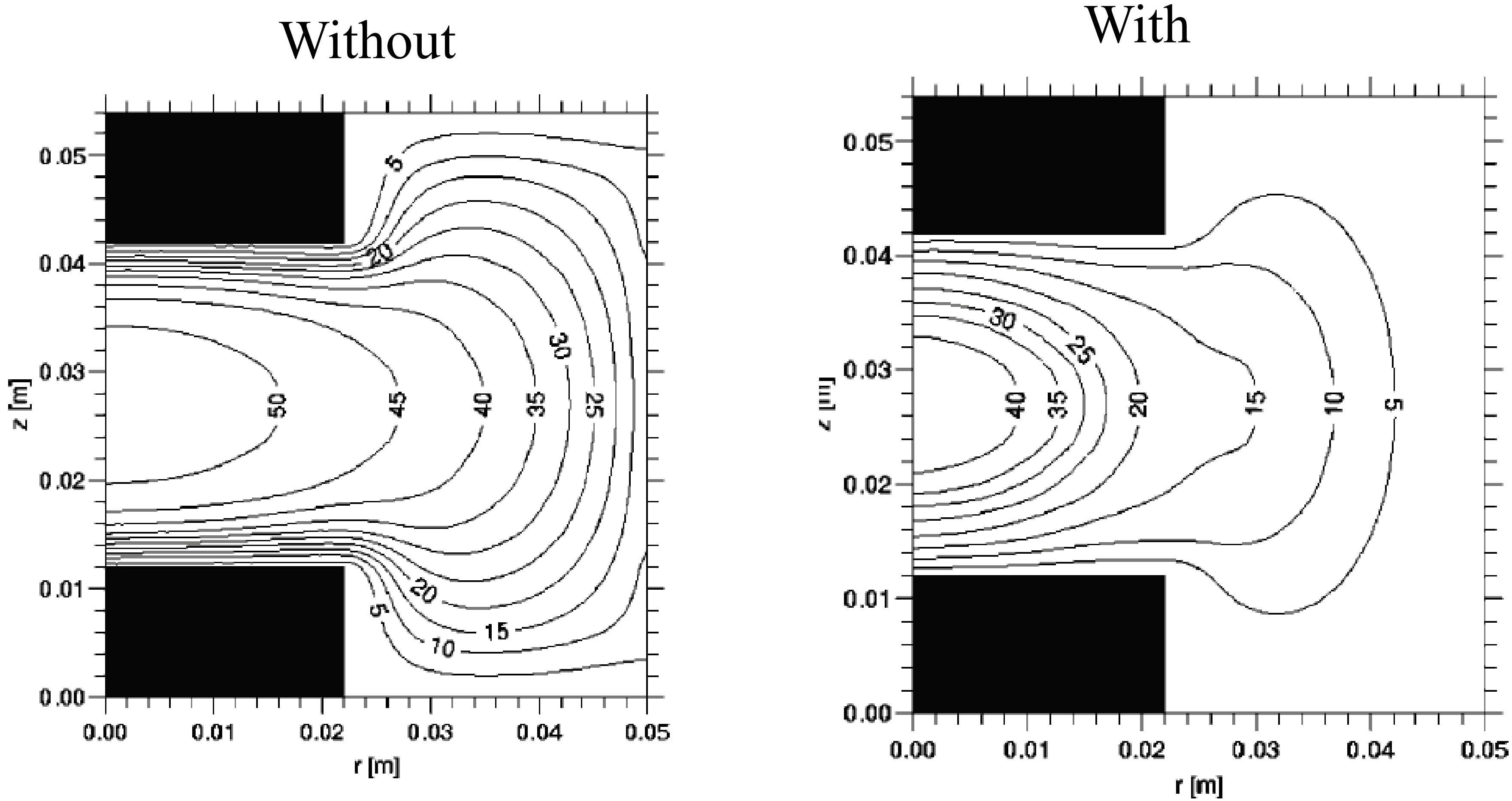
Some orders of magnitude for typical low temperature plasmas conditions from Bouchoule et al.

	a = 100 nm	a = 1 µm
Electrostatique	≈ 2.10^{-13} N	≈ 2.10^{-12} N
Entraînement par les neutres	≈ 10^{-15} N	≈ 10^{-13} N
Entraînement par les ions	≈ 5.10^{-14} N	≈ 10^{-12} N
Thermophorèse	≈ 10^{-15} N	≈ 10^{-13} N
Gravitationnelle	≈ 10-16 N	≈ 10-13 N

- **Small particles : only electrostatic and ion drag are to be considered**
- **Large particle (> 1µm) : all forces start entering into the play**

Effect of dust particles on the discharge characteristics

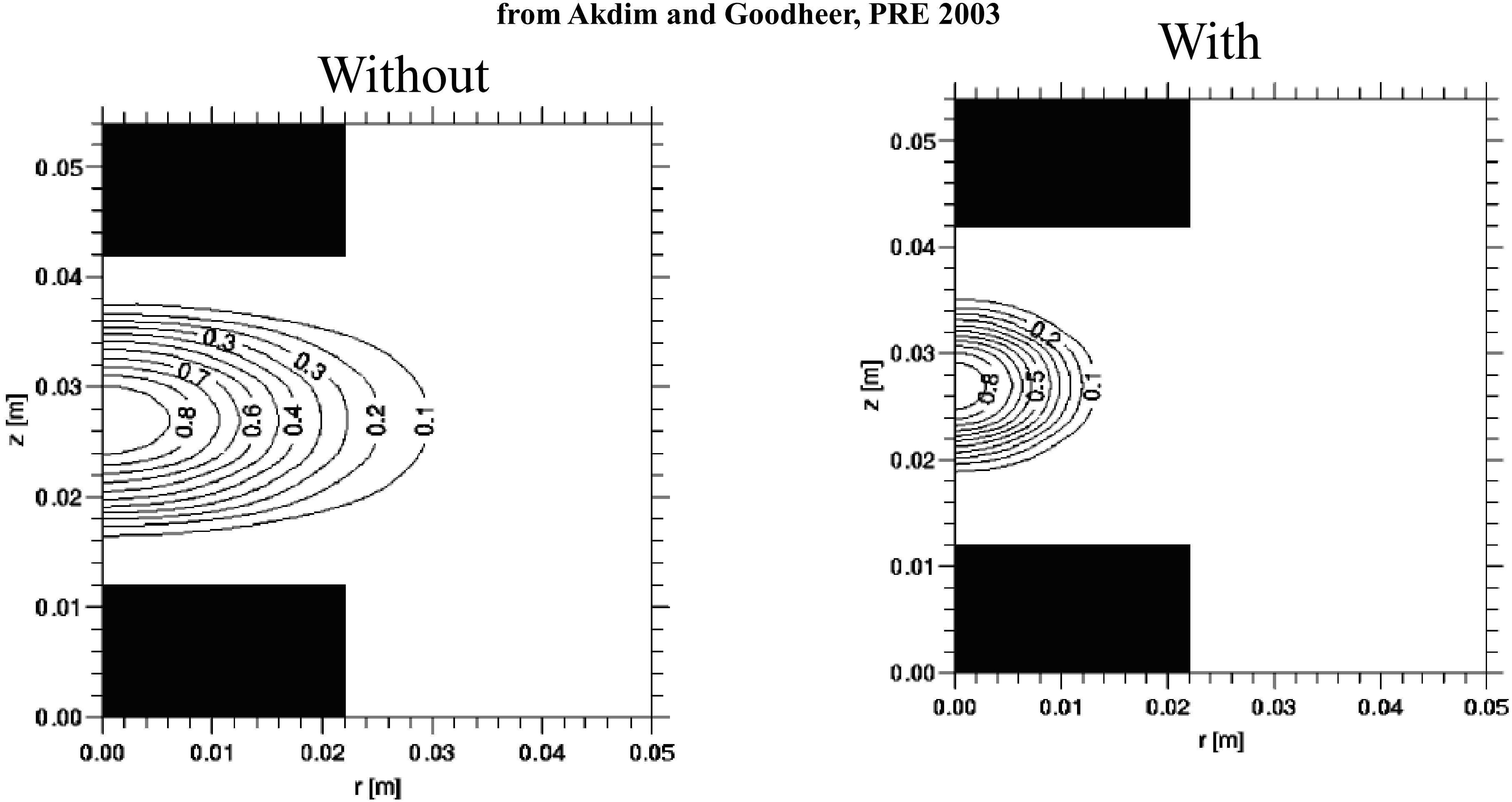
from Akdim and Goodheer, PRE 2003



Reduction of the plasma volume and decrease of the plasma voltage

Effect of dust particles on the discharge characteristics

from Akdim and Goodheer, PRE 2003

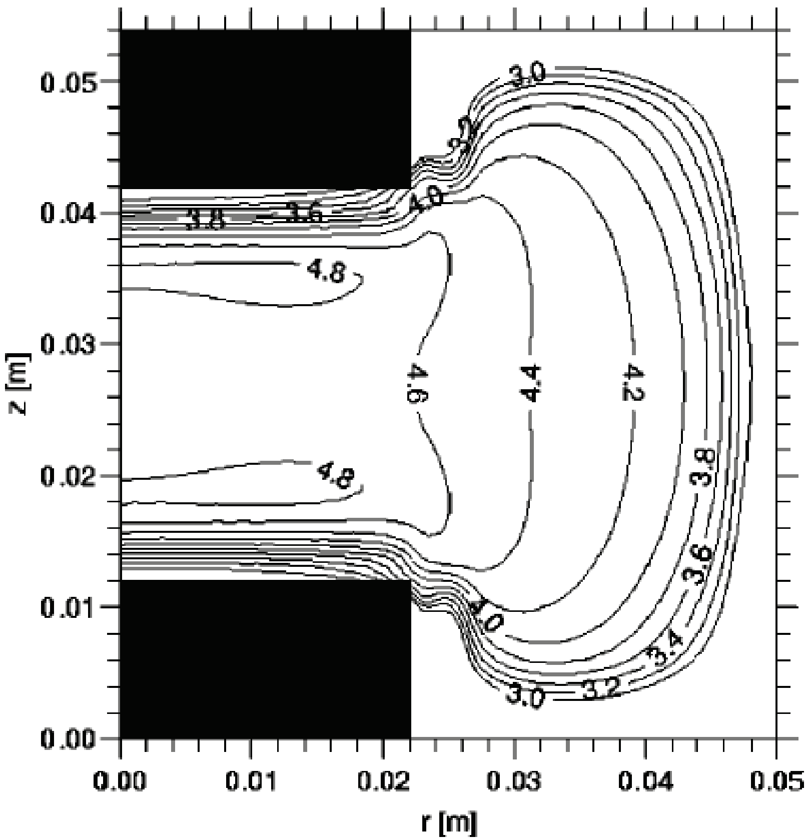


Significant depletion of the electron density and reduction in the plasma volume

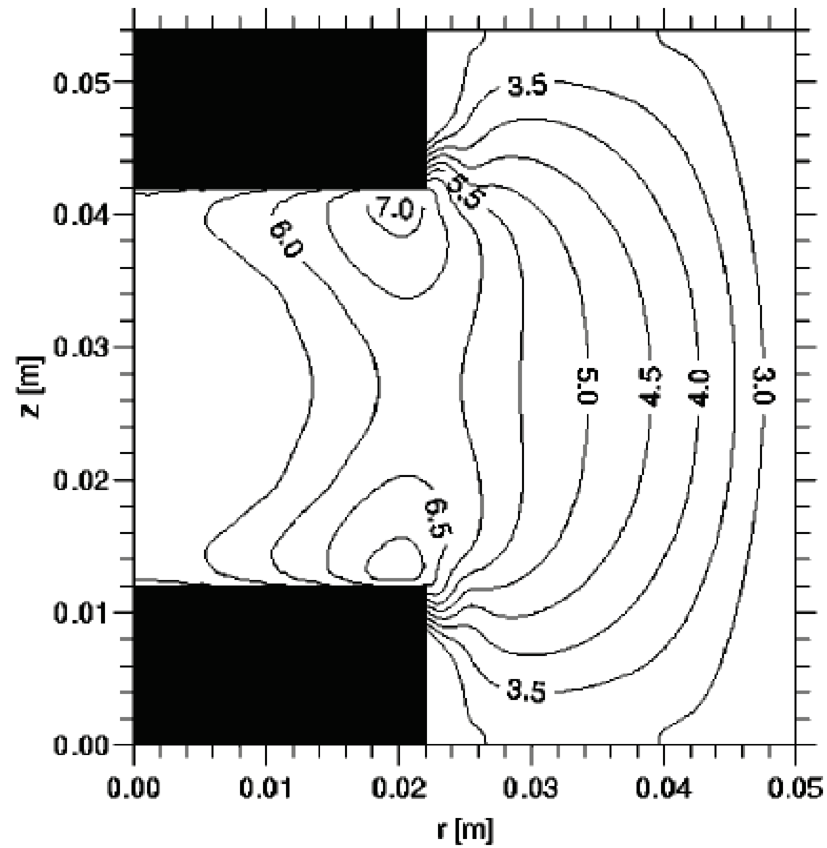
Effect of dust particles on the discharge characteristics

from Akdim and Goodheer, PRE 2003

Without



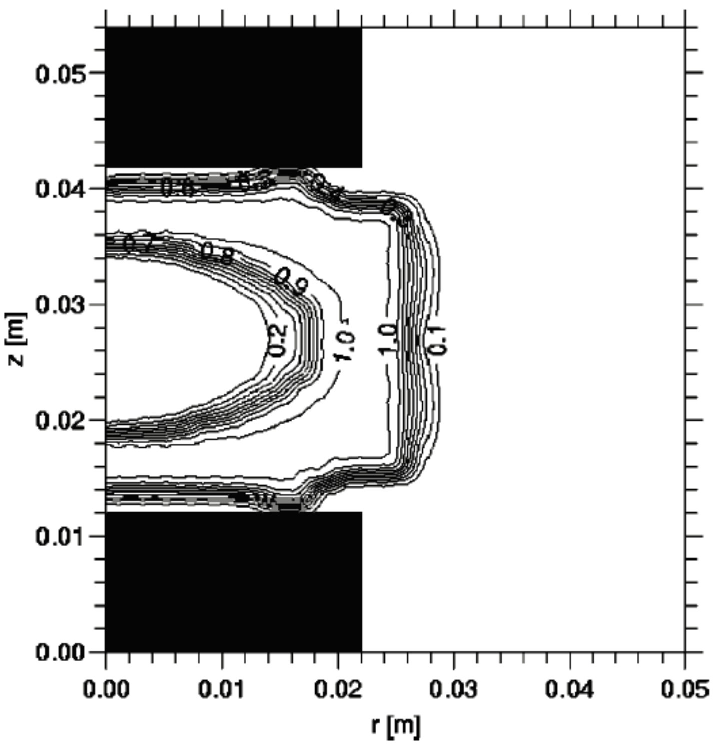
With



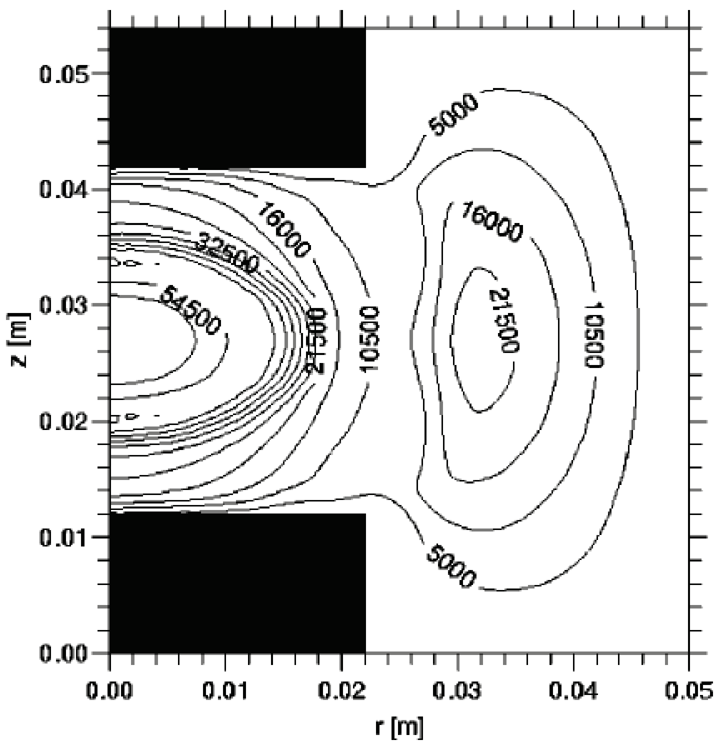
Significant increase of the electron average energy to sustain the discharge

Space distribution of dust density and charge in the discharge

density



charge



- Dust located in the vicinity of the sheath ➔ balance between electrostatic and ion drag forces
- Large charge number correlated to the plasma local parameters

Summary

- First set of studies that describe laboratory dusty plasma uses :
  - Monomodal distribution (a single size particles)
  - A given particle density

➔ Investigate the effect of the particle cloud o the discharge dynamics :

➔ particle charging and electron depletion

➔ Effect on electron temperature and ionization kinetics

➔ Charged partices dynamics and self consistent field distribution

➔ Structure of the particle cloud : void, etc.

A dust cloud has a broad size disctribution and is contantly evolving : density, size and charge

First Improvement line :
Self consistent description of aerosol and plasma dynamics

Make use of a sectional model for particles ➔ determine the size distribution, and in some cases the charge distribution

- ➔ **The size/charge distribution are governed by a set of master equations where a continuity equation is expressed for each size/charge section.**

- ➔ **The particle are no longer « inert » : small particle can appear spontaneously (nucleation) and grow through sticking and coagulation.**

$$\frac{\partial Q_l(t)}{\partial t} = \left.\frac{\partial Q_l(t)}{\partial t}\right|_{coag} + \left.\frac{\partial Q_l(t)}{\partial t}\right|_{sticking} + S_{nucleation} - \nabla F_l$$

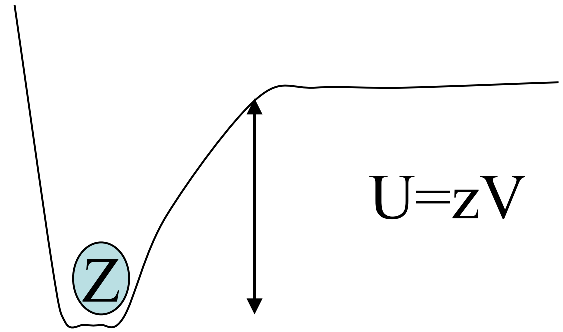
Q_l mass density for a section l

➔ **We therefore need a satisfactory description of nucleation, coagulation and sticking**

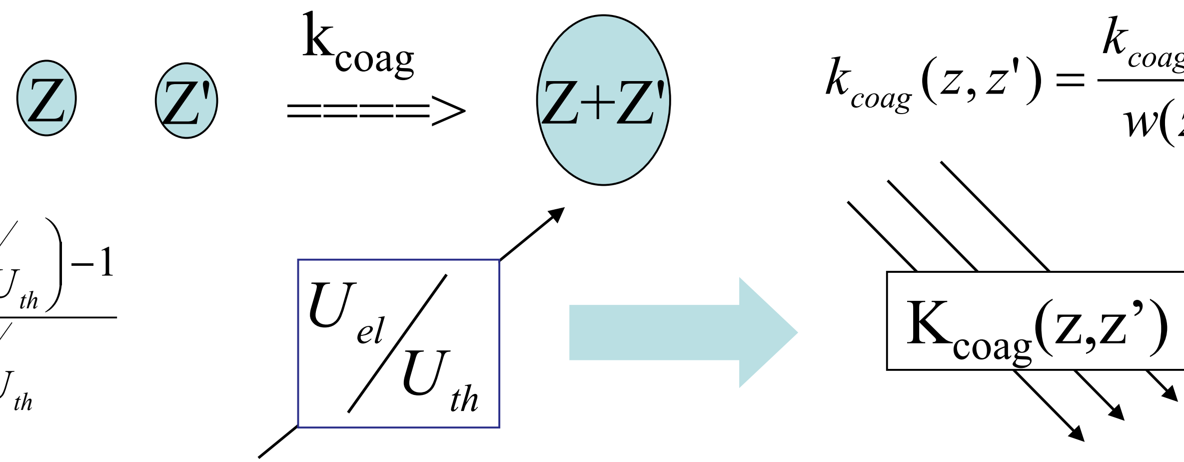
Few words on coagulation vs charging

Particle charging is a key point :

==> Enhanced particle charging insures a significant trapping and long residence time



==> Enhanced particle charging prevents coagulation and growth



$$k_{coag}(z,z') = \frac{k_{coag}(0,0)}{w(z,z')}$$

$$w(z,z') = \frac{\exp\left(U_{el}/U_{th}\right) - 1}{U_{el}/U_{th}}$$

Few words on coagulation vs charging

The only way to have growth ==> charge fluctuation and electron depletion

Possible because particle charg ing is a discrete process ➔ Dynamic fluctuation of small particles between positively and negatively charged states

➔ Coagulation takes place between two particles that has opposite instantanous charges or no charge ➔ involve small particles.

$$\tau_{coag} << \tau_{fluctuation} << \tau_{trans}$$

➔ Transport feels the average charge

$$\frac{d\overline{q}_i}{dt} = -\frac{div(\vec{J}_i - \overline{q}_i div(\vec{F}_i)}{n_i} + \frac{wq^+_{coag} - \overline{q}_i w^+_{coag}}{n_i} + \frac{wq^+_{growth} - \overline{q}_i w^+_{growth}}{n_i} + \frac{I^+ - I^-}{n_i}$$

