Some aspects of reactive thermo-chemically non-equilibrium plasmas

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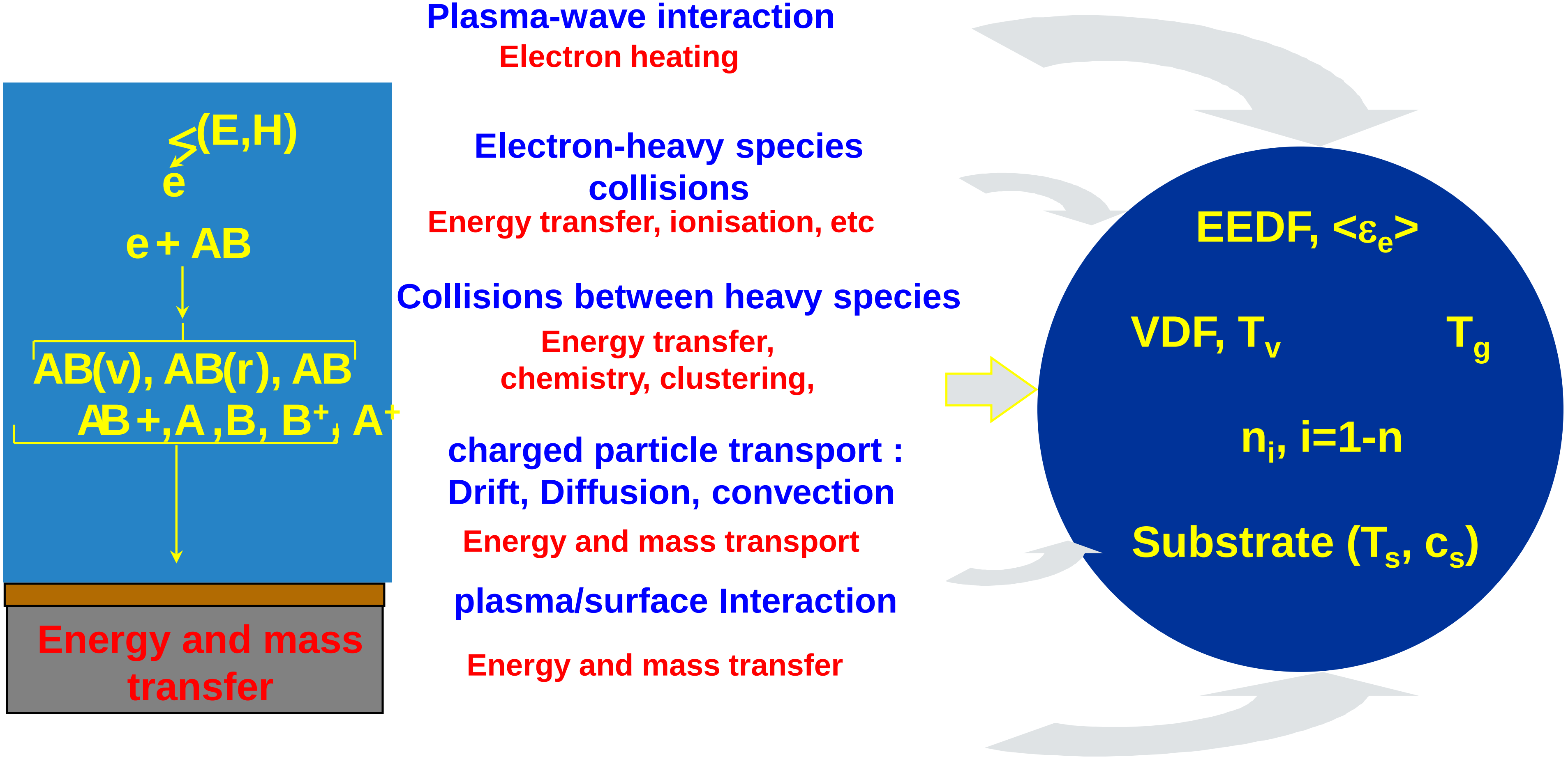
Overview

- Phenomenological description
- Electron kinetics in non-equilibrium discharges
- Reactivity and kinetics of electronically excited states– consequence on ionization kinetics and plasma characteristics : the example of hydrogen
- Vibrational kinetics and its impact on molecular dissociation : the example of molecular nitrogen
- Molecular growth, i.e., “plasma polymerization” in non equilibrium discharges :
    - Sputtering DC discharges with graphite electrodes
    - Ar/C_2H_2 capacitively coupled RF discharges
- Interplay between power coupling, energy relaxation, chemistry, and transport in reactive plasma
    - H_2/CH_4 microwave cavity plasmas
    - Ar/C_2H_2 capacitively coupled RF discharges
- Few slides on the methodology

Few words on laboratory plasmas :

a phenomenological description



(E,H)

e

e + AB

AB(v), AB(r), AB

AB^+, A, B, B^+, A^+

Energy and mass transfer

Plasma-wave interaction

Electron heating

Electron-heavy species collisions

Energy transfer, ionisation, etc

Collisions between heavy species

Energy transfer, chemistry, clustering,

charged particle transport : Drift, Diffusion, convection

Energy and mass transport

plasma/surface Interaction

Energy and mass transfer

EEDF, $<\varepsilon_e>$

VDF, T_v

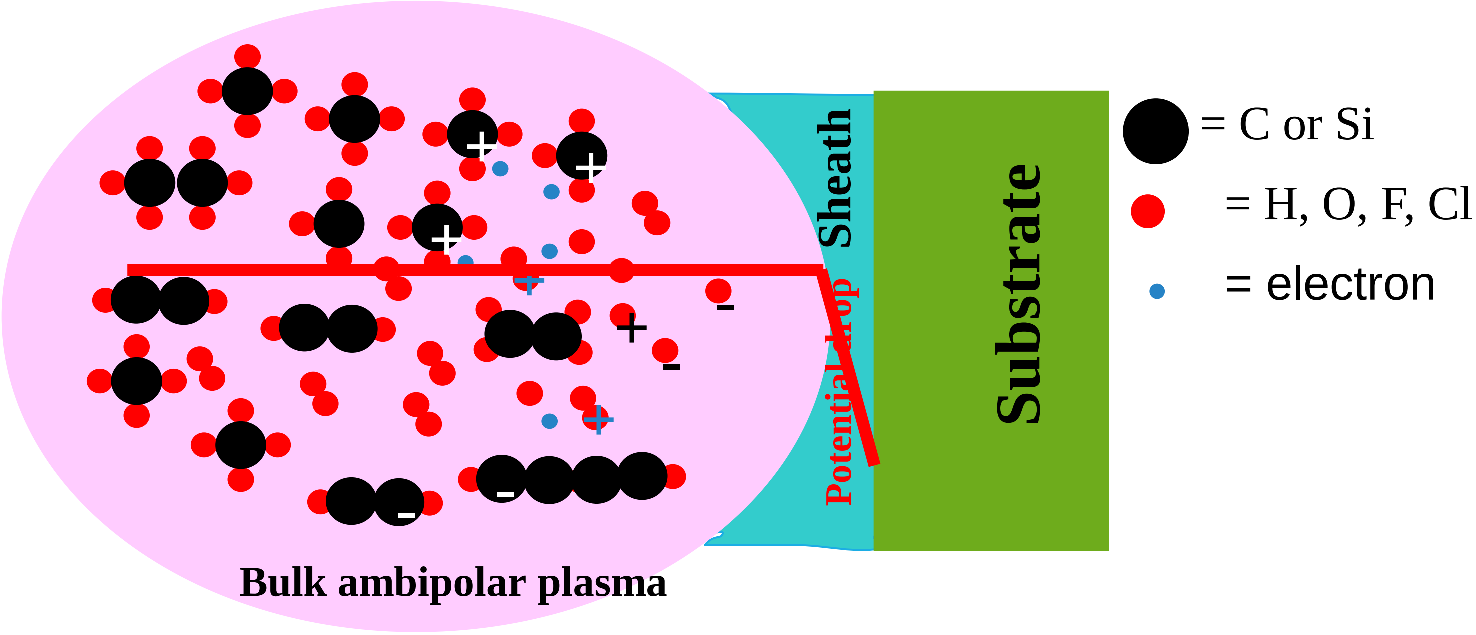
T_g

n_i, i=1-n

Substrate (T_s, c_s)

Few words on laboratory plasmas:
different types of chemical species and practical interest

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.

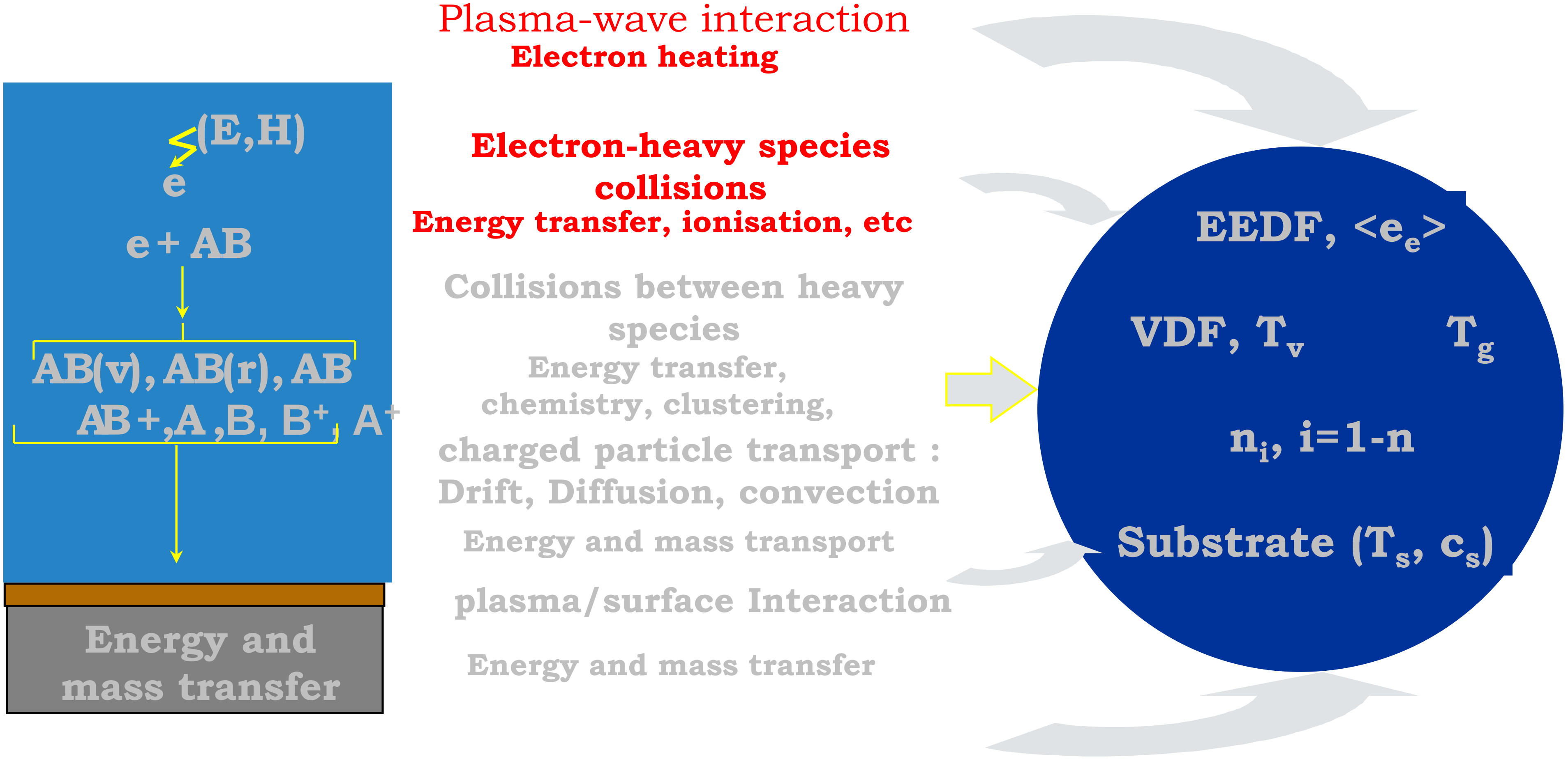
➔ Nucleation and growth of solid particles

Plasma processes

- Surface treatment
- Material deposition
- Chemical synthesis/decomposition
- Particle/nanostructure nucleation
- Active species/photons /fast particles sources

Few words on Laboratory plasmas

Phenomenological description



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T_g

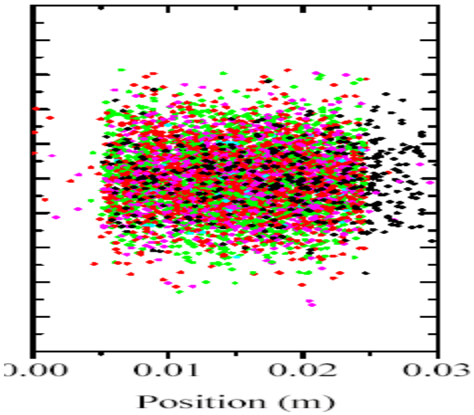
n_i, i=1-n

Substrate (T_s, c_s)

Electrons are the drivers for the plasma reactivity ➔ Electron kinetics

Electron probability density function

Electrons occupy different positions and show different velocity values



Probability Density Function in phase space : $f_e(v_e,r_e)$

$f_e(v_e,r_e)dv_edr_e$: number of electrons at positions in the position range $r_e \pm \frac{dr_e}{2}$ with velocity-values in the range $v_e \pm \frac{dv_e}{2}$

Local electron density

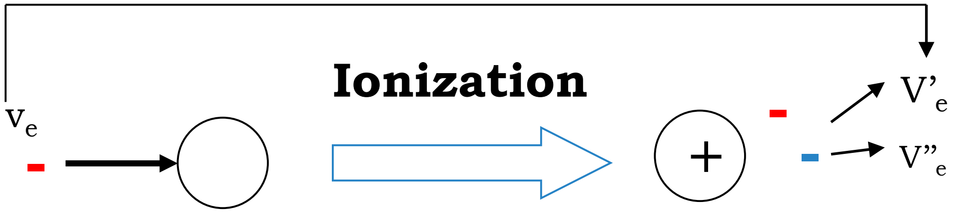
$$n_e(r_e) = \int_{v_e} \frac{d^2N_e}{dr_e} = \int_{v_e} f_e(v_e,r_e)dv_e$$

Electron states in a plasma : **electric field** , **collisions**, **transport/boundaries**

$$\frac{\partial f_e}{\partial t} + \underline{\vec{v}_e \cdot \vec{\nabla} f_e} - \underline{\frac{e}{m_e} \vec{E} \cdot \vec{\nabla}_v f_e} = \underline{C(f_e)}$$

Collision frequency and rate constant

e-HS Collisions : Local and instantaneous



Collision frequency for 1 e$^-$ in s^{-1} : $\nu_c(v_e) = \sigma_c(v_e) v_e n_{HS}$

A collision is characterized by an integral collision cross section $\sigma_c(v_e)$ in cm

For the whole electron population the collision frequency per unit volume s^{-1}cm^{-3}:

$$\boxed{\overline{\nu}_c = \int_{ve} f(v_e)dv_e v_e \sigma_e n_{tot} = k_c n_e n_{tot}}$$

Also define the rate constant

$$\boxed{k_c = \frac{\int_{ve} f(v_e)dv_e v_e \sigma_e}{\int_{ve} f(v_e)dv_e}}$$

$$\int_{v_e} f(v_e)dv_e = n_e$$

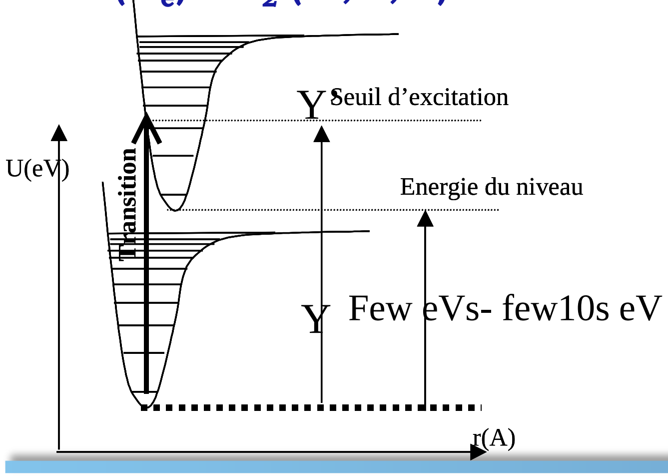
Different types of Electron/heavy species Collisions

Elastic: => e-HS Momentum and kinetic energy transfer (electron current and direct gas heating): **$e^-(v_e)$ + $A_2(v_{HS})$ => $e^-(v'_e)$ + A_2 (v'_{HS})** **Total kinetic energy (e+HS) conserved**

Inelastic non-reactive => **Excitation/de-excitation of the electronic, vibrational or rotational modes and electron cooling(superelastic)**

Electronic excitation
$e^-(v_e)$ + $A_2(Y,v,J)$

$e^-(v'_e)$ + A_2 (Y',v',J')

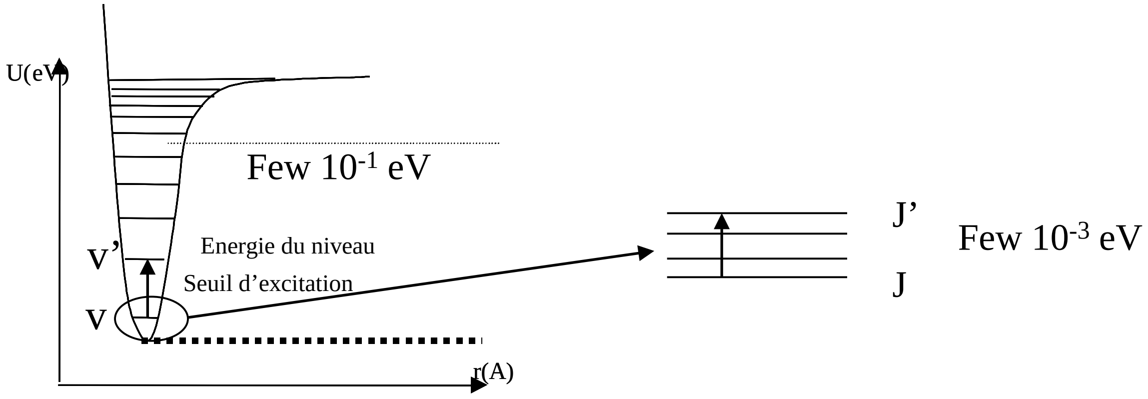


Vibrational excitation
$e^-(v_e)$ + $A_2(Y,v,J)$

$e^-(v'_e)$ + A_2 (Y,v',J')

Rotational excitation
$e^-(v_e)$ + $A_2(Y,v,J)$

$e^-(v'_e)$ + A_2 (Y,v,J')



Different types of Electron/heavy species Collisions

Reactive inelastic ➔ **Ionization, dissociation, dissociative attachment**

$e^-(v_e) + A_2(Y,v,J) \rightarrow [A_2(Y^{diss},v',J')] \rightarrow e^-(v'_e) + 2A$

$e^-(v_e) + A_2(Y,v,J) \rightarrow e^-(v'_e) + e^-(v''_e) + A_2^+(Y',v',j')$

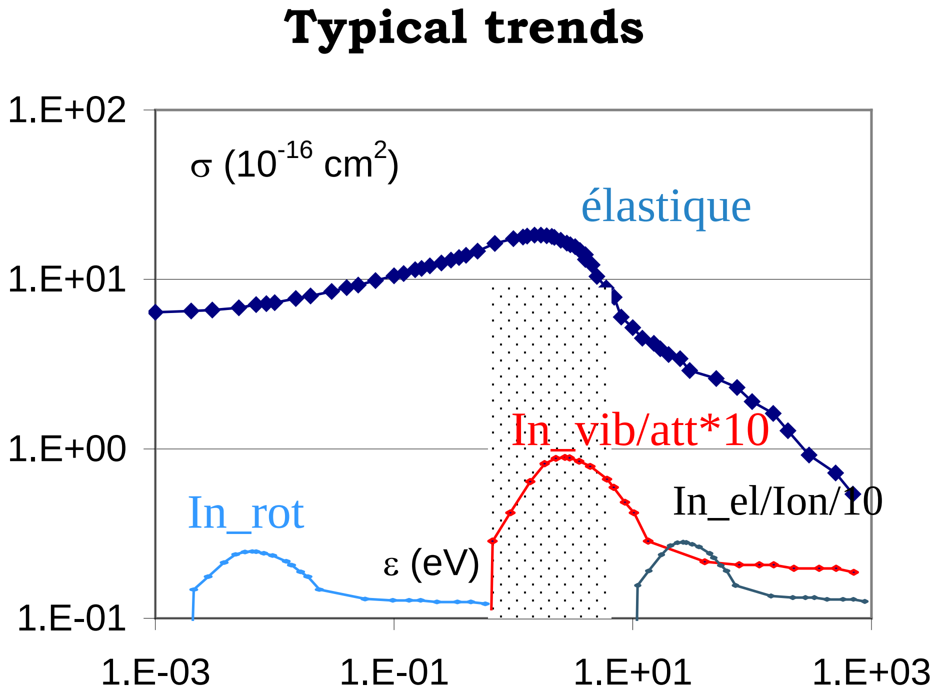
$e^-(v_e) + A_2(Y,v,J) \rightarrow [A_2^+(Y^{diss},v',j')] \rightarrow e^-(v'_e) + e^-(v''_e) + A + A^+$

$e^-(v_e) + A_2(Y,v,J) \Rightarrow A + A^-$

Super-elastic **(inelastic reverse process) ➔ internal mode de-excitation and electron heating)**

$e^-(v_e) + A_2(Y',v',J') \Rightarrow e^-(v'_e) + A_2\ (Y,v,J)$

Cross section trends, collision frequency and energy transfer rate


Typical trends

Collision frequency

$$\nu_c(v_e) = \sigma_c(v_e) v_e n_{HS}$$

Elastic >> In_vib ≥ Ine_other

Energy transfer rate:

Elastic : $\nu_{E-el}(v_e) \propto \sigma_c(v_e) v_e n_{HS} \frac{m_e}{m_{HS}} \varepsilon_e$

Inelastic: $\nu_{E-In}(v_e) \propto \sigma_c(v_e) v_e n_{HS} \varepsilon_{th}$

In_vib >=< Ine_other >> El

E-HS rate constant and electron PDF

Major questions when investigating reactive non equilibrium plasmas for a population of electrons :

1/ What are the rates of the primary e-HS collisions that sustain the plasma and generate the primary active species ? → **Chemistry**

$$r_{e-HS} = k_{e-HS} n_e n_{HS}$$

2/ What are the rates and the main channels for electron energy dissipation in the gas (self-consistent model) → **Electron energy dissipation**

$$r^{e}_{e-HS} = k_{e-HS} n_e n_{HS} \varepsilon_{th}$$

? ?

$$k_{e-HS}(r_e) = \int_{v_e} f(r_e, v_e)\sigma_{e-HS}(v_e) v_e dv_e$$

$$\int_{v_e} f(r_e, v_e) dv_e = 1$$

→ **Boltzmann equation**

$$\frac{\partial f_e}{\partial t} + \vec{v}_e.\vec{\nabla} f_e - \frac{e}{m_e}\vec{E}.\vec{\nabla}_{v_e} f_e = C(f_e)$$

Electron PDF and solution of the BE

- Three major practical situations :

1- No assumption : Solve the Boltzmann in the full phase space. Suitable for low density plasma, i.e., $n_e<10^{12}$-10^{13} cm^{-3} – no electron-electron collisions. Necessary when non local and anomalous effects (anisotropy, fluctuation, beam-like, etc.) are important : sheaths, magnetized plasmas, etc

2- Assume that the PDF is local (2a) and isotropic(2b) : develop the PDF as a LC of spherical harmonic functions and keep either only the isotropic component (classical/old) or the isotropic + the first anisotropy (newer see Hageaar and Pitchford PSST) : suitable for most of the reactive plasmas.

