Dust particle formation and field reversal in Sputtering DC Discharge Plasmas : A modelling study

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Objective / Method

Objective :

- To understand how particles originating from material sputtering/erosion can grow in a laboratory discharge.

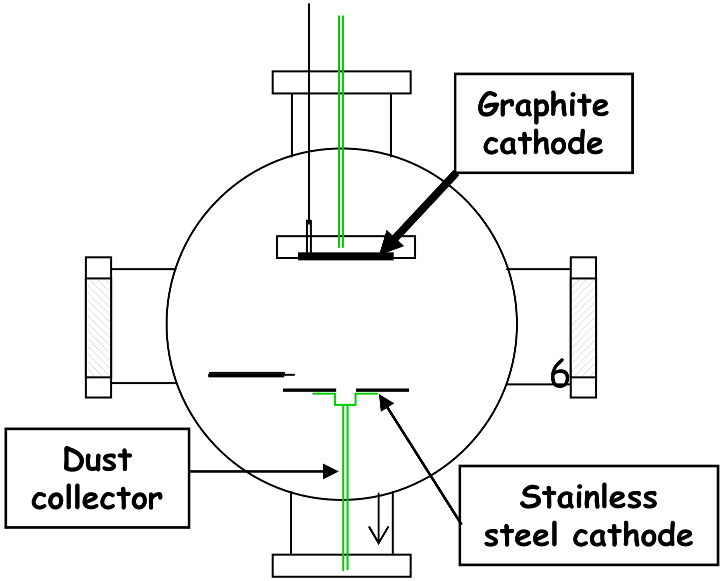
- To investigate the physical parameters that govern dust production

Method

Develop a model that describes

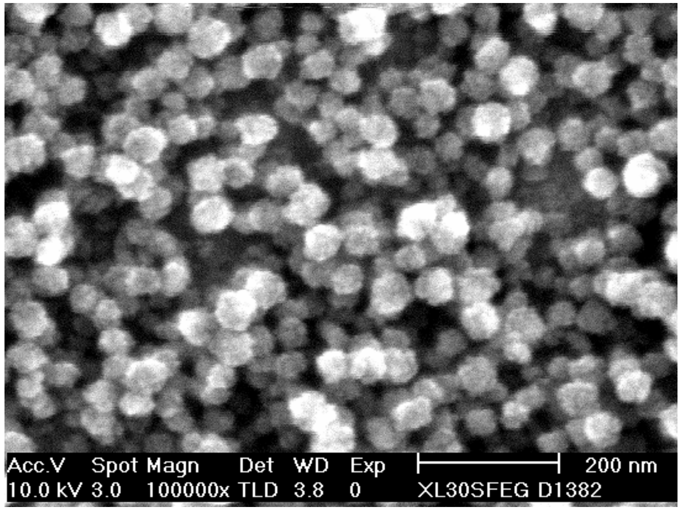
- Discharge system and cathode sputtering
- Molecular growth and transport of clusters
- Dust particle formation, growth and transport

Investigated experimental system
(From C. ARNAS, PIIM-Université de Provence)

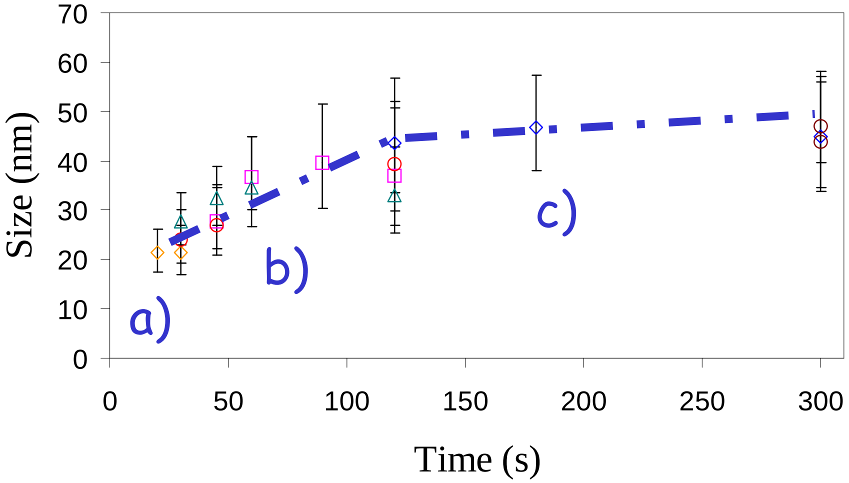


- 14 cm gap DC discharge in Argon (60 Pa ,600 V, 80 mA)
- Negative Glow : $n_e \approx 10^{10}$ cm^{-3}
- T_e ~ 3 eV
- Discharge duration < 10 min

SEM micrograph

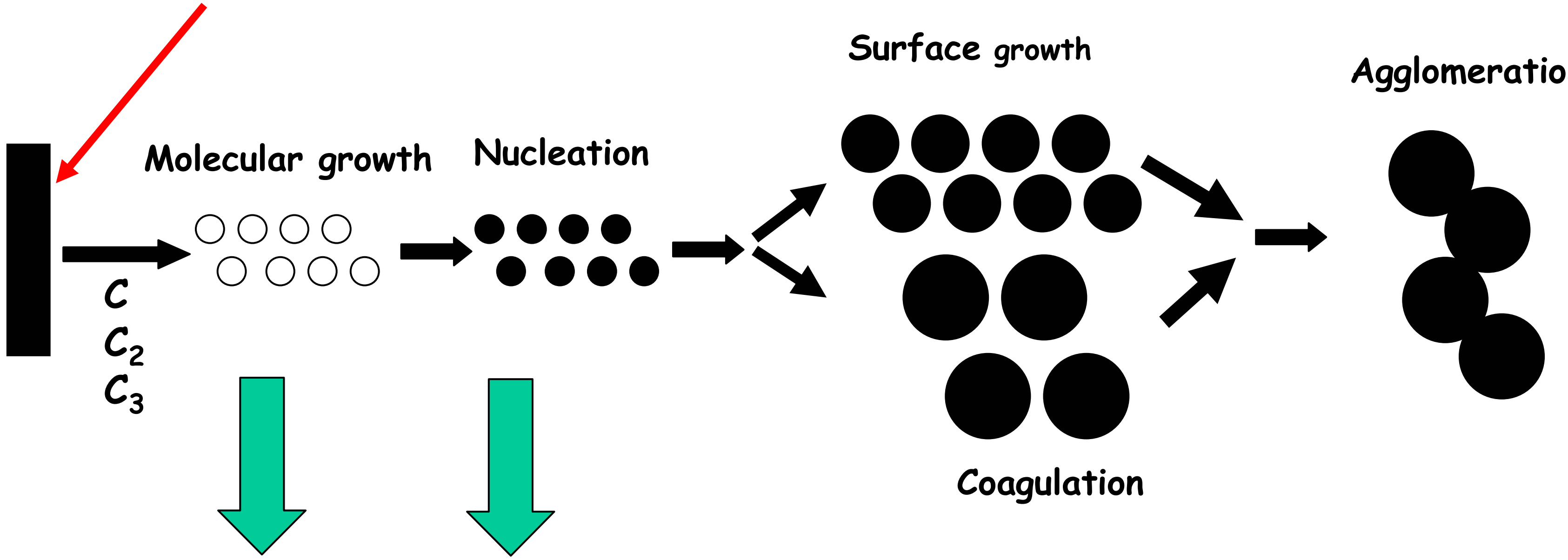


Experimental growth rate



Phenomenological description of dust particle formation

Ar^+ + Ar sputtering (Ions accelerated in the sheath – Fast neutrals created from CT)



Molecular growth

Nucleation

Surface growth

Agglomeration

C
C_2
C_3

Coagulation

possible diffusion
and loss at
surfaces

a phase

b+c phases

Some key-questions with respect to the previous description

➔ Low pressure discharge : p_g = 10-100 Pa

➔ Diffusion characteristic time = 1-10 ms very short as compared to the growth chemistry (~ min) ➔ no possibility for growth due to neutral

$$\tau_{residence} \approx \tau_{diffusion} << \tau_{growth}, \tau_{nucleation}$$

➔ Need for precursor species and particles with higher residence time :

Require trapping by external forces :

- Electric field configuration
- Ion drag induced forces

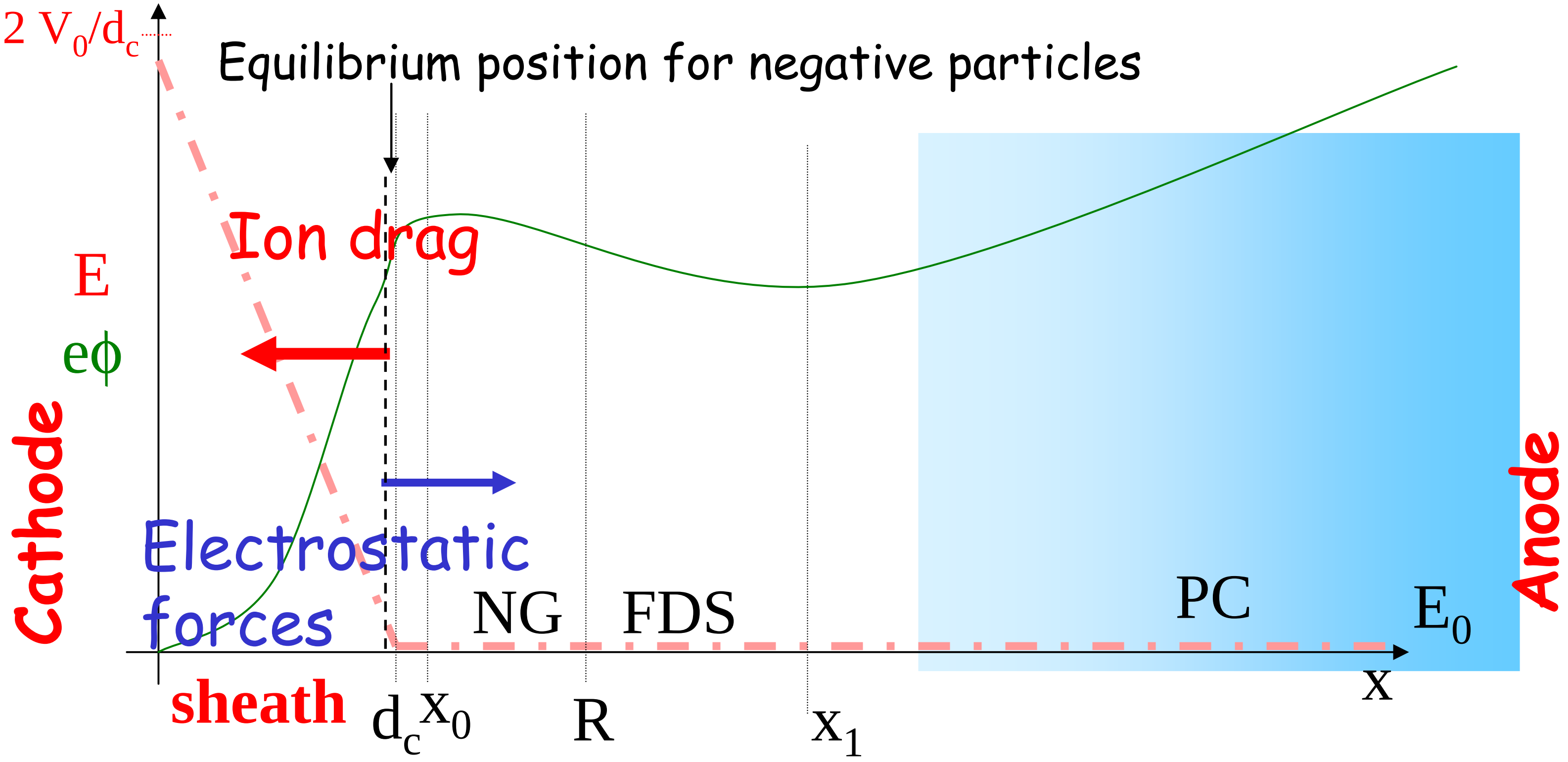
$$\tau_{residence} >> \tau_{growth}, \tau_{nucleation}$$