Coagulation feels the fluctuations

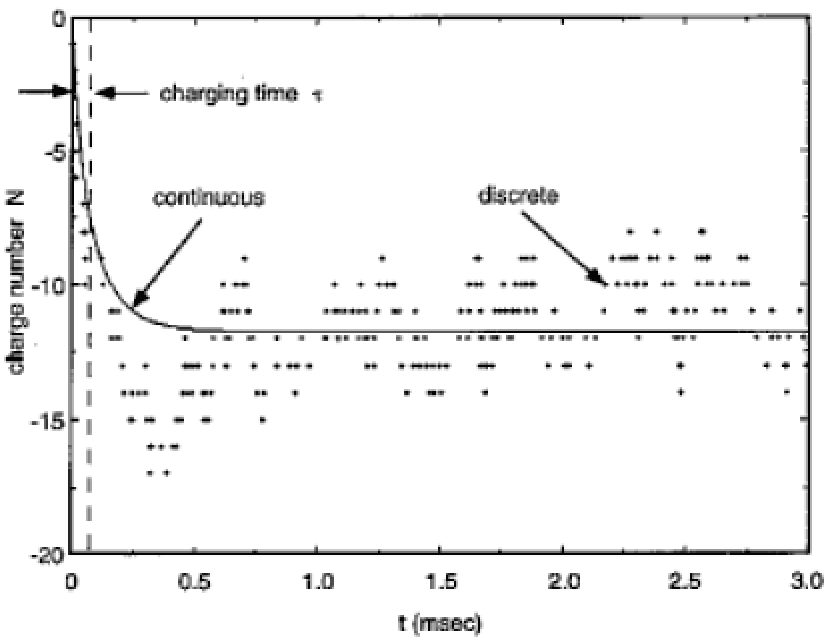
$$\psi(q, \overline{q}) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(q-\overline{q})^2}{2\sigma^2}\right] \qquad \sigma = f\left(\frac{T_e}{T}, \frac{U_{el}}{U_{th}}\right)$$

Few words on coagulation vs charging

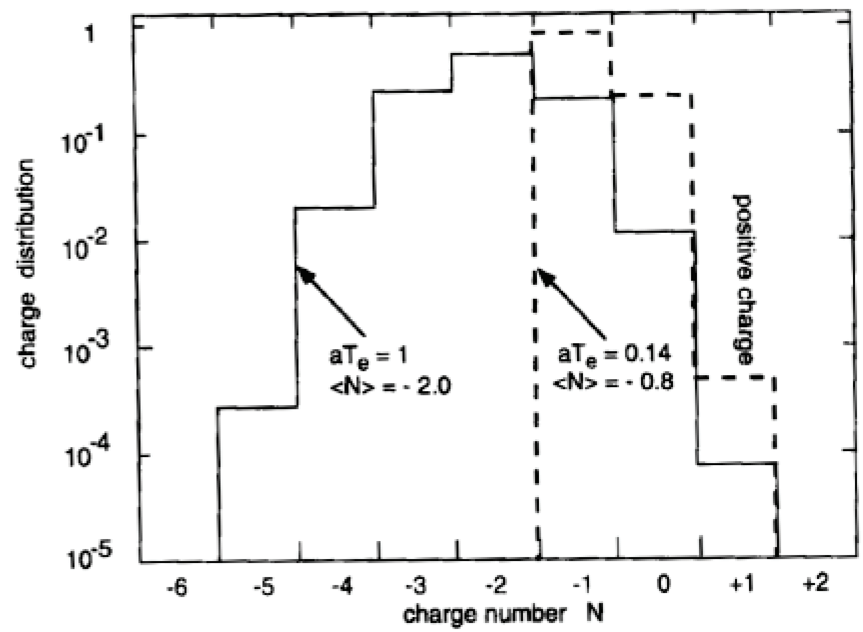
The only way to have growth ==> charge fluctuation and electron depletion

Possible because particle charging is a discrete process

➔ Dynamic fluctuation of small particles between **positively** and negatively charged states



Goree (1994)



Cui & Gorree (1994)

Few words on coagulation vs charging

➔ Coagulation takes place between two particles that has opposite instantanous charges or no charge

➔ coagulation **involves small particles**

$$\tau_{coag} << \tau_{fluctuation}$$

➔ Coagulation « feels » charge fluctuations

$$\psi(q,\bar{q}) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(q-\bar{q})^2}{2\sigma^2}\right]$$

➔ **needs to consider a detailed size distribution**

NUMERICAL MODEL (1D, TRANSIENT)
RF parallel-plate capacitively-coupled plasma

Plasma
Pop. balance eqs. for electrons & ions
Electron energy eq. (assuming Maxwellian)
Poisson's eq. for E-field

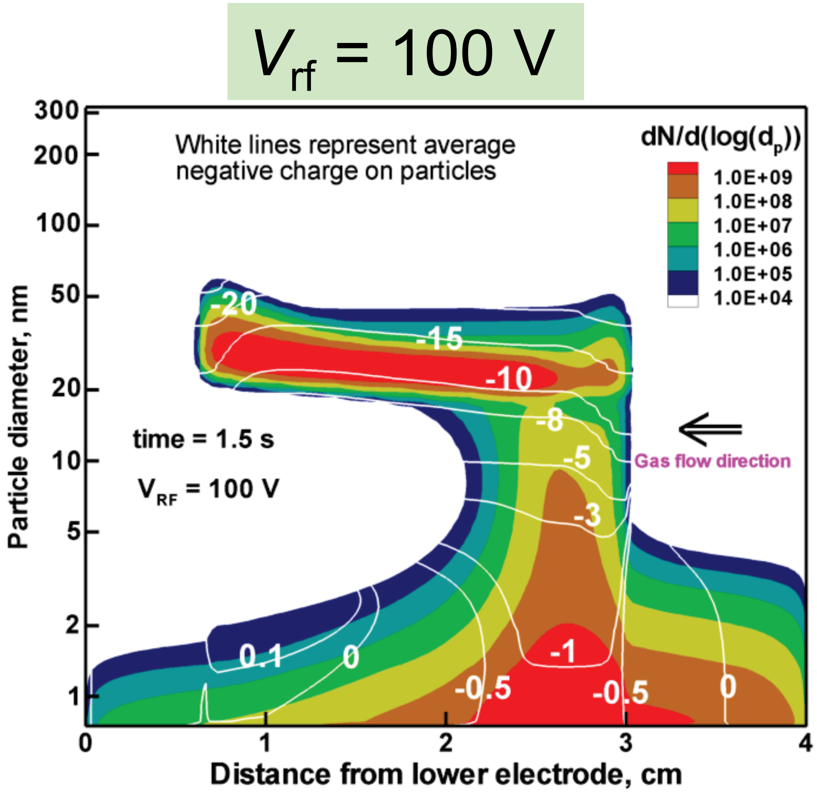
Chemistry
e, Ar, Ar*, H, H_2, H_2^+
SiH_2, SiH_3, SiH_4, SiH_2^-, SiH_3^-, SiH_3^+
Si(s),SiH(s),Si(B)

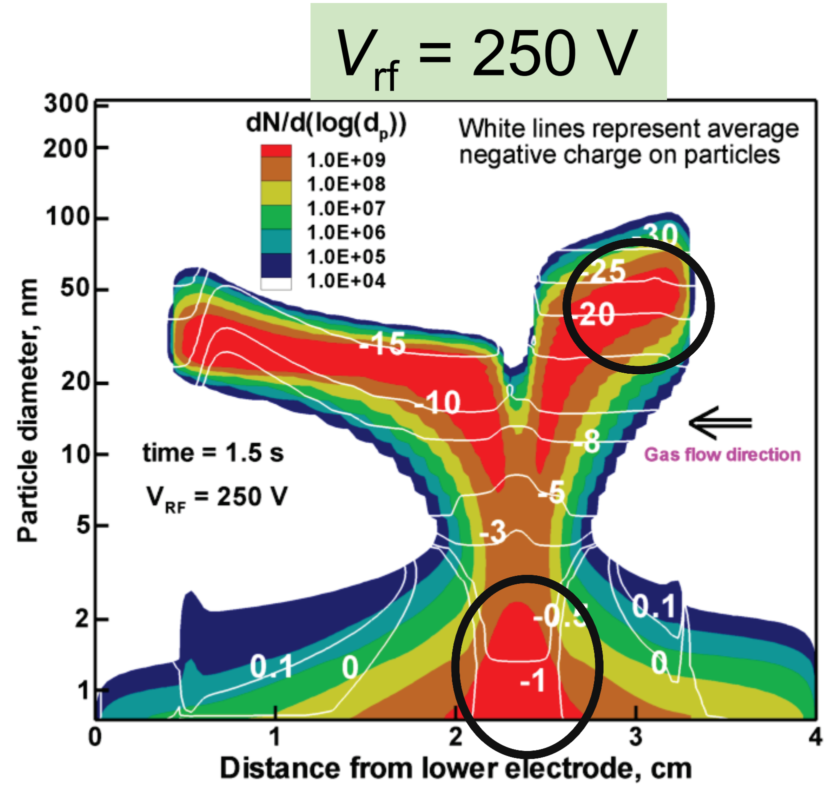
Aerosol
Sectional model for particle size & charge distributions
Finite-rate particle charging by electron & ion attachment (OML)
Coagulation (size & charge-dependent, incl. image potentials)
Transport by neutral drag, ion drag, diffusion, electric force, gravity
Nucleation rate = production rate of $Si_2H_4^-$
Particle surface growth by rxns with Si_1H_m species

Self-consistent coupling of all modules

From S. L. Girshick, University of Minnesota

PARTICLE SIZE DISTRIBUTION & AVERAGE CHARGE



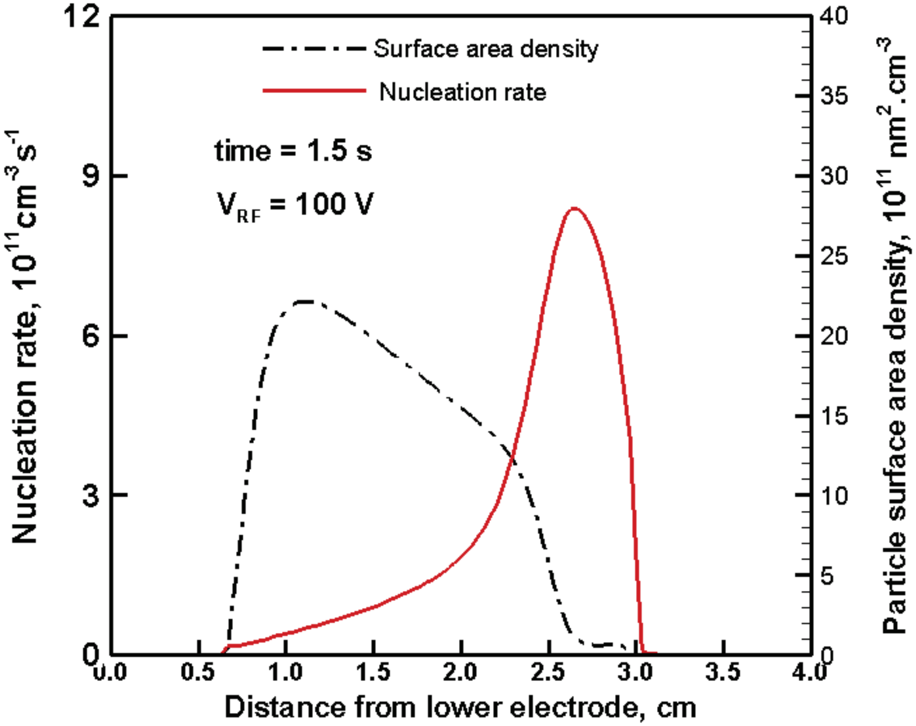


- Increasing voltage causes ion drag to increase
- Pushes large particles upstream
- Creates void in center, allowing fresh nucleation

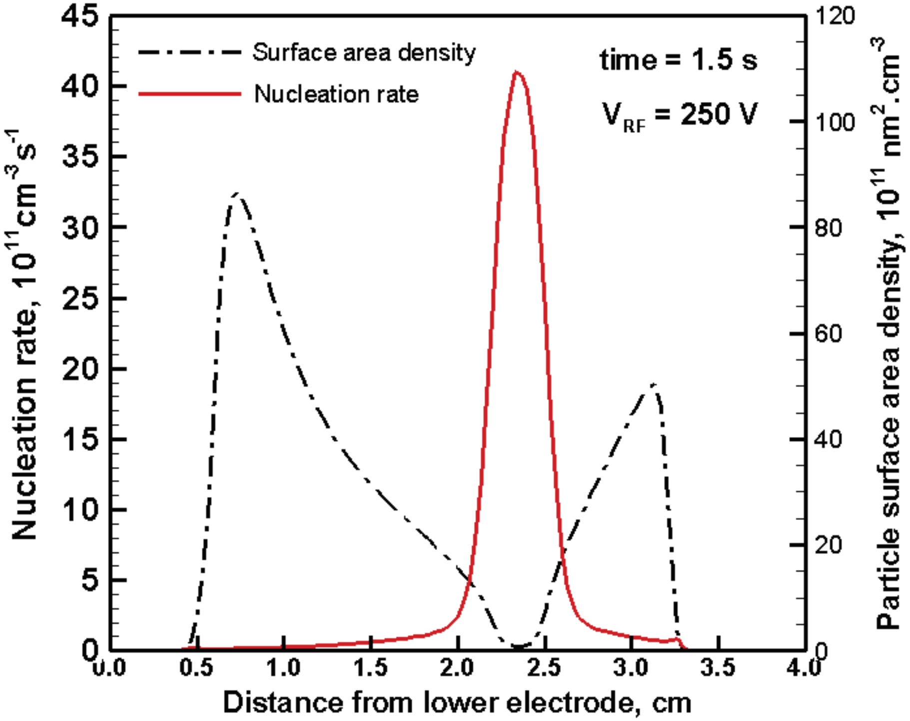
From S. L. Girshick, University of Minnessota

PARTICLE SURFACE AREA & NUCLEATION RATE

V_{rf} = 100 V



V_{rf} = 250 V

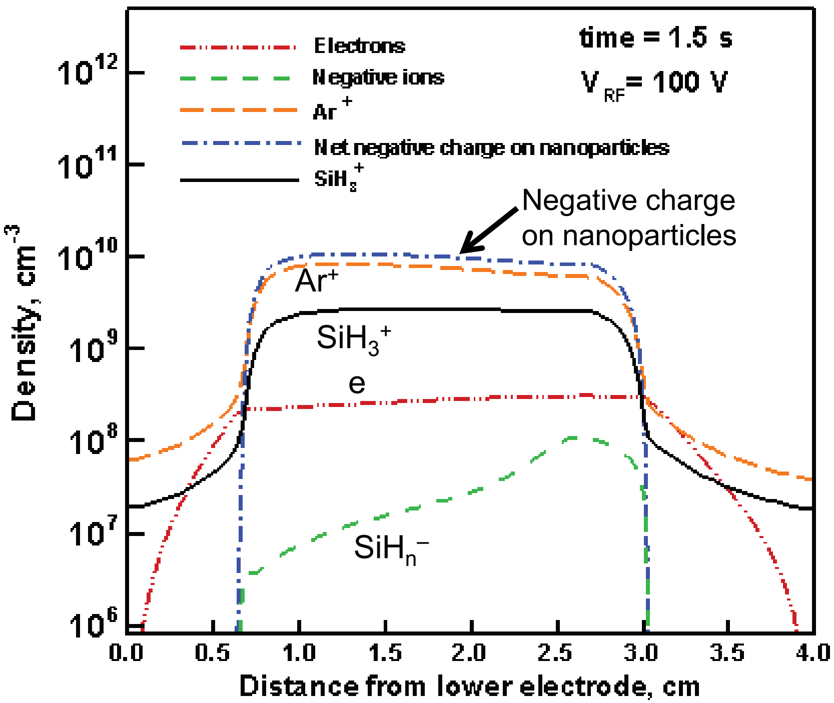


- Competition for SiH_x radicals between nucleation and surface growth
- High particle surface area concentration quenches nucleation

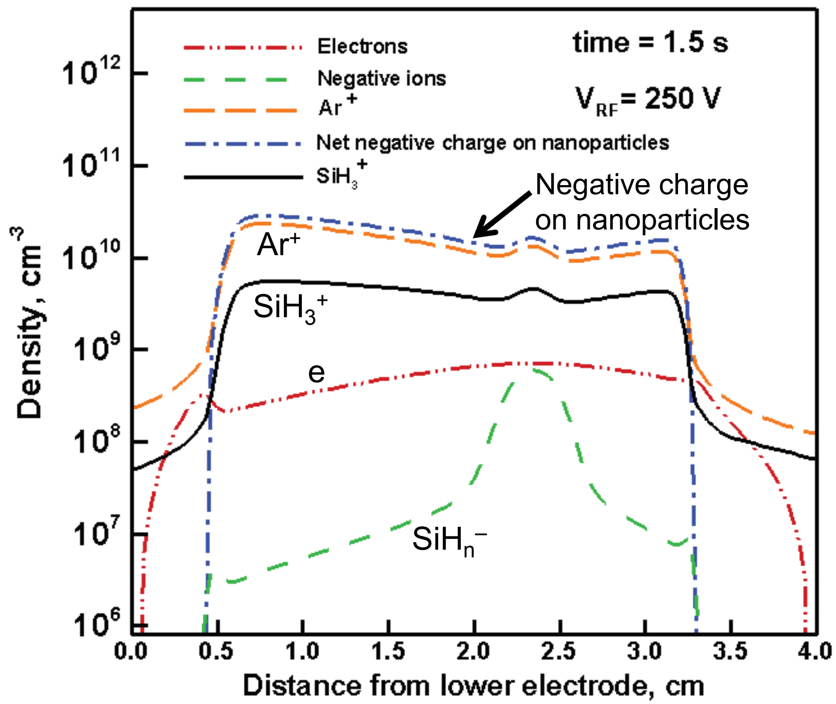
From S. L. Girshick, University of Minnesota

CHARGE CARRIER DENSITY PROFILES

V_{rf} = 100 V



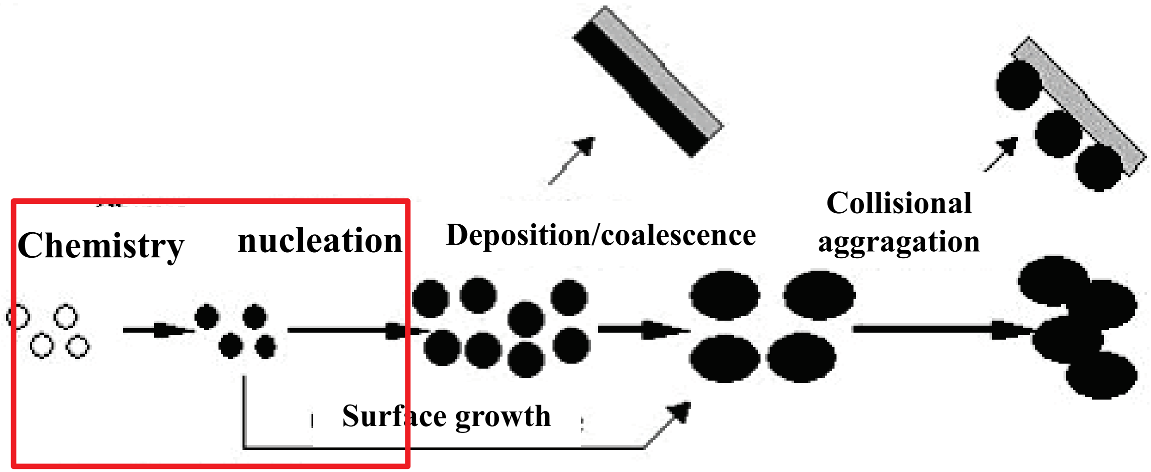
V_{rf} = 250 V



- Electrons strongly depleted by nanoparticle cloud
- Regions of high SiH_n^- density = regions of fresh nucleation

From S. L. Girshick, University of Minnesota

Second Improvement line :
Investigation of the nucleation phase : the molecular growth



Second Improvement line :
Investigation of the nucleation phase : the molecular growth

Start with a plasma model that yields the chelistry and density of small species

TABLE 1. Reaction model used to describe the chemistry of small molecular species in H_2/SiH_4 RF discharges.