3- Assume a local Maxwellian PDF suitable for large density-low pressure plasmas (enhanced electron-electron collisions ➔ Maxwell distribution)

$$f_e(v_e) = \left(\frac{m_e}{2\pi k T_e}\right)^{\frac{3}{2}} exp\left(-\frac{m_e v_e^2}{2kT_e}\right)$$

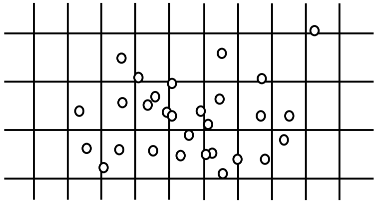
Illustration case 1 : statistical particle simulation
Electron dynamics and Particle In Cell simulation

First : charged particles (electrons) dynamics (Particle In Cell, no collisions)

Work with N *super-particles*

$$N_{s,réel} = \alpha_s . N_{s,num}$$

Distributed on a space grid



$\Delta x \leq 0{,}3\lambda_D$

Space-resolve the sheaths

For each superparticles

Time-integrate momentum equations on Δt

$$v(t+\Delta t) = v(t) + \int_{\Delta t} \frac{ez}{m} E dt$$

$$x(t+\Delta t) = x(t) + \int_{\Delta t} v dt$$

$$\Delta t \leq \frac{\Delta x}{v_{\max}}$$

For each plasma cell Compute the charge density

$$\rho_j = \frac{1}{V_c} \sum_v \lambda_v Q_v$$

Compute the selfconsistent EM field

Maxwell or Poisson's

Interpolation on superparticle positions

Illustration case 1: statistical particle simulation e-HS collisions and Monte Carlo approach

Nc collisions characterized by : $s_c(e)$ + a 'nulle' collission such : $$\boxed{\nu_{tot}(\varepsilon) = N \sum_{collisions} \sigma_c v(\varepsilon) = cste}$$

⇨ Time of flight $$\boxed{f(t) = \nu_{tot}\exp(-\nu_{tot}t)}$$

⇩

$$\boxed{t_c = -\frac{1}{\nu_{tot}}\ln\eta}$$

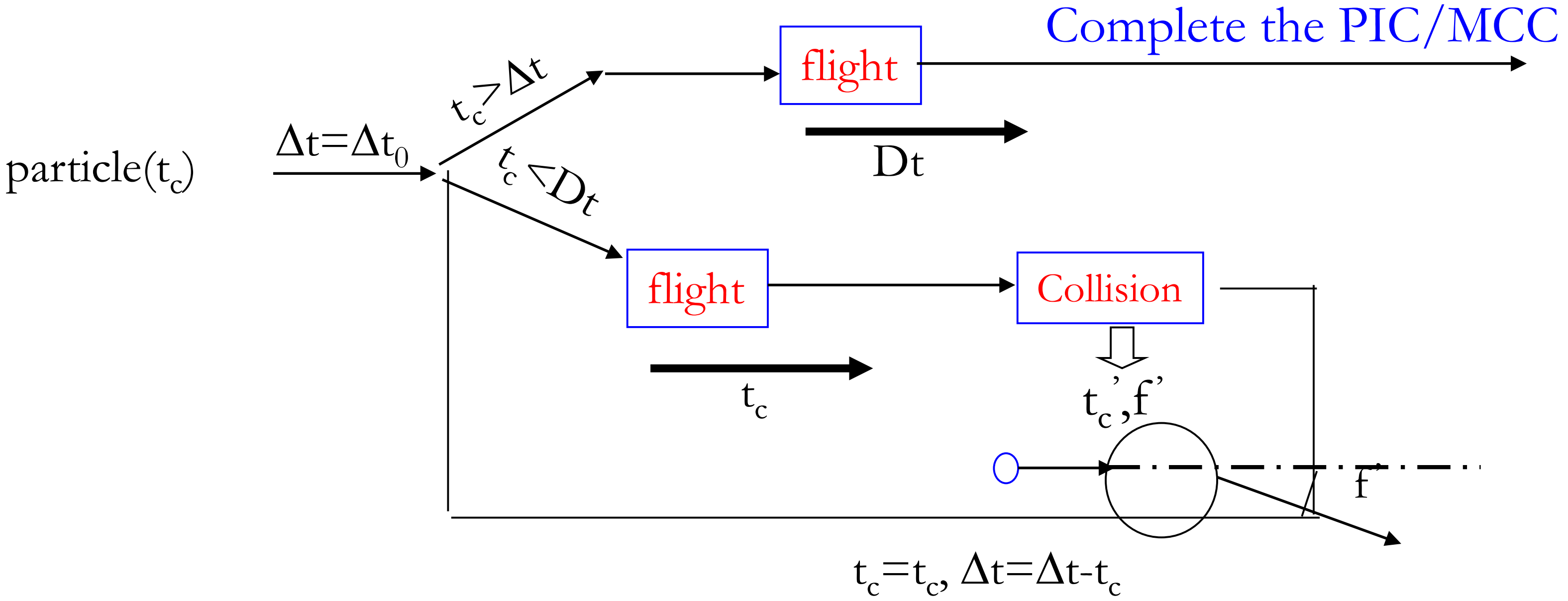
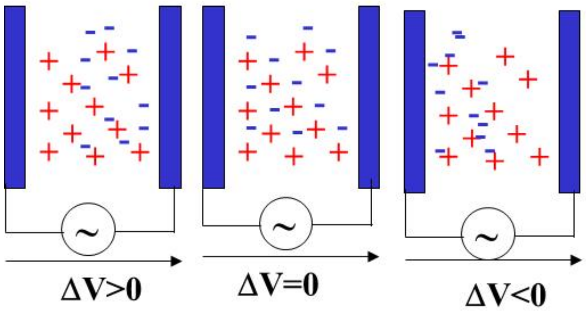
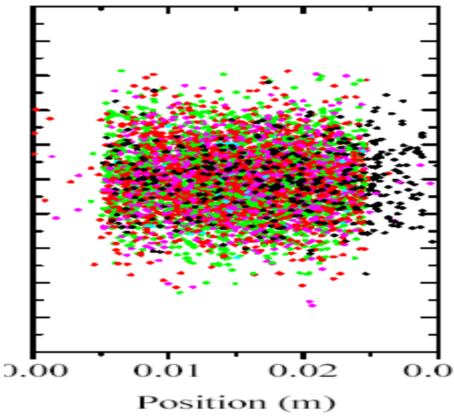
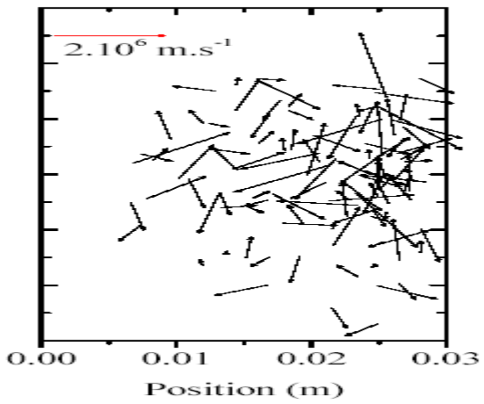


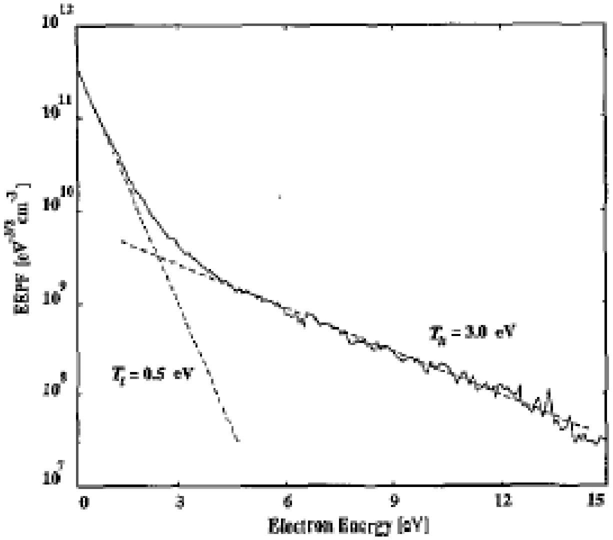
Illustration case 1: Capacitively coupled RF discharge in N_2

N_2
0.1 torr
V_{RF}=100 V
Gap=3 cm









Stochastic heating at the sheath edge

➔ **Bi-Maxwellian EEDF**

➔ Large temperature 3 eV for high energy electrons

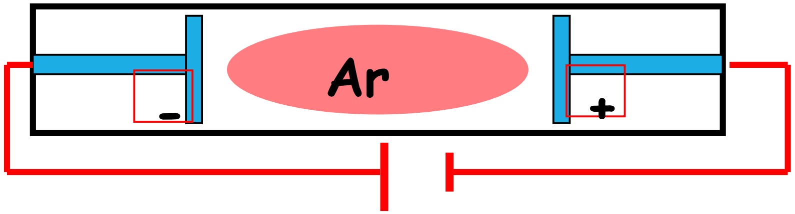
➔ Low temperature, 0.5 eV, for low energy electrons

$k_{n\text{-}max}/k_{max}>10^2$

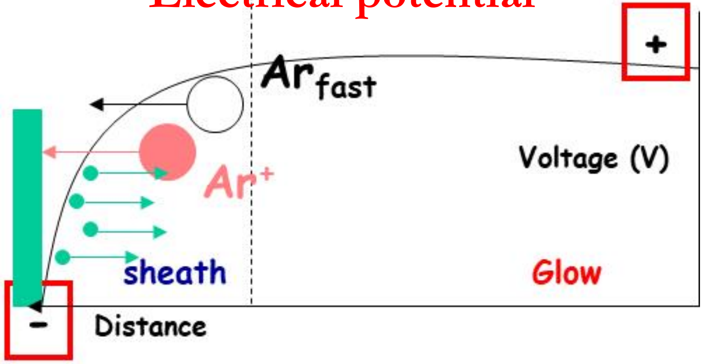
S. Longo, K. Hassouni, D. Iasillo and M. Capitelli, J. Phys. III, Fr, **7** (1997) 707-718 DOI: 10.1051/jp3:1997133
S. Longo, M. Capitelli and K. Hassouni, . *Phys. IV France **07** (1997) C4-271-C4-281*DOI: 10.1051/jp4:1997422

Illustration case 1 : electron kinetics in argon DC discharge (Monte Carlo)

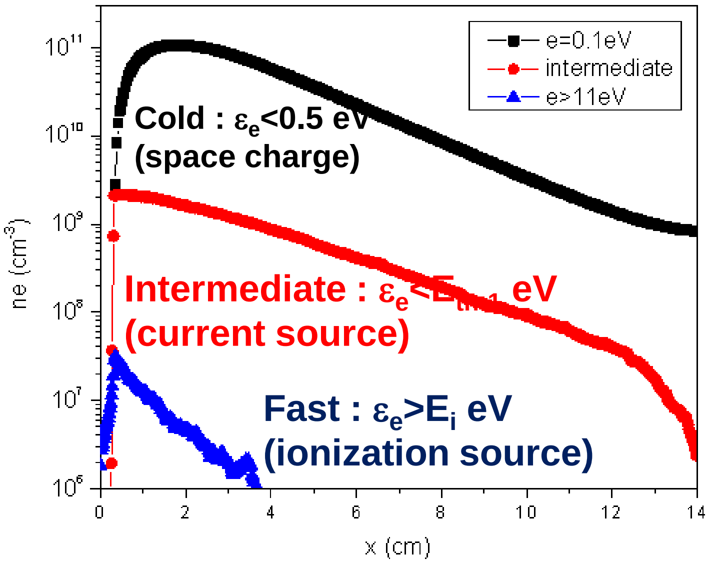
DC discharge

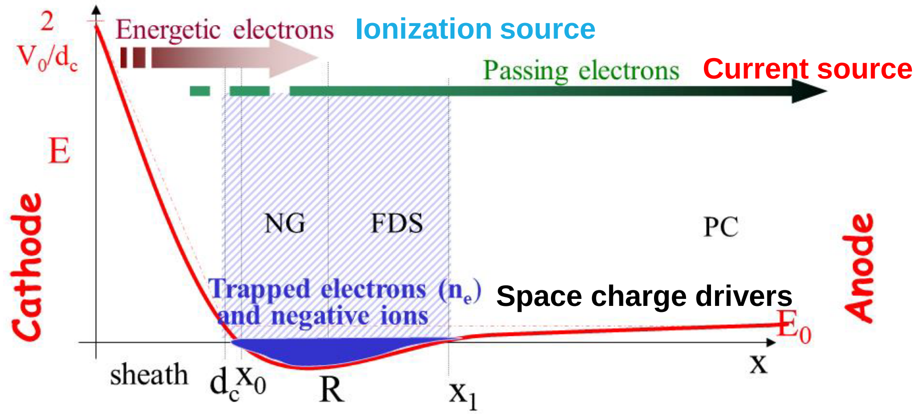


Electrical potential



Three electron populations





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

A. Michau et al. Plasma Chem. And Plasma Proc., **32**, 451-470(2012). Doi : 10.1007/s11090-012-9357-0

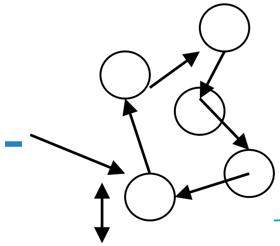
A. Michau et al. PSST, **25**, (2016), paper# 015019(16 pp) doi:10.1088/0963-0252/25/1/015019PI

Illustration case 2 : electron kinetics in moderate pressure H_2/CH_4 plasmas

Plasmas dominated by collisions and fulfilling:

- **Locality** : $\vec{v}_e \cdot \vec{\nabla} f_e$ negligible
- **Isotropy** : $v_x \Leftrightarrow v_y \Leftrightarrow v_z$ ➔ $f(v_e)=F(e_e)$

Collisions induce isotropic velocity distrbution



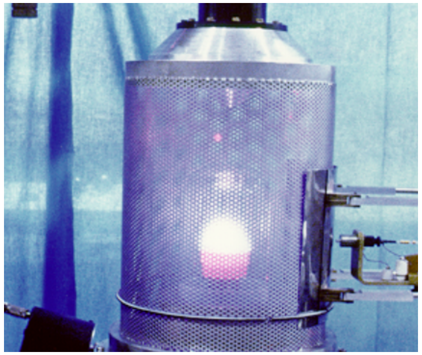
Simplification

The pdf, f_e, is approximated by the isotropic component, F_e, in its spherical harmonic expansion

$$\frac{\partial f_e}{\partial t} + \cancel{\vec{v}_e \cdot \vec{\nabla} f_e} - \frac{e}{m_e}\vec{E}\cdot\vec{\nabla}_v f_e = C(f_e)$$

Much simpler BE

$$\boxed{\frac{\partial F_e}{\partial t} + \frac{\partial}{\partial \varepsilon_e} J_E + \frac{\partial}{\partial \varepsilon_e} J_{el} = In(F_e) + Sup(F_e)}$$



What about electric-field modulation ($E=E_0\cos(\omega_{HF} t)$?

=>electron may follow the field depending on ν_{e-ex}/ω_{HF} => 2 options

1- Low pressure case : $\frac{m_e}{m}\nu_{el} + \nu_{in} \ll \omega_{HF}$ ➔ stationary situation

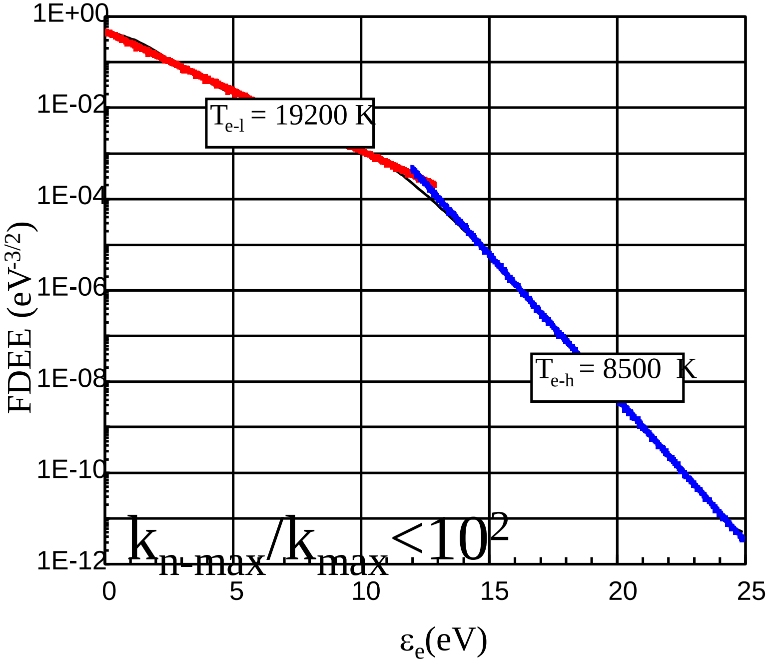
➔ Use the effective field assumption

$$\boxed{E_{eff} = \frac{E_0}{\sqrt{2}} \frac{\nu_m^e}{\left({\nu_m^e}^2 + \omega^2\right)^{1/2}}}$$

2- high pressure case : $\frac{m_e}{m}\nu_{el} + \nu_{in} \gg \omega_{HF}$ ➔non-stationary situation for electrons ➔ time-integrate the BE

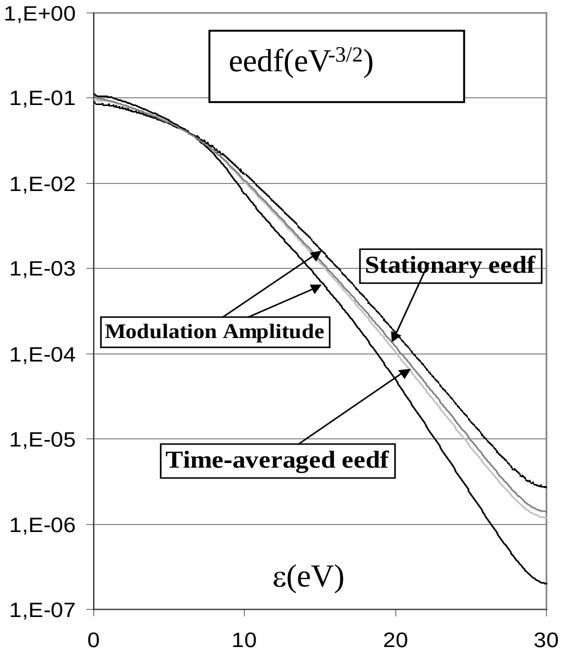
EEDF behavior in collisional high frequency plasmas