➔ Back to some basic DC discharge physics

First trapping mechanism

Equilibrium between drag and electrostatic forces at the sheath edge

see for example Hwang & Kushner, Appl. Phys. Lett. 68, 3716 (1996)



NG: Negative glow / FDS: Faraday Dark Space/ PC : positive column

➔Ion accelerated toward the cathode exerts a drag force on particles

➔ particle negatively charged ➔ E-Field in the sheath push toward the bulk

BUT works only for solid particles not for molecules and clusters

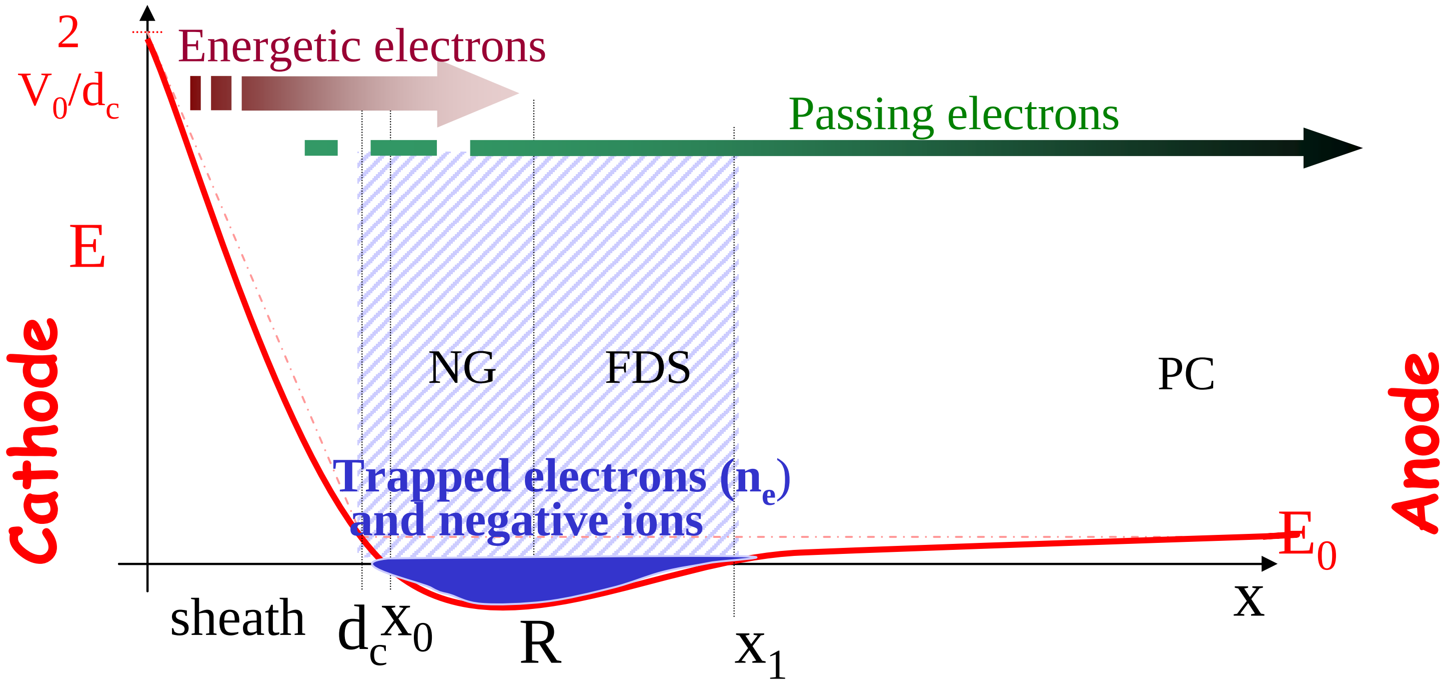
Let's look at more closely to the field structure at the sheath edge …

Second trapping possibility
Possibility of a a field reversal in the NG

(Kolobov & Tsendin, Phys. Rev. A 46 7837 (1992) ; Boeuf & Pitchford, J. Phys. D, 28 2083 (1995))

➔ confining electrical field structure

Three electron populations: fast (ionizing), intermediate (energy below the first excitation threshold), cold (trapped in the field reversal)



NG: Negative glow / FDS: Faraday Dark Space/ PC : positive column

Model of nucleation, growth and transport of dust with a field reversal configuration

3 module model

✓ Estimation of discharge main characteristics, especially field reversal strength, ion energy distribution at the cathod and electron density in the gap:

✓ Sputtering, Molecular growth and transport of carbon clusters

✓Growth, transport of solid particles

} Coupled

Discharge model in a dust-free plasma

1. **Kolobov and Tsendin Sheath dynamic model combined with a Monte Carlo simulation** Kolobov & Tsendin, Phys. Rev. A **46** 7837 (1992)

   -> Sheath dimension & Non local ionization source term

2. **Ambipolar diffusion equation for the cold electron population**

$S_i(x)$

$$-D_a \frac{d^2 n_{ce}}{dx^2} + \frac{n_{ce}}{\tau} = S_i(x) \qquad D_a = f(T_e, T_{ar+}, D_{ar+})$$

3. **Boltzmann distribution for the cold electrons**

   -> determination of the very small ambipolar field in the NG/FDS

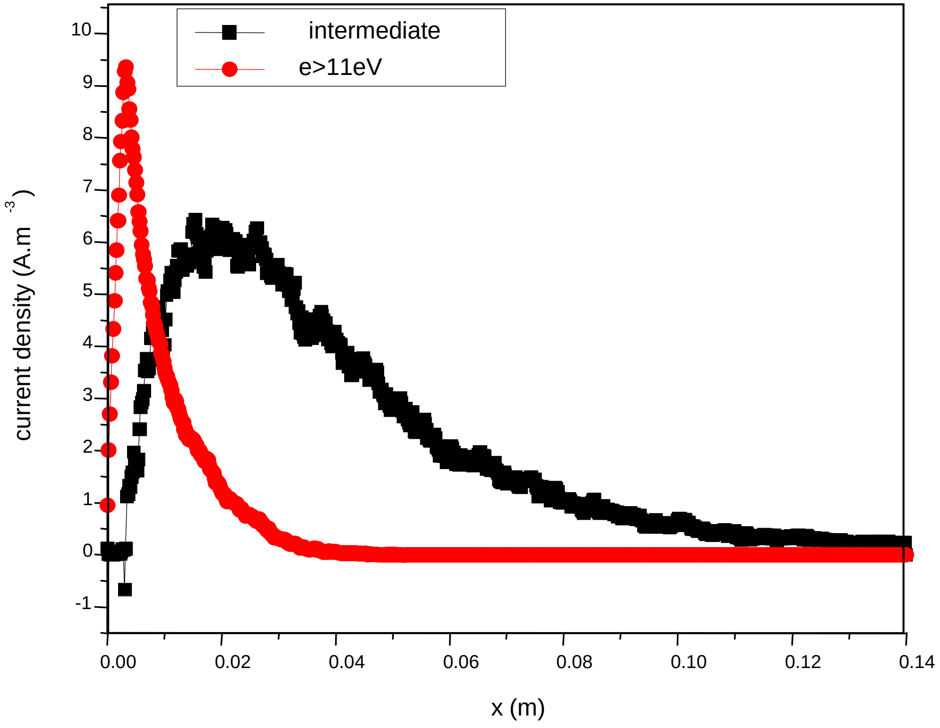
$$n_{ce} = n_{ce}^0 e^{\frac{\phi}{kT_{ce}}}$$

$$E = -\frac{kT_{ce}}{e} \nabla \ln(n_{ec})$$

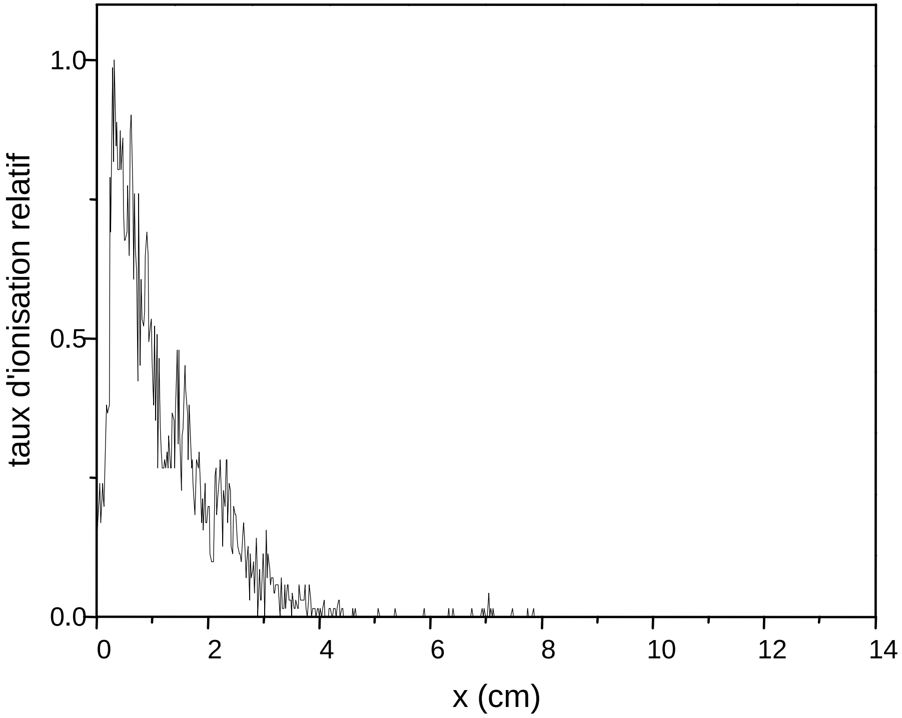
Model Parameter : Te, typically around 0.1 eV