Reaction	Reference	Reaction	Reference
$e^- + H_2(v{=}0) \to e^- + H_2(v{=}1)$	(R1) [3]	$H_2^+ + H \to H^+ + H_2$	(R25) [4]
$e^- + H_2(v{=}0) \to e^- + H_2(v{=}2)$	(R2) [3]	$H_2 + H_2^+ \to H_3 + H$	(R26) [4]
$e^- + H_2(v{=}0) \to e^- + H_2(v{=}3)$	(R3) [3]	$H + H^- \to e^- + 2H$	(R27) [4]
$e^- + H_2(v{=}0) \to e^- + H_2(v{=}4)$	(R4) [3]	$H + H^- \to e^- + H_2$	(R28) [4]
$e^- + H_2(v{=}0) \to e^- + H_2(v{=}5)$	(R5) [3]	$H^+ + H_2 \to H_2^+ + H$	(R29) [4]
$e^- + H_2 \to 2e^- + H_2^+$	(R6) [3]	$H^+ + H^- \to 2H$	(R30) [4]
$e^- + H_2 \to e^- + 2H$	(R7) [3, 5]	$H^+ + 2H_2 \to H_3^+ + H_2$	(R31) [4]
$e^- + H \to 2e^- + H^+$	(R8) [6]	$H^- + H_2^+ \to H_2 + H$	(R32) [4]
$e^- + H_3^+ \to 3H$	(R9) [7]	$H^- + H_3^+ \to 2H_2$	(R33) [4]
$e^- + H_3^+ \to H + H_2$	(R10) [7]	$SiH_3^- + SiH_2^+ \to SiH_3 + SiH_2$	(R34) [8, 9]
$e^- + H_3^+ \to e^- + H^+ + 2H$	(R11) [6]	$SiH_3^- + H_2^+ \to SiH_3 + H_2$	(R35) [8, 9]
$e^- + H_2(v{=}4) \to H^- + H$	(R12) [5, 10]	$e^- + SiH_4 \to SiH_2^- + H_2$	(R36) [8, 9]
$e^- + H_2(v{=}5) \to H^- + H$	(R13) [5, 10]	$e^- + SiH_4 \to SiH_3^+ + H + 2e^-$	(R37) [8, 9]
$e^- + H_2(v{=}6) \to H^- + H$	(R14) [5, 10]	$SiH_3^- + H_3^+ \to SiH_3 + H_2 + H$	(R38) [8, 9]
$e^- + H_2(v{=}7) \to H^- + H$	(R15) [5, 10]	$SiH_3^- + H^+ \to SiH_3 + H$	(R39) [8, 9]
$e^- + H_2^+ \to e^- + H^+ + H$	(R16) [6]	$SiH_3^- + SiH_3^+ \to SiH_3 + SiH_3$	(R40) [8, 9]
$e^- + H_2^+ \to 2H$	(R17) [6]	$SiH_2^- + SiH_2^+ \to SiH_2 + SiH_2$	(R41) [8, 9]
$e^- + H^- \to 2e^- + H$	(R18) [6]	$SiH_2^- + H_2^+ \to SiH_2 + H_2$	(R42) [8, 9]
$e^- + SiH_4 \to 2e^- + SiH_2^+ + 2H$	(R19) [8, 9]	$SiH_2^- + H_3^+ \to SiH_2 + H_2 + H$	(R43) [8, 9]
$e^- + SiH_4 \to e^- + SiH_3 + H$	(R20) [8, 9]	$SiH_2^- + H^+ \to SiH_2 + H$	(R44) [8, 9]
$e^- + SiH_4 \to e^- + SiH_2 + 2H$	(R21) [8, 9]	$SiH_2^- + SiH_3^+ \to SiH_2 + SiH_3$	(R45) [8, 9]
$e^- + SiH_4 \to e^- + SiH_4(v{=}1)$	(R22) [8, 9]	$H + SiH_4 \to SiH_3 + H_2$	(R46) [8, 9]
$e^- + SiH_4 \to e^- + SiH_4(v{=}2)$	(R23) [8, 9]	$H_2 + SiH_2 \to SiH_4$	(R47) [8, 9]
$e^- + SiH_4 \to SiH_3^- + H$	(R24) [8, 9]		

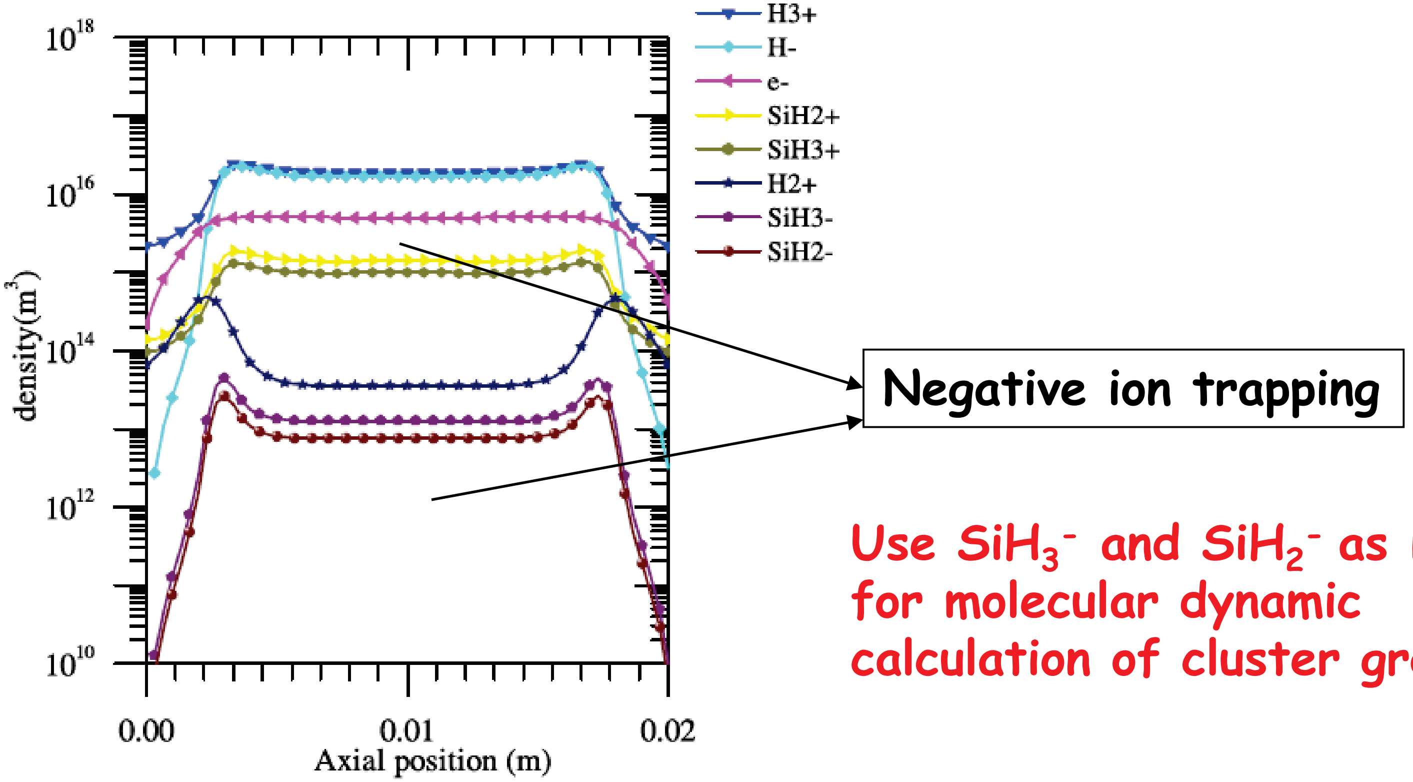
Typical results

Feed gas: H_2/SiH_4 mixture (2% SiH_4 , 98% H_2)

Excitation voltage : 100 – 500 V

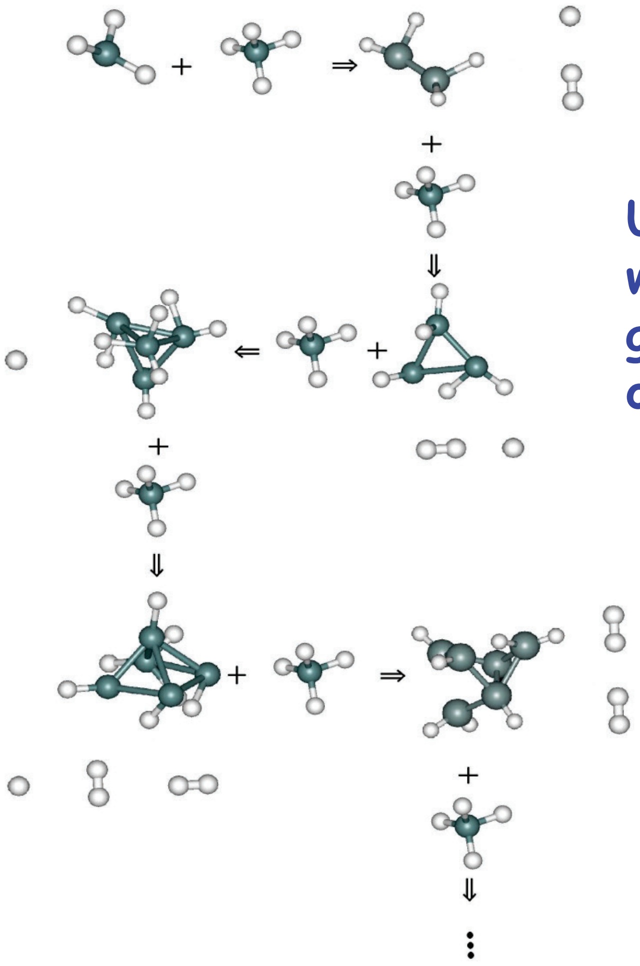
Pressure : 0.5 – 2 Torr

Time averaged species density



Use SiH_3^- and SiH_2^- as input for molecular dynamic calculation of cluster growth

Growth of Si_nH_m clusters in a plasma reactor



Using our results from the plasma modeling, we now can follow the dynamics of the cluster growth as a result of the consecutive capture of plasma radials (SiH_4, SiH_3, SiH_2…).

From Holger VACH, Q. Brulin, and Ning Ning

Approximations used in LPICM molecular dynamic code

At each time step in our MD calculation, we solve the Schrödinger equation ("on the fly"):

$$H_{tot}\Psi = E\Psi$$

$$H_{tot} = \sum_{A}\sum_{\angle B}\frac{Z_A Z_B}{r_{AB}} - \sum_{A}\sum_{i}\frac{Z_A}{r_{Ai}} + \sum_{i}\sum_{\angle j}\frac{1}{r_{ij}} - \frac{\hbar}{2\pi.m}\sum_{i}\nabla_i^2 - \frac{\hbar}{2\pi.M_A}\sum_{A}\nabla_A^2$$

For our system, it is impossible to solve Schrödinger's equation directly. Therefore, we employed the semi-empirical PM3 method to calculate the electronic structure of our system; e.g., we used three approximations for solving the electronic Schrödinger equation (reference: J.J.P. Stewart, J. Comput. Chem. **10** (1989) 209 and 221):

1) The Born-Oppenheimer's approximation :

$$H_{tot} = \sum_{A}\sum_{\angle B}\frac{Z_A Z_B}{r_{AB}} - \sum_{A}\sum_{i}\frac{Z_A}{r_{Ai}} + \sum_{i}\sum_{\angle j}\frac{1}{r_{ij}} - \frac{\hbar}{2\pi.m}\sum_{i}\nabla_i^2$$

From Holger VACH, Q. Brulin, and Ning Ning

LPICM

Approximations used in LPICM molecular dynamic code

2) The wave function can be written as a Slater determinant.

$$\Psi = (n!)^{-1/2}\left|\Psi_p^{\alpha}(1)\Psi_p^{\beta}(2)\ldots\Psi_z^{\alpha}(n-1)\Psi_z^{\beta}(n)\right|$$

where $\Psi_p^{\alpha}(1)$ is a p wave function for an electron with spin α

3) LCAO approximation:

$$\Psi_p(i) = \frac{1}{\sqrt{N_p}}\sum_k c_k^p \Phi_k(i)$$

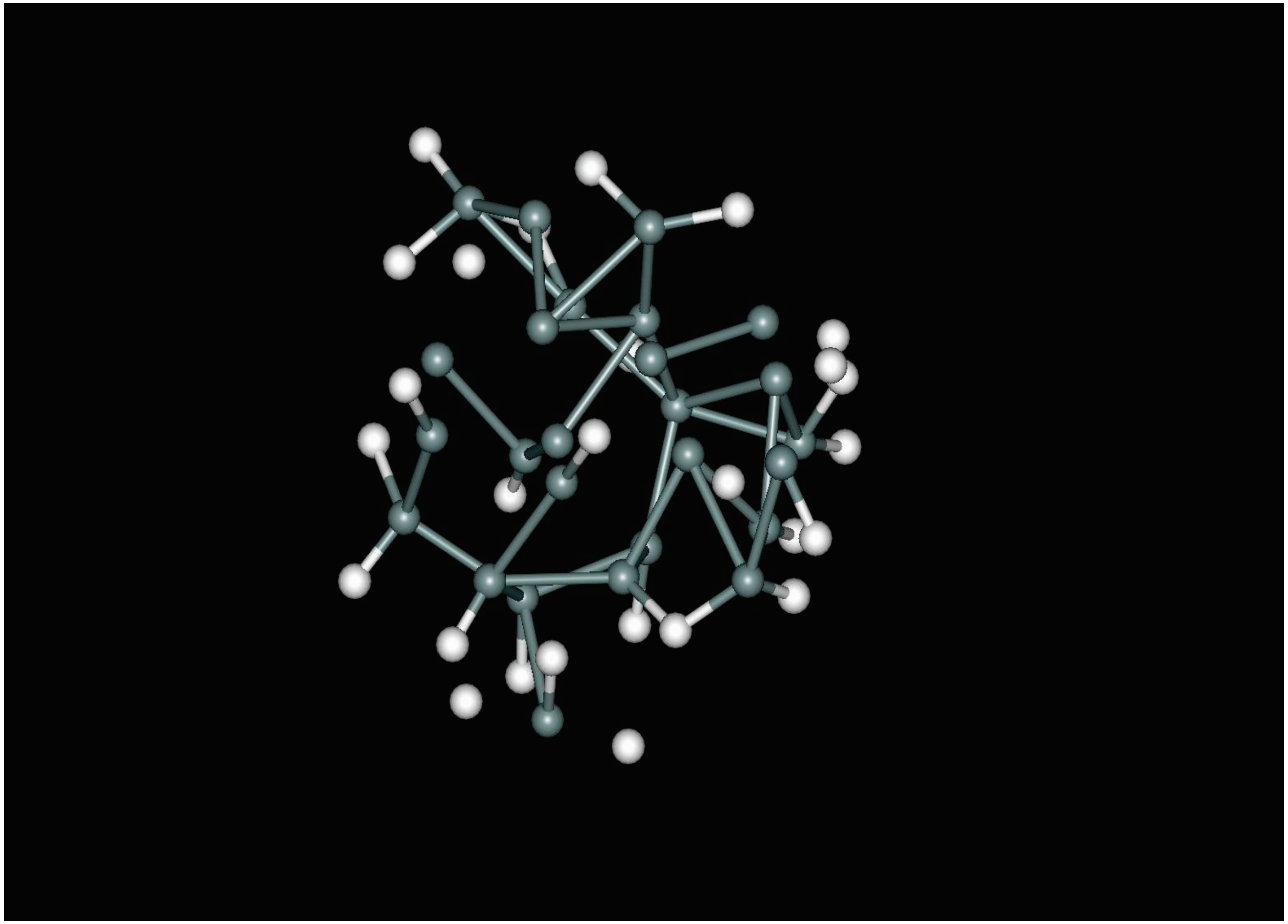
$$N_p = \sum_k \sum_l c_k^p c_l^p S_{kl}$$

Where S_{kl} is the integral overlap beetwen k and l.

Within the PM3 method, we use *s*, p_x, p_y, p_z as basis set.

From Holger VACH, Q. Brulin, and Ning Ning

Growth of $Si_n H_m$ clusters in a plasma reactor

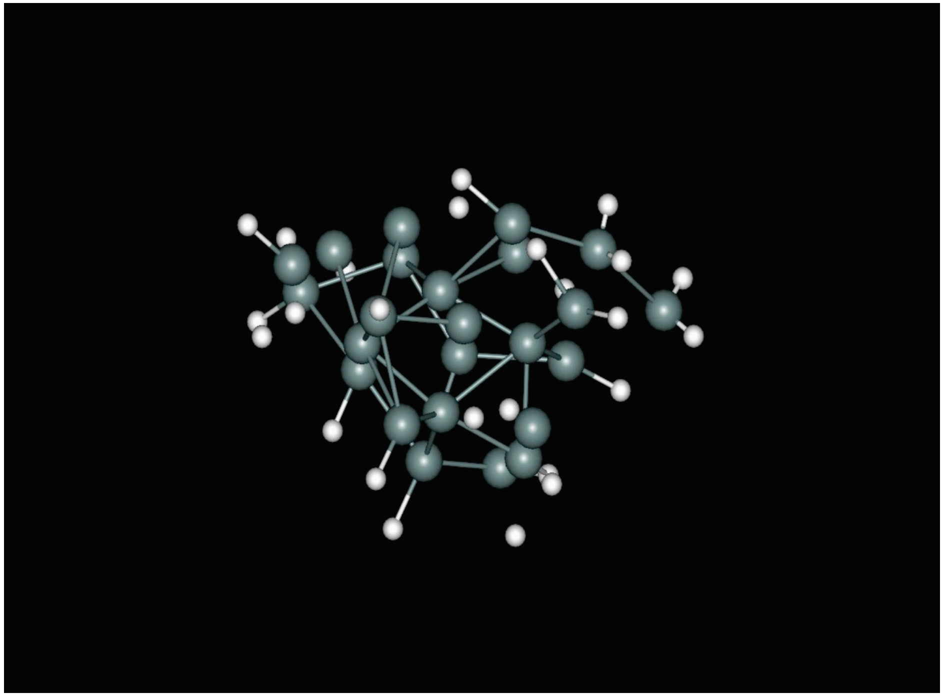


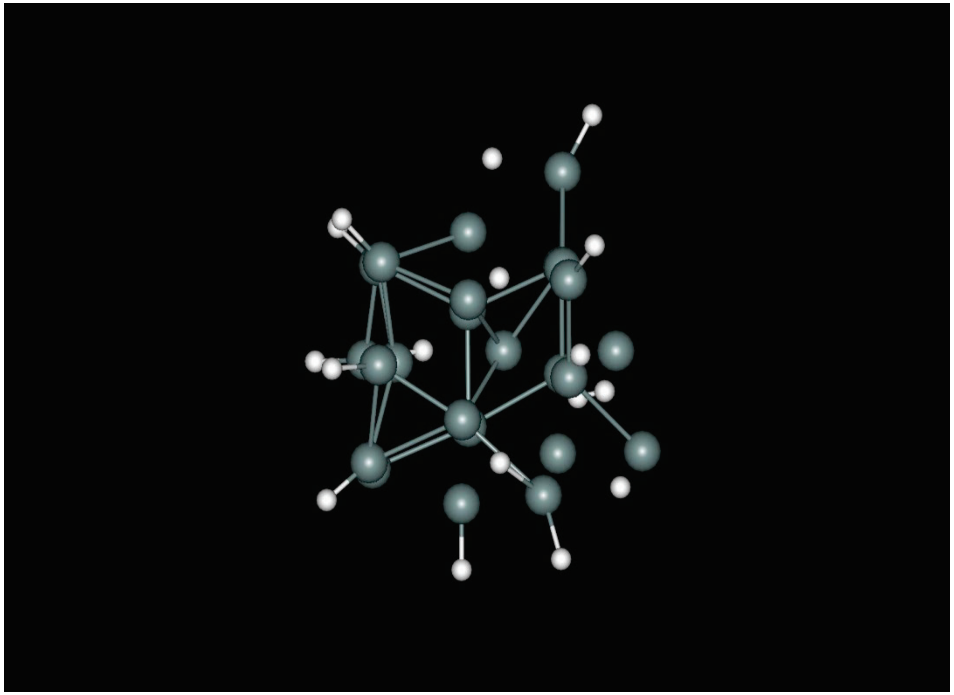
Under realistic SiH_4 plasma conditions, we always find amorphous nanostructures.