Bimodal stationary distribution

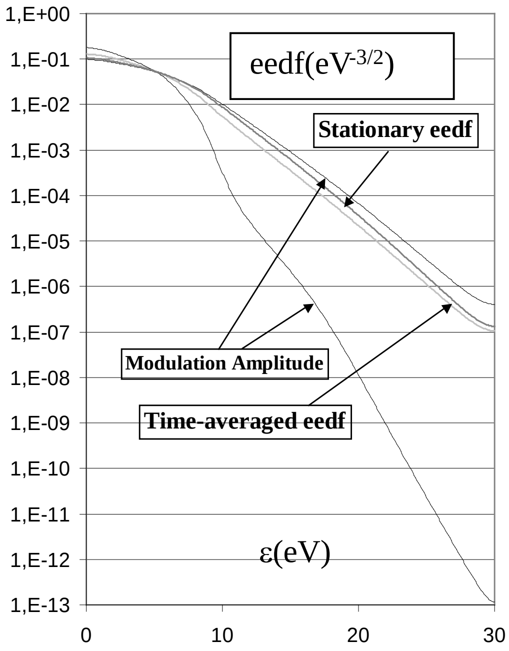


Impact of the effective field assumption

Low pressure case



High pressure case



EEDF Bimodal Te-h = f(Te-l) (univoque)
Energy balance ➔ Te-l

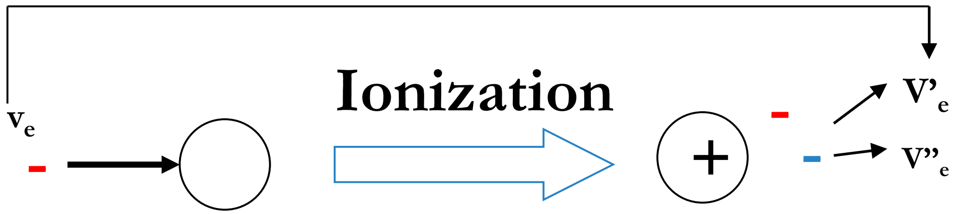
Effective field assumption and non stationary model give almost the same result

K. Hassouni et al. PSST **8**(1999), 494-512
K. Hassouni et al. Surf. Coat. Technol. **97**(1-3), 391-403 (1997)
M. Capitelli et al. Plasma Chem. And Plasma Proc. **16**, pages 153–171 (1996)

M. Capitelli et al. Phys. Rev. E **1843 (1996)**
W. Morscheidt et al. Plasma Chem. Plasma Proc. **23**, 117-140, (2003) doi: 10.1023/A:1022472904111

Discharge maintenance : Ionization kinetics

In principle : the most straightforward mechanism ➔ direct ionization :



$$e_h^- + A \rightarrow A^+ + e_{h-th}^- + e_c^-$$

But less straightforward mechanism may exist : multi-step

- Penning

$$e_h^- + A \rightarrow A^{(**)} + e_{h-th}^-$$

$$A^{(**)} + B \rightarrow A^{(*)} + B^+ + e^-$$

- step-wise

$$e_h^- + A \rightarrow A^{(*)} + e_{h-th}^-$$

$$e^- + A^{(*)} \rightarrow A^+ + 2e^-$$

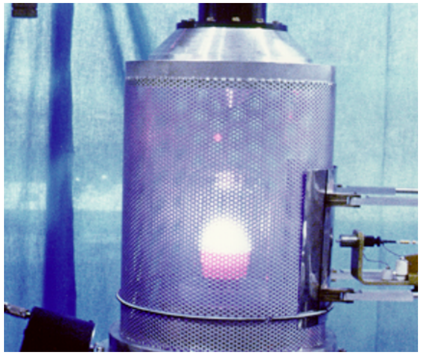
Stepwise and Penning mechanism illustration : The coupling between electronic and ionization kinetics in H_2 plasmas

Chemical species : H_2 and H

Direct Ionization : $e^- + H_2 \rightarrow H_2^+ + 2e^-$ ***and*** $e^- + H \rightarrow H^+ + 2e^-$

Closer look

H$_2$ Microwave plasmas
Microwave cavity coupling
Pressure : few tens of mbars



- Electronic excitation of : H_2 and H

- $e^- + H_2 ==> e^- + H_2^*$
- $e^- + H(n) ==> e^- + H(m)$

- Stepwise ionization involving electronically excited states

- $e^- + H_2 = [H_2^{**}]=> H_2^+ + 2e^-$
- $e^- + H(n) ==> 2e^- + H^+$

- Penning ionization through H-atom excited state :

- $H(n) + H_2 ==> [H_3^+ + e^-]$ ou [3H]

- Need to look at collisional and radiative relaxation processes

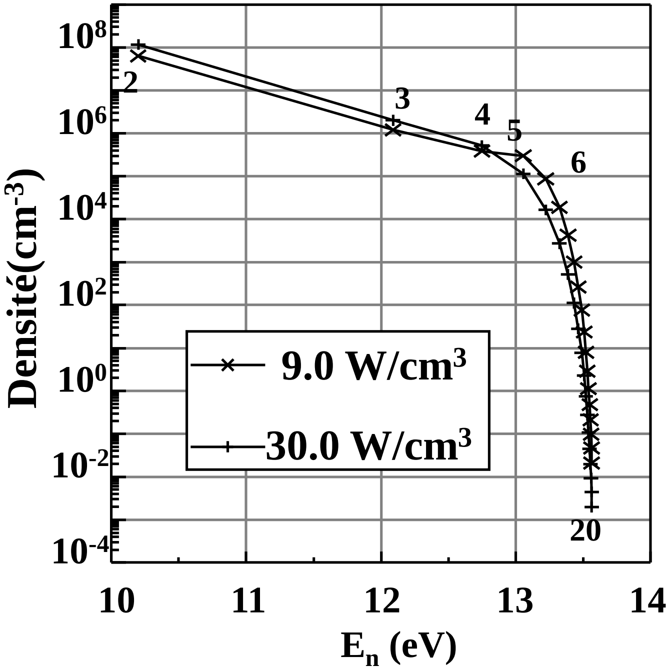
- H_2^* (+ M) ==> H_2^{**} or 2H (+M)
- H(n) + H ==> H(m) + H
- M* ==> M*' + hν (M=H or H_2)

K. Hassouni et al. PSST **8**(1999), 494-512
K. Hassouni et al. Surf. Coat. Technol. **97**(1-3), 391-403 (1997)

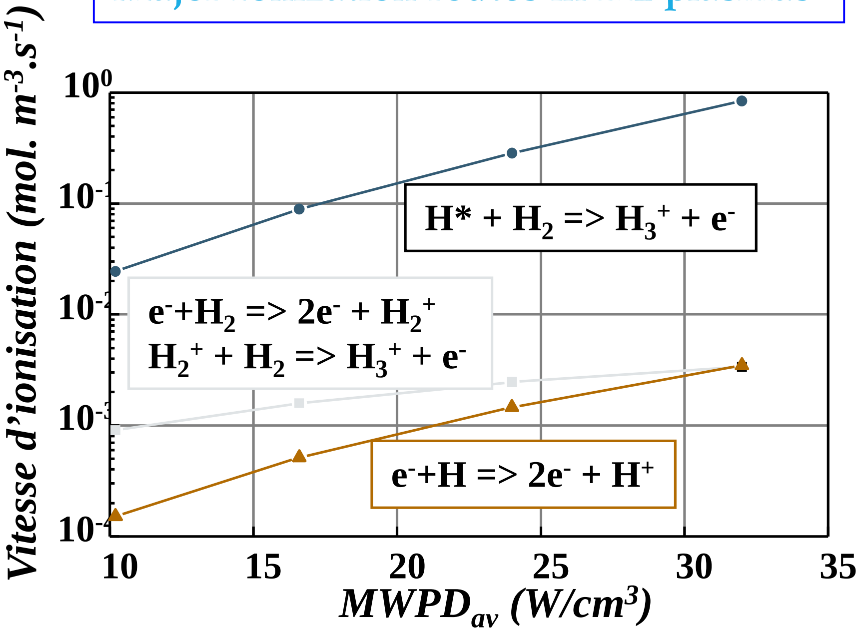
Stepwise and Penning mechanisms illustration : The coupling between electronic and ionization kinetics in H_2 plasmas

Prime importance ➔ ionization kinetics sustains the discharge

Electronically excited state distribution for H-atom



Major Ionization routes in H2 plasmas

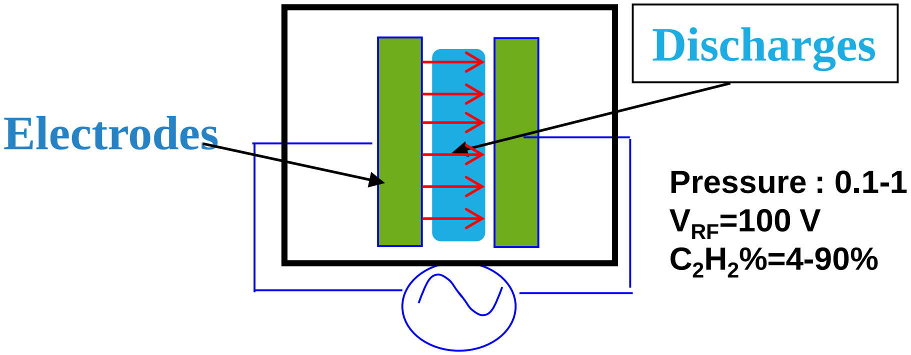


K. Hassouni et al. PSST **8**(1999), 494-512

Ionization is mainly governed by H(n=2-3) quenching

K. Hassouni et al. PSST **8**(1999), 494-512
K. Hassouni et al. Surf. Coat. Technol. **97**(1-3), 391-403 (1997)

Penning vs stepwise vs direct ionization mechanisms : the example of CCRF Ar/C_2H_2



Pressure : 0.1-1 mbar
V_{RF}=100 V
C_2H_2%=4-90%

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

Ionization routes

1- Direct on Argon :

$$e^- + Ar \rightarrow Ar^+ + 2e^- - 15\ eV$$

2- Stepwise on argon and Penning on C_2H_2

2-1. excitation of argon metastable

$$e^- + Ar \rightarrow Ar^* + e^- - 11\ eV$$

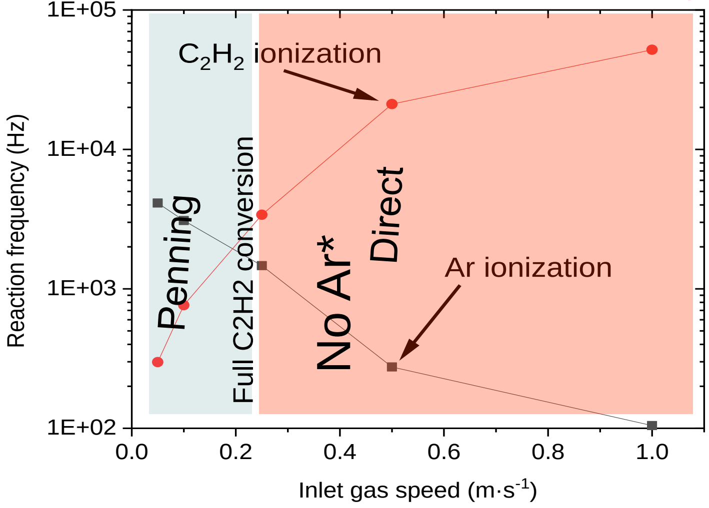
2-2-a- Ionization of Ar*

$$e^- + Ar^* \rightarrow Ar^+ + 2e^- - 4\ eV$$

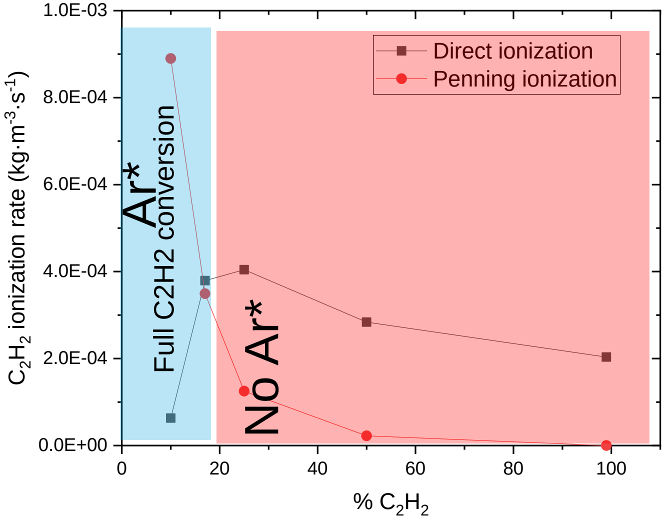
2-2-b- Collisional quenching of Ar by C_2H_2*

$$C_2H_2 + Ar^* \rightarrow {C_2H_2}^+ + Ar + e^-$$

Ionization rate vs inlet flow velocity



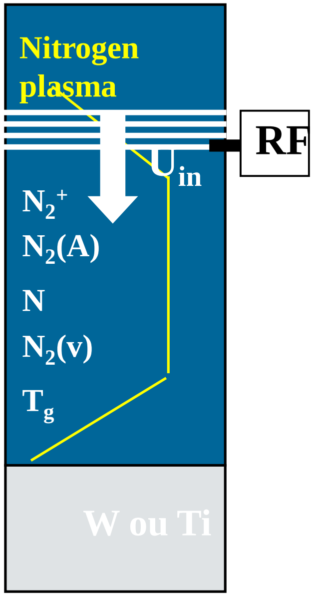
Ionization rate vs acetylene content



Ar* populated
➔ Penning >> direct

G. Tetard et al. PSST (2021), **30,** paper# 105015(22 pp) doi 10.1088/1361-6595/ac2a17

Primary activation processes : the coupling between molecular dissociation and vibrational kinetics in N_2 plasmas



What’s the main dissociation mechanism in the plasma bulk :

$N_2 + e^- + \Rightarrow 2N$? OR $N_2 + e^- \Rightarrow N_2(v=1\text{-}45) \Rightarrow N$?

How much N at the discharge exit ?

Plug flow model

$$\frac{dn_s}{dt} - W_s = 0 \qquad z = U_{in} t$$

T_g = cste ; Maxwellian eedf et T_e =cste

e-v excitation processes

$e^- + N_2(v) \Leftrightarrow e^- + N_2(w)$

Resonant v-v relaxation processes

$N_2(w) + N_2(v) \Leftrightarrow N_2(v-1) + N_2(w+1)$

V-t de-excitation process

$M + N_2(v) \Leftrightarrow M + N_2(v-1)$

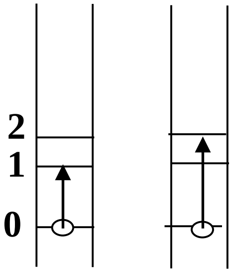
dissociation

$M + N_2(v_{\text{élevé}}) \Leftrightarrow M + 2N$

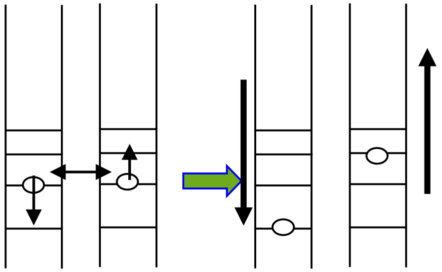
$N_2(v_{\text{élevé}}) + N_2(v) \Leftrightarrow N_2(v-1) + 2N$

K. Hassouni et al. Computer and Chem. Eng. (1993), **17**(Supp. 1), S505-S510
S. Longo et al. , J. Phys. III, Fr, **7** (1997) 707-718 DOI: 10.1051/jp3:1997133
S. Longo et al. . *Phys. IV France **07** (1997) C4-271-C4-281*DOI: 10.1051/jp4:1997422

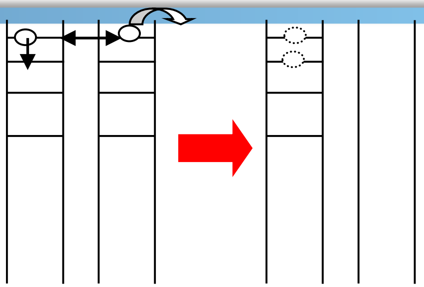
Primary activation processes : the coupling between molecular dissociation and vibrational kinetics in N_2 plasmas



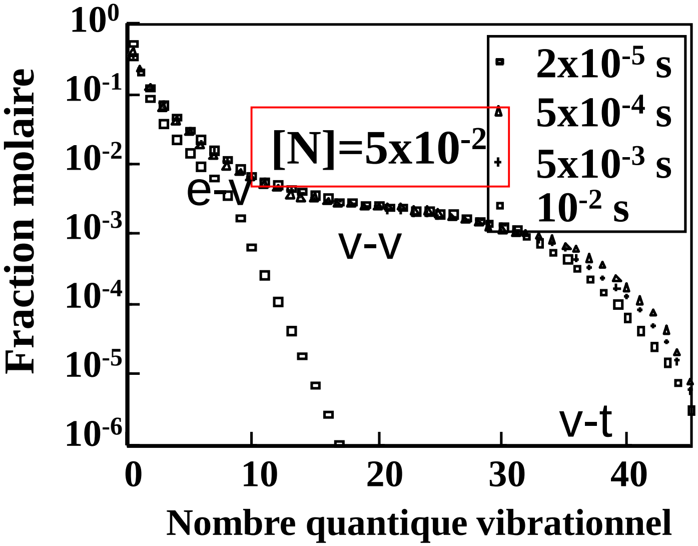
$e^- + N_2(v=0) \Rightarrow e^- + N_2(v=1\text{-}4)$
pompage sur les bas niveaux

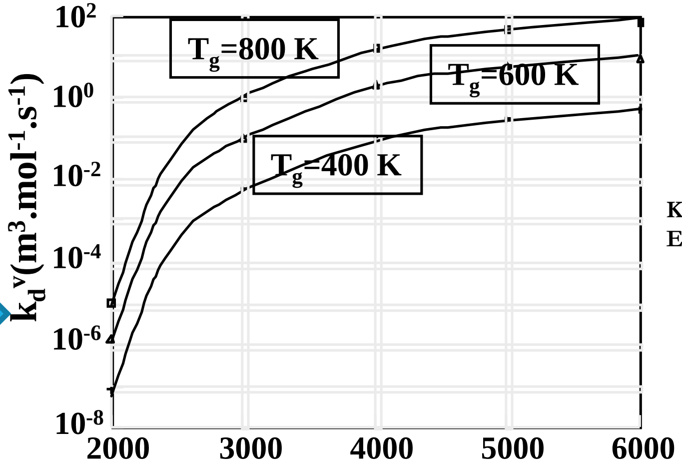


$N_2(v) + N_2(w) \Rightarrow N_2(v-1) + N_2(w+1)$
Montée dans l 'échelle vibrationnelle



$N_2(vl) + N_2(v)$ (ou M) $\Rightarrow 2N + N_2(v-1)$ (ou M)
Dissociation du dernier niveau par collision avec un lourd

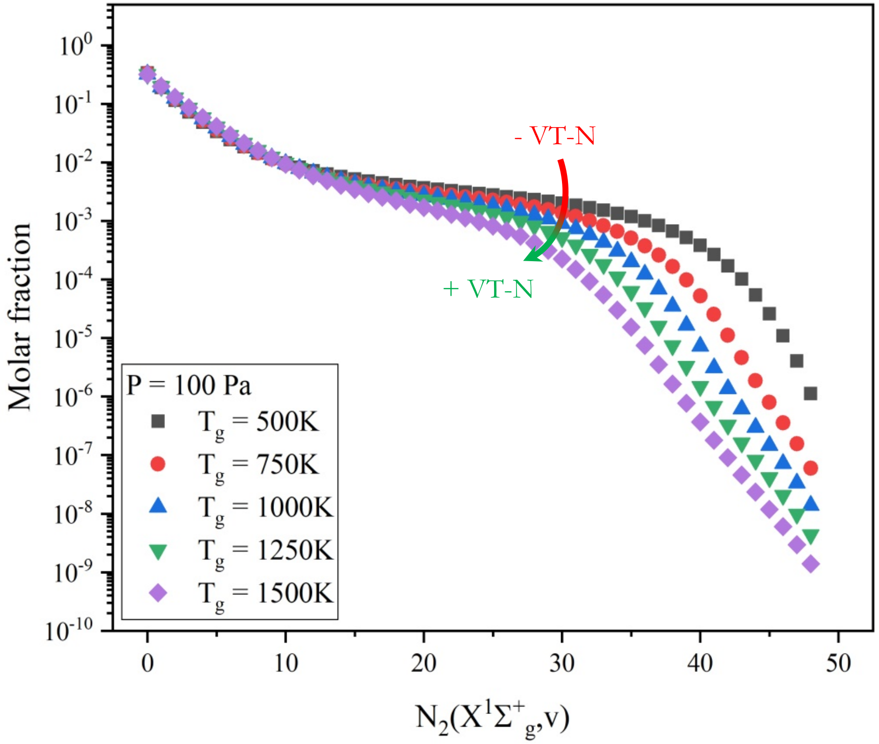




K. Hassouni et al. Computer and Chem. Eng. (1993), 17(Supp. 1), S505-S510

$(n_e\ T_e)$ ➔ T_v THEN (T_vT_g) ➔ dissociation kinetics : $2N_2 \Rightarrow 2N + N_2$ $[k_d^v = f(T_v, T_g)]$

Self-limiting effects for the vibrational dissociation mechanism in N_2 plasmas



Maxwellian	Non-Maxwellian
Low plateau	Large plateau
VT-N processes	VV relaxation

Self-limiting mechanism of N-atoms to molecular dissociation via v-D mechanism

How to enhance N-atom production?

VT-N:

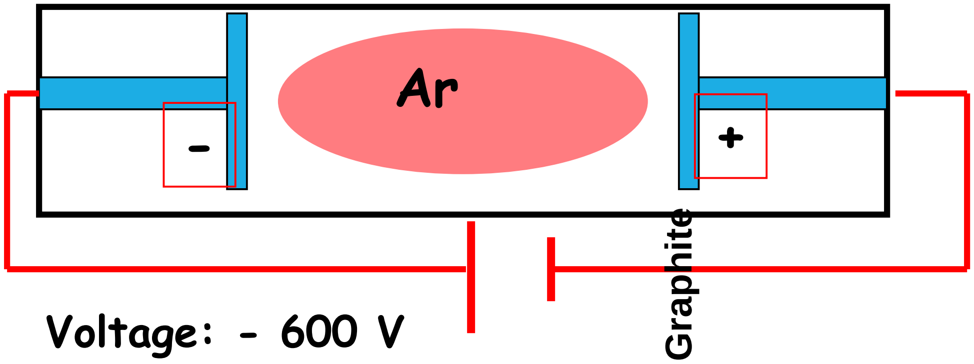
$$N_2(X^1\Sigma^+_g, v) + \bigcirc\!\!\!\!\!N \rightarrow N_2(X^1\Sigma^+_g, v \pm 1) + N$$

By pulsing the discharge!