Fast electrons and non local ionization

Fast and intermediate electrons



Relative variation of the non local Ionization rate



-NG size of the order of 4 cm

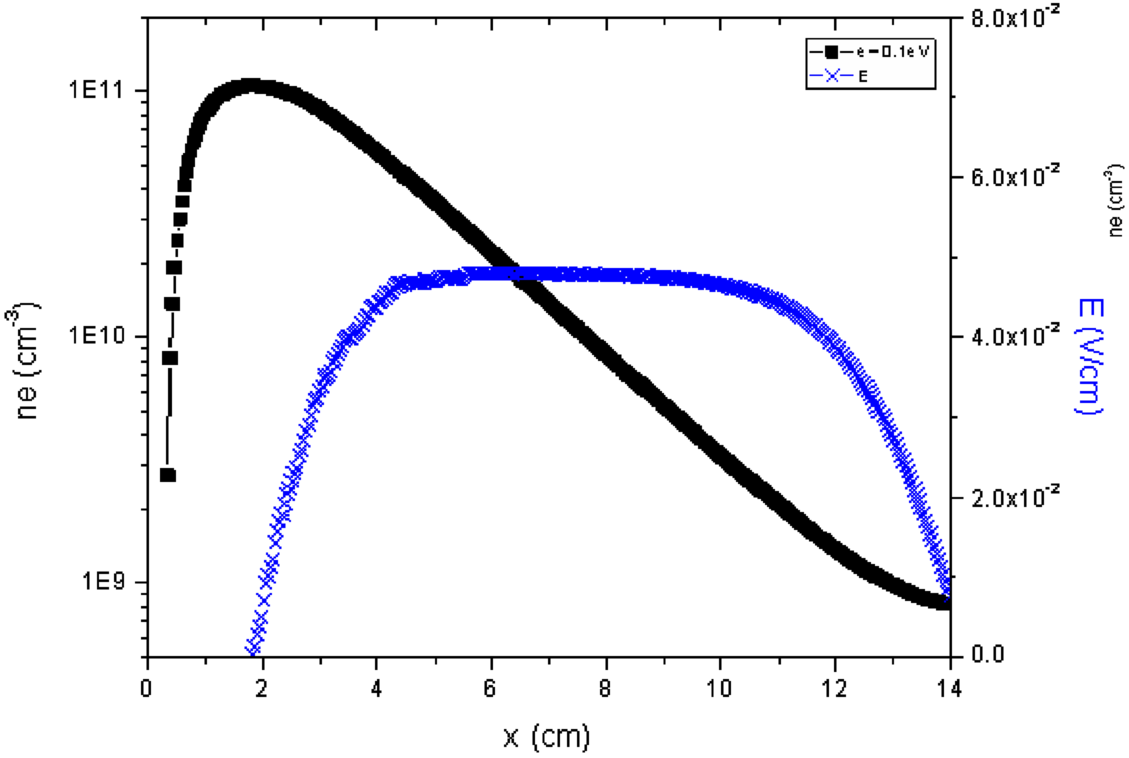
-Fast electron dominating in the sheath

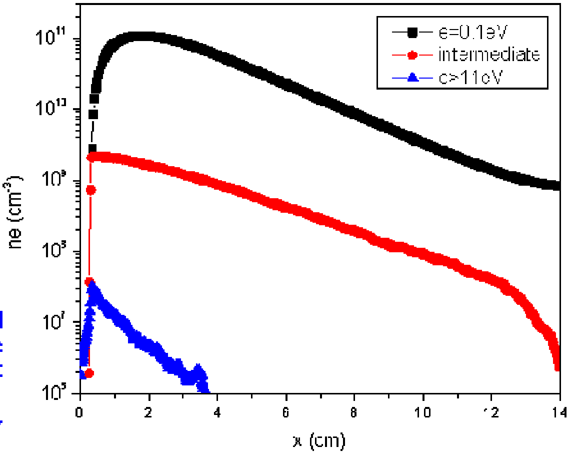
Absolute value from Kolobov-Tsendin model

Then use this rate in cold electron equation

Cold electron distributions and electric field reversal strength

Cold electrons and electric field





Cold electron density maximum ⇔ field reversal

Field reversal strength ⇔ cold electron temperature (model parameter)

Very small as compared with the cathod fall (1V/m vs 10^6 V/m)

Model for molecular growth, and dust nucleation, growth and transport in DC discharges

- ✓ 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)
  - ✓ Carbon clusters are described through their density $n_i(x,t)$ assuming T=Tg
  - ✓ The present results are obtained for n=1-30 with several isomers per size (≈140 clusters)

- ✓ Nucleation of carbon dusts from clusters: *Assumption of 'Largest Molecular Edifice'*

- ✓ Growth, transport and wall losses of dusts
  - ✓ Dust particles are described through their number density $n_p(x,t)$
  - ✓ In principle size distribution is needed : we limit ourselves to the average size : $d_p(x,t)$
  - ✓ In principle charge distribution is needed : we limit ourselves to the average charge : $q_p(x,t)$

Model equations

Molecular balance

Sticking at dust surface

$$\frac{\partial n_{i,z}}{\partial t} = -\vec{\nabla}\left(-D_i\vec{\nabla}n_i + \mu_{i,z}nz\vec{E}\right) + \boxed{W_i} - \boxed{W_{st}^{i}} - \boxed{P_{rad}^{i}}$$

Diffusion drift

Production rate of C_i

Radial loss at the wall

clusters

Nucleation

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

n_l is the size of the largest molecular edifice

Solid particle number, mass and charge balances

$$\frac{\partial n_p}{\partial t} = -\vec{\nabla}\left(\vec{F}_p\right) + W_{nuc} - W_{coag} \qquad \vec{F}_p = -D\vec{\nabla}n_p + \mu\overline{z}\vec{E}$$

Dust particles

Sticking

$$\frac{\partial n_p.m_p}{\partial t} = -\vec{\nabla}\left(m_p.\vec{F}_p\right) + W_{nuc}.m_{nuc} + \sum_{i=1}^{ncluster} W_{st}^{i}.m_{cluster}^{i}$$

Sticking

$$\frac{d\overline{q}_p}{dt} = -\frac{div(\vec{J}_p) - \overline{q}_p div(\vec{F}_p)}{n_p} + \frac{w_{coag}}{n_p} + \frac{w_{nuc}^{-} - \overline{q}_p w_{nuc}^{tot}}{n_p} + \frac{w_{st}^{-}}{n_p} + \frac{I^{+} - I^{-}}{n_p}S$$

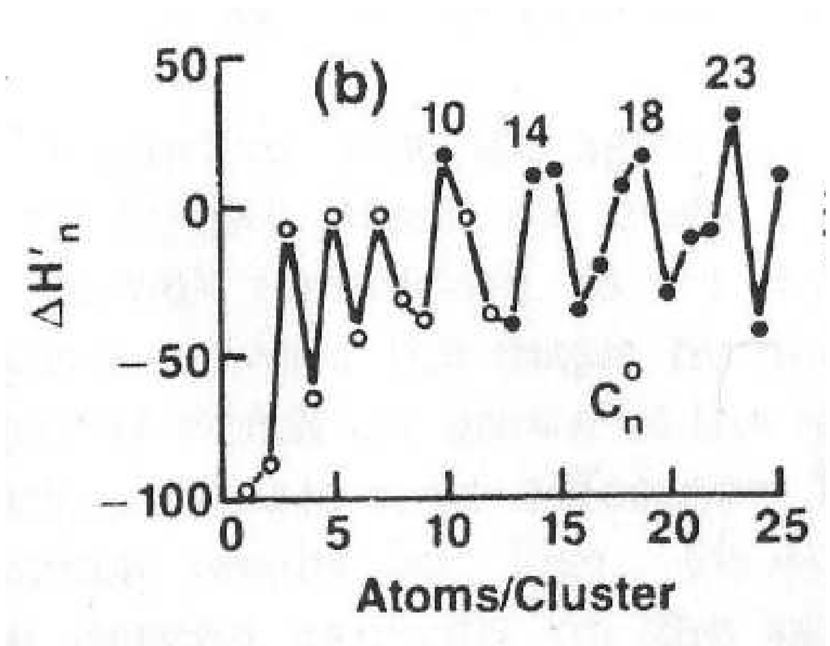
Wnuc= nucleation
Wcoag= coagulation
Wst= sticking

Few words on molecular growth processes and their collisional data

- **Major molecular growth process :**

$$C_n + C_x \rightarrow C_{n+x} \quad x<4$$
$$C_n^- + C_x \rightarrow C^-_{n+x} \quad x<4$$
$$C_n + C_x^- \rightarrow C^-_{n+x} \quad x<4$$

·formation enthalpies are taken into account ➔ magic number effect



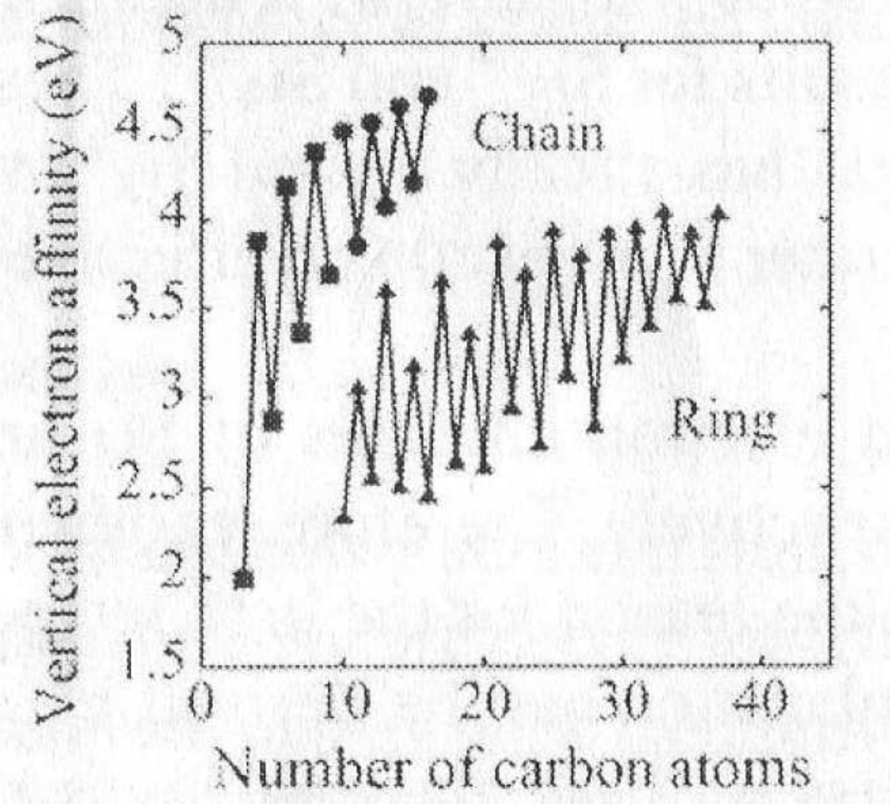
To estimate the rate constants ➔ We combine two data sources (Bernholc & Schweigert)

$$\boxed{k_{ij} = V_{th}\sigma_{ij}\sqrt{\frac{i+i}{i.j}}.exp\left(-\frac{Eb}{RT}\right).exp\left(-\gamma\frac{\left(\Delta G_i+\Delta G_j\right)}{kT}\right)}$$

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

From J. Bernholc, J. C. Phillips, 1986 Journal of Chemical Physics **85**, p. 3258
V. A. Schweigert, A. L. Alexandrov, *et al.*, 1995 *Chemical Physics Letters* **238**, p. 110

Few words on the key-processes involved in negative cluster formation



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

- **Attachment** $C_n + e^- \rightarrow C_n^-$ $n \geq 4$

Rate computed according to radiative attachment processes

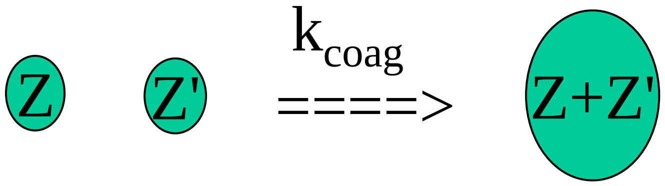
- **Detachment** $C_n^- + e^- \rightarrow C_n + 2e^-$