Holger VACH, Q. Brulin, and Ning Ning

Growth of $Si_n H_m$ clusters in a plasma reactor

Role of atomic H for the crystallization of an amorphous $Si_{24}H_{25}$ nanoparticle





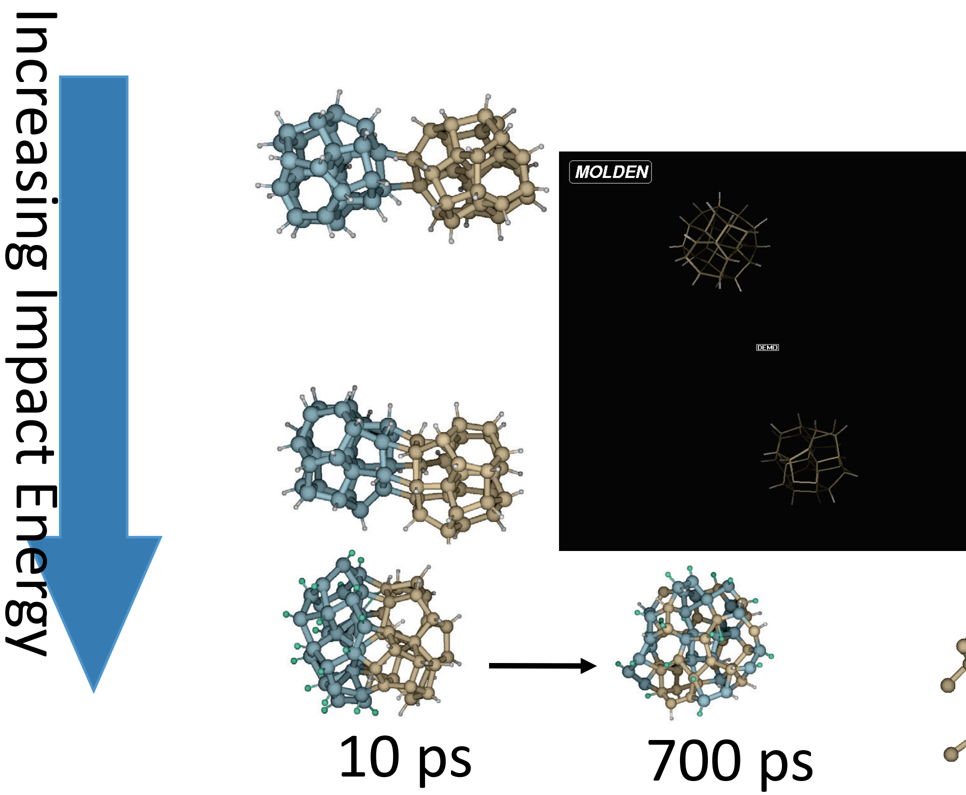
BEFORE … ***AFTER …***

… the collision with 10 thermal H atoms

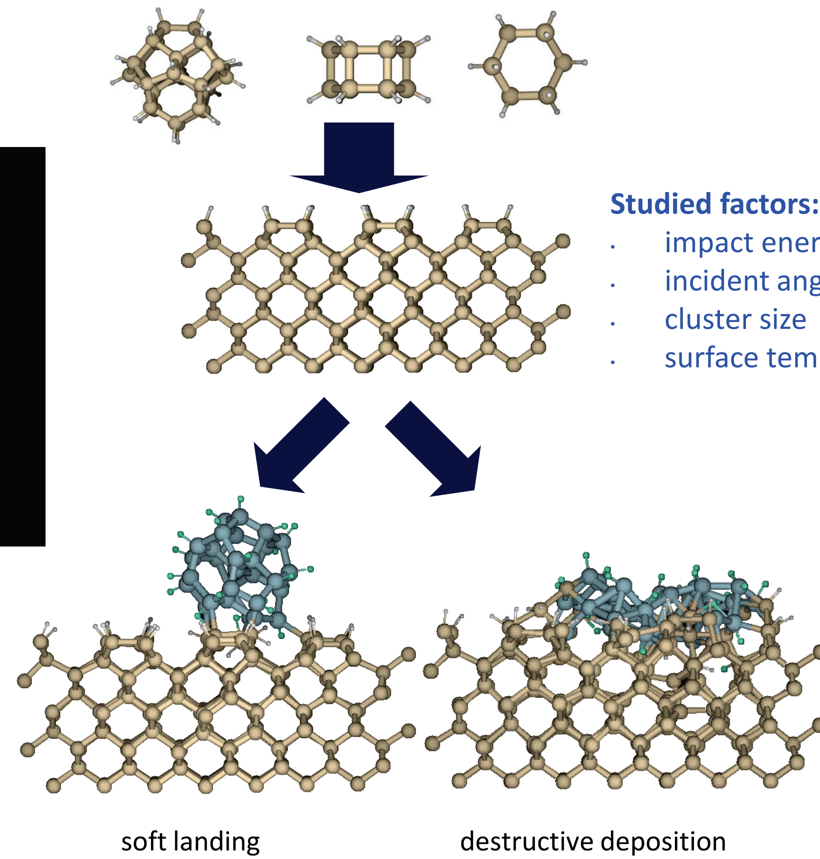
Holger VACH, Q. Brulin, and Ning Ning

•Hydrogenated silicon nanoparticle coagulation and deposition

Coagulation of hydrogenated silicon particles in the gas phase using classical MD simulation method



Deposition dynamics of hydrogenated silicon clusters on a crystalline silicon substrate under typical plasma conditions.

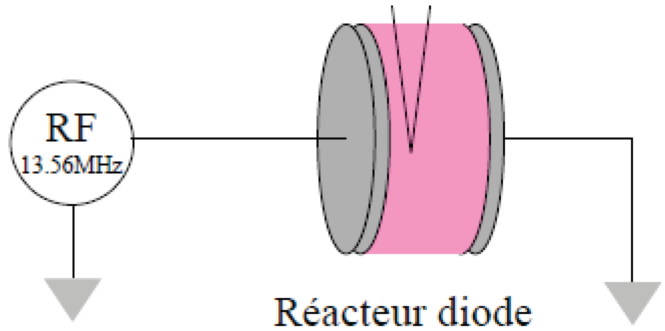


Studied factors:
- impact energy
- incident angle
- cluster size
- surface temperature

N. Ning and H. Vach, J. Phys. Chem. A 114, 3297 (2010).

Particle formation in other discharge configuration

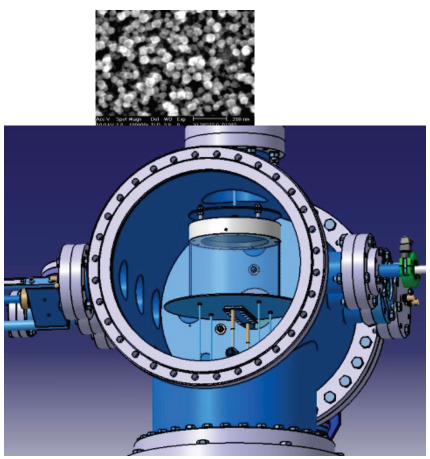
So far :



Particle formation driven by Negative ion clustering

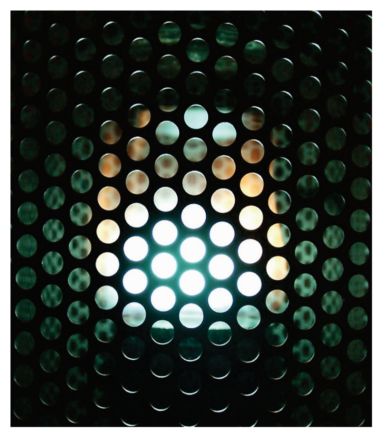
Particle are also observed in :

DC discharge



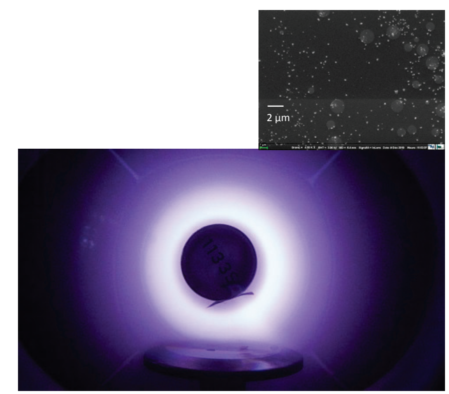
Particle formation driven by Negative ion clustering

MW discharge



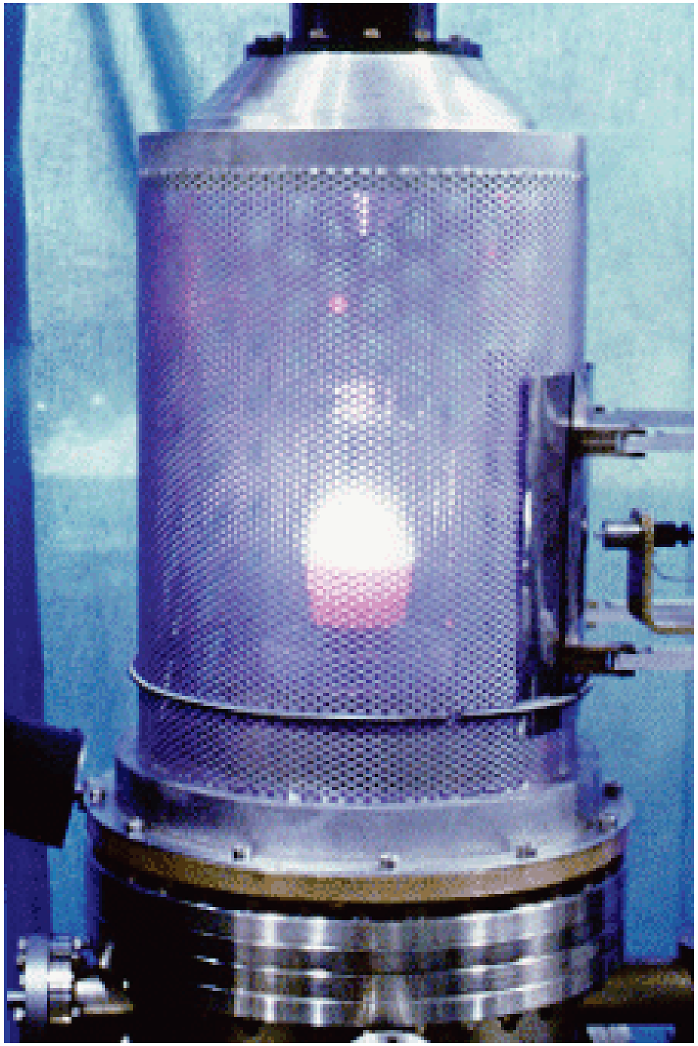
Particle formation driven by neutral clustering

Magnetized discharge



?

Neutral species driven dust (soot) particle The example of diamond deposition plasma processes



Bell Jar Reactor type

- 2-6 kW
- P=25-200 mbar

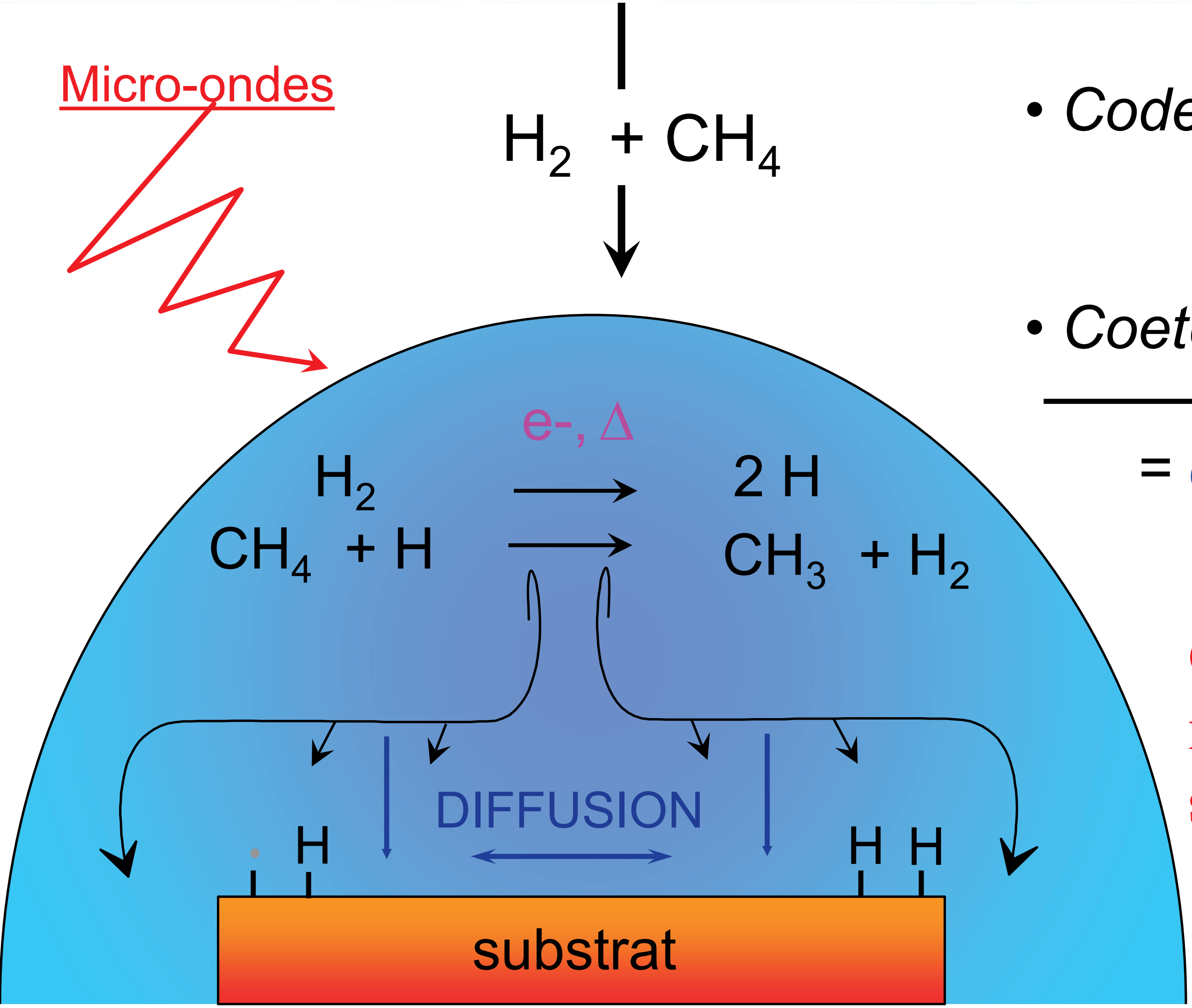
Deposition parameters

- $\%CH_4$: 0.25 - 16 %
- Ts : 400 - 1000°C
- dP_{MW} : 9 - 30 W/cm^3
- t : 0.5 - 600 h

Sheath

few tens of microns
totally collisional for ions
very small potential drop (floating)
→very low energy ions
→Low ion flux (vs atom and radicals)

PACVD of diamond principle



- *Codeposition of* (sp_2, sp_3)

+

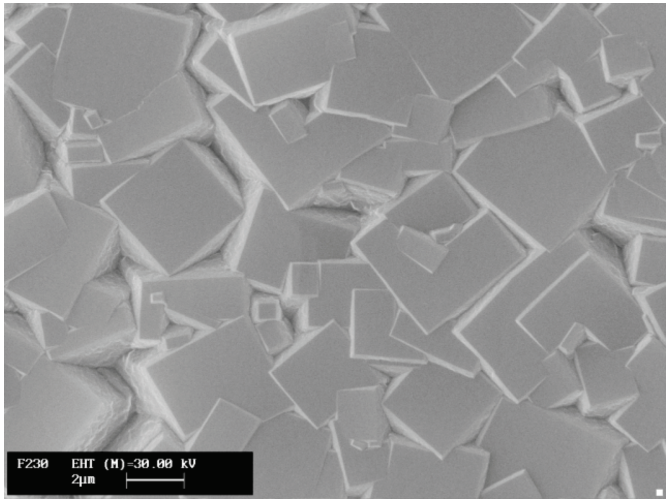
- *Coetching* (sp_2, sp_3)

= *diamant polycristallin*

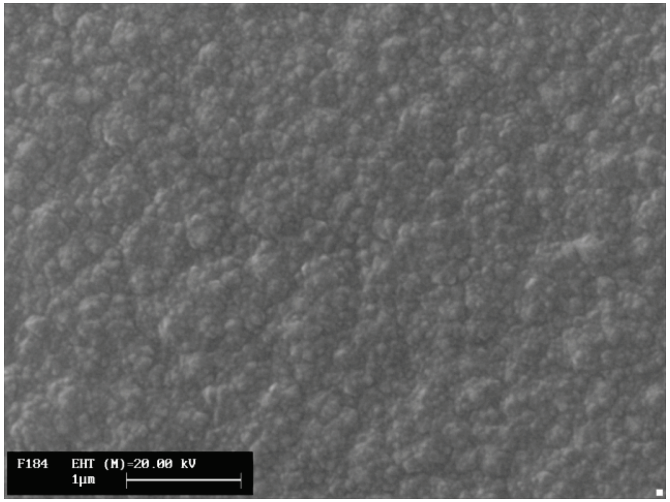
Only neutral chemistry involved in the plasma surface interaction

Consequence on the film morphology and texture

- selective secondary nucleation :
  - Stable (100) faces
  - unstable (111) faces

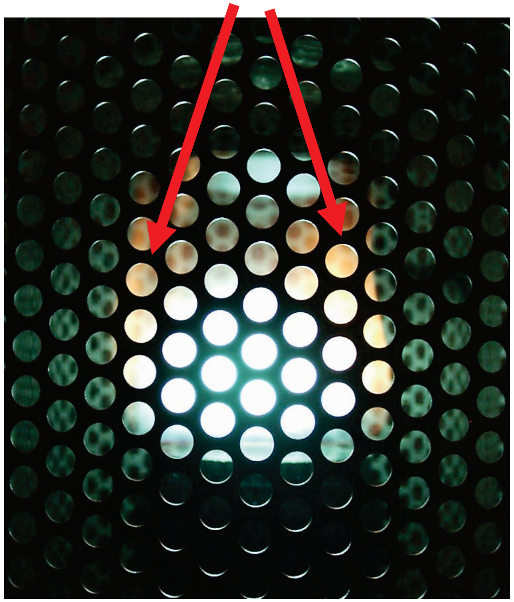


- *«isotropic» secondary nucleation :*
  - *unstable (100) faces*
  - *Unstable (111) faces*



From H_2/CH_4 to $H_2/Ar/CH_4$
From PCD to NCD

Redish soot particles



Molecular and particle growth in gas phase

- Homogeneous chemistry
  - Radicalar route
  - Ionic route
- Heterogeneous processes

Implication
on the growth ?
and change in the film microstructure ?

Understanding the soot formation
A modeling approach : quasi-homogenous plasma assumption

Modeling objective : **estimate the gas and electron temperatures, species densities, particle size distribution (or its moments) in the uniform plasma bulk**

Small molecules → **large molecular edifices** → **Nucleus smallest *solid* particle** → **Complex particle population**

Plasma chemistry → **Nucleation ??** → **Aerosol dynamic**

2 LME ➔ nucleus

heterogenous nucleation is not considered

Heterogenous chemistry on particle surface

- **nucleation**
- **Growth**
- **Coagulation**
- **Aggregation**
- **Transport losses**

Solutions of the coupled set

- $<\varepsilon_e>$ eq.
- Total energy eq.
- Species eq.
- Aerosol dynamic eq.

→ **T_g, composition, $<\varepsilon_e>$, particle-size distribution (or its moments)**

2C-model (1)

Based on the kinetic models developed for H_2/CH_4 discharges[1,2]:

- **38 species (with e^-)**
  - **Neutral and charged hydrogen compounds:**

    H_2, H, H(n=2), H(n=3), H^+, H_2^+ and H_3^+
  - **Hydrocarbon molecules up to 2 C-atoms and their corresponding ions:**

    C_xH_y (x = 1-2, y = 0-6), $^1CH_2$, C^+, CH_{3-5}^+, C_2^+, $C_2H_{1-6}^+$
  - **Argon based compounds:**

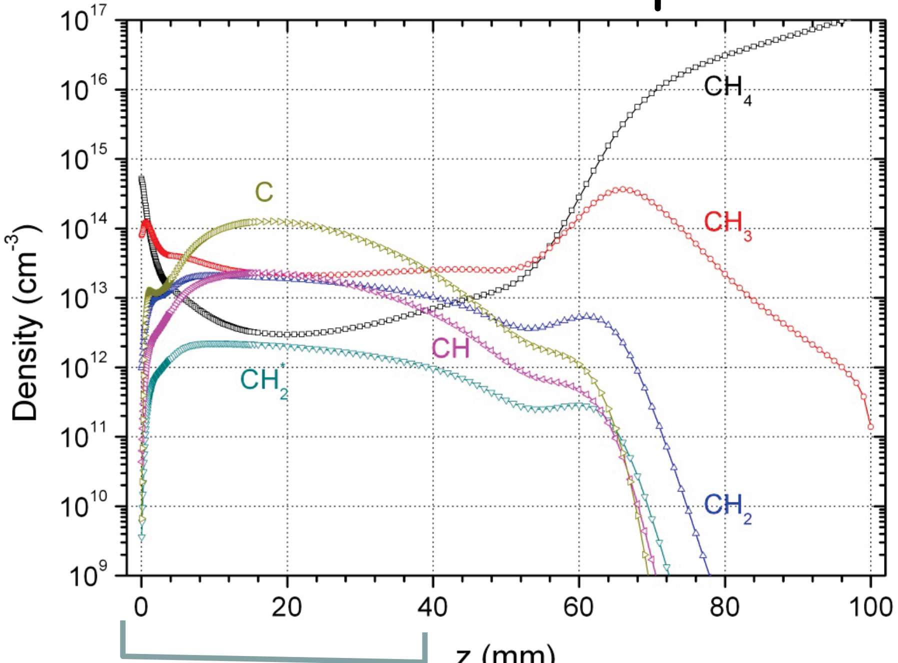
    Ar, Ar^*, Ar^+, ArH^+ and ArH^{+*}

- **147 chemical reaction mechanism describing**
  - **the chemistry of pure hydrogen discharge**
  - **the thermal hydrocracking of H_2/CH_4 mixture**
  - **the chemistry of hydrocarbon ions**
  - **the reactions due to the presence of argon**

(1) *Hassouni et al., Plasma Chem. Plasma. Process. (1998)*
(2) *Hassouni et al., Plasma Sources Sci. Technol. (1998)*

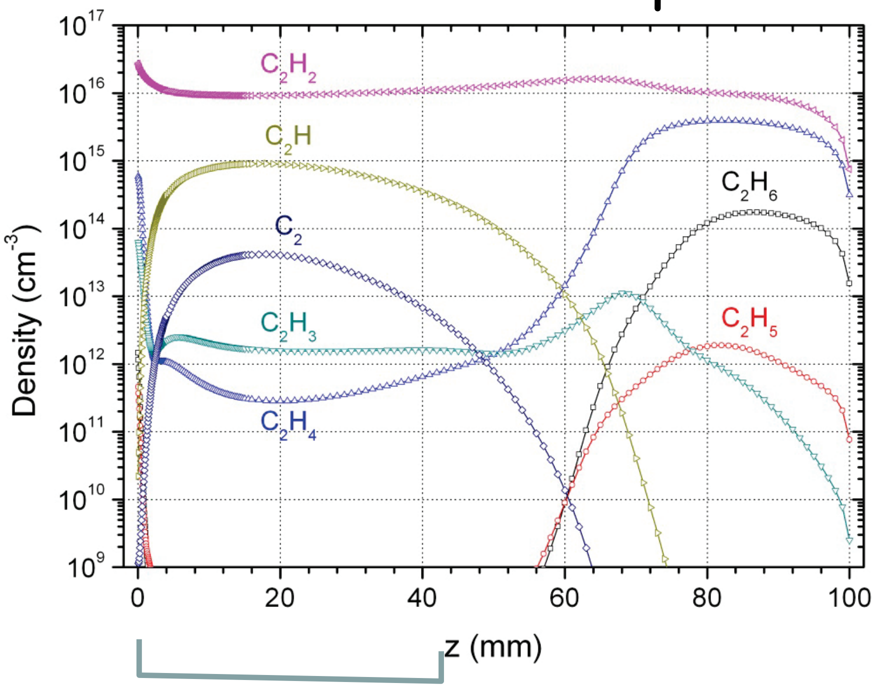
Species distribution in the plasma reactor