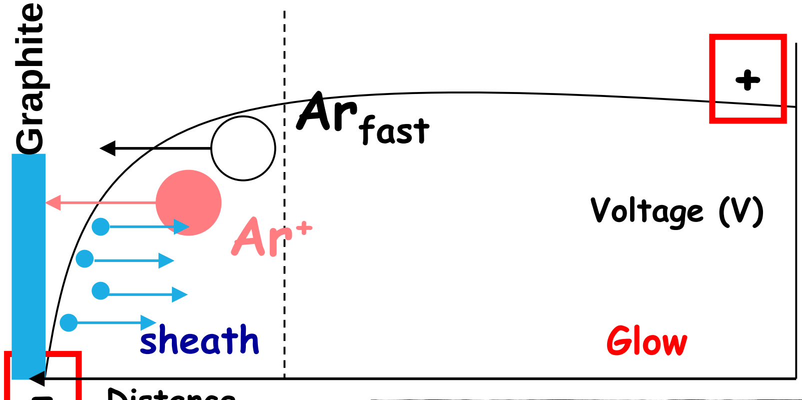
S. Prasanna et al. to be submitted to PoP

Attachment and molecular growth kinetics in non equilibrium plasmas : the case of sputtering DC discharges

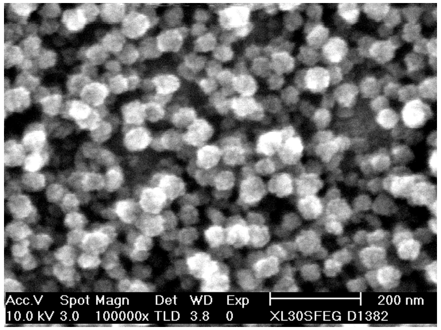
DC dicharge



Voltage: - 600 V
Gap distance: 14 cm
Electrode diameter: 5 cm
Current: 8x10^{-2} A



C. Dominique and C. Arnas,
J. Appl. Phys. (2007) 101(12),
10.1063/1.2748365



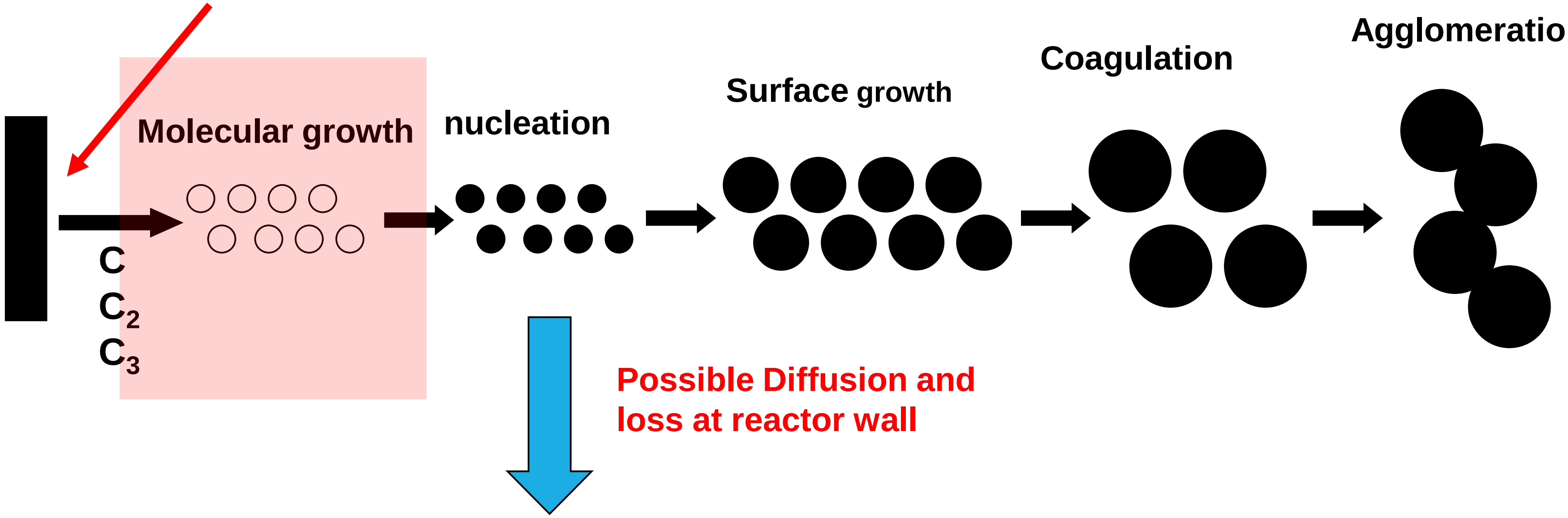
Dusts are produced by the sputtering of the graphite cathode:

- Argon ions accelerated in the sheath
- Fast neutrals resulting from charge transfer $Ar_{slow} + Ar^+ \rightarrow Ar^+ + Ar_{fast}$

What is the mechanism responsible for dust formation ?

Attachment and molecular growth kinetics in non equilibrium plasmas : the case of sputtering DC discharges

Ar^+ + Ar sputtering (Ion accelerated in the sheath – Fast neutral created from charge exchange)



Molecular growth

C

C_2

C_3

nucleation

Surface growth

Coagulation

Agglomeration

Possible Diffusion and loss at reactor wall

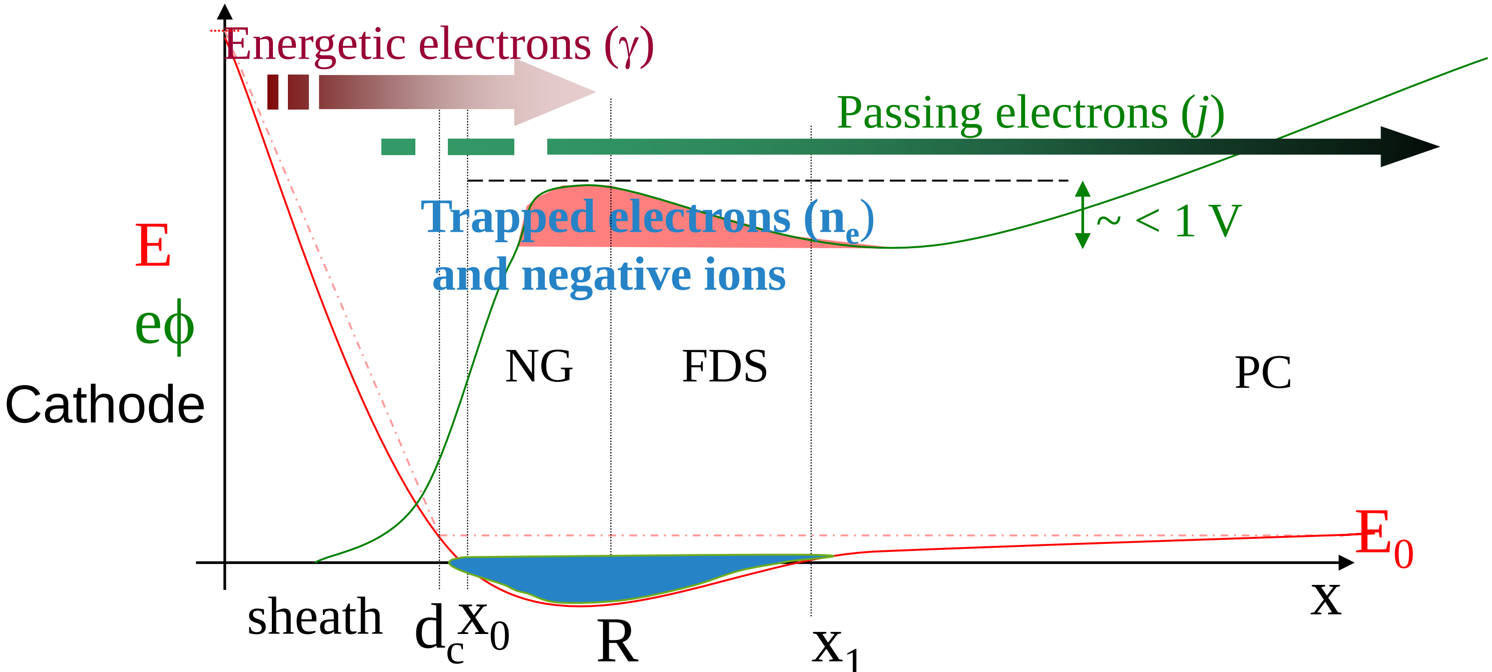
$T_{growth} \sim 100.T_{diffusion\text{-}neutral}$

➔ Neutral cannot grow

➔ charged species : electrostatic trapping ?

Attachment and molecular growth kinetics in non equilibrium plasmas : Confining effect of field reversal in DC discharges

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



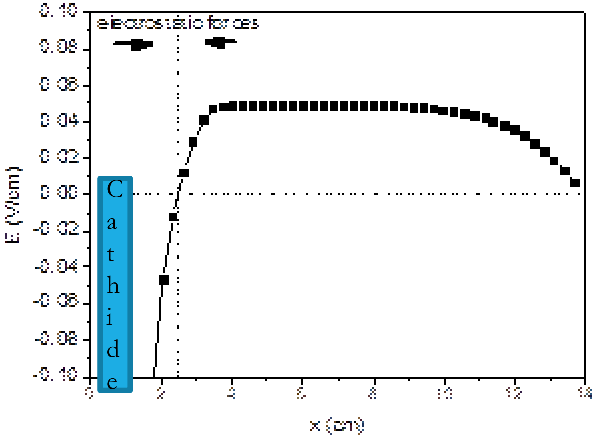
NG: Negative glow / FDS: Faraday Dark Space / PC: Positive Column

Existence of a field reversal

➔ **electrical potential structure is confining for negatively charged species**

Attachment and molecular growth kinetics in non equilibrium plasmas : field reversal and molecular growth in DC discharges

Electric field reversal



Field-reversal at 2 cm from the cathode.

➔ **Electrostatic trapping of negative species is possible**

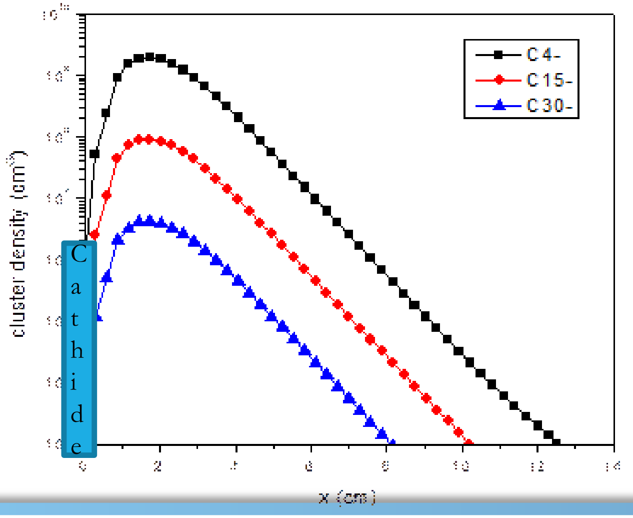
sputtered C, C_2, C_3 induce a molecular growth :

$$C_{x=1-3} + C_{x'=1-3} \rightarrow C_{x+x'}$$

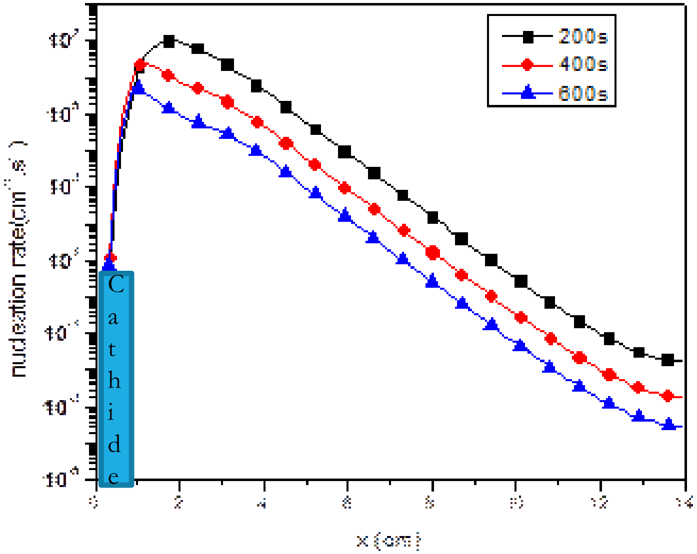
$C_n + e^- \rightarrow C_n^-\ (n \geq 4) + h\nu$ **radiative attachment**

$C_n^- + C_x \rightarrow C_{n+x}^-\ (n \geq 4)$ **growth**

Negatively charged clusters



Nucleation rate

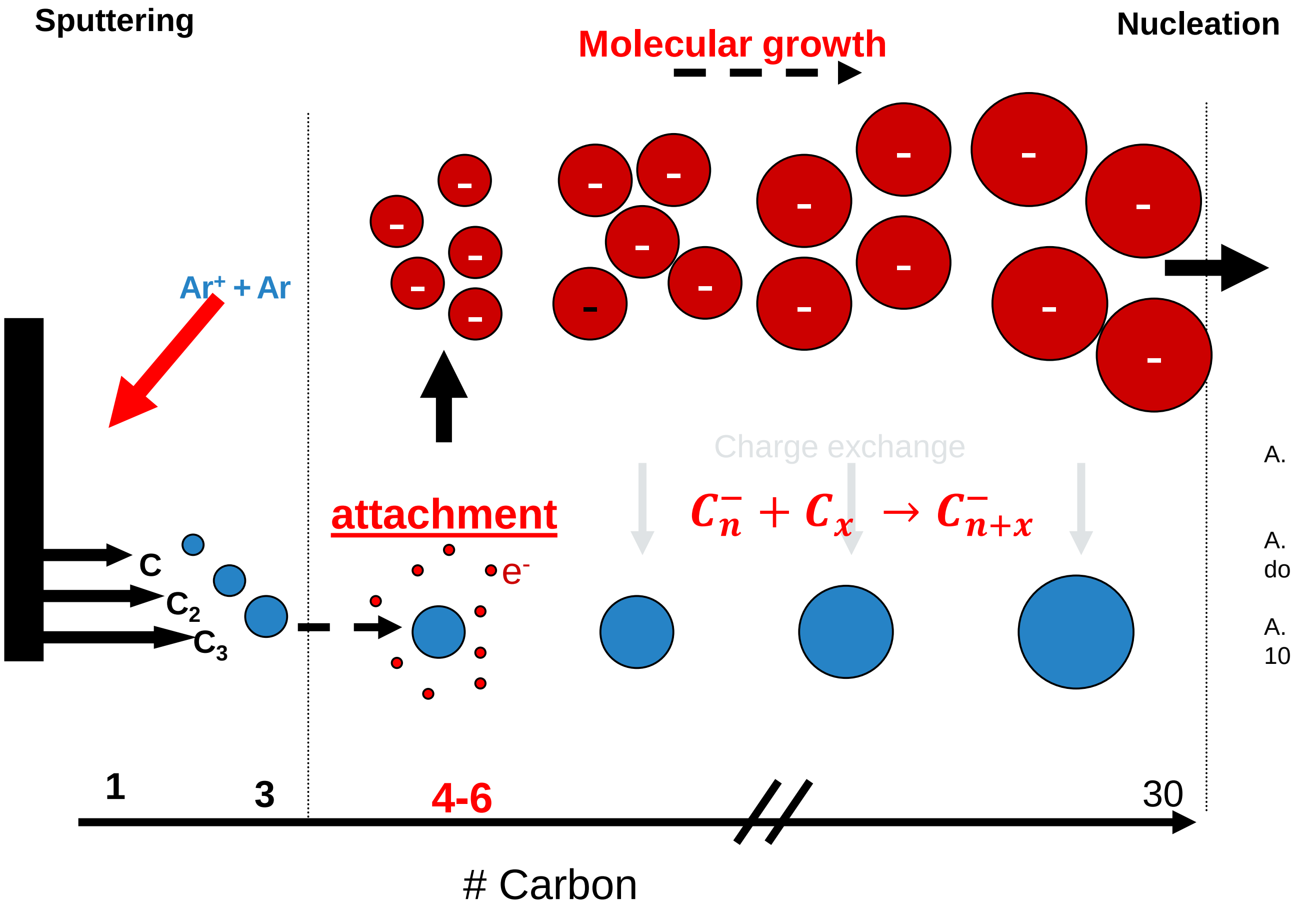


A. Michau et al. Plasma Chem. And Plasma Proc., **32**, 451-470(2012). Doi : 10.1007/s11090-012-9357-0

A. Michau et al. PSST, **25**, (2016), paper# 015019(16 pp) doi:10.1088/0963-0252/25/1/015019Pl

A. Michau et al. PSST (2010) paper „ 034023(7pp) doi 10.1088/0963-0252/19/3/034023

Attachment and molecular growth kinetics in sputtering DC discharge



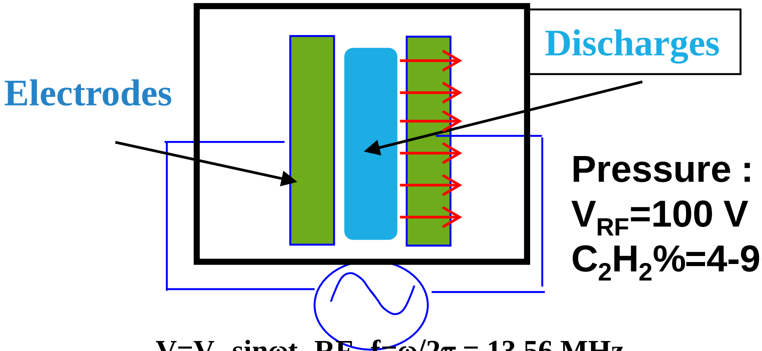
A. Michau et al. Plasma Chem. And Plasma Proc., **32**, 451-470(2012). Doi : 10.1007/s11090-012-9357-0

A. Michau et al. PSST, **25**, (2016), paper# 015019(16 pp) doi:10.1088/0963-0252/25/1/015019PI

A. Michau et al. PSST (2010) paper „ 034023(7pp) doi 10.1088/0963-0252/19/3/034023

Key-role of Field reversal and negatively charged species for molecular growth

Ionization and molecular growth kinetics in Ar/C_2H_2 CCRF plasmas



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

Pressure : 0.1-1 mbar
V_{RF}=100 V
C_2H_2%=4-90%

Dust formation is often (if not always) observed
What is the mechanism for particle nucleation ?