- **Charge exchange** $C_n^- + C_x \rightarrow C_n + C_x^-$

Rate takes into account electronic affinities

$$T_{ij} = V_{th}\sigma_{ij}\sqrt{\frac{i+i}{i.j}}.\exp\left(-\zeta\frac{\left(\left|Ea_i - Ea_j\right|\right)}{kT}\right)$$

Another key-issue : How to treat coagulation in a model where only the average charge is used



$$Z \quad Z' \xrightarrow{k_{coag}} Z+Z'$$

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

➔ coagulation depends on the charge of the colliding particles :

zz′ ↗ -> w(zz′) ↗↗ -> k_{coag}(zz′) ↘↘↘

- We need to take into account charge fluctuation effects originating from the discrete nature of the charging phenomenon …

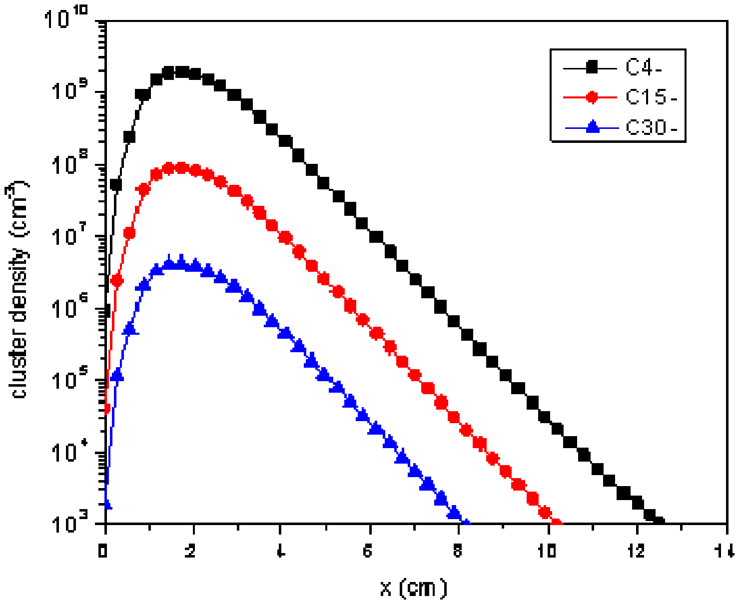
charge distribution derived by Matsoukas et al.

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

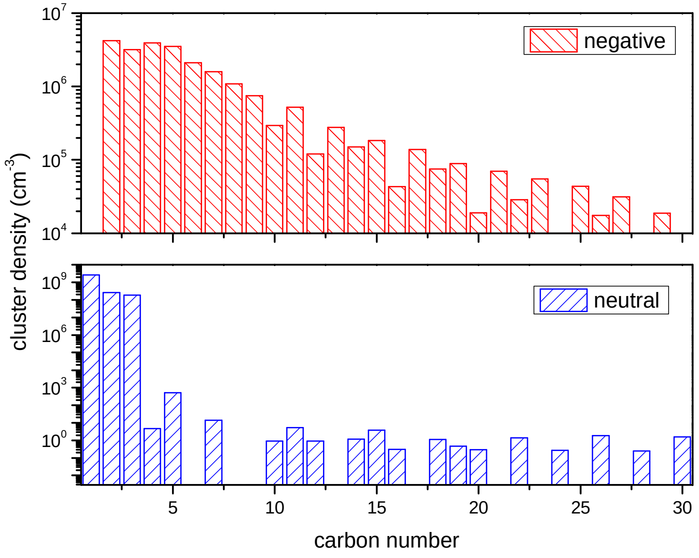
T. Matsoukas, M. Russell, 1995 *Journal of Applied Physics* **77**, p. 4285

Some results
Space and size distributions of clusters

Space distribution of some clusters at 600 s

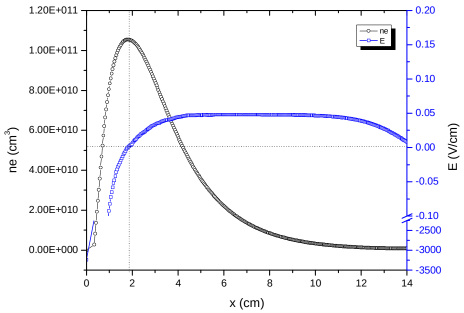


Size distribution of n=1-30 clusters at 600 s and 7 cm



- Clusters localized at the field reversal position

Note the logarithmic scale



- Mainly negative clusters

- Neutral clusters $C_{n<4}$

Inferred Cluster Growth mechanism

Once the emission of neutral C, C_2, C_3 takes place

1. growth of neutrals up to C_4

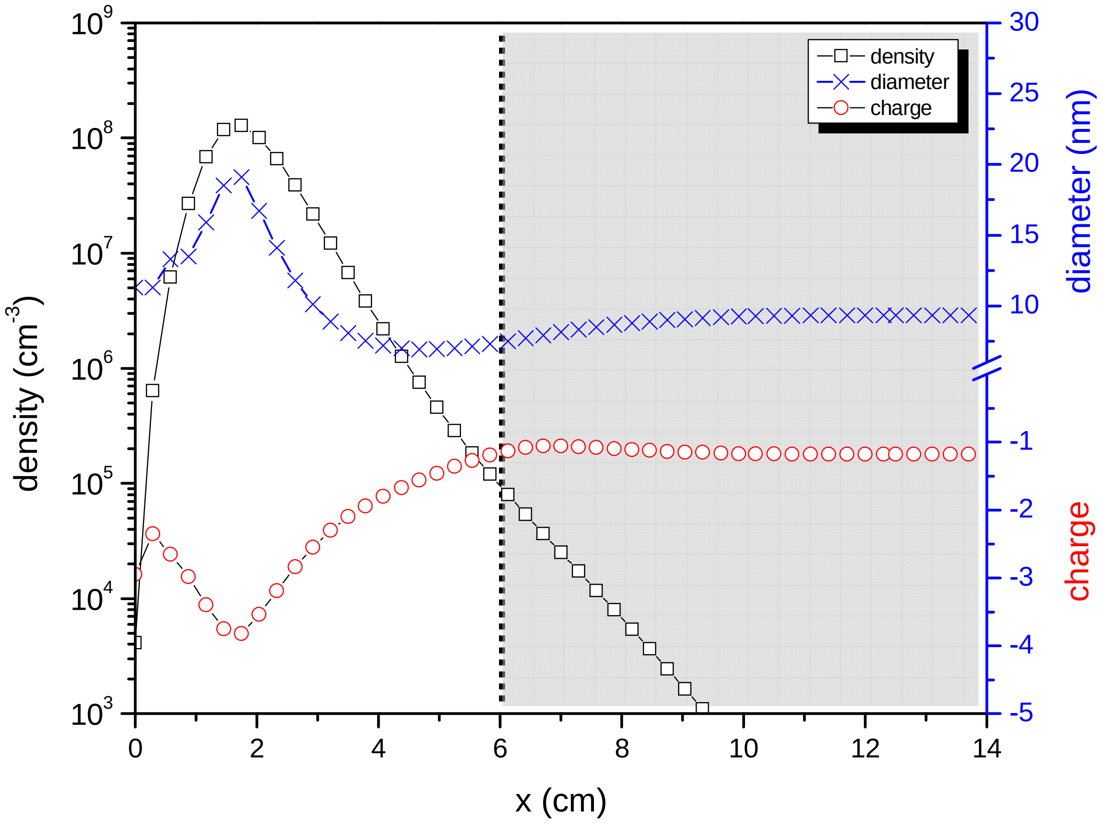
2. Electron attachment on C_4 ➔ C_4^- and beyond

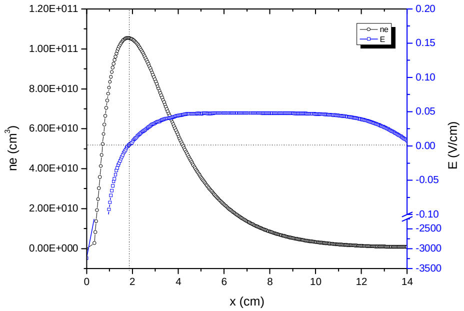
3. only negative clusters can grow through coagulation with the emitted small clusters : $C_n^- + C_x \rightarrow C^-_{n+x}$ $x<4$

4. $C_{n>4}$ neutral cluster populations are produced by charge transfer processes from large negatively charged clusters

Space distributions of dust density, average size and average charge

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

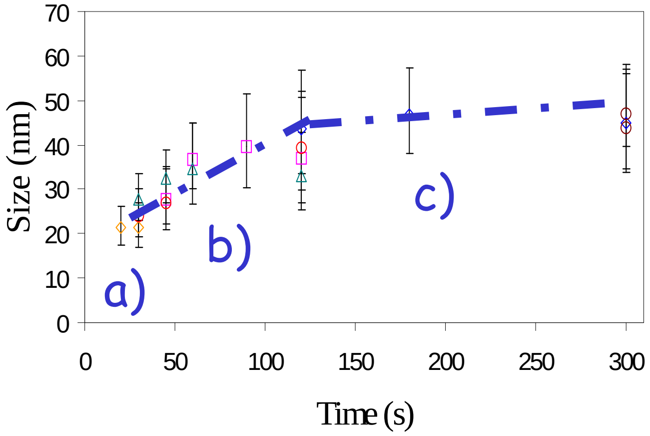




- •Particle cloud also localized at the field reversal position
- •Particle diameter is around 20 nm in the cloud
- •Maximum average charge : -4 ➔ close to OML equilibrium