One-carbon species



Plasma region

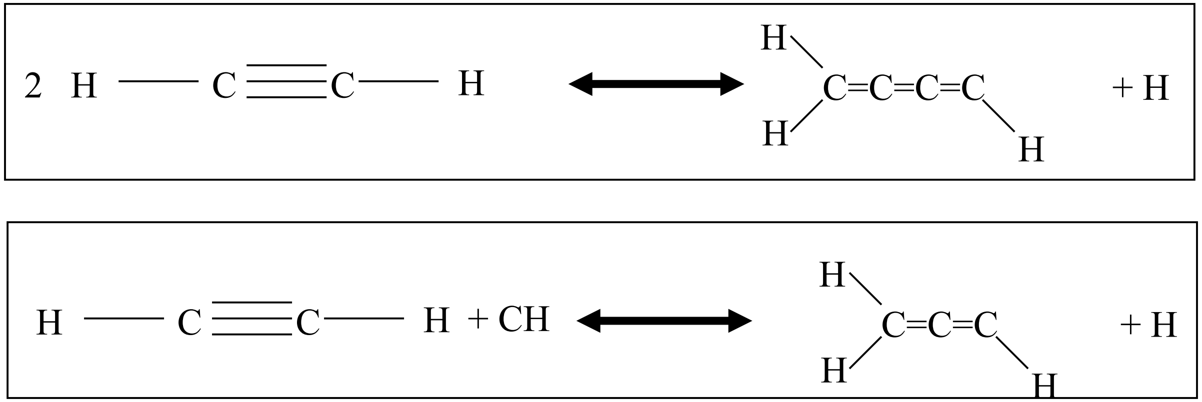
Two-carbon species



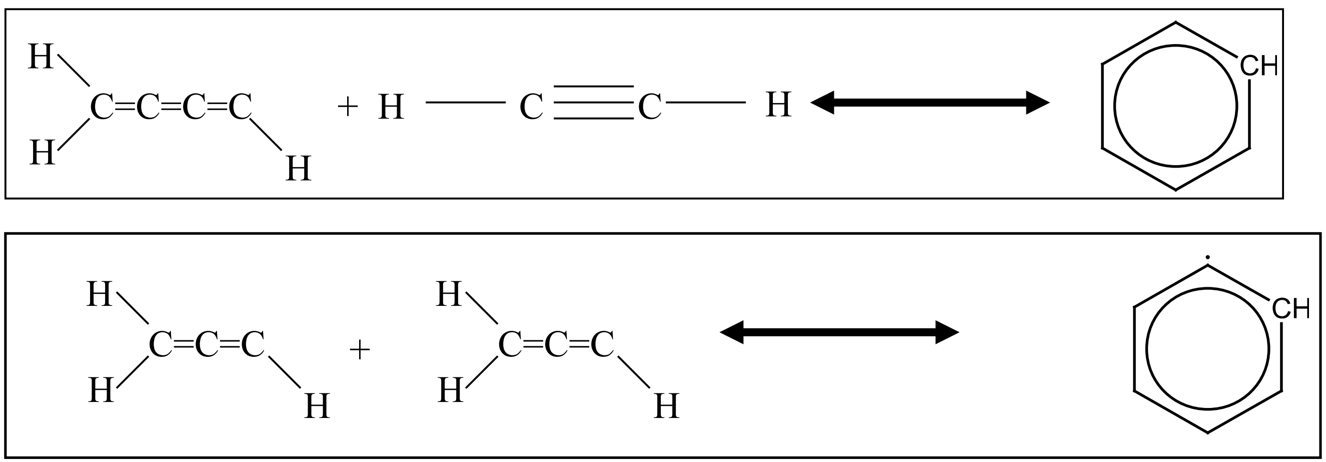
Plasma region

A4/A9 models (1)
Radicalar growth of PAH and nucleation mechanism

- **Mechanism of Poly-Aromatic Hydrocarbons (PAHs) formation[1]**



Linearization

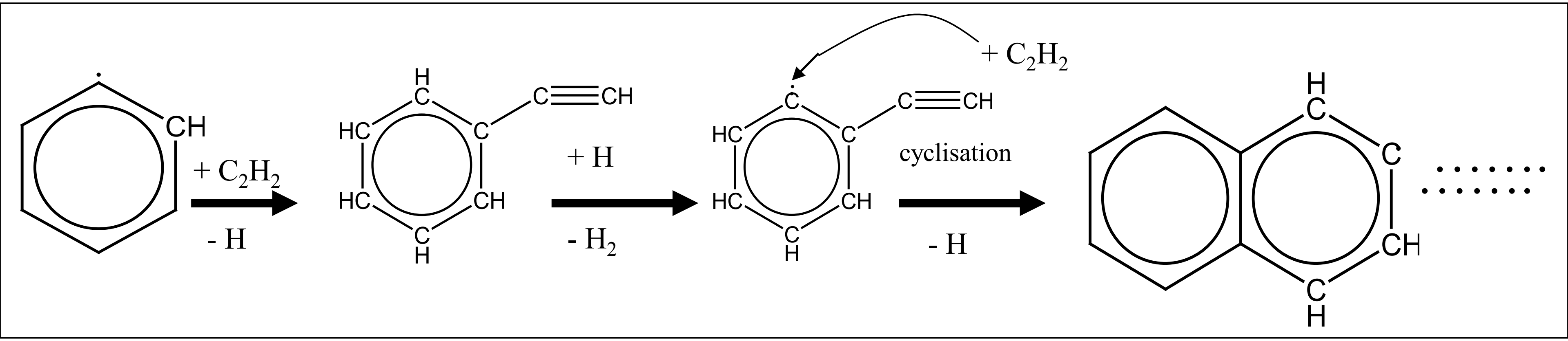


Cyclization

[1] *Wang et Frenklach., Comb. Flame (1997)*

Radicalar growth of PAH and nucleation mechanism

Hydrogen Abstraction Carbon Addition (HACA)



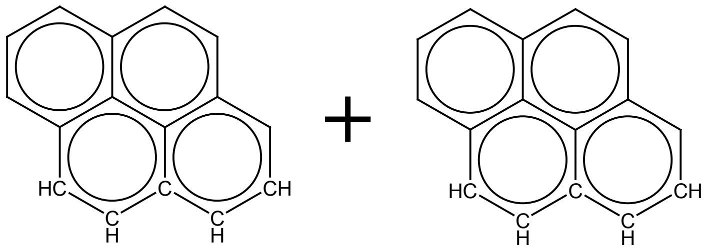
[(1)] *Wang et Frenklach., Comb. Flame (1997)*

A9/A4 models (3)
Nucleation mechanism

- **Nucleation of soot particles**

2 models were considered

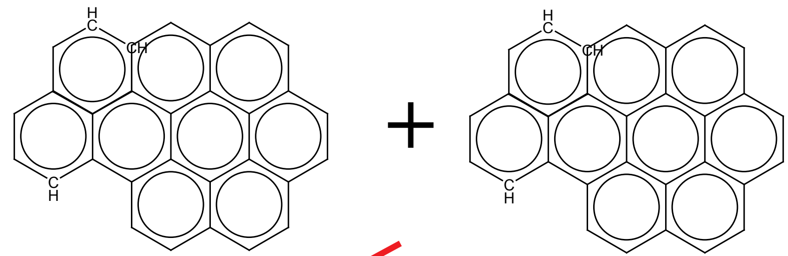
Condensation of 2 pyrene molecules



A4 + **A4**

A4-model

Condensation of 2 dibenzo-coronene molecules



A9 + **A9**

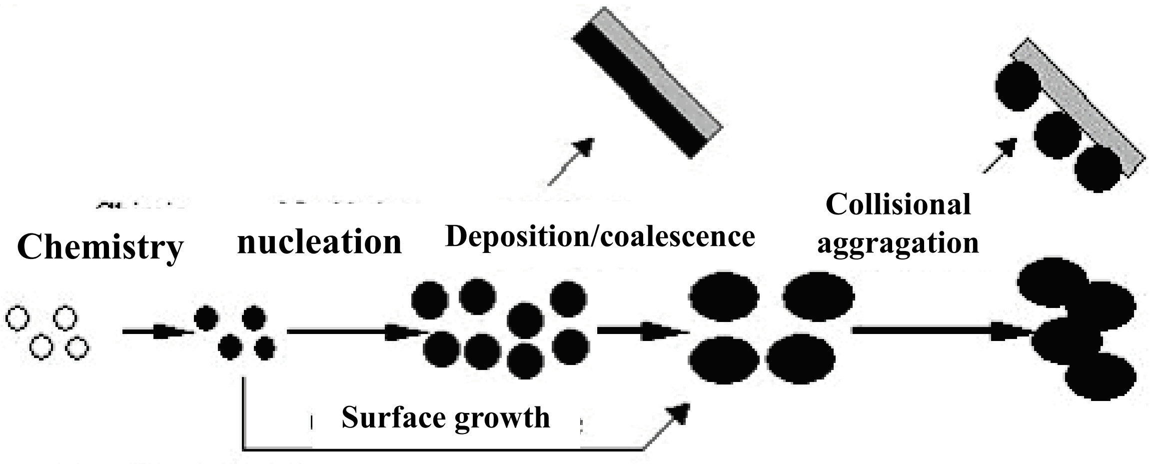
A9-model

Soot nucleus

Soot particle

See the work of Frenklach group

The aerosol dynamic governing equations



$$\frac{dN_i}{dt} = \tilde{R}_i + \tilde{G}_i + \tilde{W}_i + \tilde{T}_i$$

N_i : density of particles with a size i
R = nucleation rate (estimated from the chemical kinetics model)
G = <u>coagulation</u> rate (2 particles ➔ larger particles)
W = growth rate (surface growth - hetergenous chemistry)
T = particle losses due to transport : diffusion, thermophoresis, drag, etc..

Approach : Fractional moment
Frenklach et al., combustion and flame

Master equation for a particle size i (i=1-∞)

$$\frac{dN_i}{dt} = \widetilde{R}_i + \widetilde{G}_i + \widetilde{W}_i + \widetilde{T}_i$$

R = nucleation (from molecular growth model)
G = coagulation (increase the size and decrease density)
W = Sticking (increase the size and keep the density constant)
T = transport (mainly diffusion, thermophoresis in MW)

rth order moment :

$$M_r = \sum_{i=1}^{\infty} m_i^r . N_i$$

0 order moment ➔ total density
1st order moment ➔ total mass and volume fraction
1/3rd moment ➔ average diameter
2/3 rd moment ➔ avergae surface …

The moment approach

Try to derive governing equations for the moment of the distributions : $M_r = \sum_{i=1}^{\infty} m_i^r . N_i \quad \mu_r = \frac{M_r}{M_0}$

These contain the most relevant information : numerical density (0th order), mass density (1th order), mean diameter (1/3th order) , specific surface (2/3th order), optical properties, etc.

$$\frac{dN_i}{dt} = \tilde{R}_i + \tilde{G}_i + \tilde{W}_i + \tilde{T}_i \Longrightarrow \frac{dM_r}{dt} = \frac{\sum_i dN_i m_i^r}{dt} = \sum_i \left(\tilde{R}_i + \tilde{G}_i + \tilde{W}_i + \tilde{T}_i\right) m_i^r \Longrightarrow \frac{dM_p}{dt} = R_p + G_p + W_p + T_p$$

* The major difficulty ➔ express R_p, G_p, W_p, T_p. These often depend on fractional moments

Exp: $G_0 = K_c M_0^2 \left[\left(1 + \mu_{-1/3}\mu_{1/3}\right) + \gamma\left(\mu_{-1/3} + \mu_{1/3}\mu_{-2/3}\right)\right]$ (For collisionnal regime)

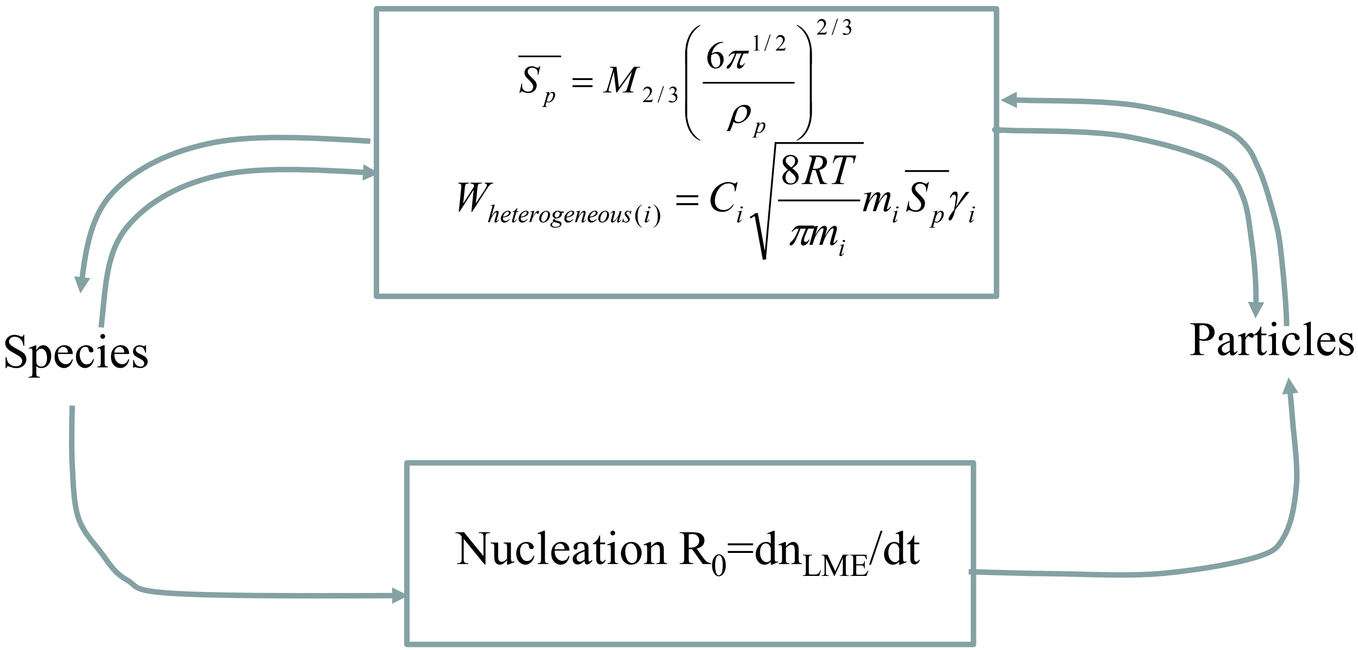
How can we get these fractional moments from integer ones ?
➔ Use Lagrange Interpolation:

$$\log \mu_{q/p} = L_{q/p}\left(\log \mu_0, \log \mu_1, \ldots, \log \mu_{r\max}\right)$$

Coupling between the soot and the plasma

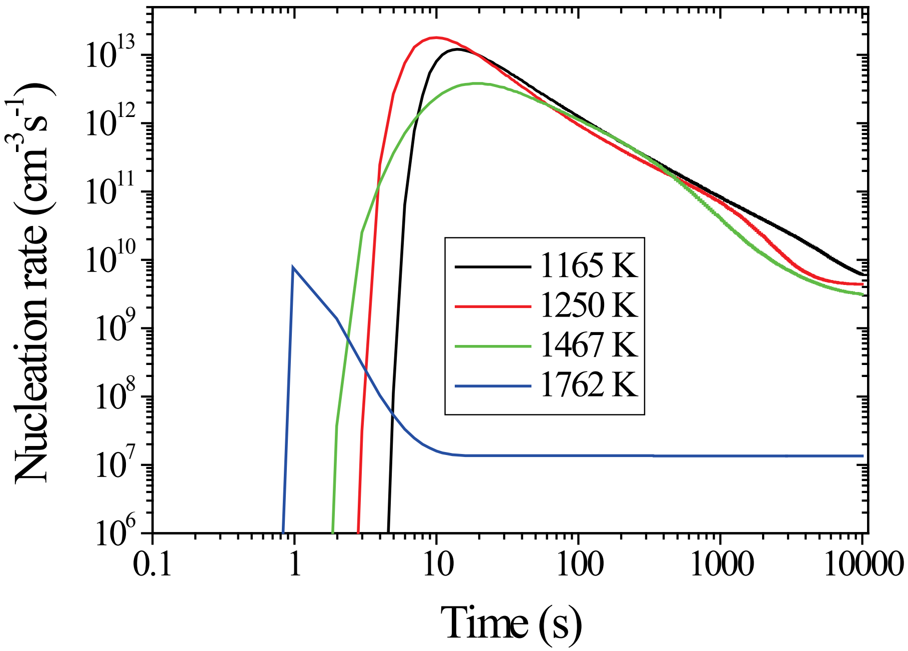
Soot is almost neutral in these conditions : fairly high temperature (> 1500 K)
➔strong themoelectronic emission for negatively charged species

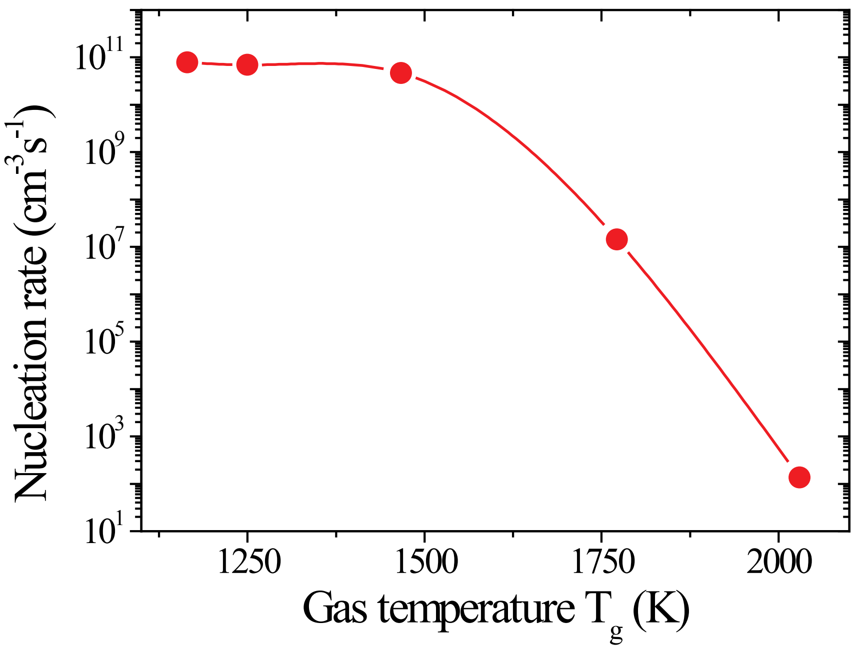
The coupling is thermochemical : energy balance (soot radiate) and species balance (species react on soot surface, molecular growth leads to soot)



Radical mechanisms
Models : A4-model (8)