Answer :

- RF plasmas fluid model (G. Tetard et al. PSST (2021), **30,** paper# 105015(22 pp) doi 10.1088/1361-6595/ac2a17)

Handle large time-scale chemistry

- Growth model (from M. Mao et al., J. Phys D (2008) 225201(14 pp))

$C_2H + C_{2n}H_2 \rightarrow C_{2n+2}H_2 + H$ k~ 3.10^7 $m^3.mol^{-1}.s^{-1}$
$C_2H_2 + C_{2n}H \rightarrow C_{2n+2}H_2 + H$ k~4.10^7 $m^3.mol^{-1}.s^{-1}$

$C_2H_2 + C_{2n}H^- \rightarrow C_{2n+2}H^- + H_2$ k~6.10^5 $m^3.mol^{-1}.s^{-1}$

$C_2H_2 + C_{2n}H_y^+ \rightarrow C_{2n+2}H_y^+ + H_2$, (n>2,y=6) k~$6.10^7$ $m^3.mol^{-1}.s^{-1}$

The growth starts with

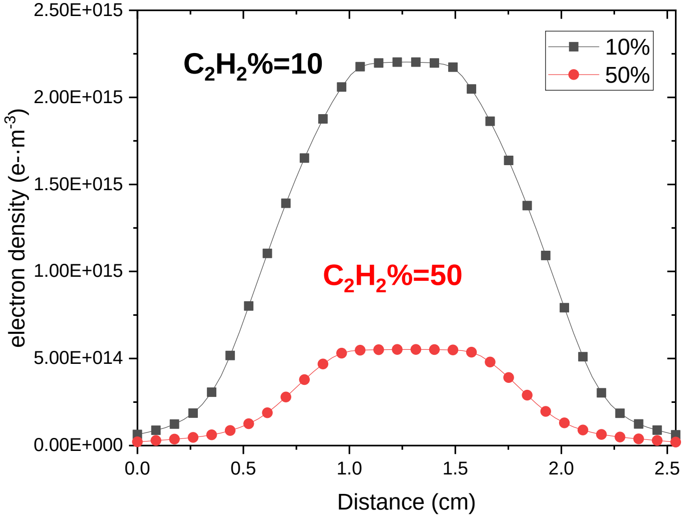
$e^- + C_2H_2 \rightarrow e^- + C_2H + H$

$e^- + C_2H_2 \rightarrow C_2H^- + H$

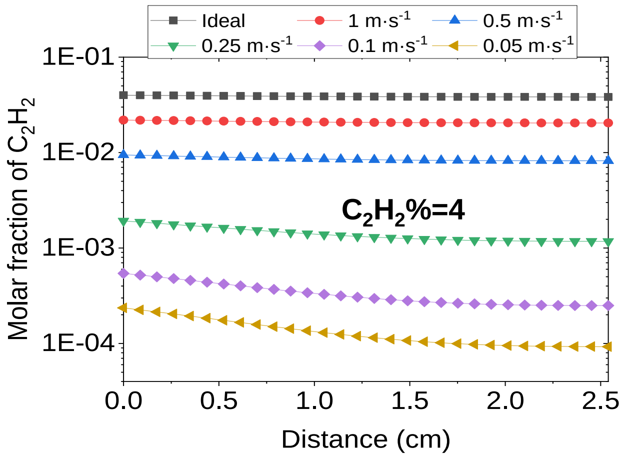
$e^- + C_2H_2 \rightarrow C_2H_2^+ + 2e^-$ Or
$Ar^* + C_2H_2 \rightarrow C_2H_2^+ + Ar + e^-$

Ionization and molecular growth kinetics in Ar/C_2H_2 CCRF plasmas : discharge structure and composition

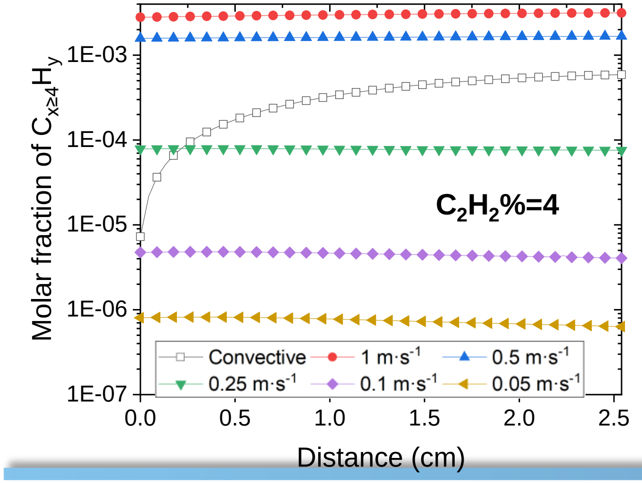
Electron density in the gap



C_2H_2 density in the gap



Large HC density in the gap

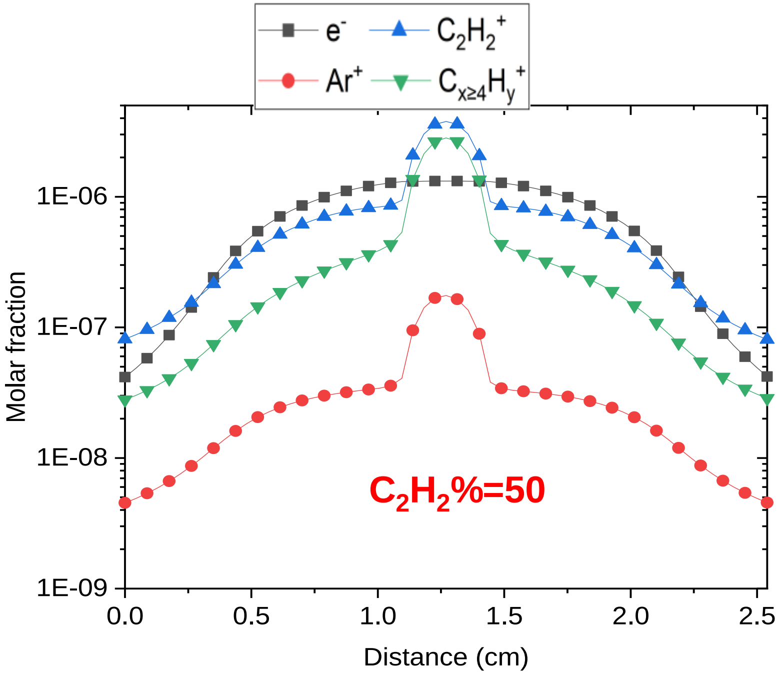


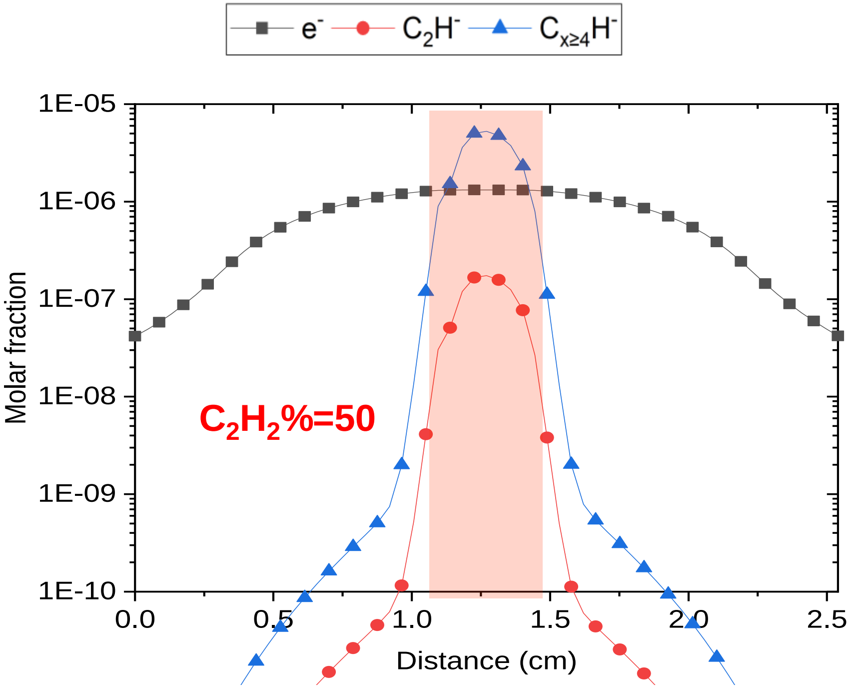
- Total acetylene conversion at low flow inlet-velocity
- Substantial conversion (50%) at large flow velocity
- Substantial production of large molecular edifice at low residence time !

G. Tetard et al. PSST (2021), **30,** paper# 105015(22 pp) doi 10.1088/1361-6595/ac2a17
G. Tetard et al. Submitted to Plasma Process and Polymer - 2021

Université Sorbonne Paris Nord

Ionization and molecular growth kinetics in Ar/C_2H_2 CCRF plasmas : Charge species in the gap





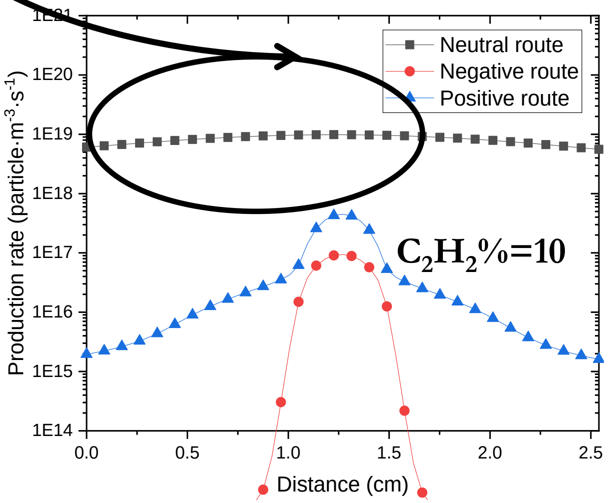
Narrow highly electronegative region in the center of the gap
Electropositive plasma elsewhere

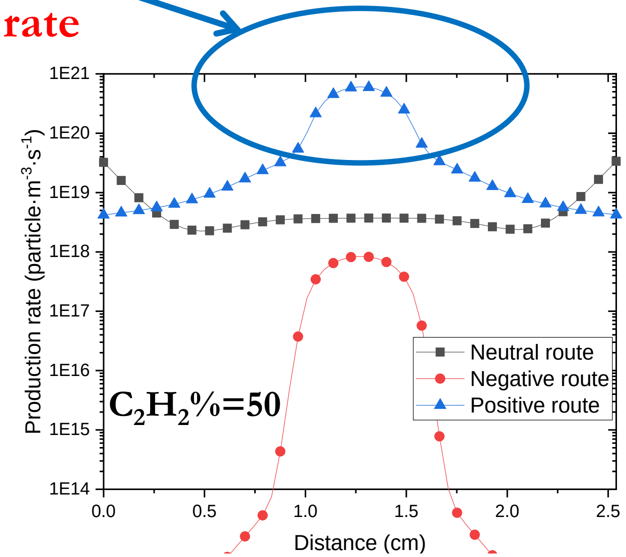
G. Tetard et al. PSST (2021), **30,** paper# 105015(22 pp) doi 10.1088/1361-6595/ac2a17
G. Tetard et al. Submitted to Plasma Process and Polymer - 2021

Ionization and molecular growth kinetics in Ar/C_2H_2 CCRF plasmas : major molecular growth routes

$C_2H + C_{2n}H_2 \rightarrow C_{2n+2}H_2 + H$	k~ 3.10^7 $m^3.mol^{-1}.s^{-1}$
$C_2H_2 + C_{2n}H \rightarrow C_{2n+2}H_2 + H$	k~4.10^7 $m^3.mol^{-1}.s^{-1}$
$C_2H_2 + C_{2n}H^- \rightarrow C_{2n+2}H^- + H_2$	k~6.10^5 $m^3.mol^{-1}.s^{-1}$
$C_2H_2 + C_{2n}H_y^+ \rightarrow C_{2n+2}H_y^+ + H_2$, ($n>2$, $y=6$)	k~6.10^7 $m^3.mol^{-1}.s^{-1}$

$C_{n\geq8}H_2$ production rate





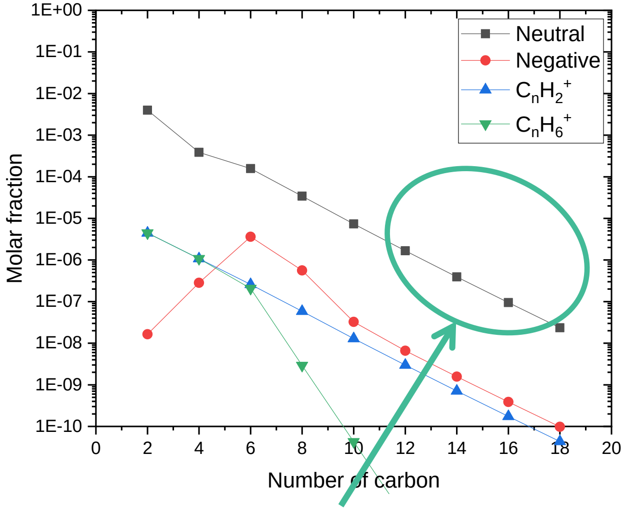
- Neutral route dominate when C_2H_2 density is low in the gap
- Positive ion route dominate when C_2H_2 density is significant in the gap

G. Tetard et al. Submitted to Plasma Process and Polymer - 2021

Ionization and molecular growth kinetics in Ar/C_2H_2 CCRF plasmas : Molecular growth and nucleation

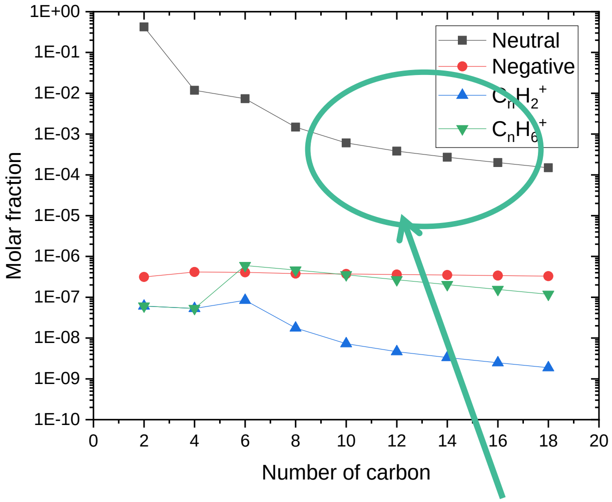
Size distributions of hydro-carbons

10 % C_2H_2 in the feed gas



Several orders of magnitude exponential population decrease with size

50 % C_2H_2 in the feed gas



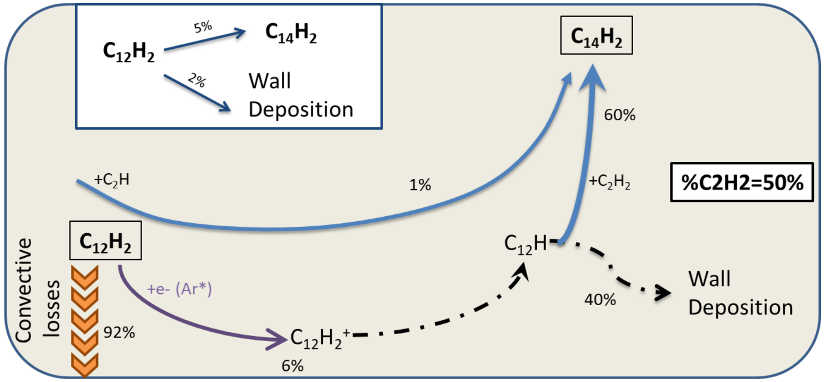
Mass accumulation over all the size distribution (very slight or no decrease)

Only the positive ion route can lead to nucleation … in this growth model !!!

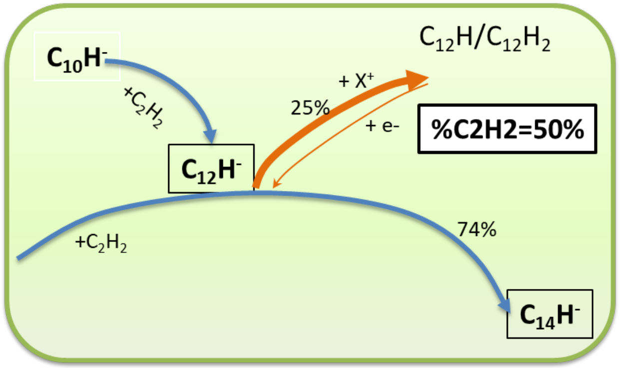
G. Tetard et al. Submitted to Plasma Process and Polymer - 2021

Competitive processes for molecular growth

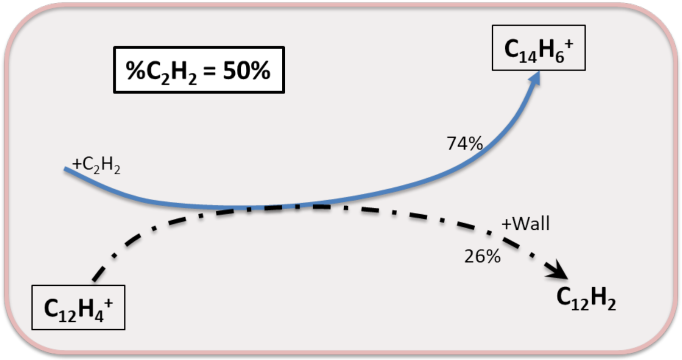
Neutral molecule route



Negative ion route



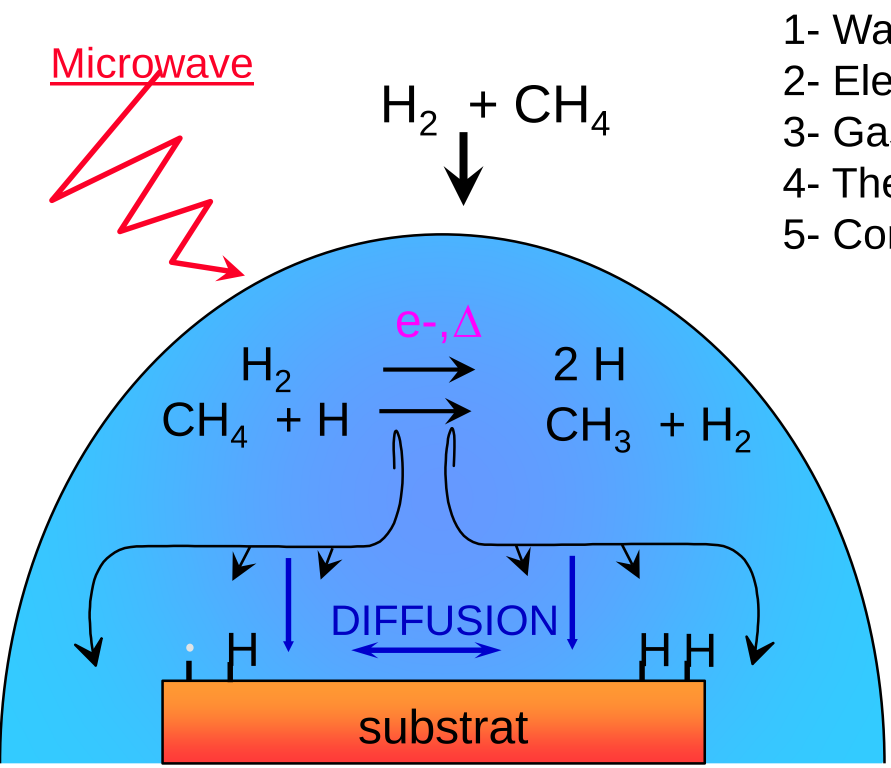
Positive ion route



- **Convective losses of neutral clusters are highly dominant which explains the limited contribution of this route in the nucleation process**
- **Significant competition between molecular growth and wall deposition for the neutral route**
- **Molecular growth is dominant for both negative and positively charged clusters**

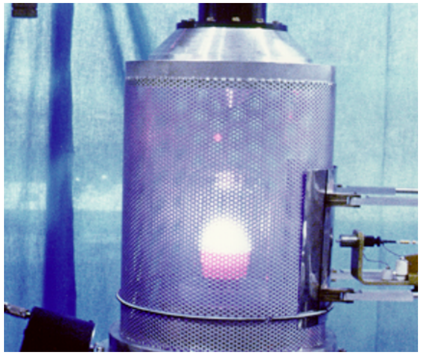
G. Tetard et al. Submitted to Plasma Process and Polymer - 2021

Complex chemistry and the coupling between thermal, chemical and transport phenomena in hydrocarbon containing microwave plasmas



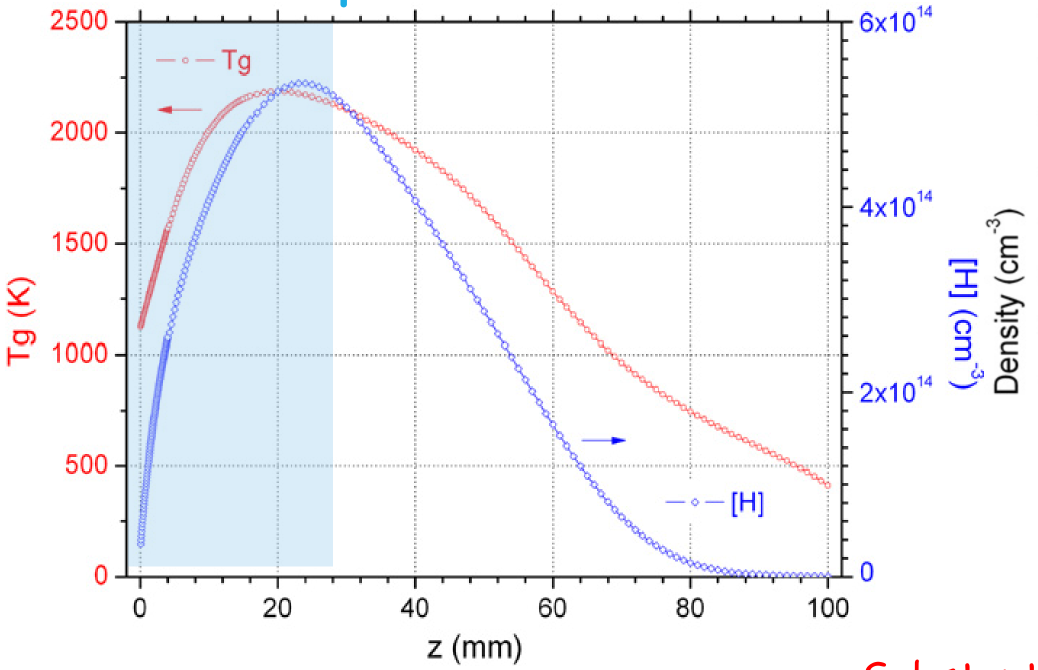
1- Wave-plasma interaction – energy deposition
2- Electron heating and collisional relaxation
3- Gas excitation and heating
4- Thermal and electron-impact chemistry
5- Composition change

Strong coupling

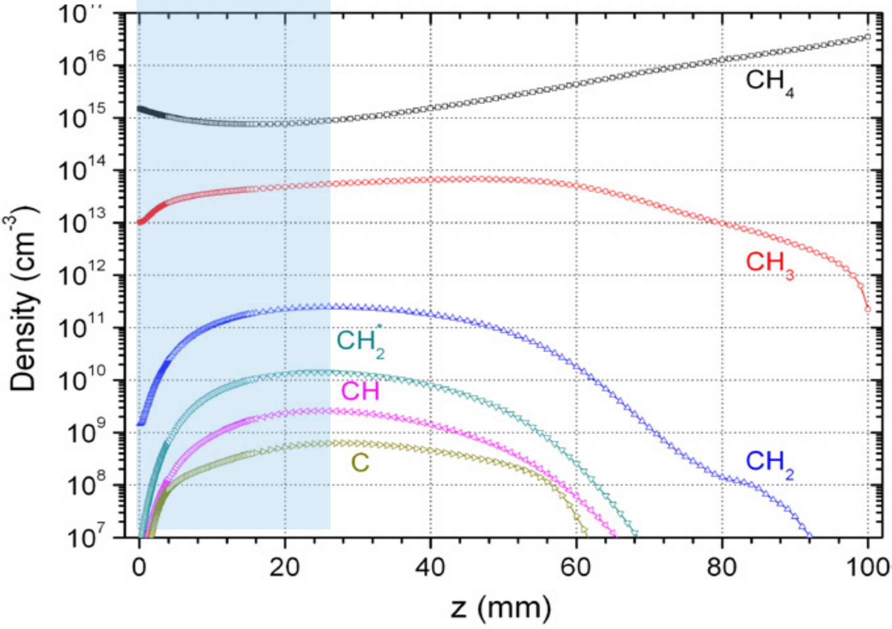


Plasma composition at low power density-low pressure (9 W/cm^3, 2500 Pa)