Qualitative comparison with experiment
Solid particle growth kinetics

Experimental growth rate

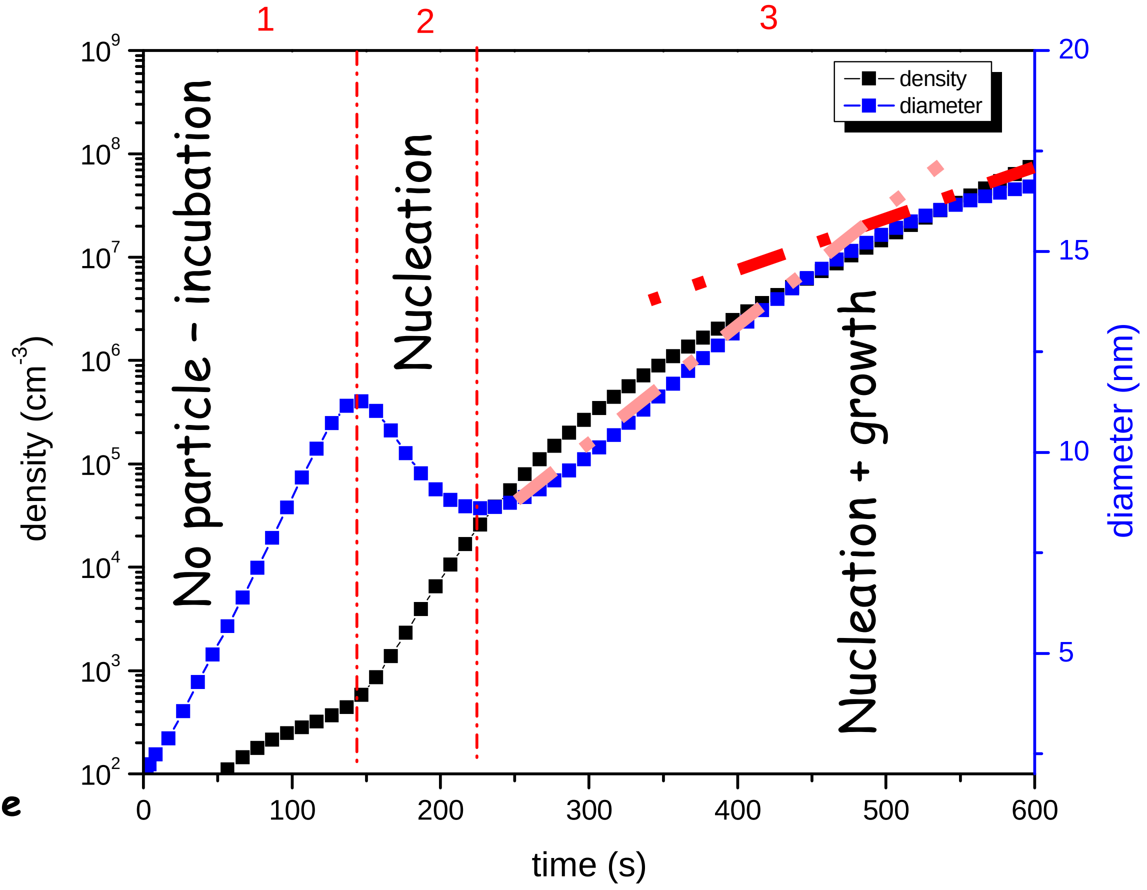


Three phase kinetics

1- incubation ➔ molecular growth phase

2- nucleation burst ➔ decrease of the average diameter

3- nucleation + growth ➔ increase of both density and average diameter

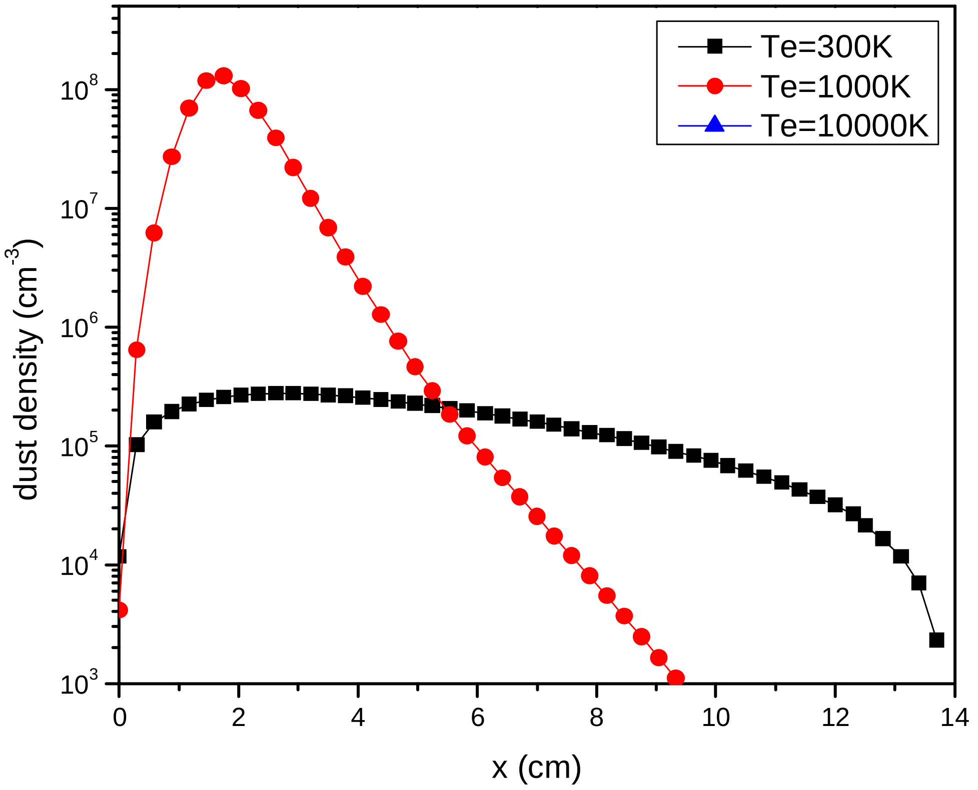


Despite many approximations the model gives similar size magnitude and growth characteristic times.

Effect of some key-model parameters
Temperature of cold electron

When Te increases :

- The field reversal and the confinment effect are stronger
  ➔ favors molecular and particle growth
- The attachment process becomes very slow
  ➔ negative clusters production decreases



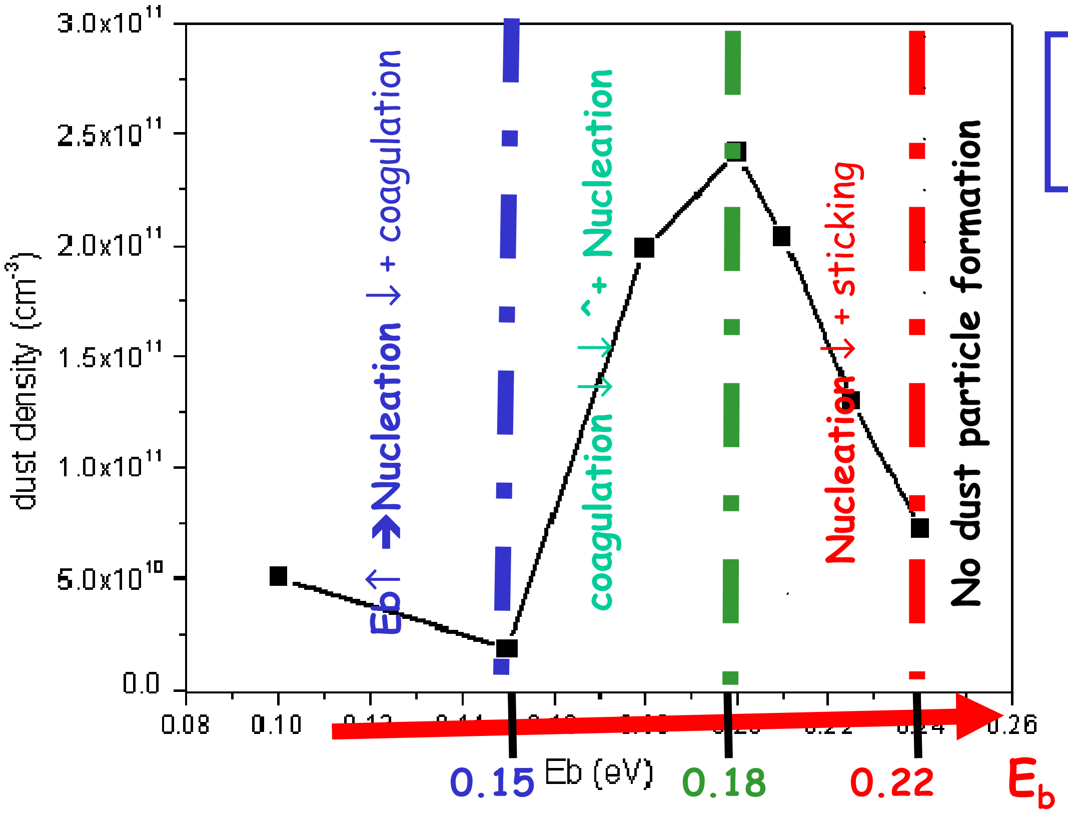
- T_e = 0.025 eV ➔ trapping not effective
- Te = 1eV ➔ no particle formation !!!

(cannot produce C_4 and initiate the attachment growth procedure)

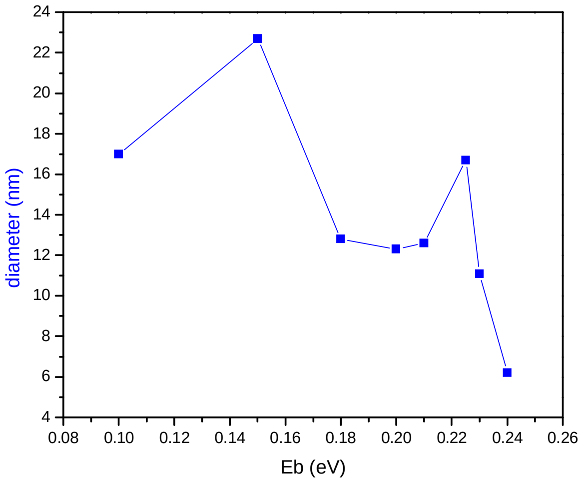
Dust production is significant only in a narrow window of cold electron temperature

Effect of some model parameters

activation energy for cluster coagulation process



$$k_{ij} = V_{th}\sigma_{ij}\sqrt{\frac{i+i}{i.j}}.exp\left(-\frac{Eb}{RT}\right).exp\left(-\gamma\frac{\left(\Delta G_i+\Delta G_j\right)}{kT}\right)$$



- Eb<0.15 eV : clusters ➔ nucleation AND coagulation ➔ Dust growth

- Eb> 0.22 eV : no dust particle formation

Coupling between cluster growth dust formation and discharge characteristics

So Far :

- We clearly show that field reversal can induce dust particle formation

- The effect is strongly sensitive to dicharge and collisional data (nonlinearity)

BUT No coupling between discharge and cluster/dust particle

What happens if we take into account this coupling ?

•Cold electron density balance takes into account the presence of neutral clusters charged clusters and dustparticles ➔ n_e:

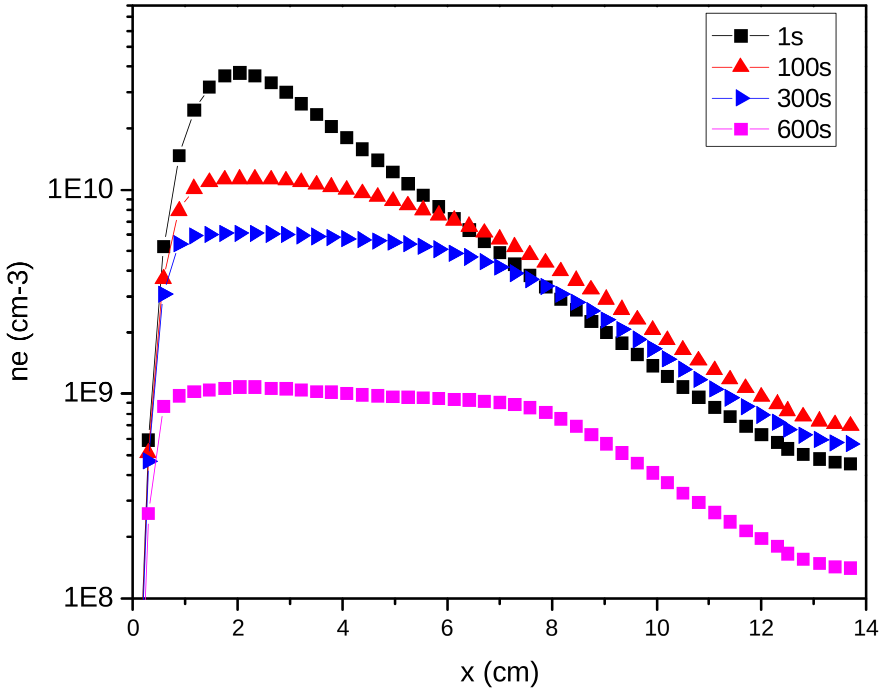
$$\frac{\partial n_e}{\partial t} = -\vec{\nabla}\left(-D_e\vec{\nabla}n_e + \mu_e n_e \vec{E}\right) + S_i(x) - P^e_{dust} - P^e_{attach} - P^e_{rad}\left(\frac{n^-}{n_e}\right)$$