✓ Nucleation of soot particles





↳ **Time-scale for soot formation ≈ 1-10 s**

↳ **High nucleation rate below 1500 K**

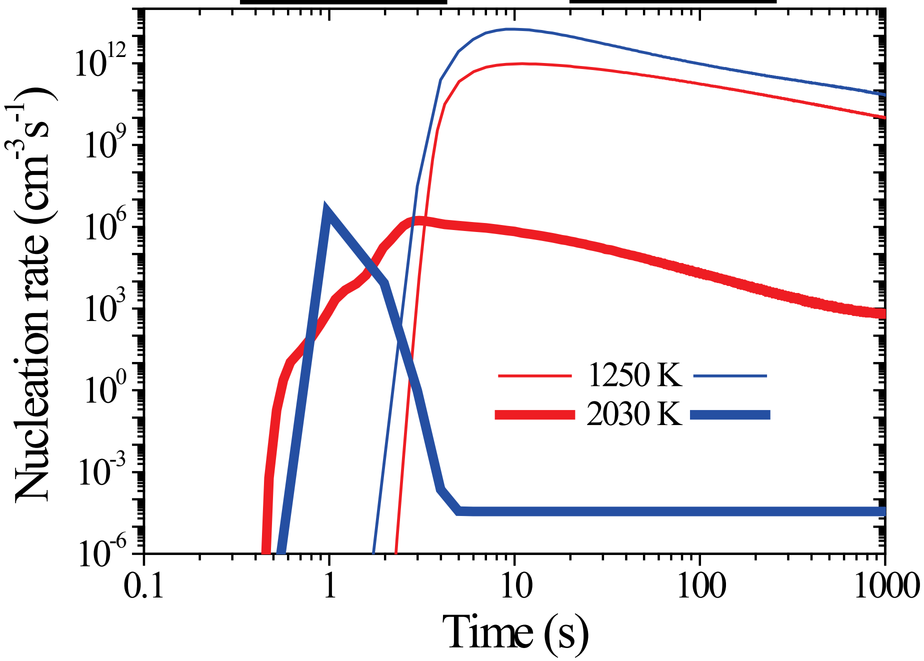
↳ **Strong decrease for higher T_g**

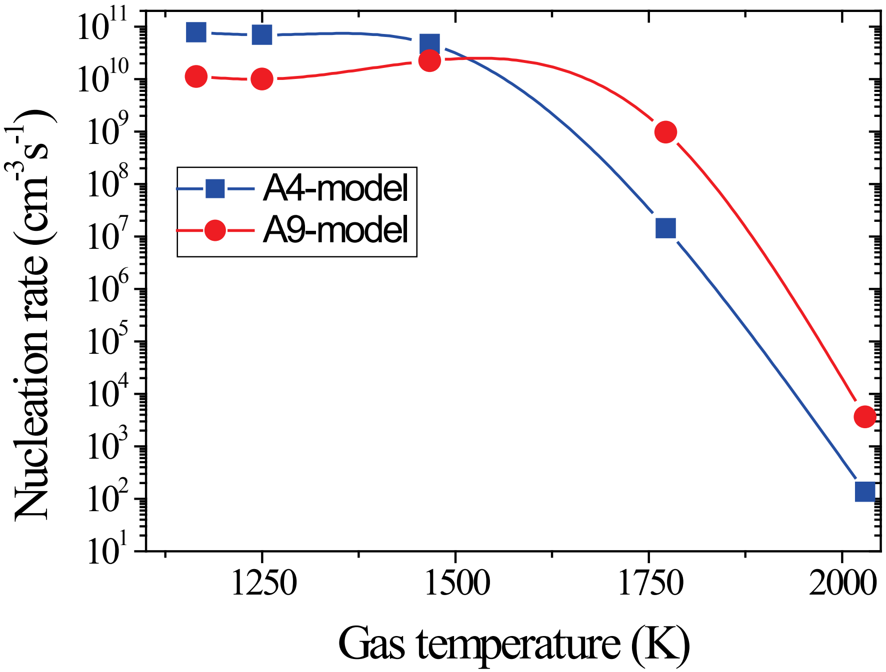
K. Hassouni, F. Mohasseb, F. Bénédic, G. Lombardi and A. Gicquel, PAC, Vol. 78, Issue 6, p. 1127

Radical mechanisms models: A9-model (13)

✓ Nucleation of soot particles

A4-model   A9-model





➯ Except at high temperature the trends are essentially the same

➯ A9 model yields a somewhat wider temperature domain for nucleation

K. Hassouni, F. Mohasseb, F. Bénédic, G. Lombardi and A. Gicquel, PAC, Vol. 78, Issue 6, p. 1127

Self consistent modeling of chemistry and aerosol dynamic

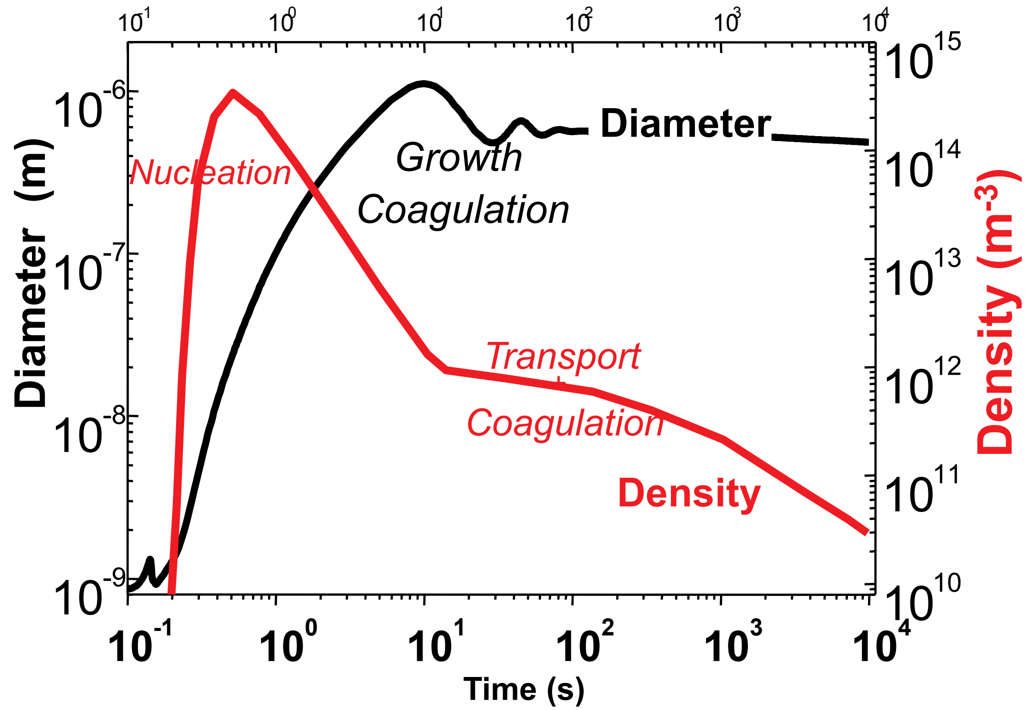
Feed-back of soot particles on the plasma chemistry takes place through heterogeneous condenstation reactions which depends on the 2/3 order moment (soot surface per unit volume).

$CH_4/H_2/Ar$ (1/2/97 %),

200 mbar

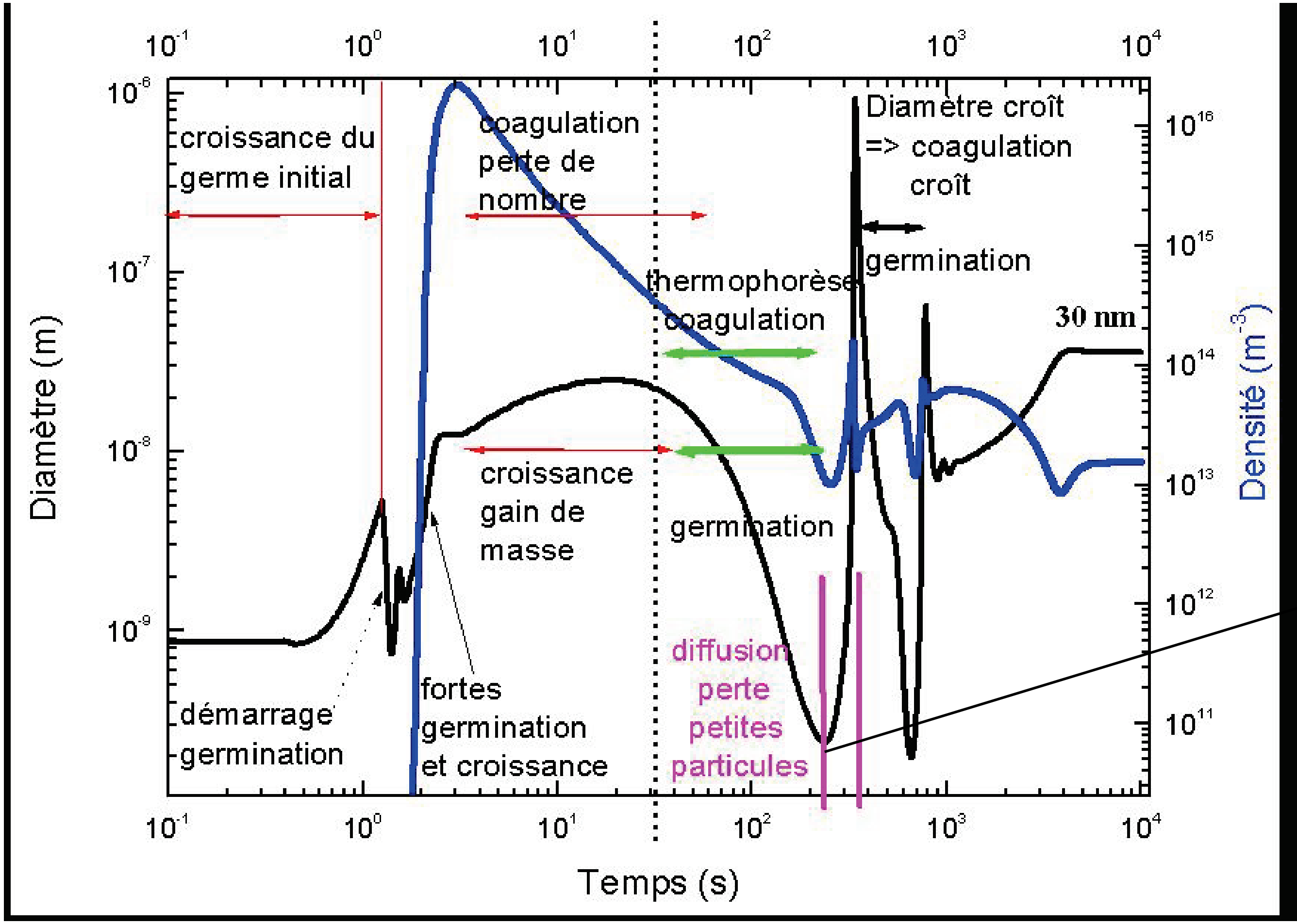
T_g = 1450 °C

condensation coefficient on soot = 10^{-3}



K. Hassouni, F. Mohasseb, F. Bénédic, G. Lombardi and A. Gicquel Vol. 78, Issue 6, p. 1127

Self consistent modeling of chemistry and aerosol dynamic

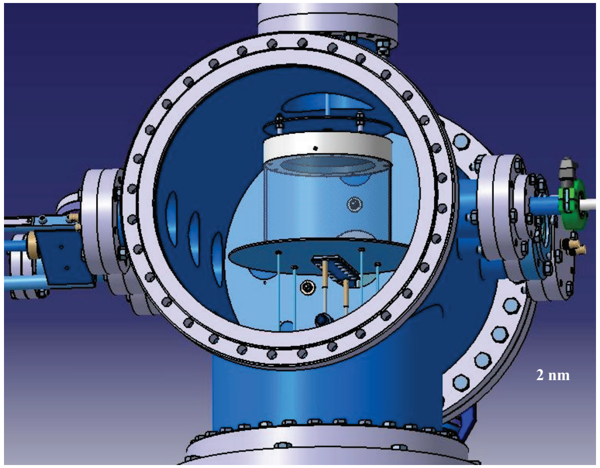


Very high particle fluxes on the substrate

Significant nucleation (10^7 cm^{-3}) in the cold region of the plasma
Up to H/C = 16 !!!! ➔ implication on film growth ????

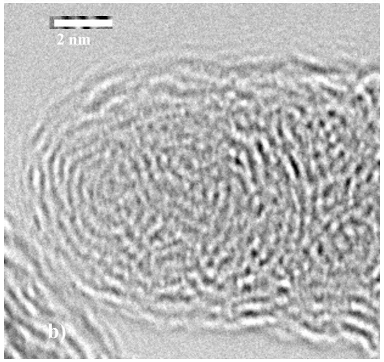
Argon DC Discharge - graphite Cathode

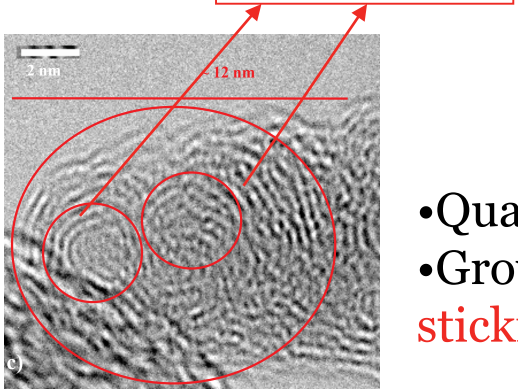
C. Arnas PIIM



- **Conditions**
  - A 14 cm gap
  - voltage V_d ~ - 600 V
  - Current = 80 mA
  - Pressure = 0.6 mbar
  - Discharge Duration 5 mn
  - Volume ~1 L

TEM Images of a 12 nm particle produced after a 60 s plasma discharge





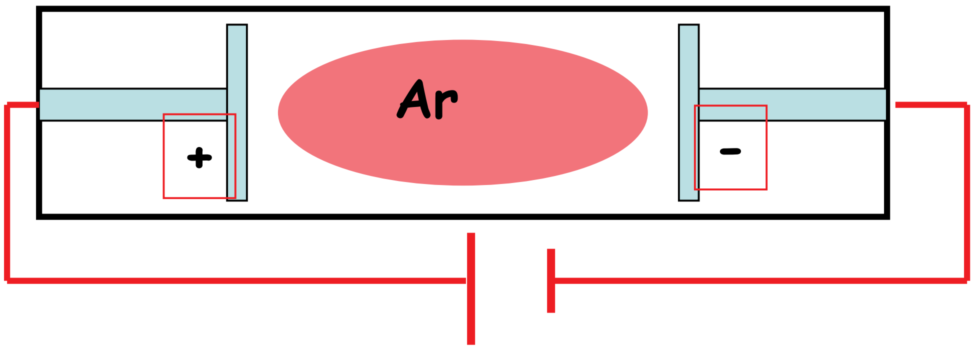
2 nucleides of 2-3 nm

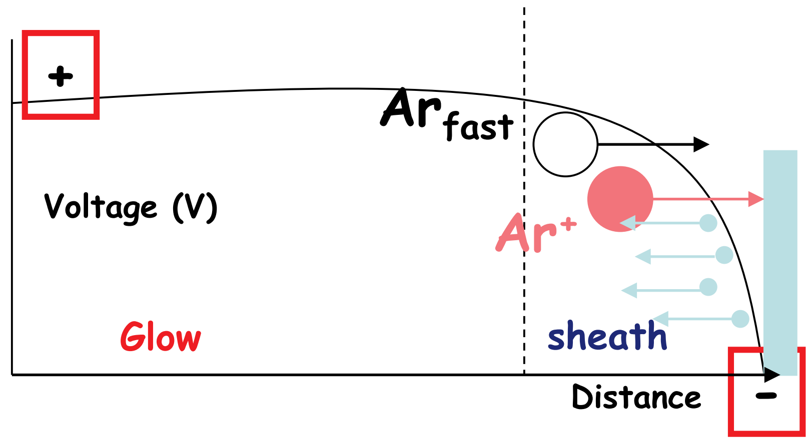
- Quasi spherical Particles
- Growth by coagulation and molecular sticking

T_{growth} ~ 100.$T_{diffusion}$ electrostatic trapping of charged species

Model of nucleation, growth and transport of dust in Ar DC discharges

PIIM device





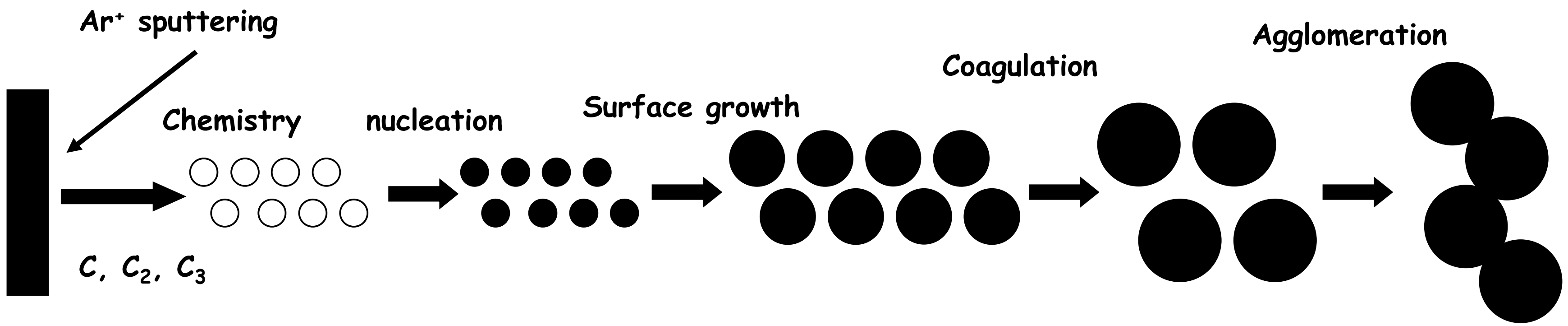
Voltage: - 600 V
Inter-electrode distance: 14 cm
Electrode diameter: 5 cm
Current: 8×10^{-2} A

$Ar_{slow} + Ar^+ \rightarrow Ar^+ + Ar_{fast}$

Dusts are produced by the sputtering of the graphite cathode:

- Argon ions accelerated in the sheath
- Fast neutrals resulting from charge transfer

Dust formation : speculated mechanism



- Estimation of discharge main characteristics: *flux and ion energy distribution or ion average energy on the cathode*
- Extraction of C_1, C_2 et C_3
- Formation of $C_{n=1,nl}$ clusters, where n_l is arbitrary chosen (n_l=30 or 60)
- Nucleation of carbon dusts from clusters: *Assumption of 'Largest Molecular Edifice'*
- Growth, transport and wall losses of dusts
- Dust charging
- Size distribution of dusts

Molecular growth modelling of carbon clusters and dusts

Molecular growth

$$\frac{\partial n_{i,z}}{\partial t} = -\vec{\nabla}\left(-D_i\vec{\nabla}n_i + \mu_{i,z} n z \vec{E}\right) + W_i$$

Diffusion — Mobility — Production rate of the C_i cluster

clusters

Nucleation

$$\frac{\partial n_{n_l,z}}{\partial t} = W_{n_l}(n_l) = N$$

$n_{i,z}$ = density of the cluster C_i of charge z

Dust Transport

$$\frac{\partial n}{\partial t} = -\vec{\nabla}\left(-D.\vec{\nabla}n + \mu.n.\overline{z}.\vec{E}\right) + N - C$$

$$\frac{\partial \rho}{\partial t} = -\vec{\nabla}\left(\left(-D.\vec{\nabla}n + \mu.n.\overline{z}.\vec{E}\right)\overline{M}\right) + N + A$$

N = nucleation
C = coagulation
A = condensation

$\Rightarrow$ Determination of the average diameter d_p

Carbon cluster growth reactions**

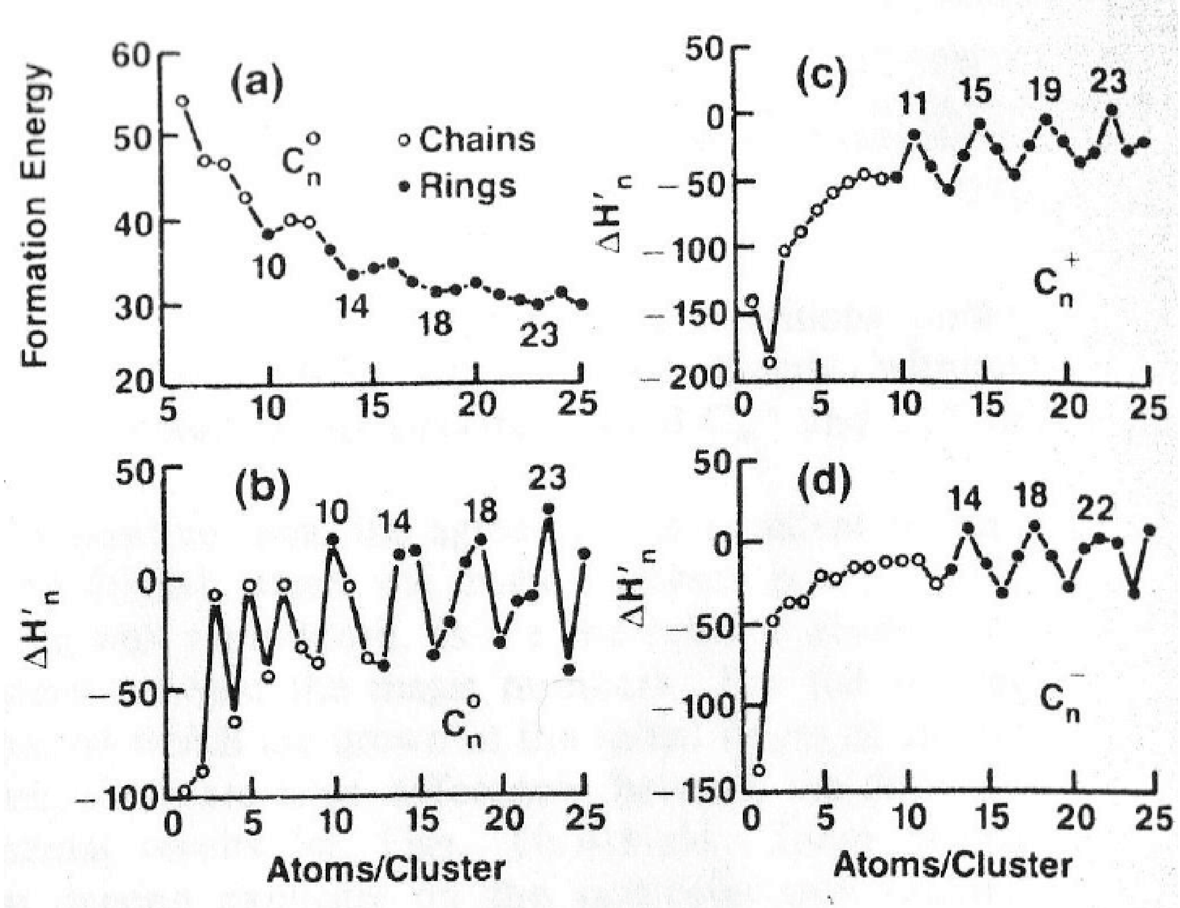
Bernholc & Schweigert models (classical models) (**):