Gas temperature and H-atom



1 carbon species



Moderate temperature increase

Electron-impact dissociation of H-atom

Non-equilibrium H-atom density

Substantial conversion of CH_4

Smooth evolution of the plasma composition

Slightly reactive boundary layer

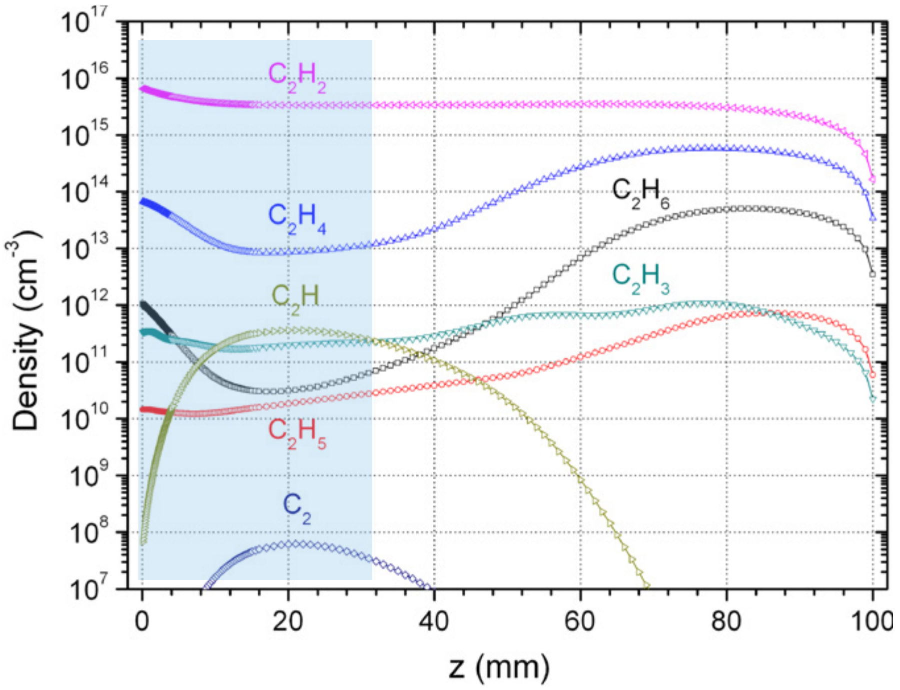
Both thermal and electron-impact chemistry

K. Hassouni et al. J. Phys. D: Appl. Phys. 43 (2010) 153001 (45pp)
F Silva et al 2009 J. Phys.: Condens. Matter 21 364202

G. Lombardi et al. PSST **14**(2005), 440-450, doi : 10.1088/0963-0252/14/3/005
G. Lombardi et al., J. Appl. Phys. **98**, 053303 (2005); https://doi.org/10.1063/1.2034646

Plasma composition at low power density-low pressure (9 W/cm^3, 2500 Pa)

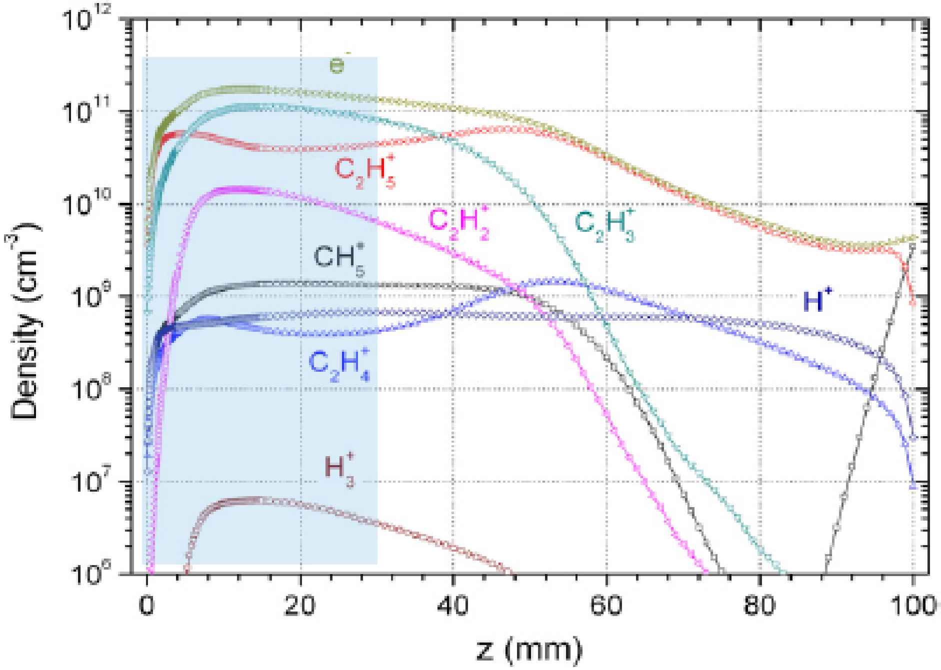
2 carbon species



From CH_4 feed to Acetylene plasma
Substantial but still 'smooth' variation of the Composition in the BL

K. Hassouni et al. J. Phys. D: Appl. Phys. 43 (2010) 153001 (45pp)
F Silva et al 2009 J. Phys.: Condens. Matter 21 364202

Ions



Dominated by hydrocarbon ions

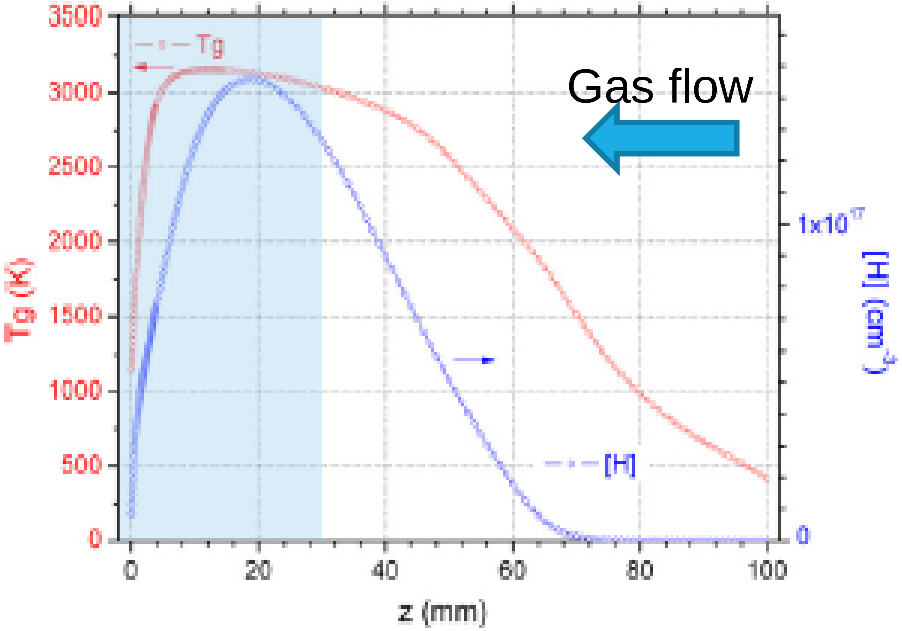
Hydrogen ionization followed by ion conversion processes

$H(n) + H_2$ ==> $[H_3^+ + e^-]$ ou $[3H]$

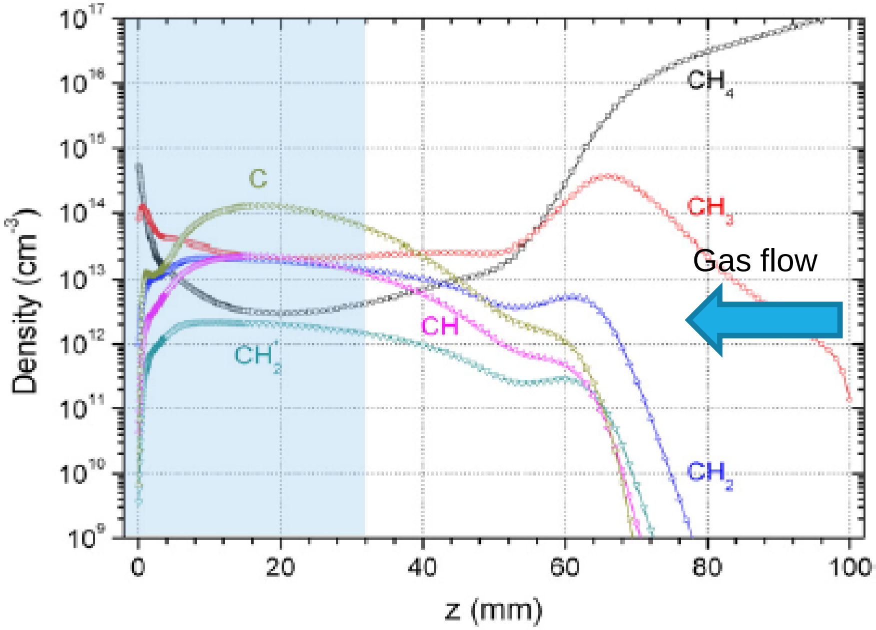
$H_3^+ + C_xH_y \rightarrow C_xH_{y+1}^+ + H_2$

G. Lombardi et al. PSST **14**(2005), 440-450, doi : 10.1088/0963-0252/14/3/005
G. Lombardi et al., J. Appl. Phys. **98**, 053303 (2005); https://doi.org/10.1063/1.2034646

Plasma composition at high power density-high pressure ($50\ W/cm^3$, 10000 Pa)



Gas temperature and H-atom



1 carbon species

Large temperature increase
Thermal dissociation of H-atom
Large dissociation yield
Still non-equilibrium H-atom density

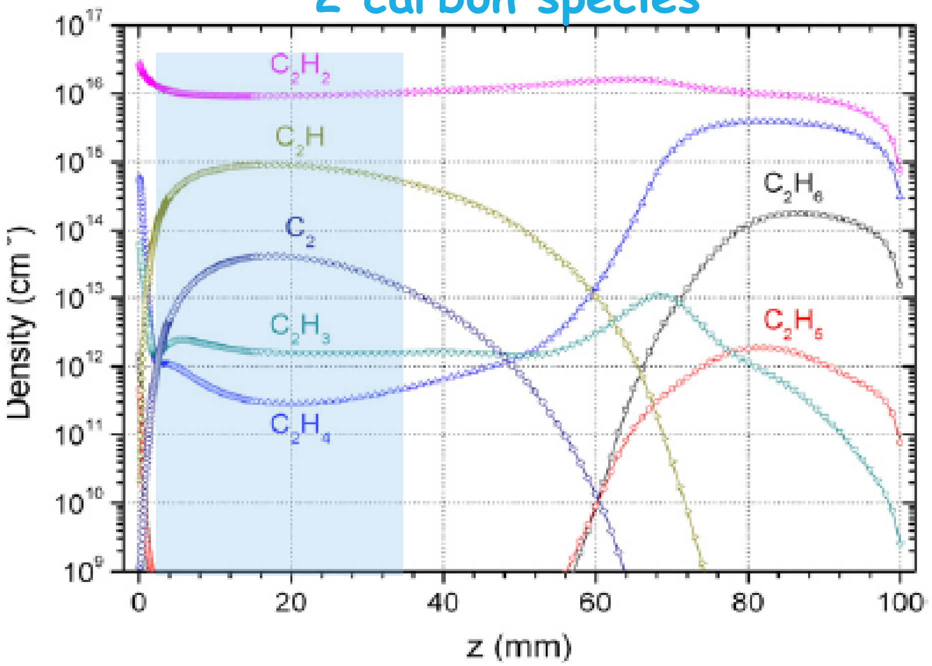
Full conversion of CH_4 before reaching the plasma bulk
Highly reactive boundary layer

K. Hassouni et al. J. Phys. D: Appl. Phys. 43 (2010) 153001 (45pp)
F Silva et al 2009 J. Phys.: Condens. Matter 21 364202

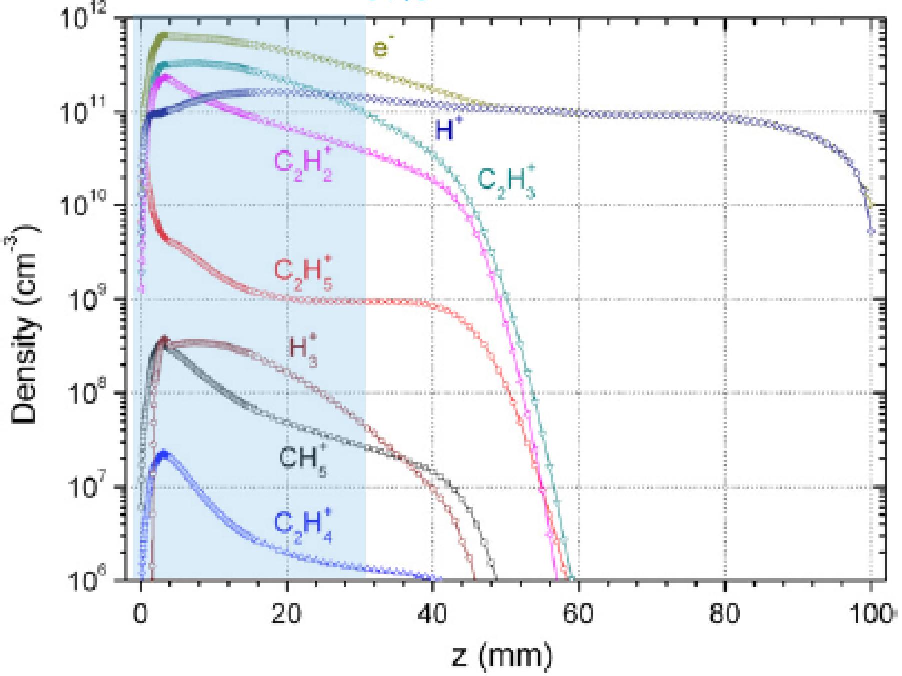
G. Lombardi et al. PSST **14**(2005), 440-450, doi : 10.1088/0963-0252/14/3/005
G. Lombardi et al., J. Appl. Phys. **98**, 053303 (2005); https://doi.org/10.1063/1.2034646

Plasma composition at high power density-high pressure (50 W/cm^3, 10000 Pa)

2 carbon species



Ions



Still C_2H_2 plasma !
Very large variation in the BL
Driven by H-atom and T_g

H_2 ionization and Charge transfer in the plasma
Substantial H-atom ionization
Very large and highly ionized post-discharge

Electron (microwave) ➔ T_g ➔ H-atom THEN T_g and H-atom ➔ hydrocarbon chemistry

K. Hassouni et al. J. Phys. D: Appl. Phys. 43 (2010) 153001 (45pp)
F Silva et al 2009 J. Phys.: Condens. Matter 21 364202

G. Lombardi et al. PSST **14**(2005), 440-450, doi : 10.1088/0963-0252/14/3/005
G. Lombardi et al., J. Appl. Phys. **98**, 053303 (2005); https://doi.org/10.1063/1.2034646

Few words on the methodology (modeling)

Investigating the reactivity

Discharge physics (power coupling, electron heating)

Energy modes relaxation (energy conversion)

Species and energy transport

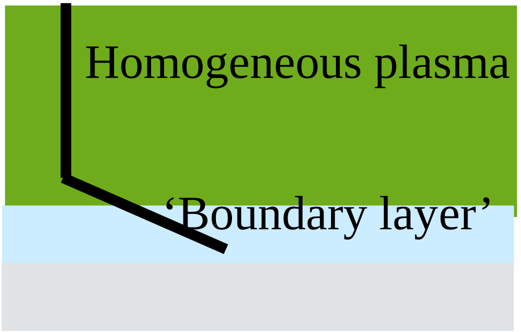
Interaction with the walls

We have a multi-physics problem

May addressed using several level of details/complexity

First approach (the simplest one) : Quasi-homogeneous or plug flow plasma model

Quasi-homegenous plasma



Suitable for stationary glow discharges and plasma

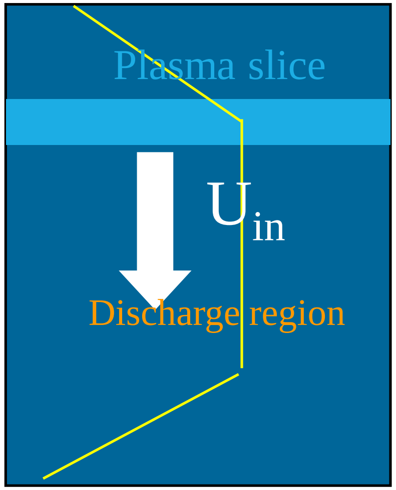
Objective : To get a first idea on what is happening in trms of energy relaxation and chemistry

Though it light be not accurate quantitaively.

We can :

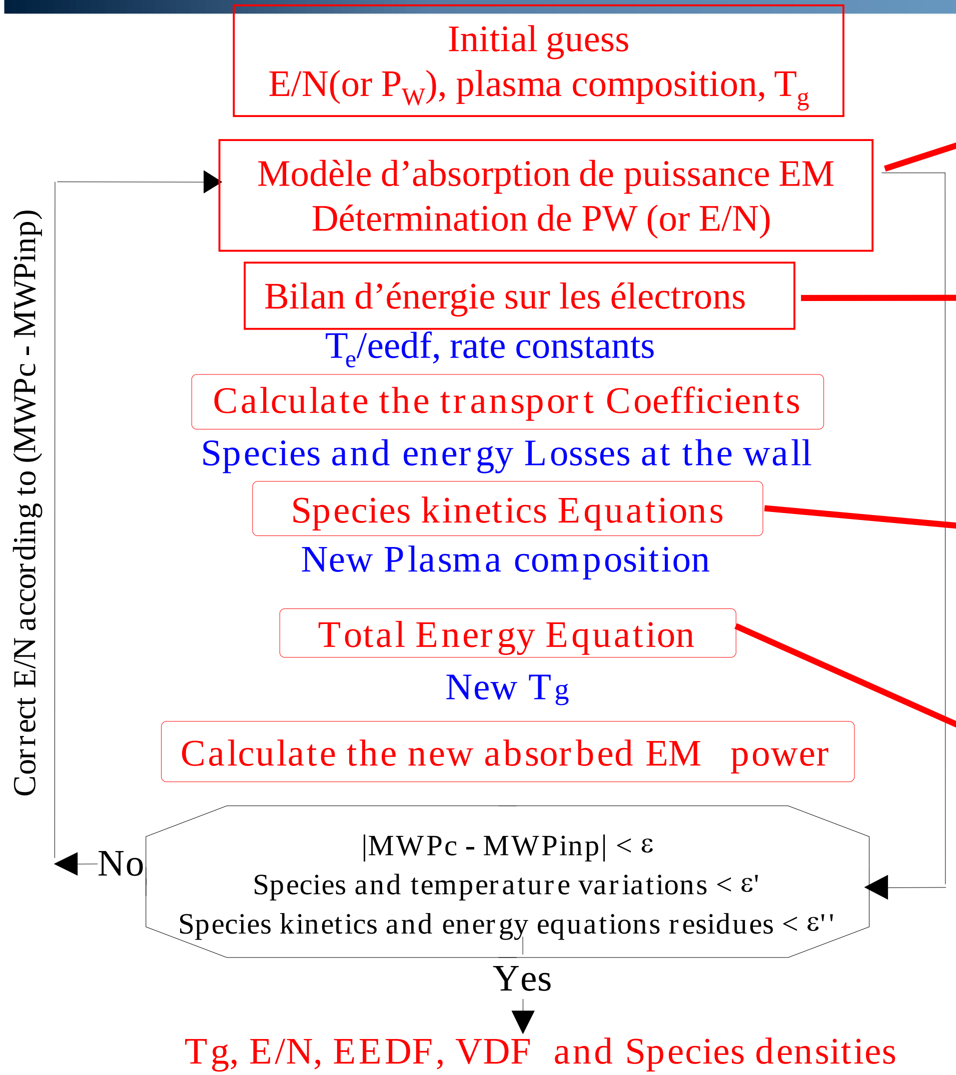
- build up very detailed CR models
- infer the major elementary processes
- setup simplified models

Plug flow plasma



C. D. Scott et al. JTHT(1996), **10**(3), 10.2514/3.807
K. Hassouni et al. PSST **8**(1999), 494-512
K. Hassouni et al. J. Phys. D: Appl. Phys. 43 (2010) 153001 (45pp)

Typical components involved in a quasi-homogeneous plasma model



Initial guess
E/N(or P_W), plasma composition, T_g

Modèle d'absorption de puissance EM
Détermination de PW (or E/N)

Bilan d'énergie sur les électrons
T_e/eedf, rate constants

Calculate the transport Coefficients
Species and energy Losses at the wall

Species kinetics Equations
New Plasma composition

Total Energy Equation
New T_g

Calculate the new absorbed EM power

|MWPc - MWPinp| < ε
Species and temperature variations < ε'
Species kinetics and energy equations residues < ε''

No

Correct E/N according to (MWPc - MWPinp)

Yes

Tg, E/N, EEDF, VDF and Species densities

- Relationship Power / Electric field

- Determination of the whole eedf and 'accurate', electron-impact reaction rate constants and electron transport coefficients-

- Determine the overal species densities

- Determine the overal ('mean') gas temperature

K. Hassouni et al. PSST **8**(1999), 494-512
K. Hassouni et al. *Plasma Sources Sci. Technol.* (2001), **10**(1), 61
K. Hassouni et al. J. Phys. D: Appl. Phys. 43 (2010) 153001 (45pp)