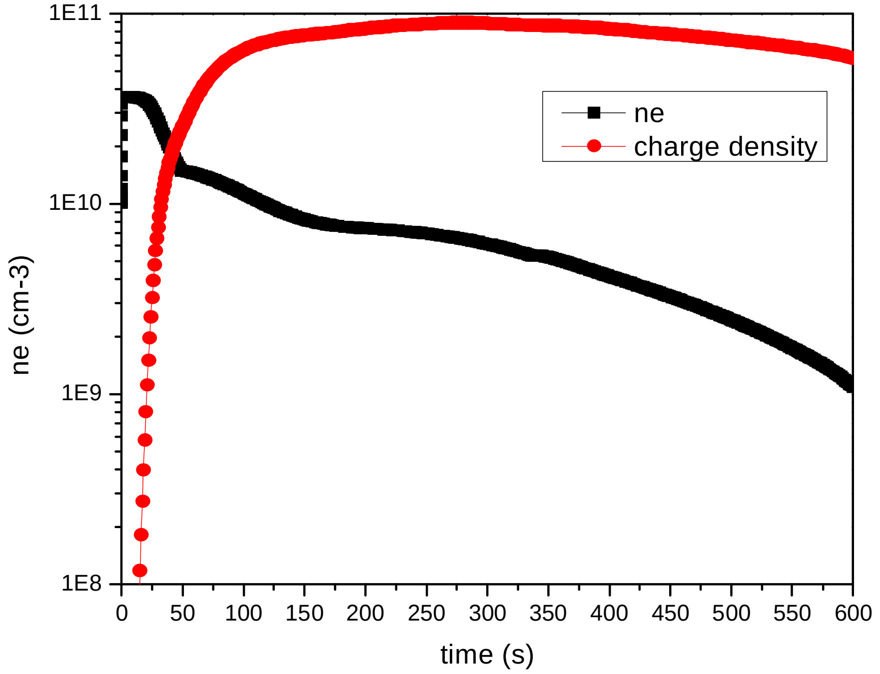
•Ambipolar field computed by current balance involving electron, ions, clusters and dust particles

$$\sum q_i(-D_i\nabla n_i + q_i\,\mu_i n_i) = 0$$

Electron depletion and electronegative discharge

(Results for strongly sputtering discharges)



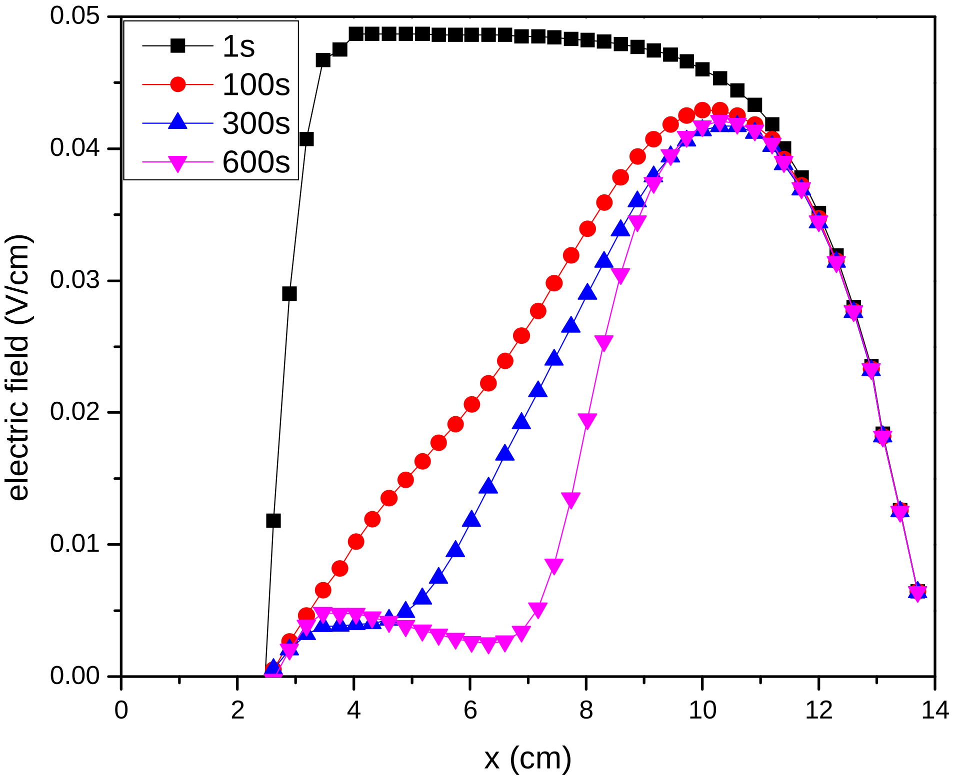


1- Cold electron concentration decrease by more than 1 order of magnitude

2- Discharge electronegativity is almost 100 (n^-/n_e) !!!

3- Electron distribution becomes almost flat in the NG

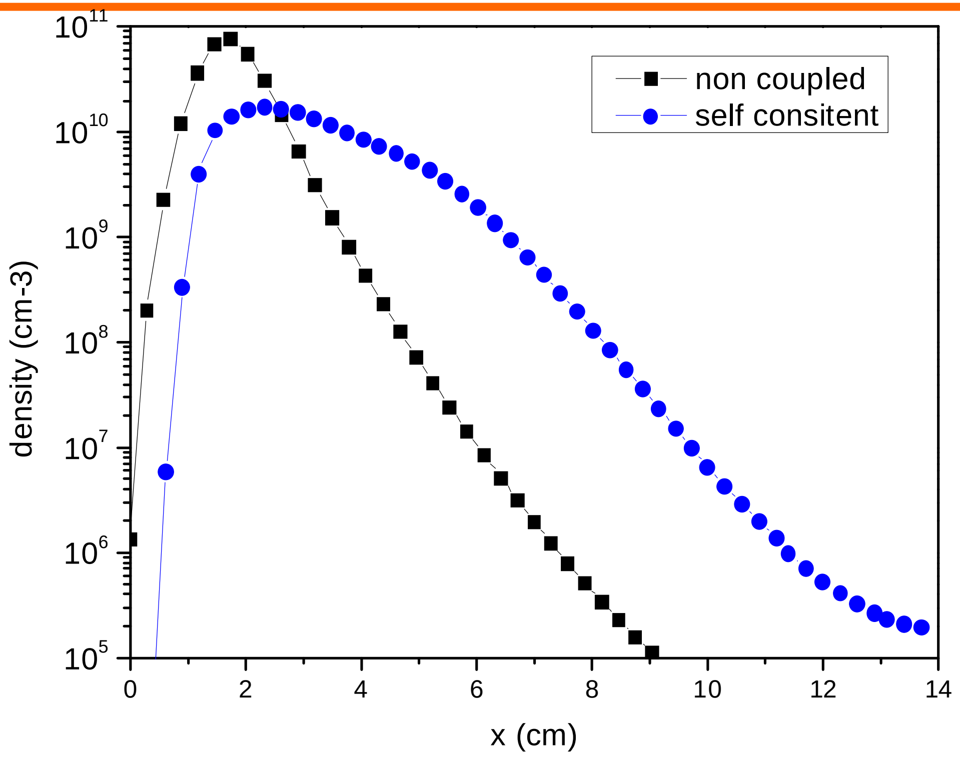
Change in the electric field configuration
(Results for strongly sputtering discharges)

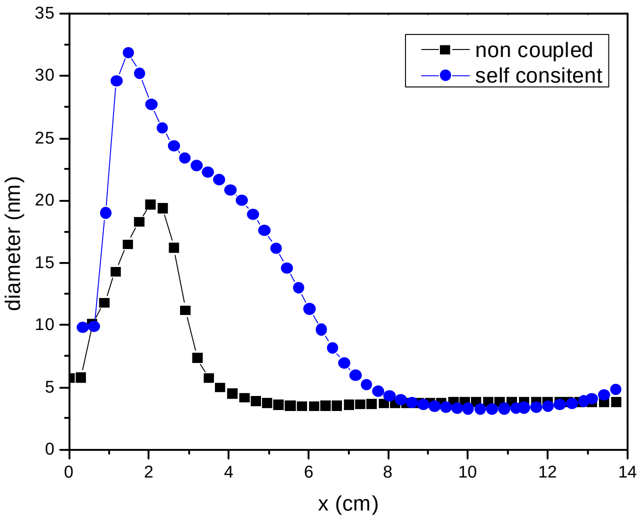


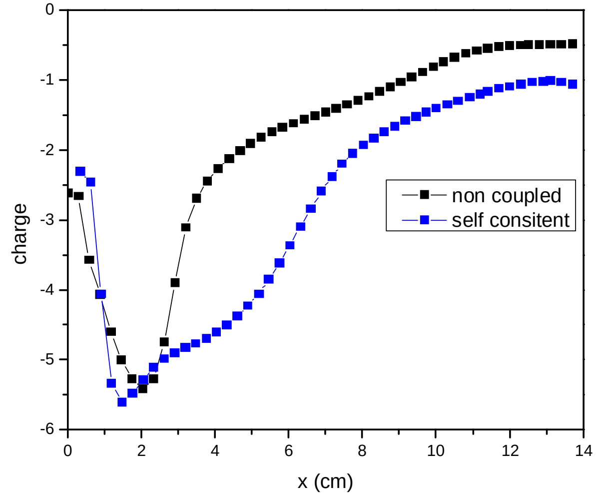
1- Field reversal is much weaker
2- It becomes almost zero i the NG
3- Less Confinement in the NG

Change in the dust particle growth kinetics

(Results for strongly sputtering discharges)







1- There is still dust production !!!

2- But broader distribution with smaller maximum
(smaller reversal weaker confinment, smaller nucleation)

3- Somewhat larger diameter (more sticking + coagulation for long discharge duration)
(Better agreement with experiment for diameter and dust density value)

4- Similar charges for coupled and non coupled situations !!!

Conclusion

- The scenario based on negative particle trapping in the the field reversal of the NG can explain dust formation in DC discharge.