• Growth = one single process ($C_n + C_x \rightarrow C_{n+x}$), but take into account the stability of the C_n clusters

• First version of the model took into account neutral clusters

- Molecular growth of clusters
  - Rates computed according to formation enthalpies
  - Clusters have configurational isomers (chains, rings, multi-cycles) distinguished by cyclization entropy (20 kcal/mol/cycle)
  - Extrapolation for unknown values according to cluster periodicities

Formation enthalpies & nombres magiques



$$k_{ij} = \alpha R_{ij}^3 e^{-\gamma \frac{(\Delta G'_i + \Delta G'_j)}{kT}}$$

$$\Delta G'_i = n(\Delta G_{i+1} - \Delta G_i) = n(\Delta H_{i+1} - \Delta H_i) - nT(\Delta S_{i+1} - \Delta S_i)$$

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Molecular growth modelling of neutral carbon clusters and dusts

➔Low pressure discharge : p=10-100 Pa

➔Diffusion characteristic time =1-10 ms very short as compared to the growth chemistry ➔ no possibility for growth of neutral

➔ Need for species with higher residence time :

Negative clusters

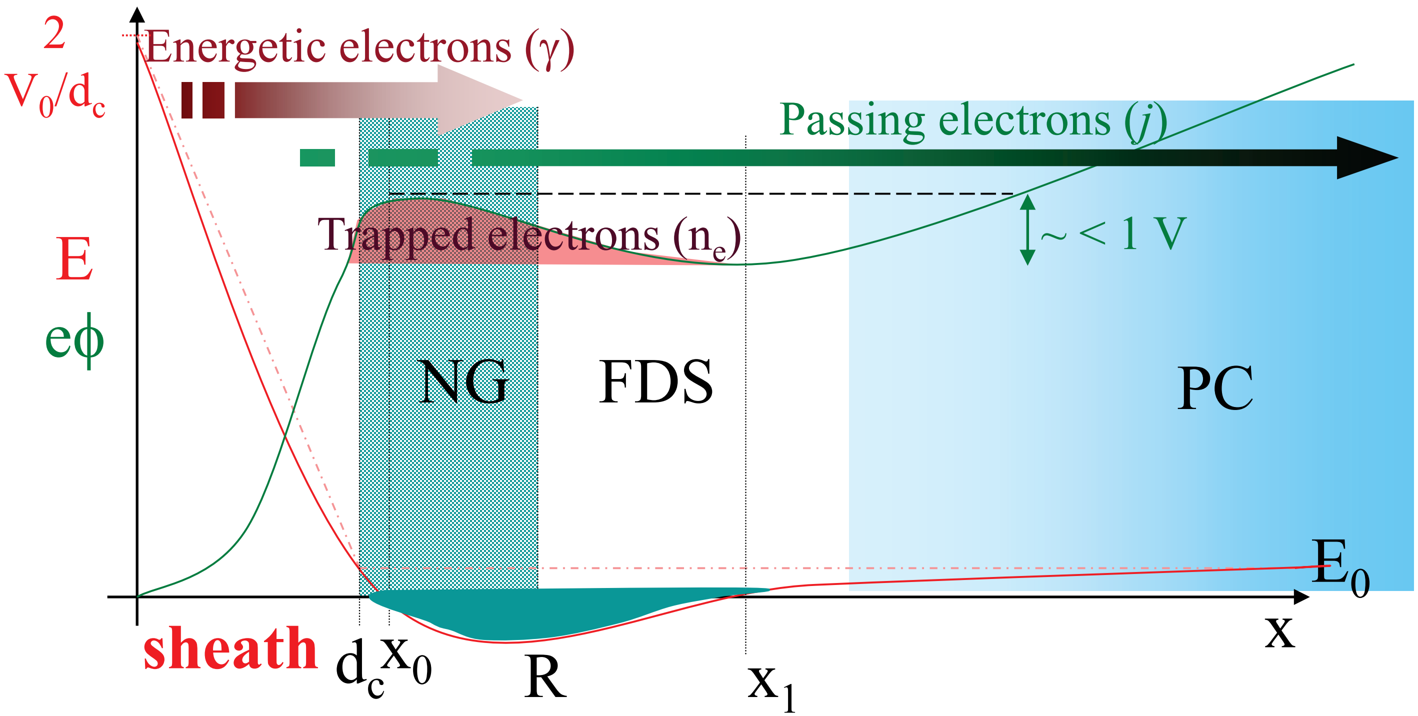
And

Trapping electric field configuration

➔ Back to some basic DC discharge physics

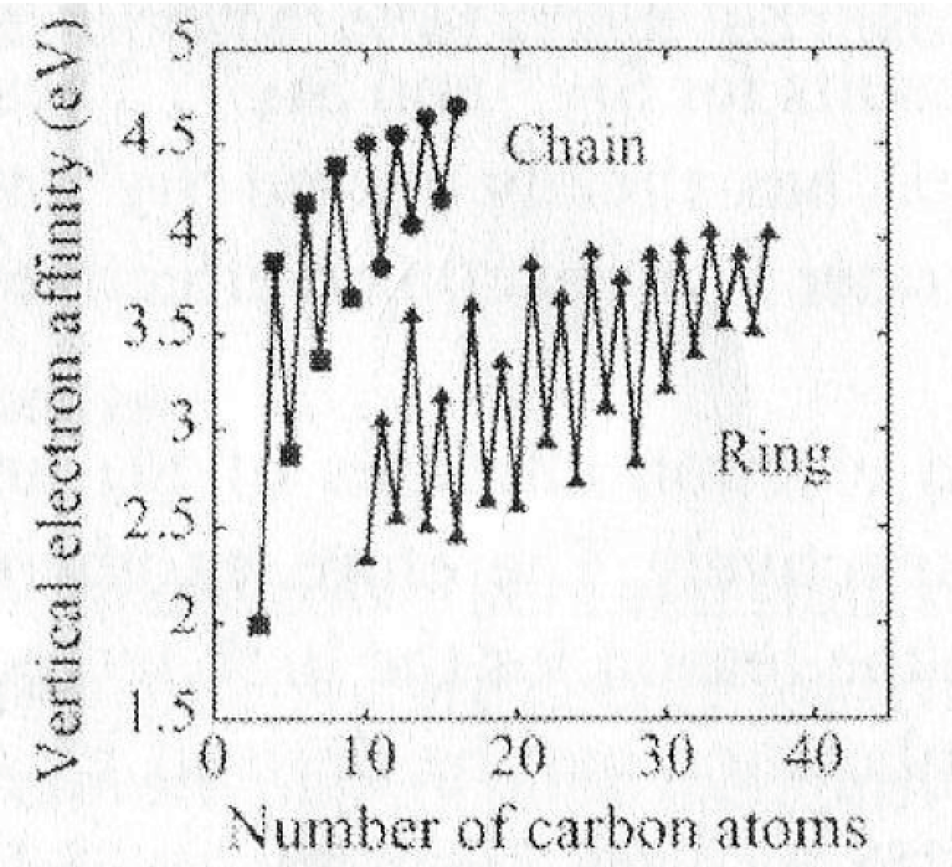
Electric field reversal and molecular growth of negative clusters

- Charging of dust particles **only effective if electric field is confining** !
- Where is the confining electric field ? ➔ Kolobov & Tsendin, Phys. Rev. A **46** 7837, Boeuf & PitchFord, J. Phys. D, (1994)
  - **Self-consistent electric field reversal: confinement**
  - Three electron populations: energetic, passing, trapped



NG: Negative glow / FDS: Faraday Dark Space / PC: Positive Column

Negative carbon cluster growth reactions



From Y. Achiba et al., J. Elect. Spect. Related Phen. 142, 231 (2005)

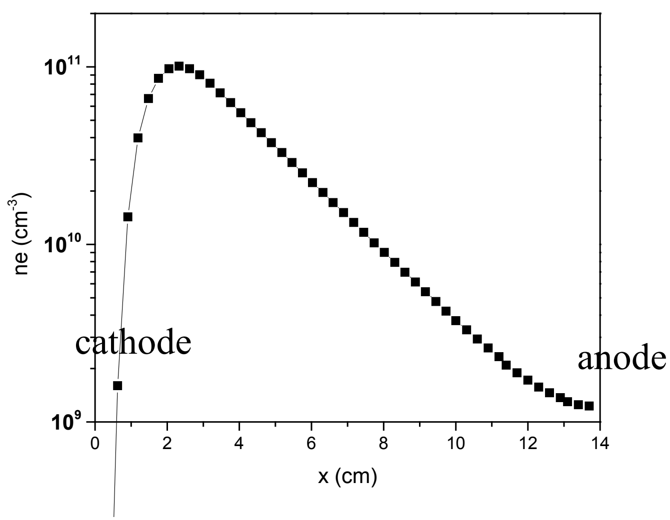
- **Attachment** $C_n + e^- \rightarrow C_n^-$
  - Rates computed according to electronic affinities
- **Charge exchange** $C_n^- + C_x \rightarrow C_n + C_x^-$
  - Electronic affinities

$$T_{i^- j} = \alpha R_{ij}^3 e^{-\xi^- \frac{\Delta A_i + \Delta H_j}{kT}}$$

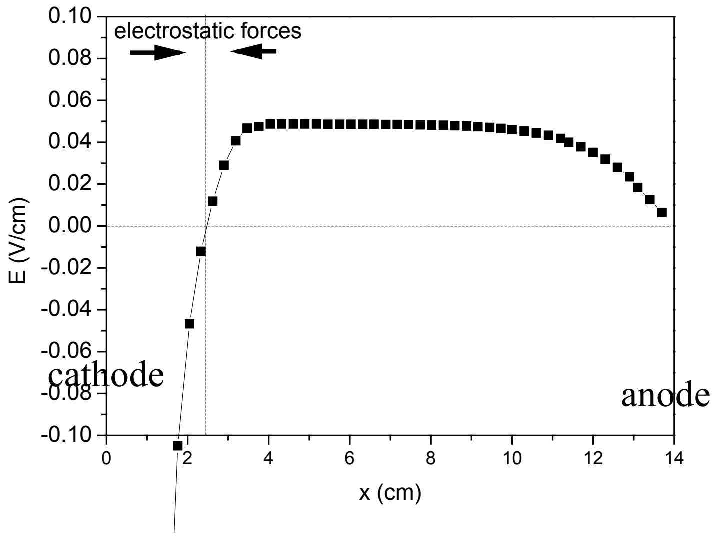
- **Dust agglomeration** (sticking)
- **Detachment** $C_n^- + e^- \rightarrow C_n + 2e^-$

Plasma Characteristic

Electron Density



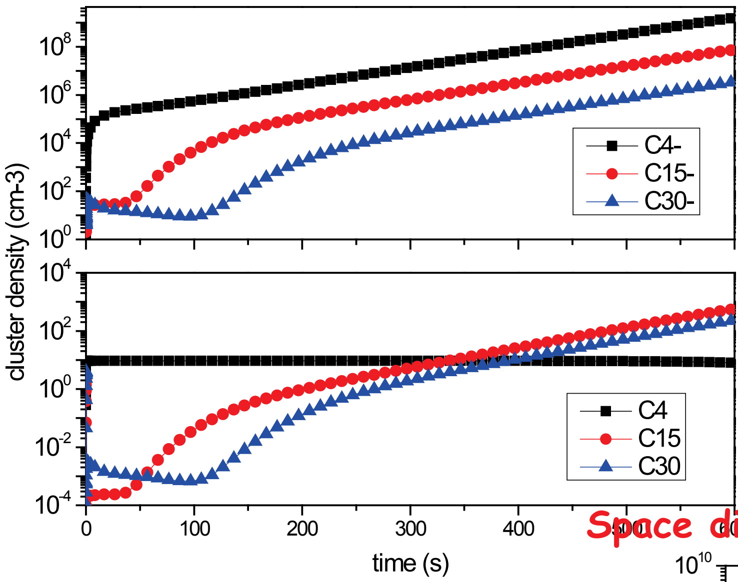
Electric Field



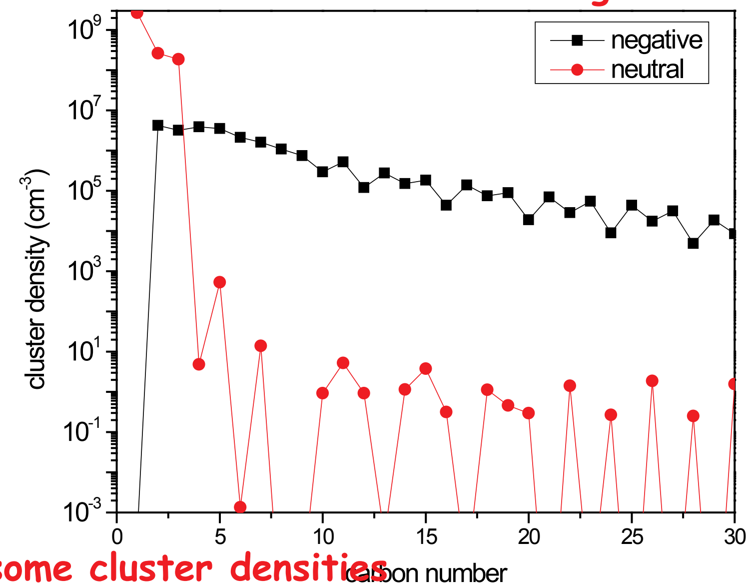
- Electron density in good agreement with experimental results
- High density for 1-4 cm from the cathode – strong decrease in FDS
- Reversal at 2 cm from the cathode.
- Electrostatic trapping of negative species at this position

Cluster population : time, space and size distributions

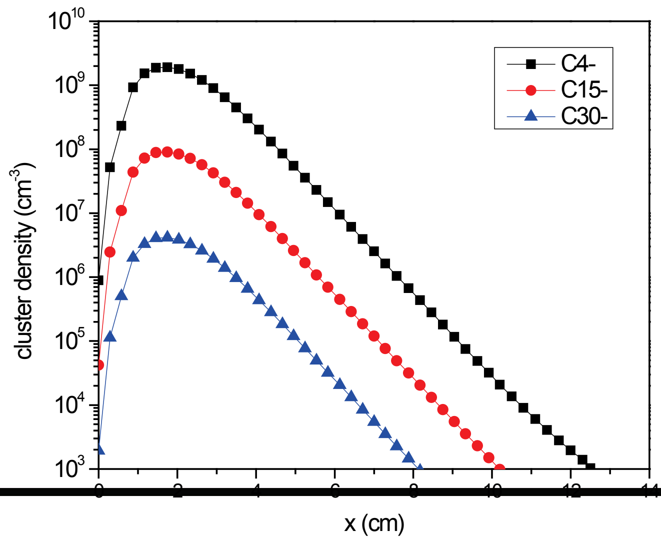
Time-evolution of some cluster densities



Size distributions of neutral and negative cluster

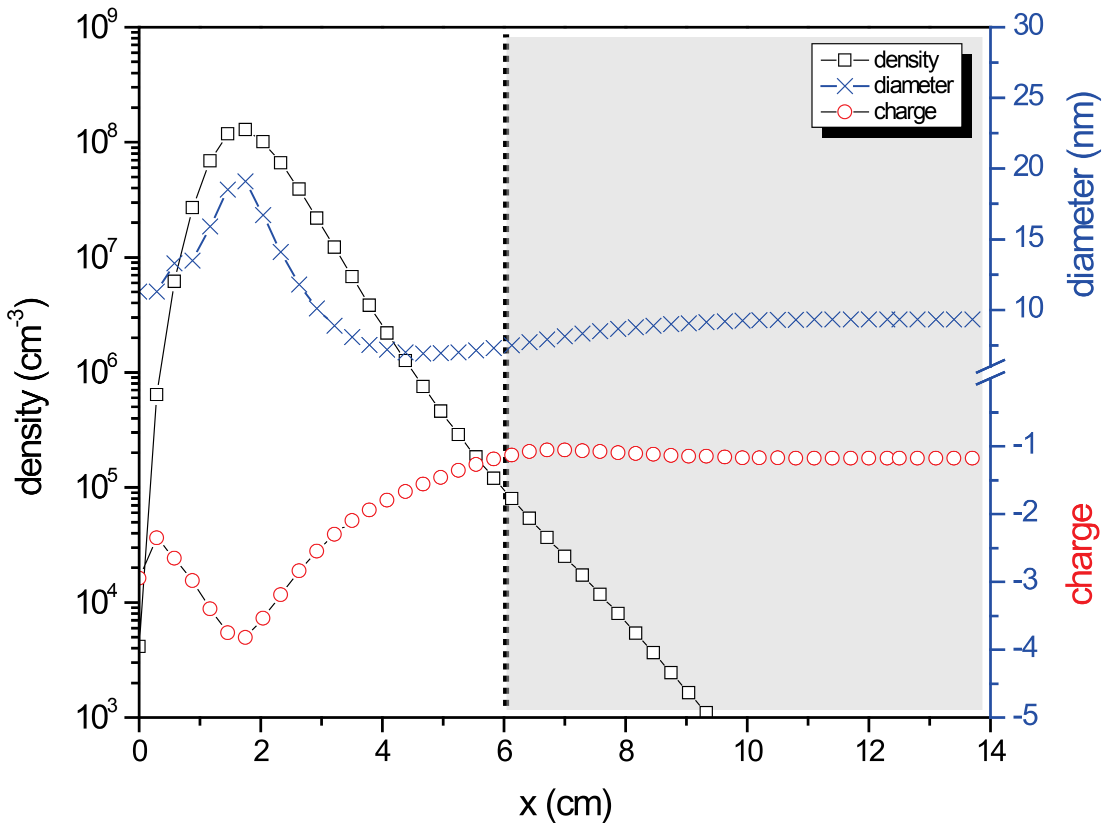


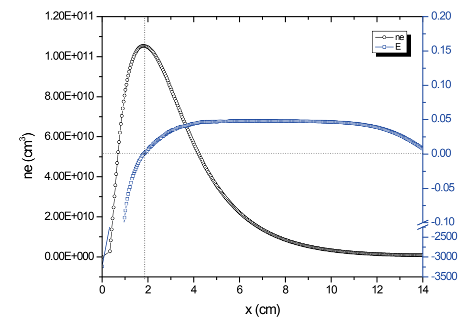
Space distribution of some cluster densities



Space distributions of dust density, average size and average charge

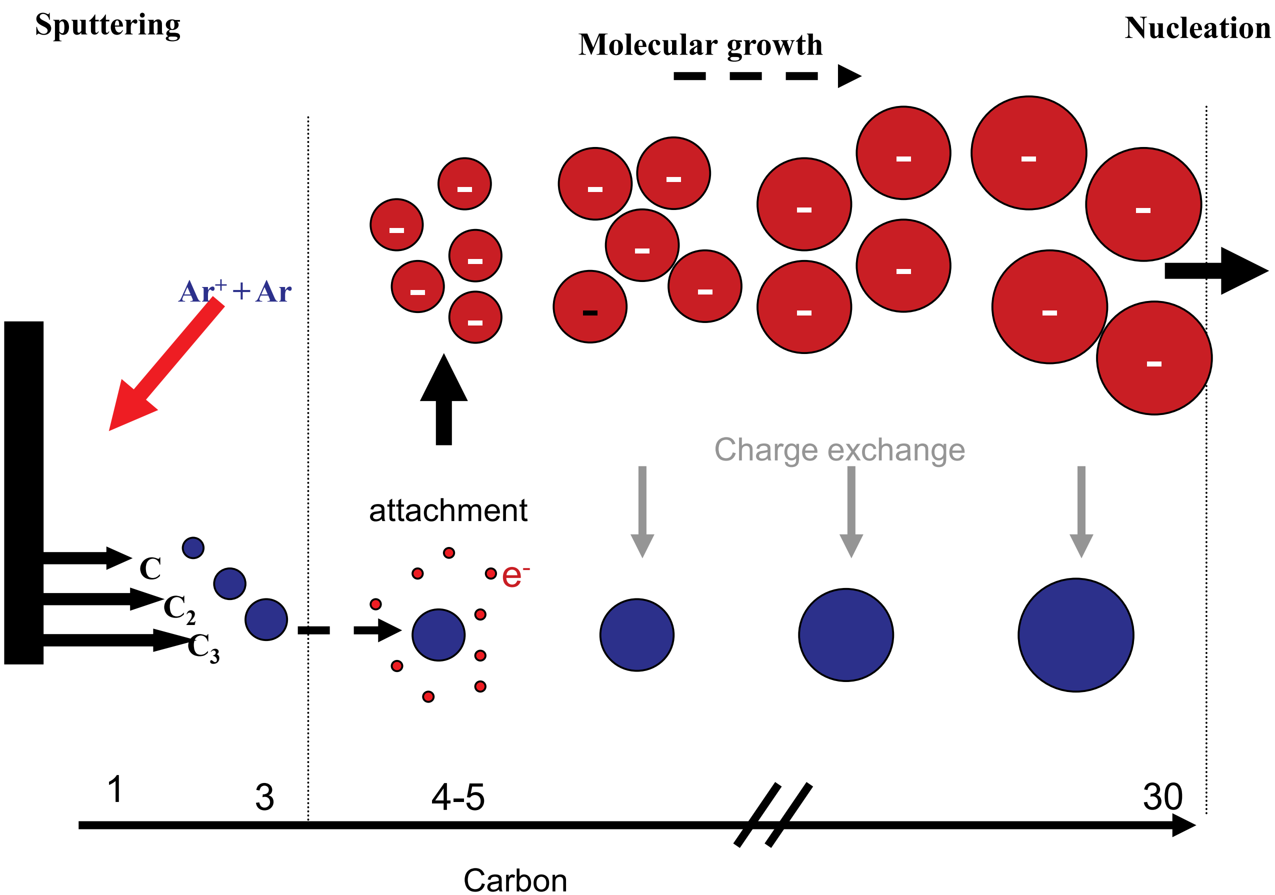
dust density, average charge, and average size after 600 s discharge