Typical equations involved in quasi-homogeneous plasma model

-Relationship between power and electric field

$$P_{Ohm} = \omega_p \left(\frac{\omega_p}{\nu_{qm}} \right) \frac{1}{(\omega / \nu_{qm})^2 + 1} \frac{\varepsilon_0 E_0^2}{2}$$

-Determination of the eedf

-Or the average electroln energy f(e)=exp(-e/kT$_e$)

$$\frac{\partial f(\varepsilon,t)}{\partial t} = -\frac{\partial J_E}{\partial \varepsilon} - \frac{\partial J_{el}}{\partial \varepsilon} - \frac{\partial J_{e-e}}{\partial \varepsilon} + Q_{in} = 0$$

$$\frac{\partial \tilde{E}_e}{\partial t} = \left[PMW - Q_{e-v} - Q_{e-t} - Q_{e-X} \right] \frac{1}{\rho}$$

-Determination of the plasma composition

$$\frac{dY_s}{dt} = \frac{W_s}{\rho}$$

-Estimation of the gas temperature

$$\frac{\partial \tilde{E}}{\partial t} = \left[PMW - Q_{rad} - S_P \right] \frac{1}{\rho}$$

K. Hassouni et al. PSST **8**(1999), 494-512
K. Hassouni et al. *Plasma Sources Sci. Technol.* (2001), **10**(1)**,** 61
K. Hassouni et al. J. Phys. D: Appl. Phys. 43 (2010) 153001 (45pp)

Typical models for low pressure discharges with a local electron kinetics in the frame of the fluid approach

X Ions in thermal equilibrium with the neutrals : T_i=Tg

X E= E_{drift} + $E_{thermal}$ with E_{drift} >> $E_{thermal}$ (at least in the sheath)

A Continuity equation for each neutral, ion and electron

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

An energy equation for electrons

Requires assumption on the eedf

$$\frac{\partial n_e < \varepsilon_e >}{\partial t} = -\nabla\left(-2/3\kappa_e \vec{\nabla} < \varepsilon_e > +5/3 \vec{J}_e < \varepsilon_e >\right) + e.\vec{J}_e \bullet \vec{E} - \sum_{coll} k_{coll} n_e n < \varepsilon_{th-coll} >$$

A momentum equation for each charged species

$$\frac{\partial \rho_s \vec{u}_s}{\partial t} - \nabla \cdot \left(p_s\right) = e\rho_s \vec{E} - \nu_{s-qm} \rho_s \vec{u}_s$$

Simplification #1 : drift-diffusion transport

Suitable for cases with : $\lambda_{Debye} \approx d_{syst}$ et $\omega << \omega_s$

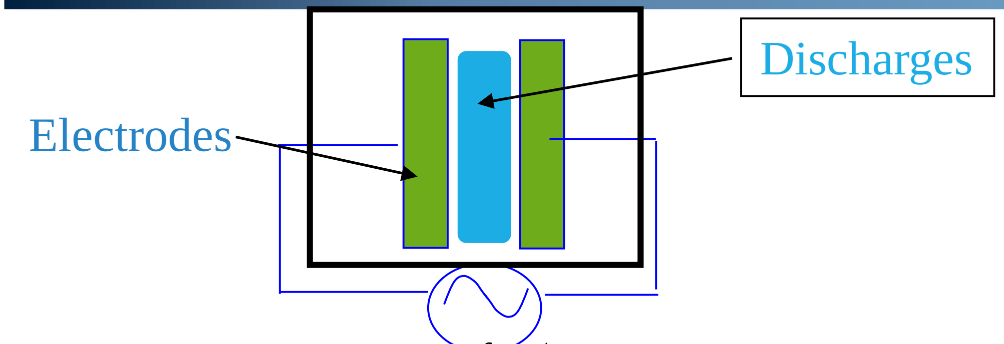
$$\frac{\partial \rho_s \vec{u}_s}{\partial t} = 0 \Longrightarrow \vec{u}_s = z_s \mu_s \vec{E} - D_s \frac{\vec{\nabla} n_s}{n_s} \Longrightarrow$$

(Requirfe the estimation of D_s et μ_s)

(advantage : no momentum equation)

Application : Fluid model for RF ; streamer propagation, …

Discharges with space charge separation : the drift-diffusion model. The example of CCRF discharges



p=0.1-1 torr, T_g=300-600 K,
Puissance =few 0.1 to few W

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

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

$\omega_{p\text{-}i} << \omega_{RF} << \omega_{p\text{-}e}$

① Space charge is taken into account
(some region may be non neutral)

② Now wavelength affect :
Electrostatic assumption

Drift-diffusion assumption

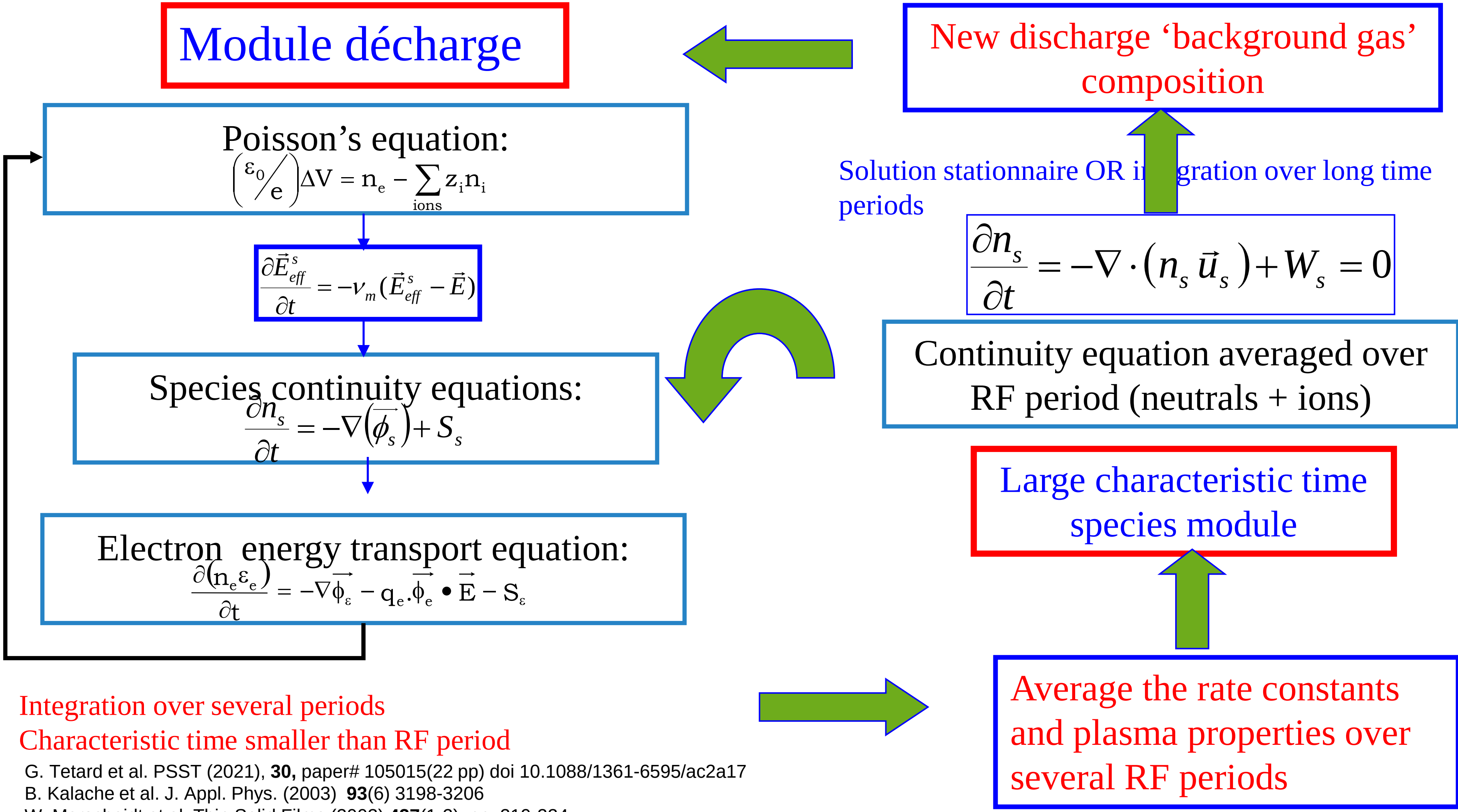
- OK for electrons
- Not valid for ions => ion oscillation is damped

momentum equations required

A solution is to use : an effective electric field experienced by ions.

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

Typical simultion of reactive CCRF discharges



Module décharge

Poisson’s equation:

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

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

Species continuity equations:

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

Electron energy transport equation:

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

Integration over several periods
Characteristic time smaller than RF period

Average the rate constants and plasma properties over several RF periods

Large characteristic time species module

Continuity equation averaged over RF period (neutrals + ions)

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

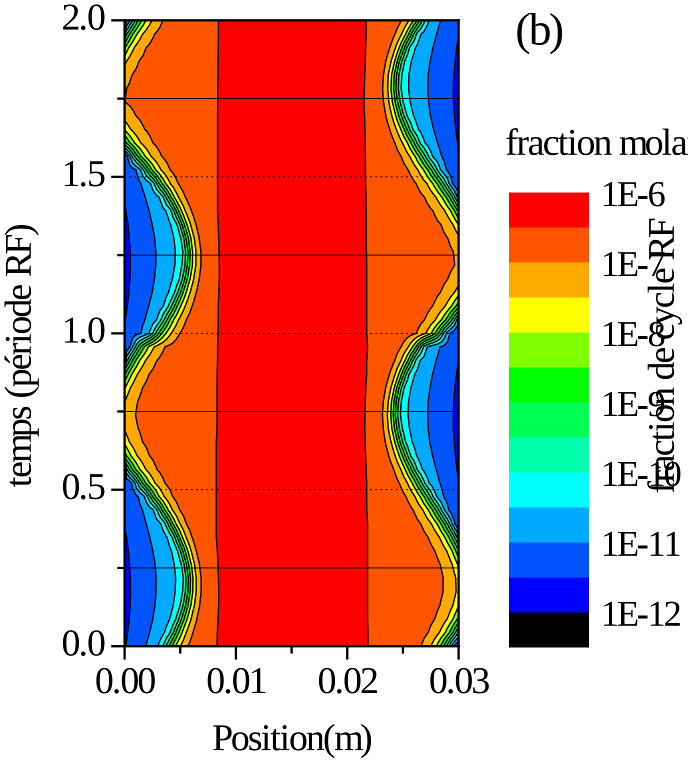
Solution stationnaire OR i gration over long time periods

New discharge ‘background gas’ composition

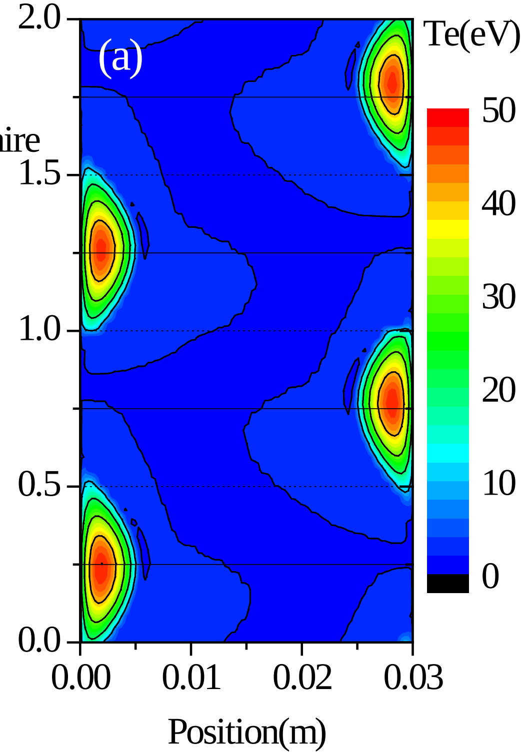
G. Tetard et al. PSST (2021), **30,** paper# 105015(22 pp) doi 10.1088/1361-6595/ac2a17
B. Kalache et al. J. Appl. Phys. (2003) **93**(6) 3198-3206
W. Morscheidt et al. Thin Solid Films (2003) **427**(1-2), pp. 219-224

Discharge dynamics – space-time distributions of electron-mole fraction, electron-emperature and power density

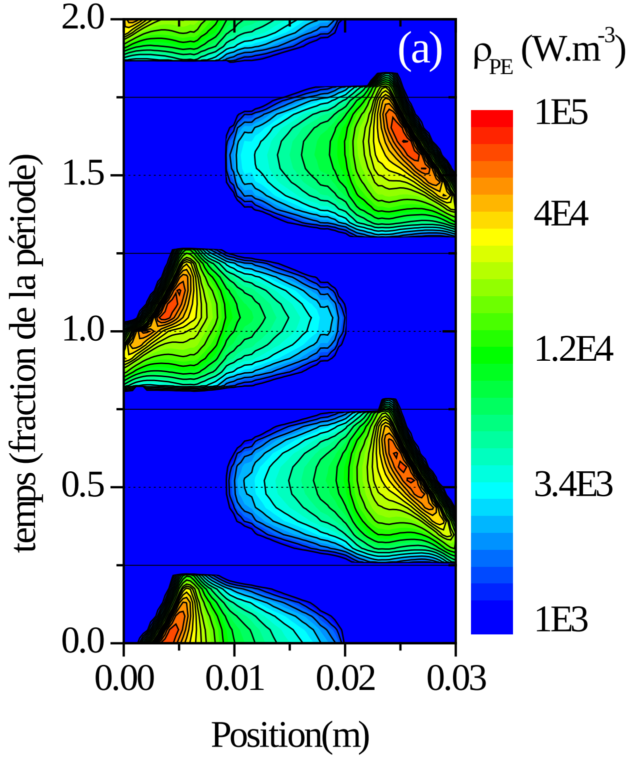
$[e^-]$



T_e



RF power-density



N_e and T_e are out of phase
Either very hot few electrons or a lot of warm electrons

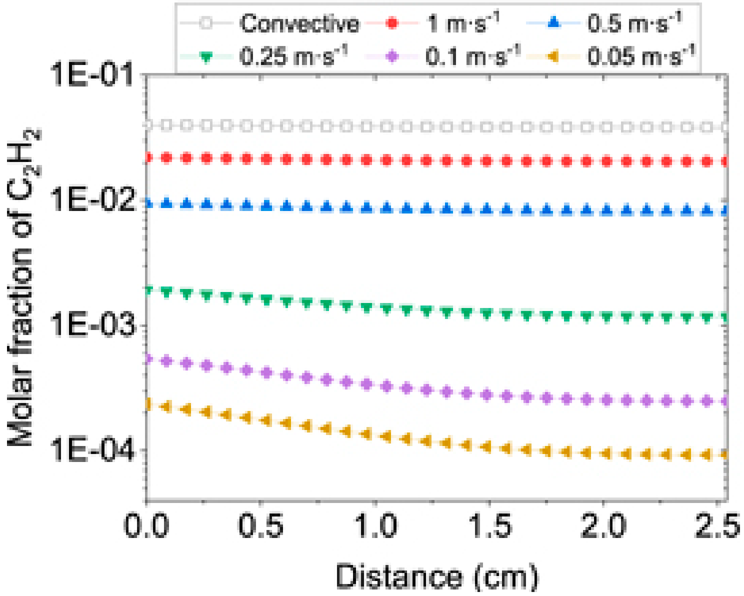
- The absorbed power is a kind of compromise between n_E and T_e
- We need as much hot electron as possible ➔ the heating takes place during the anode=>cathode transition

W. Morscheidt et al. Thin Solid Films (2003) **427**(1-2), pp. 219-224

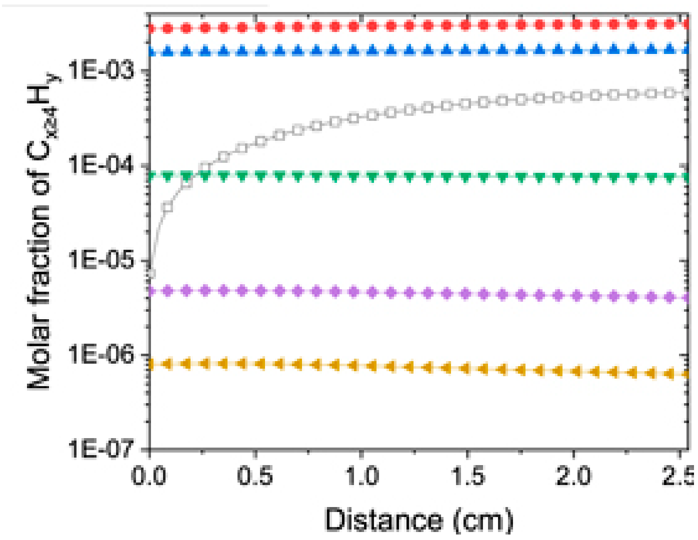
Background gas composition

Acetylene conversion in Ar/C_2H_2 discharges 4% acetylene)

Acetylene fraction for different values of the inlet velocity (flow rate)



Fraction of the $C_{2n}H_2$(n≥4) molecules, for different values of the inlet velocity (flow rate)



The precursor may be almost totally converted and the plasma is therefore generated in a gas composition that is strongly diferent from the feed gas one !

G. Tetard et al. PSST (2021), **30,** paper# 105015(22 pp) doi 10.1088/1361-6595/ac2a17
G. Tetard et al. Submitted to Plasma Process and Polymer - 2021

Transport and chemistry in low pressure plasmas
No charge separation + fluid approach

Simplification #2 : Ambipolar diffusion

May be used when : $\lambda_{\text{Debye}} << d_{\text{système}}$ ➡

$$\sum_i z_i n_i = 0$$

$$\sum_i z_i J_i = 0$$

Special case of 1 ion + 1 électron

$$-\mu_e n_e E_{amb} - D_e \nabla n_e = \mu_i n_i E_{amb} - D_i \nabla n_i$$

$$E_{amb} = \frac{D_i - D_e}{\mu_i + \mu_e} \frac{\nabla n_e}{n_e} \qquad J_i = -\frac{\mu_e D_i + \mu_i D_e}{\mu_i + \mu_e} \nabla n_i = \boxed{-D_{amb} \nabla n_i}$$

Advantage : Continuity equation = diffusion equation if no flow (no drift ➔ easier)

$$\frac{\partial n_i}{\partial t} + \nabla \times \left(-D_a \vec{\nabla} n_i + \vec{u}\, n_i \right) - W_i = 0$$

Disadvantages : not so straightforward in the case of multicomponent plasmas (sevetral ions , negative ions, ...)

Multi-temperature ambipolar plasmas models

Continuity equation for each species => density $$\frac{\partial n_i}{\partial t} + \nabla \times \left(-D_i \vec{\nabla} n_i + \vec{u}\, n_i \right) - W_i = 0$$

Overall momentum => flow velocity

Electron energy => T_e $$\frac{\partial E_e}{\partial t} + \mathrm{div}(u_e h_e - \lambda_e \nabla T_e) - P_{EM} + Q_{e-t} + Q_{e-v} + Q_{e-X} = 0$$

Vibration modes => T_v $$\frac{\partial E_{v-m}}{\partial t} + \mathrm{div}(u_m E_{v-m} - \lambda_{v-m} \nabla T_{v-m}) + Q_{v-t} - Q_{e-v} + Q_{v-X} = 0$$

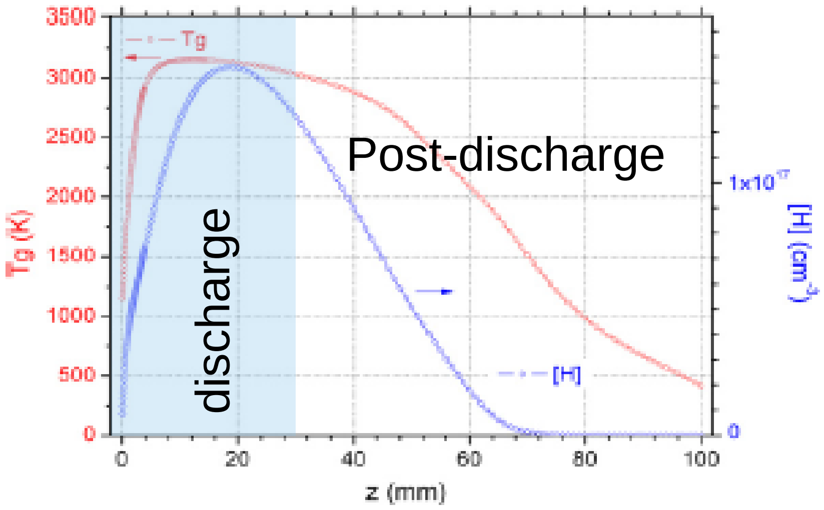
Coupling nodes

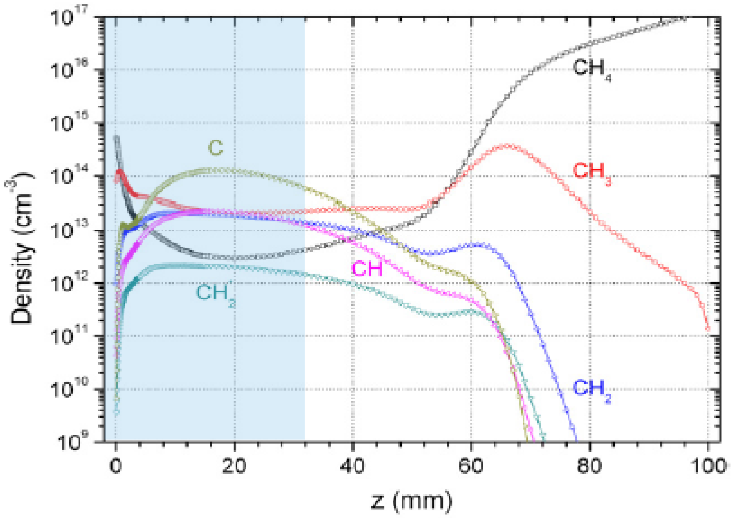
Total energy => Tg $$\frac{\partial E}{\partial t} + \mathrm{div}[\Sigma u_i h_i - \lambda_{t-r} \nabla T - \Sigma \lambda_{v-m} \nabla T_{v-m} - \lambda_e \nabla T_e] - P_{EM} + Q_{rad} = 0$$