- Dust partice formation would be very sensitive to some discharge parameters and small clusters coagulation and attachment collisional data

- Despite the simplified description or the aerosol dynamics, the model reproduces the qualitative trends observed experimentally

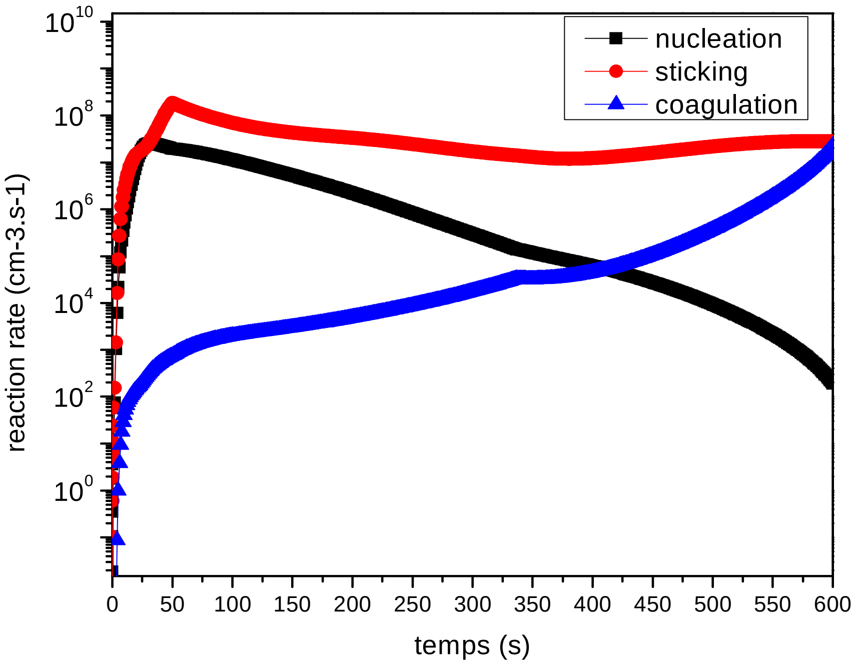
- First results show that the coupling between the discharge characteristics, cluster growth kinetics and particle aerosol dynamics affect the observed dust particle distribution especially for long discharge duration or strong sputtering conditions

Improvement :

Take into account the details of size and charge distribution for more quantitative prediction of the aerosol dynamic

RESERVE

A revoir


10^{10}
10^{8}
10^{6}
10^{4}
10^{2}
10^{0}
reaction rate (cm-3.s-1)
0
50
100
150
200
250
300
350
400
450
500
550
600
temps (s)
nucleation
sticking
coagulation

Coupling between dust and discharge

New DC discharge model：

- The negative species are lumped in a single average negative ion

  ➔3 species : Ar+, <ion>-, cold electrons

- Ambipolar field computed by current balance of the three species

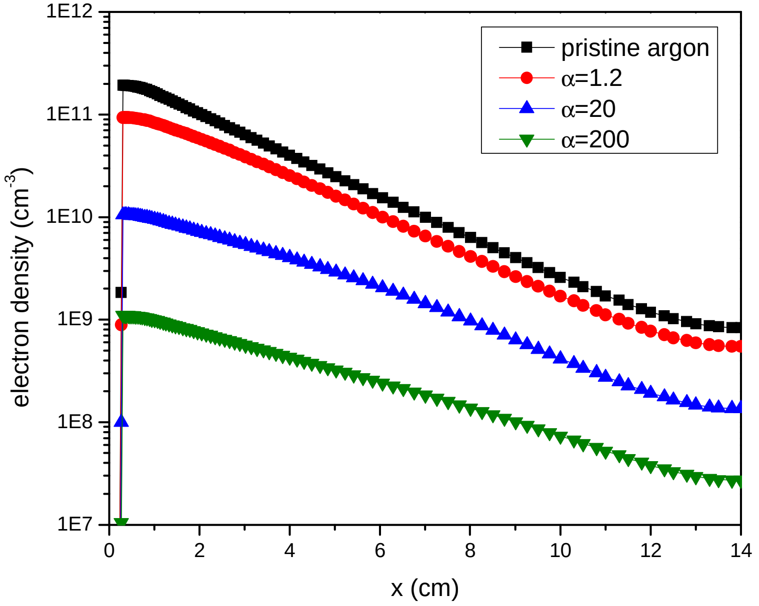
$$\sum q_i(-D_i \nabla n_i + q_i\, \mu_i n_i) = 0$$

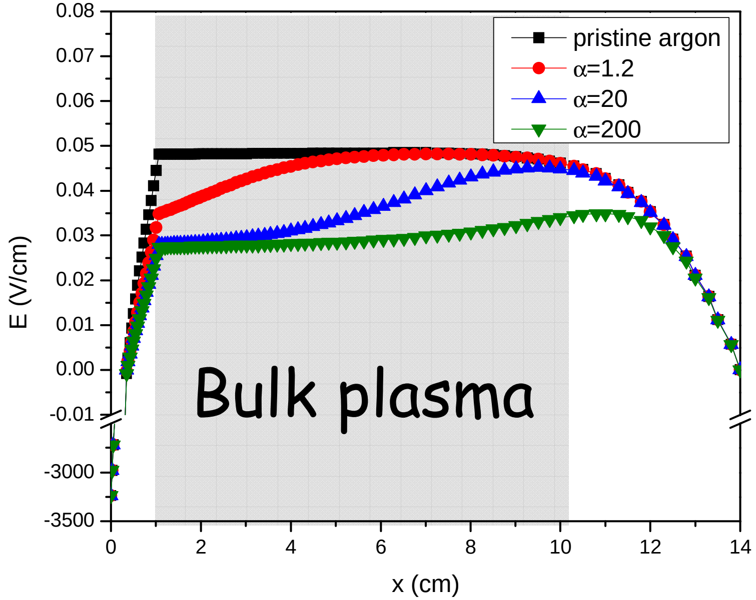
- Electron density balance ➔ n_e:

$$\frac{\partial n_e}{\partial t} = -\vec{\nabla}\left(-D_e \vec{\nabla} n_e + \mu_e n_e \vec{E}\right) + S_i(x) - P^{e}_{dust} - P^{e}_{attach} - P^{e}_{rad}\left(\frac{n^-}{n_e}\right)$$

Simple self consistent electronegative plasma simulation

Effect of the attachment kinetics (in terms of plasma electronegativity α)



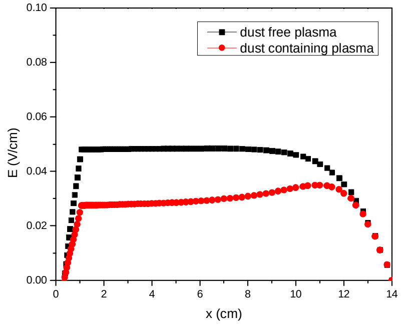


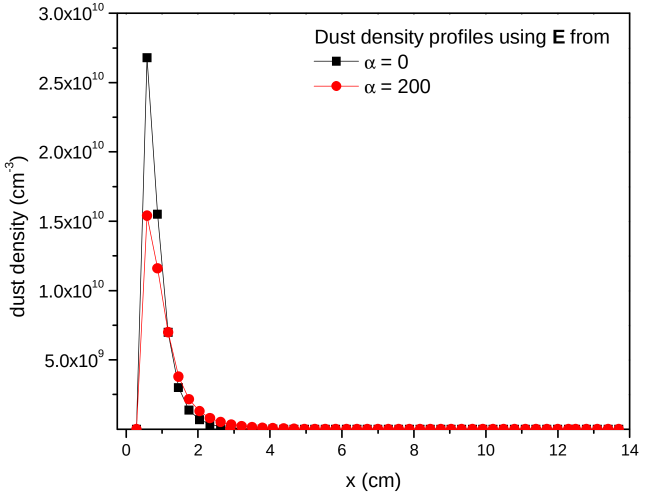
- Hudge (2 orders of magnitude) increase of α yields only slight decrease less than a factor 2 of the ambipolar electric field

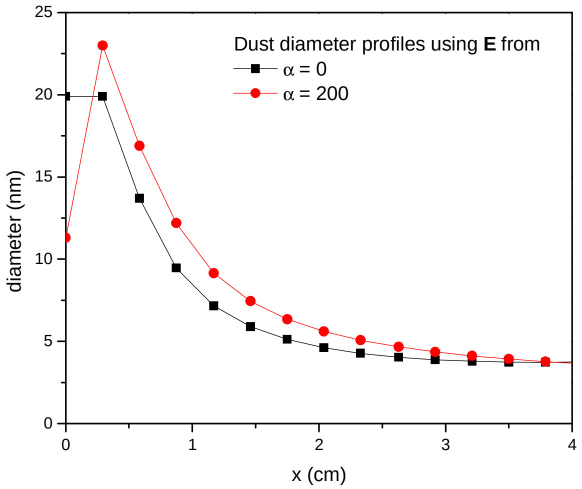
Effect of the ambipolar electric field

Detailed Cluster-dust model + electron balance with specified ambipolar field profiles

We make use of the upper and lower limit determined from the simplified model



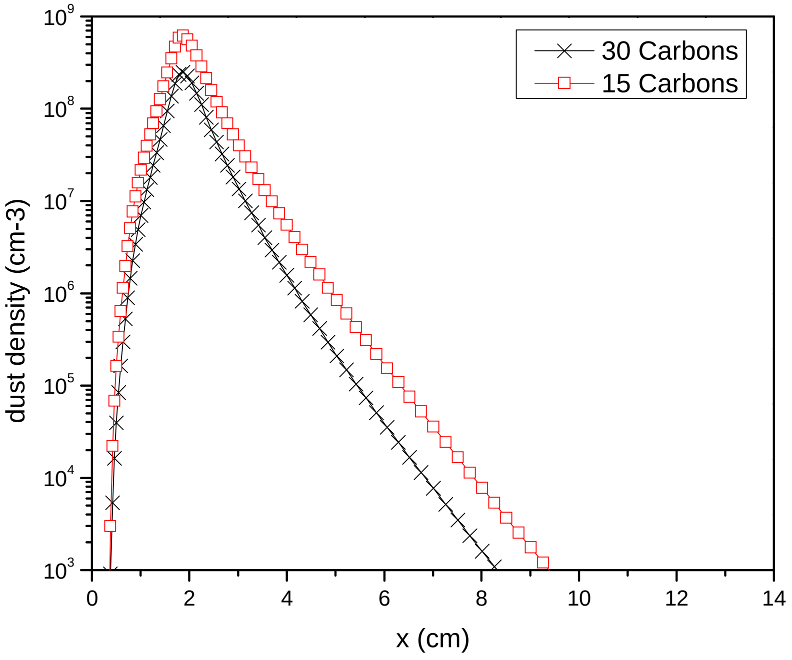


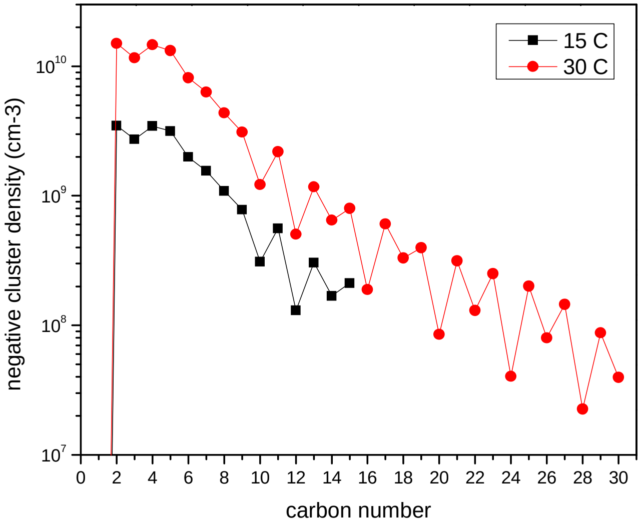


Decrease of the E-field indices the decrease of the peak dust density by a factor 2
The average diameter remains almost constant.