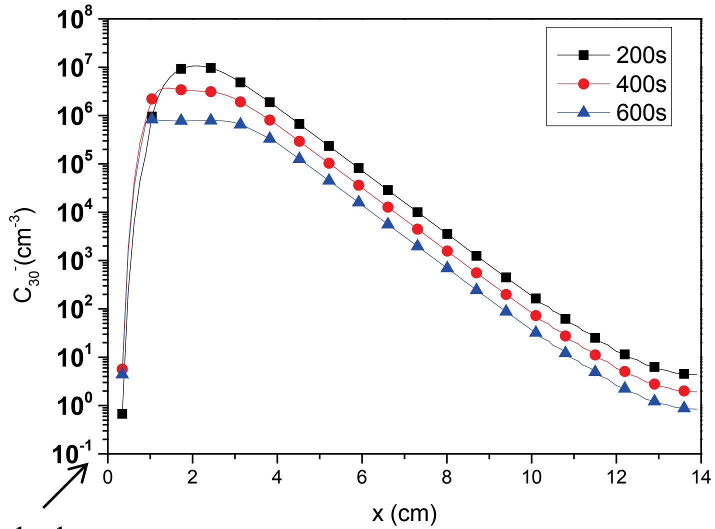
- Particle cloud also localized at the field reversal position
- Particle diameter is around 20 nm in the cloud
- Maximum average charge : -4 ➔ close to OML equilibrium

Infered cluster growth mechanism



Nucleation

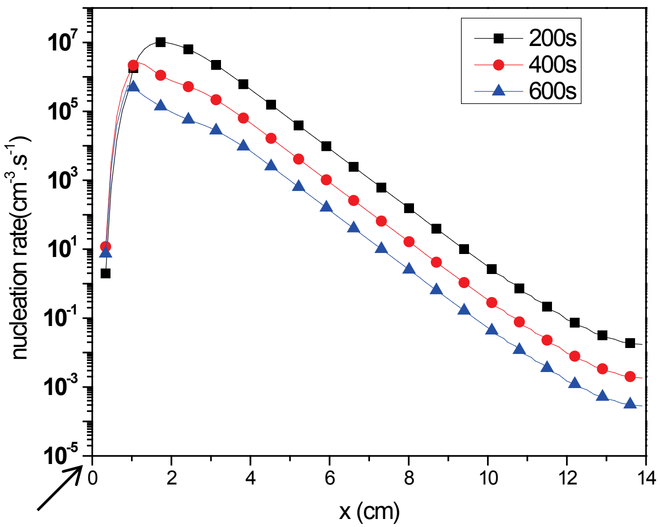
Largest negative cluster density



Cathode
Sputtering

Anode

Nucleation rate

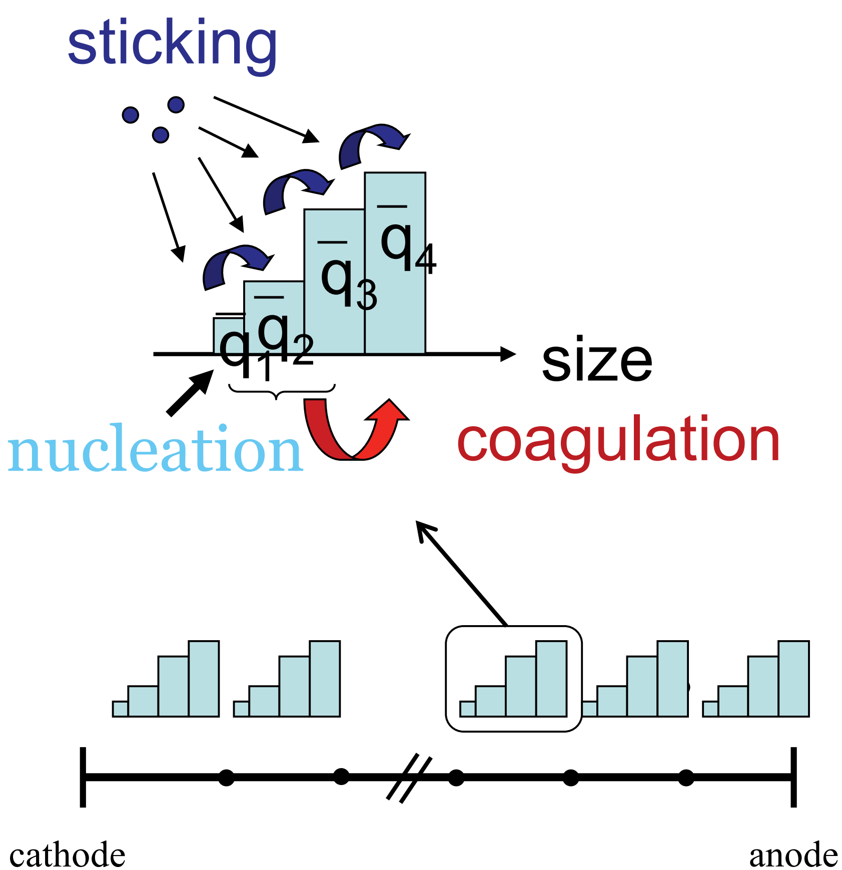


Cathode
Sputtering

Anode

- Nucleation due to growth of C_{30}^-
- Particle nucleation remains during all discharge duration
- Decrease of nucleation rate due to consumption of clusters sticking on existent particles

Aerosol Model : Particle Volume



- Nucleation
- transport
- Growth by sticking
- Growth by coagulation

Volume balance

$$\frac{\partial Q_l(t)}{\partial t} = \left.\frac{\partial Q_l(t)}{\partial t}\right|_{coag} + \left.\frac{\partial Q_l(t)}{\partial t}\right|_{sticking} + S_{nucleation} - \nabla F_l$$

Gelbard *J. of Colloid and Int Sci* **76**, 1980
Warren *Aerosol Sci and Tech*, 4 1985

Aerosol Model : Particle Charge

$$k_{coag}(q\ ,q') = k_{coag}(0,0).w(q,q')$$

->need for charge distribution for each section in each point

Solution adopted

Charge balance : **averaged** particle charge for each section

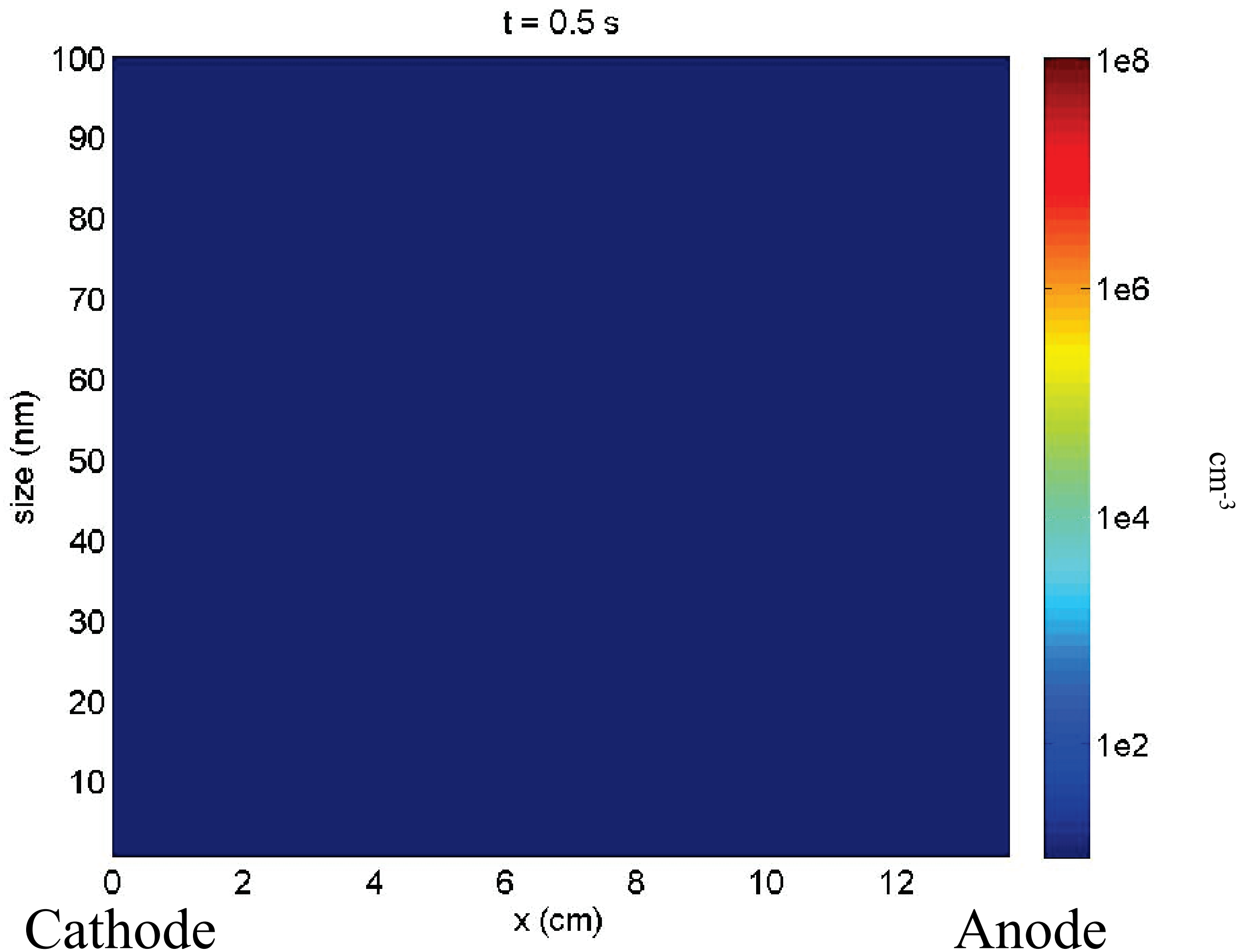
$$\frac{\partial q_l}{\partial t} = -\frac{\vec{\nabla}(q_l \vec{F}_l)}{Q_l} + \left(I_{e-slow} + I_{e-fast} + I_i\right).S_l + S^q{}_{nuc} + S^q{}_{coag} + S^q{}_{sticking}$$

Fluctuation ⇔ Poisson's charge distribution : $\Psi(q, \bar{\boldsymbol{q}})$

$$\psi(q,\bar{q}) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(q-\bar{q})^2}{2\sigma^2}\right] \qquad \sigma = f\left(\frac{T_e}{T}, \bar{q}, d_p\right)$$

T. Matsoukas, M. Russell, 1995 *Journal of Applied Physics* **77**, p. 4285

Aerosol Dynamics Results



Cathode

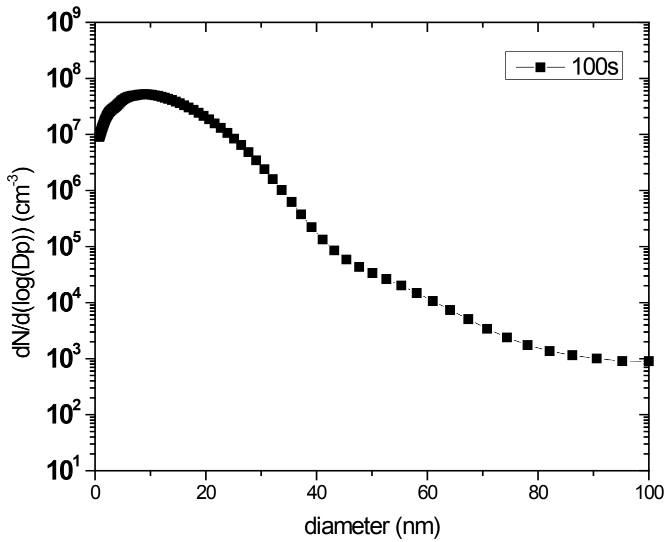
Anode

Aerosol Dynamics Results
Particle growth mechanism at 100 s

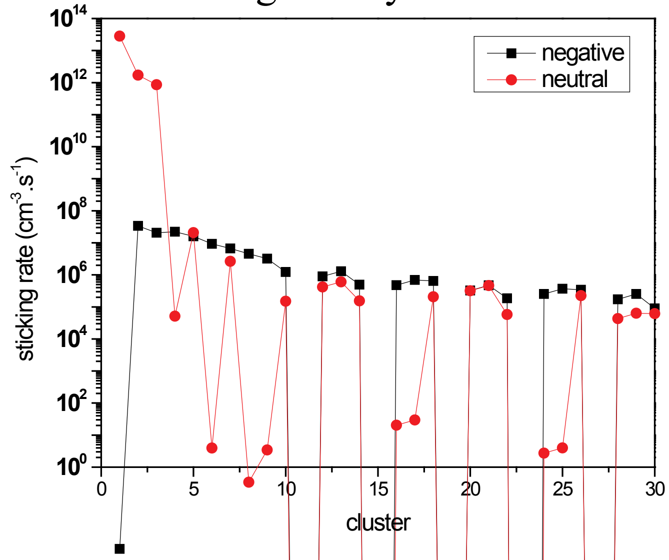
x= 2 cm

Size distribution

Particle Density



Sticking rate by cluster size



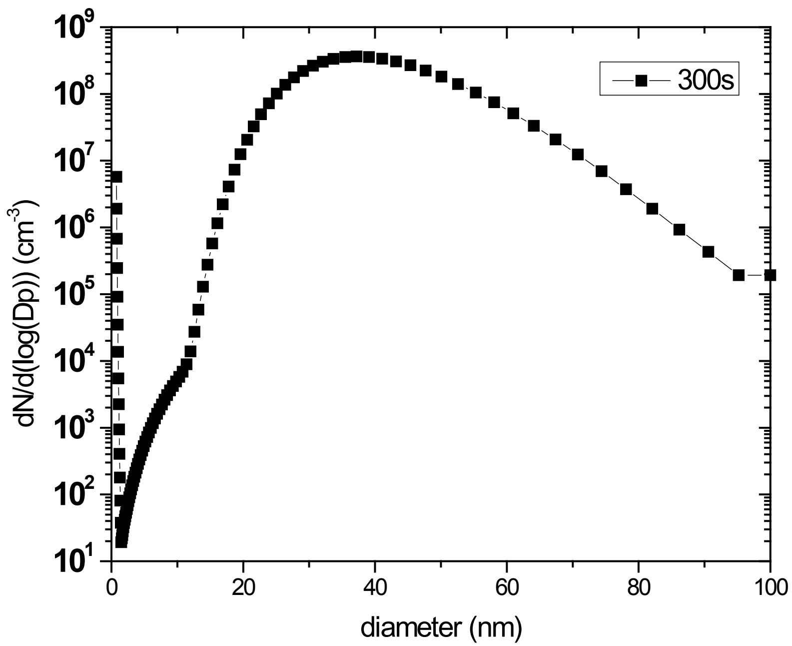
Growth due mainly to molecular sticking

- C, C_2, C_3 from sputtering

Aerosol Dynamics Results
size distribution for long duration

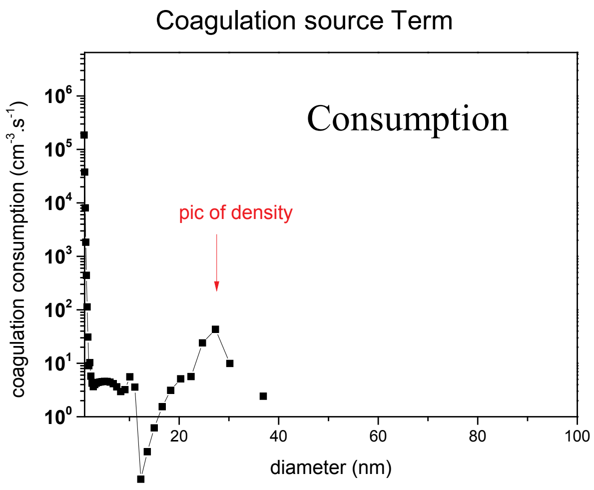
x= 2 cm

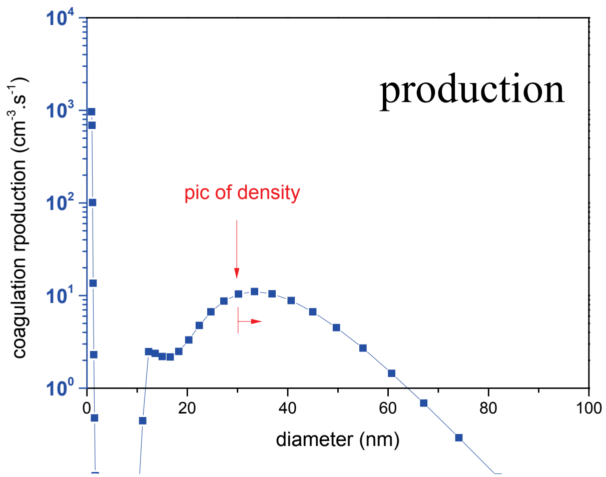
Particle Density

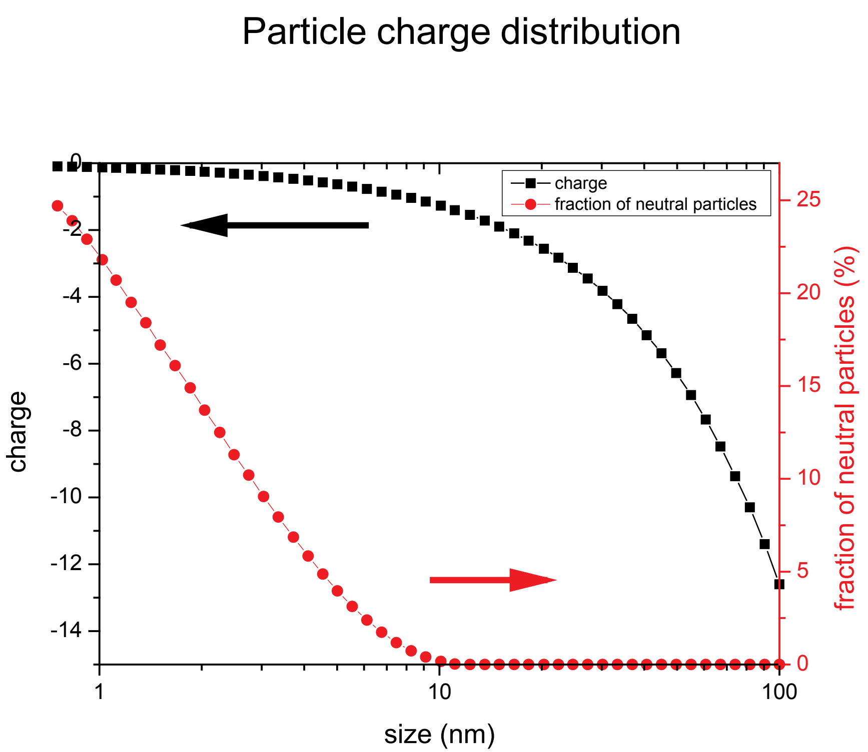


Two-population distribution with a strong depletion between 2 and 10 nm

Aerosol Dynamics Results
Coagulation kinetics for long discharge duration







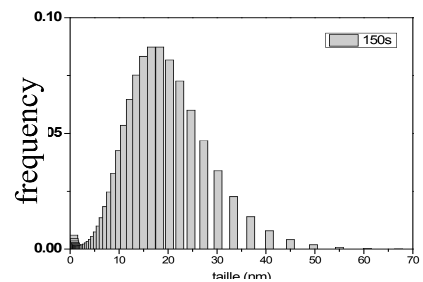
Coagulation = 1 neutral particle of 1-2 nm + 1 negative particle

Comparison with experimental Results

Density : Particle density 10^8 cm^{-3} close to measurements

Size distribution :

Model **120 s** x= 2cm



Diameter (nm)
d=18 nm

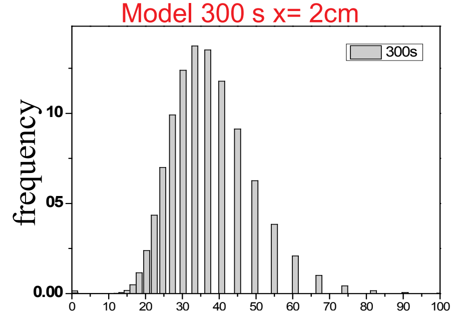
Experiment **120 s**

frequency

Diameter (nm)
d=35 nm

Good agreement at 300 s

Model 300 s x= 2cm



Diameter (nm)
d=34 nm

experiment 120 s

frequency

Diameter (nm)
d=35 nm

Delay may be due to time variation of the sputtering yield
$Y=10^{-2}$
$\Gamma=6.10^{15}$ $cm^{-2}.s^{-1}$

Conclusion

- Plasma poudreux ou dusty plasmas : thématique de +50 ans mais il **reste beaucoup à faire**
  - Physique des plasmas : instabilités, transitions de phases, distributions de charge et de taille
  - Physique atomique et moléculaire : croissance molécuaire
  - Physique de la matière condensée (agrégats) : transition de phase (agrégats), nucléation,
  - Matériaux : structure, propriétés, manipulations, etc….