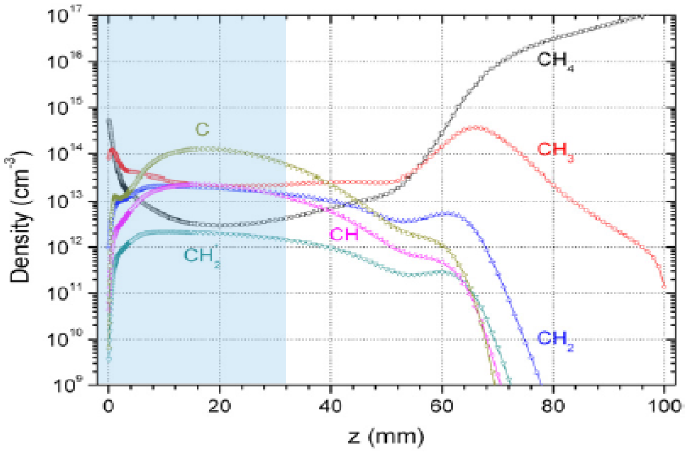
K. Hassouni et al., Plasma Chem. And Plasma Proc. (1998), **18**, 325-362
K. Hassouni et al. J. Phys. D: Appl. Phys. 43 (2010) 153001 (45pp)
G. Lombardi et al. PSST **14**(2005), 440-450, doi : 10.1088/0963-0252/14/3/005
G. Lombardi et al., J. Appl. Phys. **98**, 053303 (2005); https://doi.org/10.1063/1.2034646

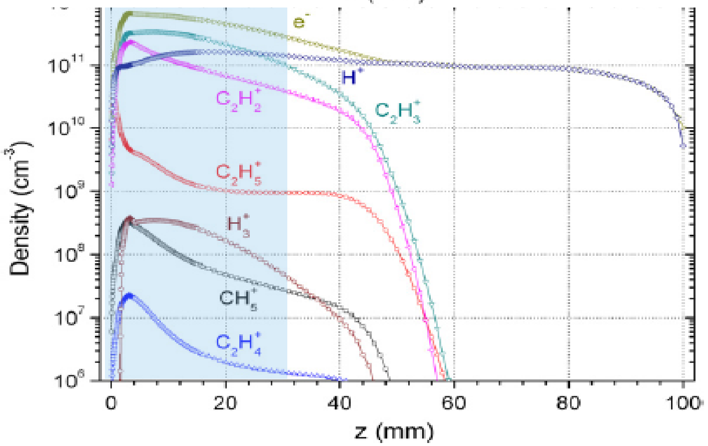
The approach is close to the one used in combustion

Results : space distributions of temperature and species (no current, no sheath and electroneutral plasma)-example of CH_4/H_2 microwave plasmas







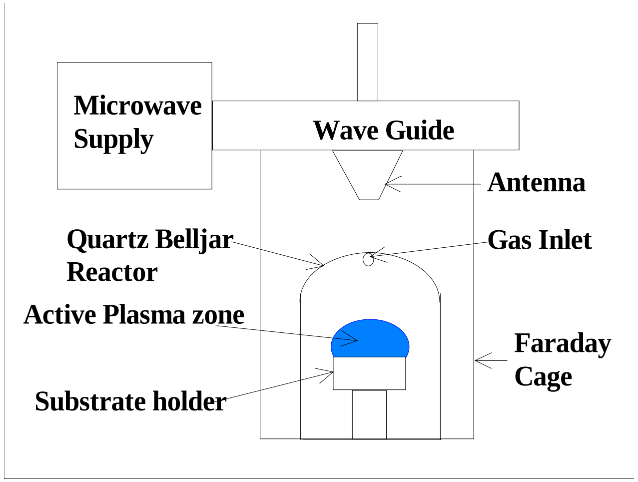


K. Hassouni et al. J. Phys. D: Appl. Phys. 43 (2010) 153001 (45pp)
F Silva et al 2009 J. Phys.: Condens. Matter 21 364202

G. Lombardi et al. PSST **14**(2005), 440-450, doi : 10.1088/0963-0252/14/3/005
G. Lombardi et al., J. Appl. Phys. **98**, 053303 (2005); https://doi.org/10.1063/1.2034646

Plasma-wave interaction: The example of microwave cavity generated plasmas

Microwave coupling , p=20-150 torr, PMW=0.6-6 kW



Ion balance ==> T_e = 1-2 eV
power balance ==> 10^{11}-10^{12}cm^{-3}

$\lambda_{Debye} \approx 0.1$ mm $<< d_{syst}$

1 Ambipolar plasma

2 $\lambda_{\mu wave} \approx 12$ cm $\approx d_{syst}$
We have a wavelength effect:
Quasistatic assumption not valid

Eq. Maxwell => E_{HF}

3 $\omega_{p\text{-}i} << \omega \approx \omega_{p\text{-}e}$

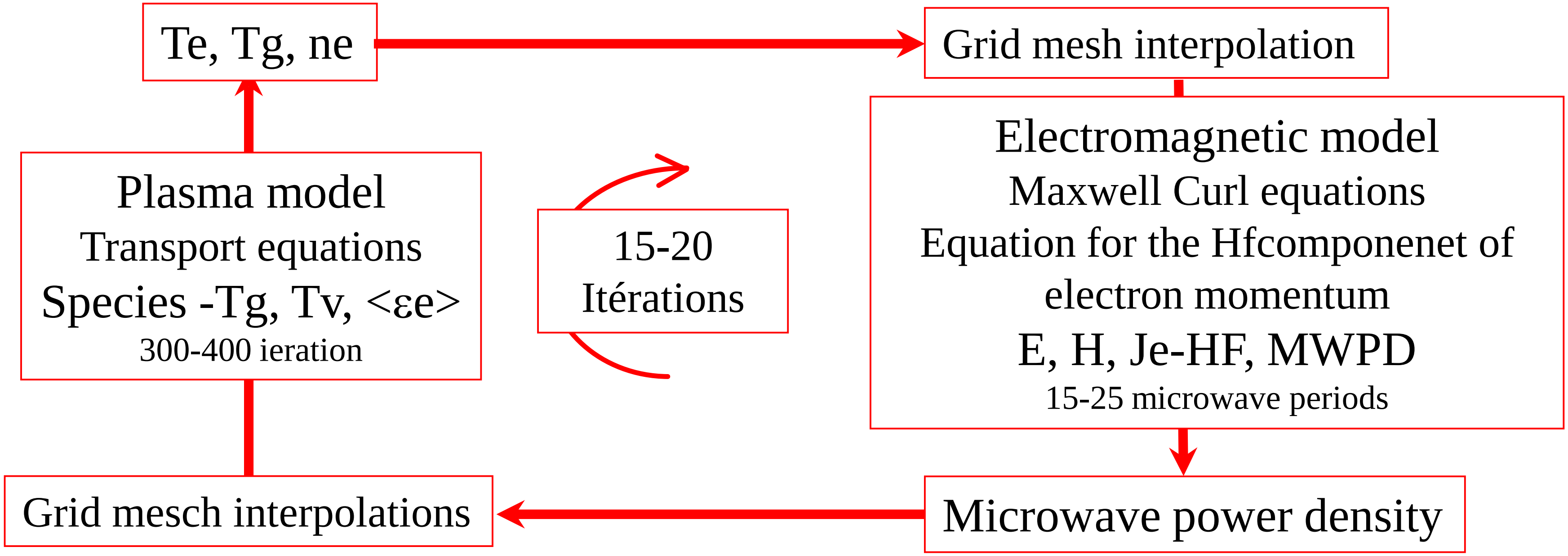
Coupling with the electrons through their high frequency current that lay be excited by microwave

Eq. de QM-HF
pour les é => J_{HF}

$J_{HF}.E_{HF}$ = PMW

Plasma-wave interaction: The example of microwave cavity generated plasmas

2. 2D self consistent model



Te, Tg, ne

Grid mesh interpolation

Electromagnetic model
Maxwell Curl equations
Equation for the Hfcomponenet of electron momentum
E, H, Je-HF, MWPD
15-25 microwave periods

Microwave power density

Grid mesch interpolations

Plasma model
Transport equations
Species -Tg, Tv, <εe>
300-400 ieration

15-20
Itérations

Maxwell module

$$\nabla \times E = \frac{\partial H}{\partial t}$$

$$\nabla \times H = J_{HF} + \varepsilon_0 \frac{\partial E}{\partial t}$$

$$m_e \frac{d\mathbf{v}_{HF}}{dt} = -q\mathbf{E} - m_e \upsilon_{eff} \mathbf{v}_{HF}$$

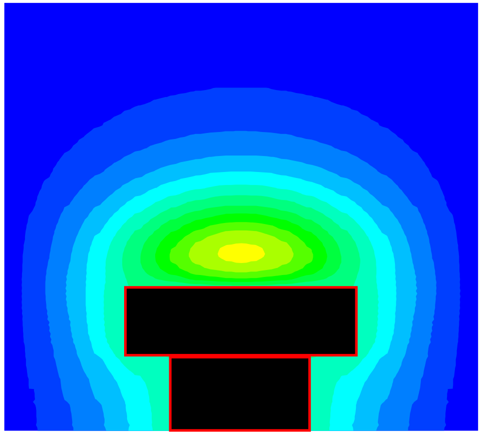
$$\mathbf{J}_{HF} = -q_e n_e \mathbf{v}_{HF}$$

K. Hassouni et al. J. Appl. Phys **86** (1999), 134-145.
G. Hagelaar et al. J. Appl. Phys **96** (2004), 1819
K. Hassouni et al. J. Phys. D. 43 (2010) 153001 (45pp)
S. Prasanna et al. PSST 26 (2017) 097001 (6pp)
S. Prasanna et al. PSST 25 (2016) 045017 (10pp)

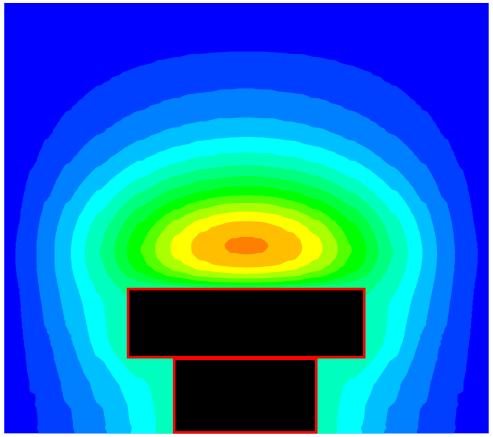
Plasma-wave interaction. H_2 microwave plasma used for diamond deposition

Optimal microwave coupling – pressure = 2500 Pa

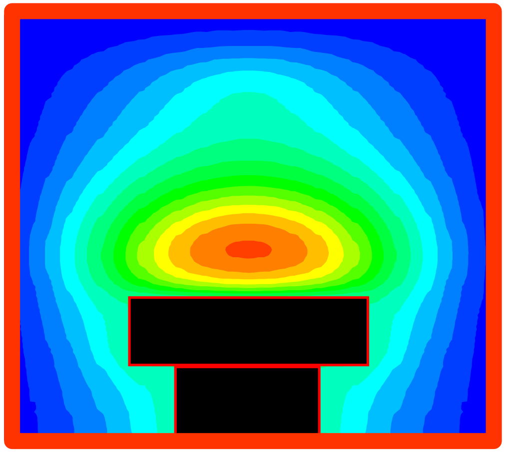
300 W



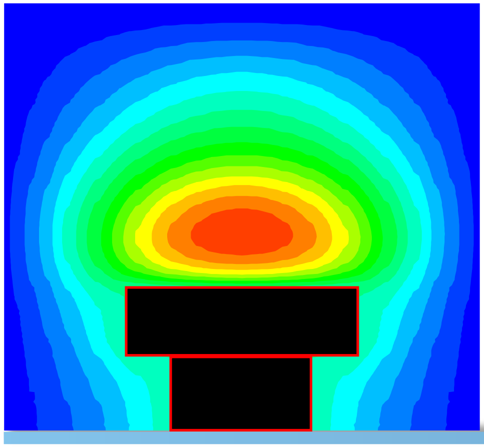
500 W



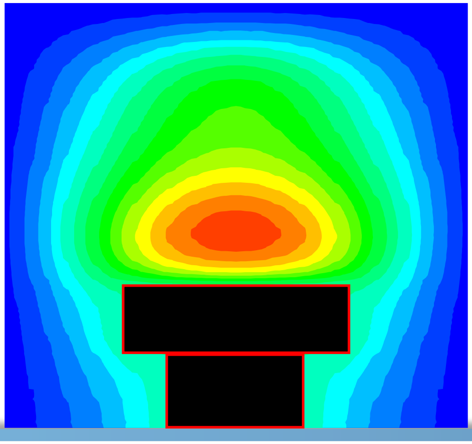
700 W



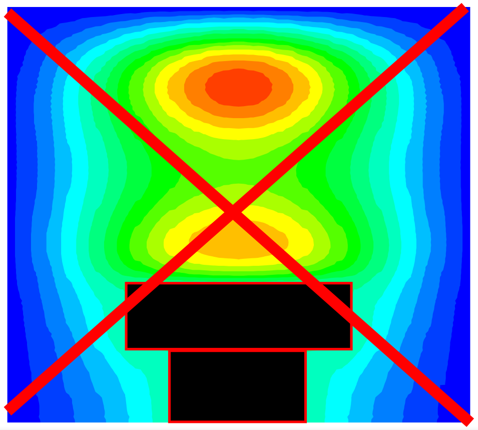
800 W



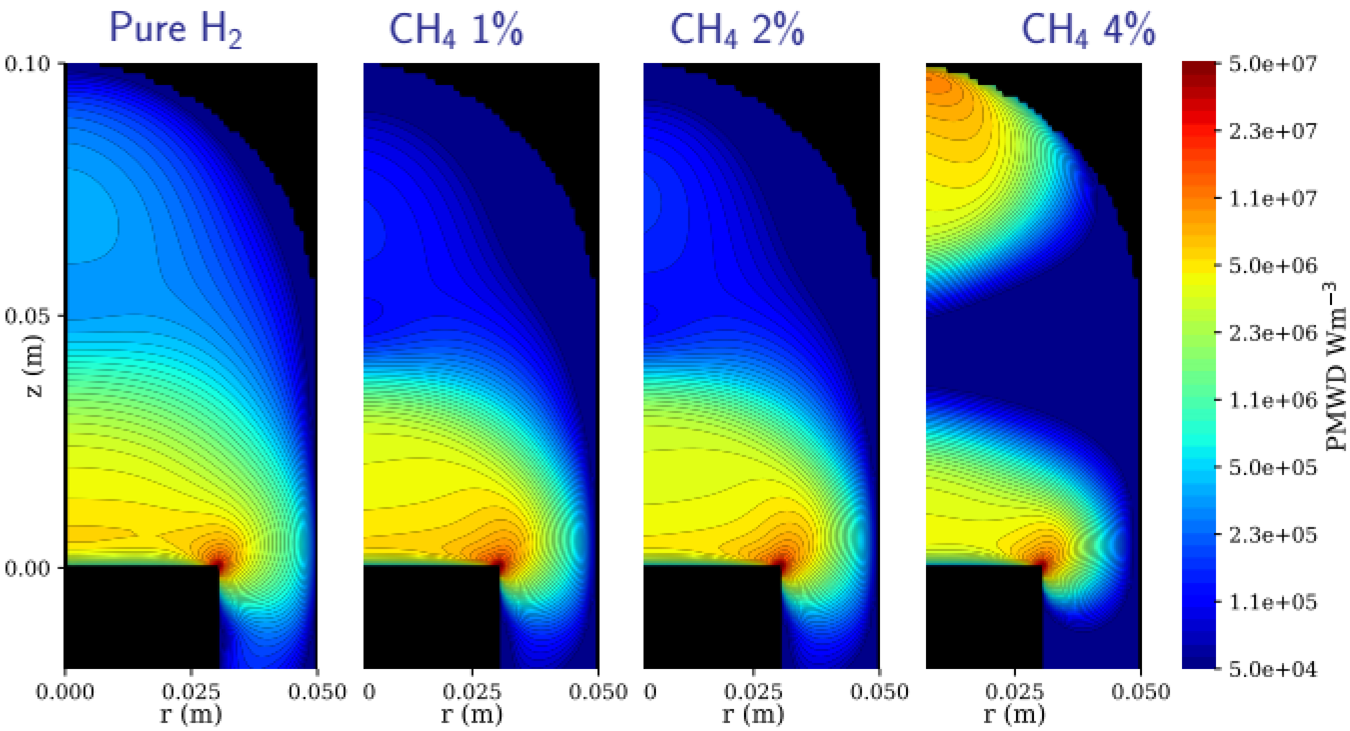
900 W



1000 W



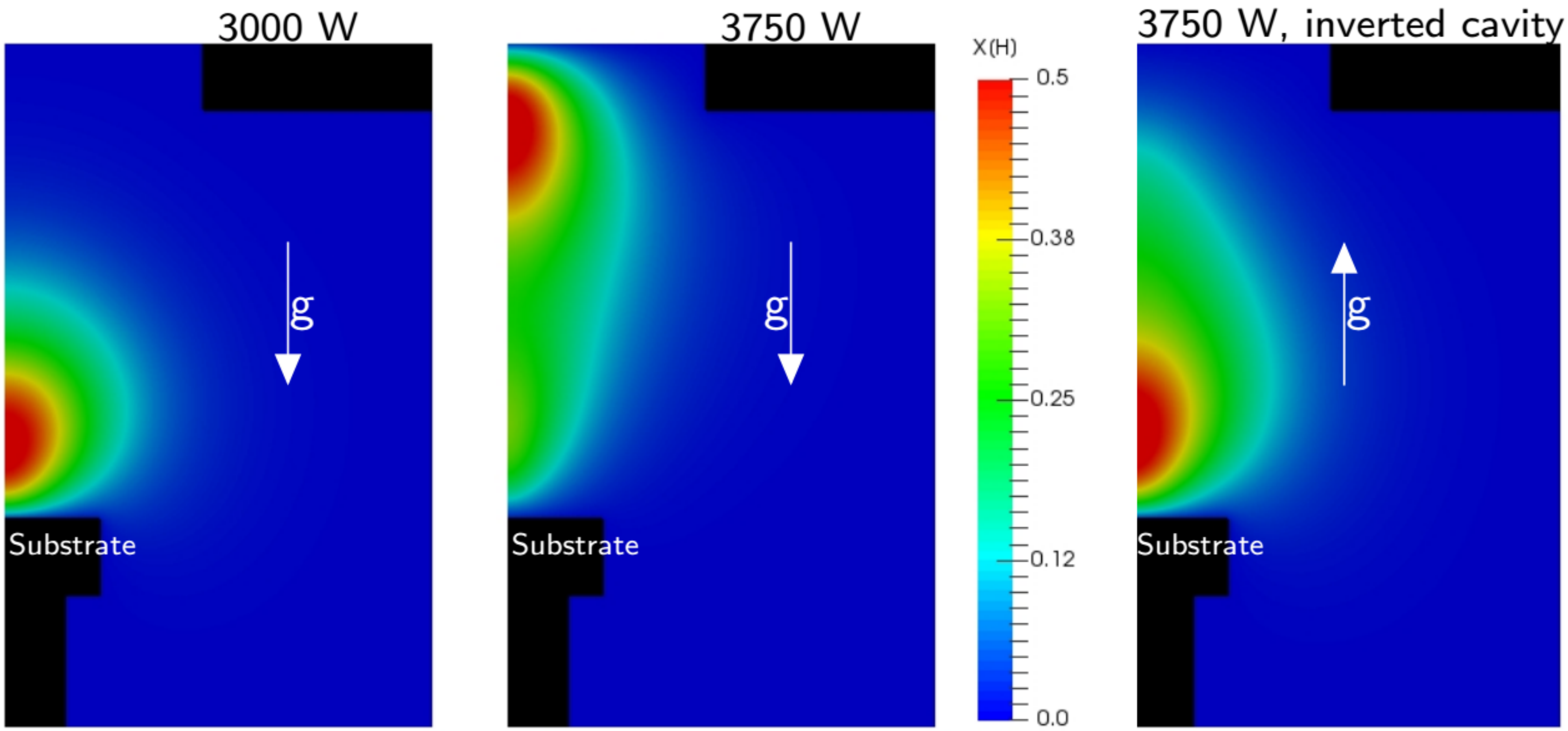
Effect of the feed gas composition on power coupling



S. Prasanna et al. PSST 26 (2017) 097001 (6pp)

The power coupling may substantially change even with a small change in the feed gas composition

Effect of buoyancy on power coupling



S. Prasanna et al. PSST 25 (2016) 045017 (10pp)

The power coupling may be significantly coupled to gas flow effects
Here we show the fact that the power coupling is very sensitive to the buoyancy forces and the natural convection

Conclusion

- Reactivity in non equilibrium plasmas : Rich and diverse
- Non-equilibrium effects are also rich and diverse

- Cannot be treated without considering discharge and plasma physics, as well as energy relaxation (molecular and atomic physics)

- Usually strongly coupled sets of phenomena

- Usually Huge space and time stiffness : key consequences on both experiments and modeling

- I did not discuss some major open questions (among others …) :
  - Plasma Surface Interaction and its feed back on the plasma behavior
  - Collisional data issues
  - Methodological issues (still not always straightforward)
  - Multiscale approaches

Thanks for listening

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