Effect of some model parameters
size of the largest molecular edifice (LME)

Comparison between 15 and 30 carbon : largest molecular edifice

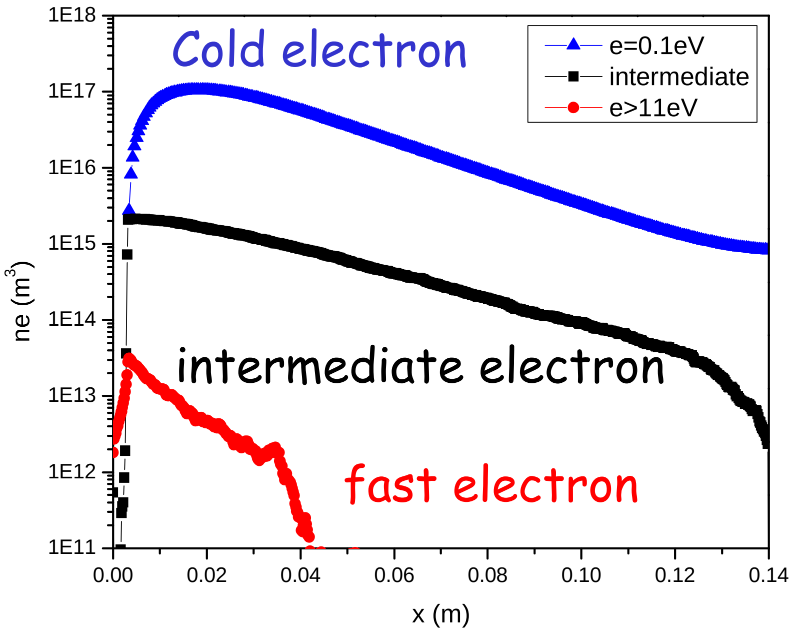




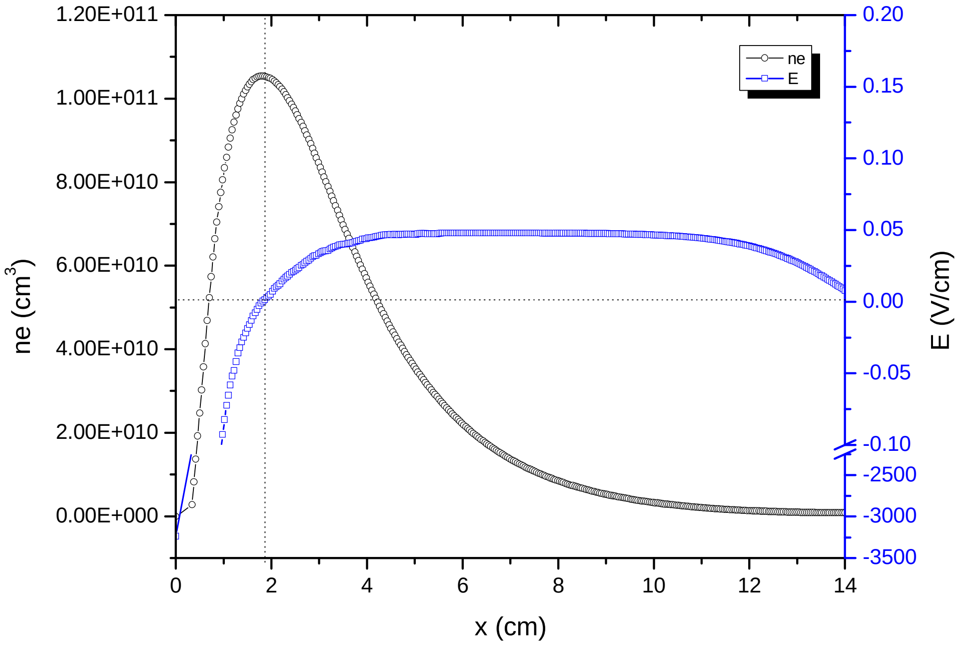
Smaller LME Overestimate the dust density
by a factor 2-3 (Reasonable)

Discharge characteristics

Electron density



Cold electron and electric field



Fast electron➔ ionisation
Intermediate electron ➔ current
Cold electron ➔ space charge/attachment

Cold electron density maximum ⇔ field reversal
Field reversal strength ⇔ cold electron temperature (model parameter)
Short discharge : Sheath, NG and FDS

Discharge model

1- Kolobov and Tsendin Sheath dynamic model

Kolobov & Tsendin, Phys. Rev. A **46** 7837 (1992)

➔ sheath thickness d_c, secondary emission γ_{sec}, absolute non local ionization : S_i^{sh}

$$\frac{dJ_{fe}^{sh}(x)}{dx} = \boxed{\alpha} J_{fe}^{sh}(x) = \boxed{S_i^{sh}} \qquad \boxed{J_{tot}} = \frac{4\varepsilon_0 \mu_i \boxed{V_c^2}\left(1+\boxed{\gamma_{sec}}\right)}{\boxed{d_c^3}}$$

$$m_e \frac{\boxed{dv_{fe}^{sh}}}{dt} = -eE(x) - N_{tot} * L(\varepsilon) \qquad E(x) = E_0\left(1-\frac{x}{d_c}\right), x < d_c$$

2- Monte Carlo simulation

➔relative densities and currents of fast, intermediate and slow electrons

➔Relative variation of the non local Ionisation in the whole discharge gap

3- (1 & 2) ➔ absolute value of the non local ionisation source term in the whole discharge gap

Carbon cluster growth reactions**

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

- Growth = one single process : $C_n + C_x \rightarrow C_{n+x}$

- take into account the stability of the C_n clusters

  - formation enthalpies are taken into account ➔ magic number effect

  - Clusters have configurational isomers (chains, rings, multi-cycles) distinguished by cyclization entropy (20 kcal/mol/cycle) ➔ some sizes may be stabilized by a single configuration

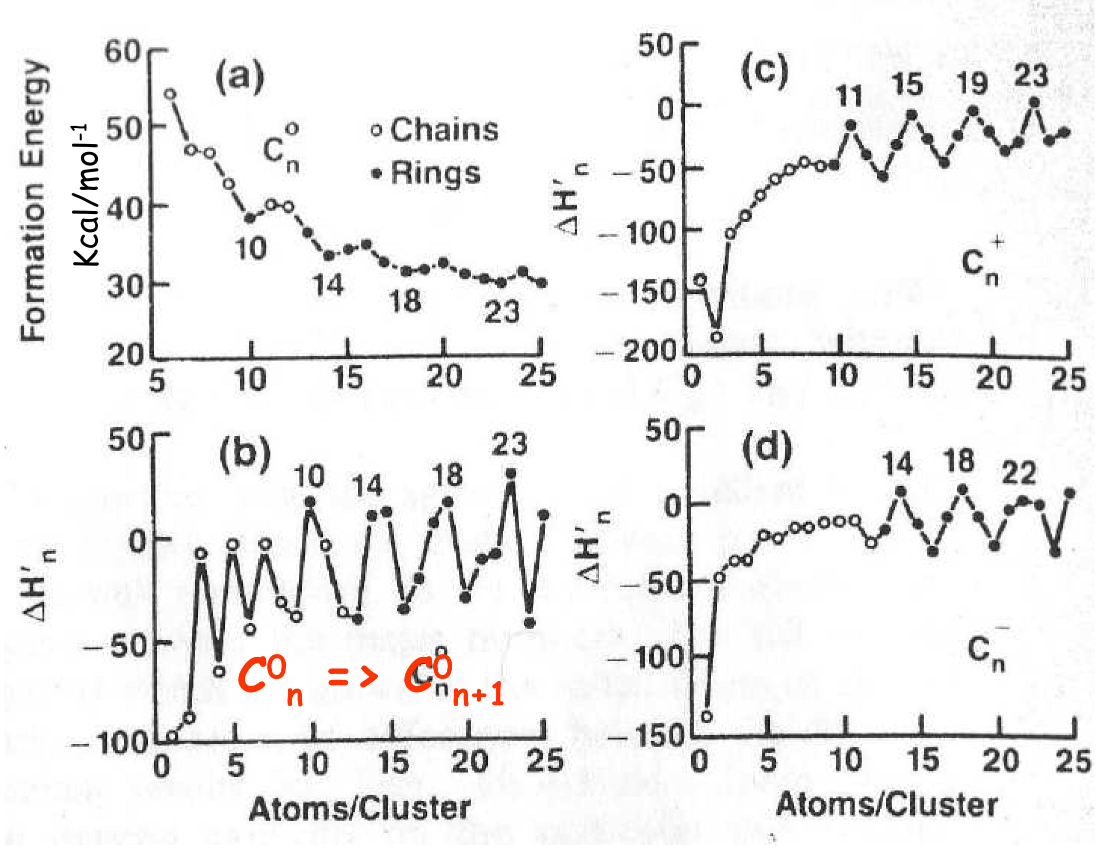
  - Data do not exist for all the sizes ➔ extrapolation for unknown values according to cluster periodicities

Coagulation rate constant estimation and formation enthalpy

$$k_{ij} = V_{th}\sigma_{ij}\sqrt{\frac{i+i}{i.j}}.\exp\left(-\frac{Eb}{RT}\right).\exp\left(-\gamma\frac{(\Delta G_i+\Delta G_j)}{kT}\right)$$

Model parameters : E_b, γ

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



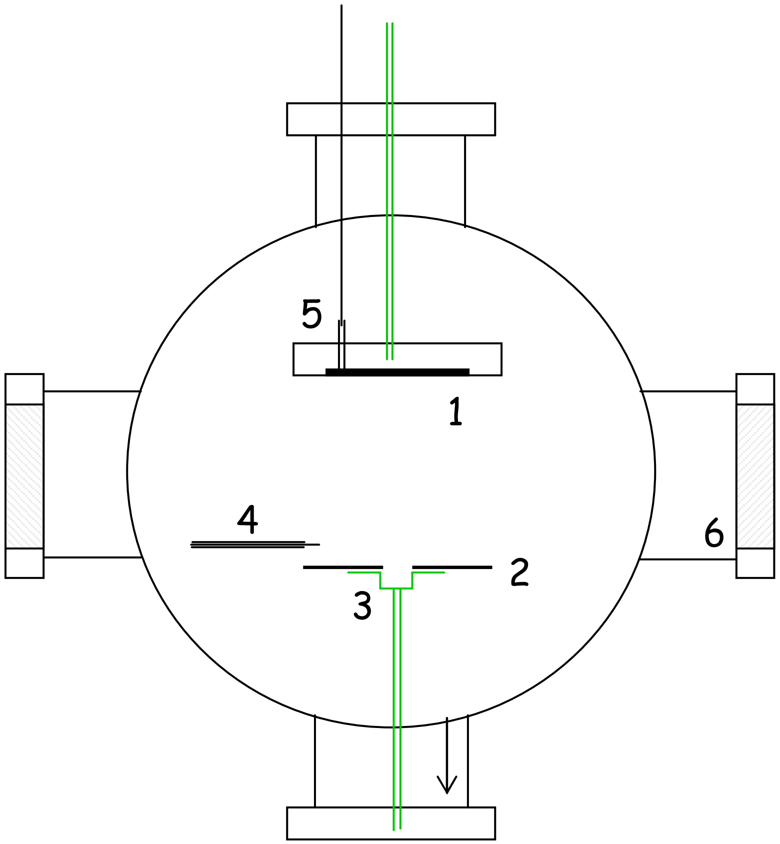
C^0_n => C^0_{n+1}

Formation enthalpies

Particle generation through plasma surface interaction in a DC discharge system

Experiment developped by C. Arnas
at PIIM-CNRS, Université de Provence

- DC discharge in Argon
- Inter-electrode distance 14 cm
- Bias V_d ~ - 600 V
- Discharge current = 80 mA
- $N_e = N_i = 10^{10}\ cm^{-3}$ in the negative glow
- T_e ~ 3 eV
- Pressure = 0.1 - 1mbar (typically 0.6 mbar)
- The only carbon source is the graphite cathode
- Discharge duration < 10 min



1 : Graphite cathode
2 : Anode
3 : Dust collector
4 : Langmuir probe
5 : Thermocouple
6 : Optical window