Numerical simulation tools for plasma chemistry

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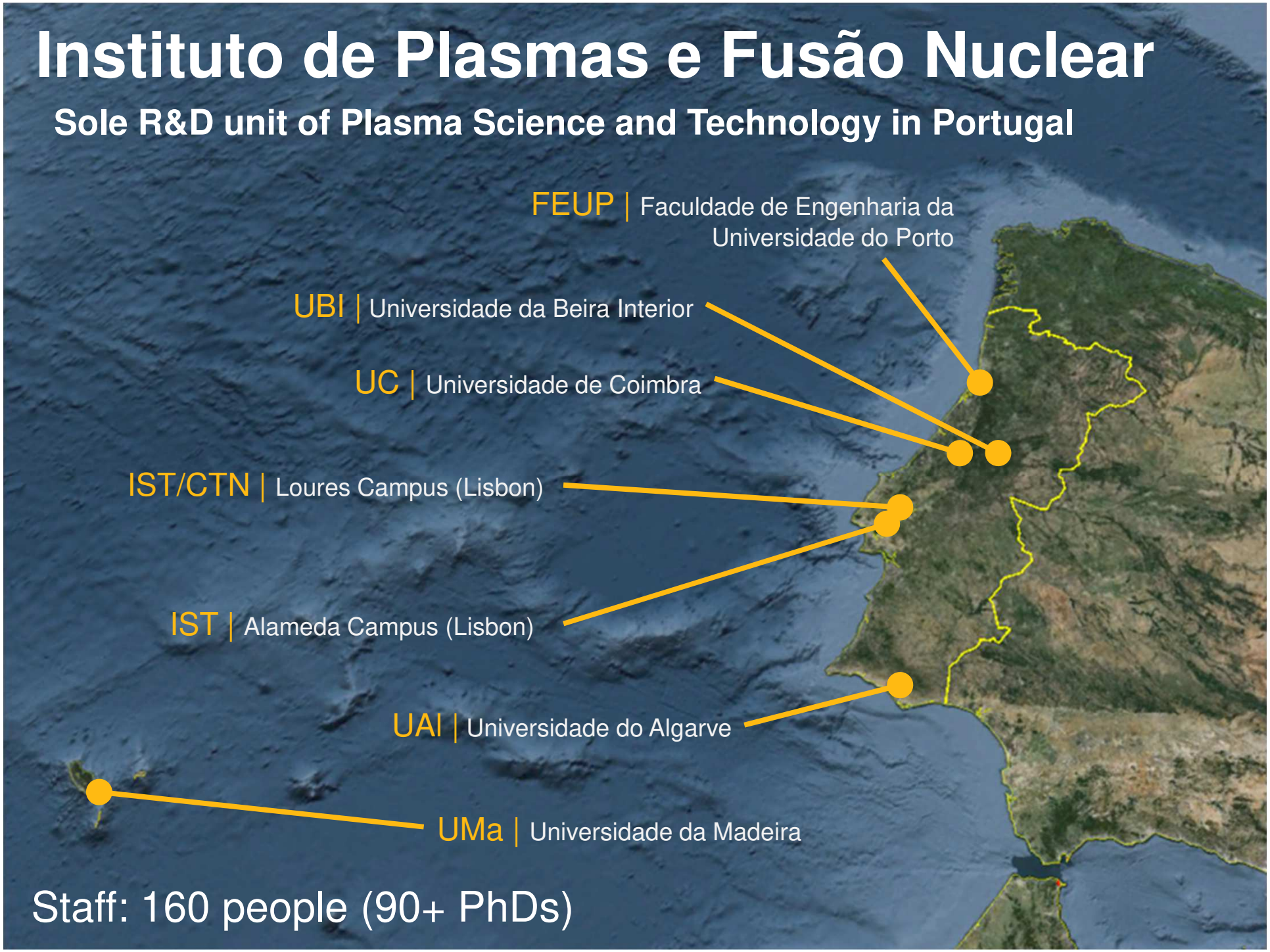
14-19 July, 2019, Sapporo, Japan


Instituto de Plasmas e Fusão Nuclear
Sole R&D unit of Plasma Science and Technology in Portugal
FEUP | Faculdade de Engenharia da Universidade do Porto
UBI | Universidade da Beira Interior
UC | Universidade de Coimbra
IST/CTN | Loures Campus (Lisbon)
IST | Alameda Campus (Lisbon)
UAl | Universidade do Algarve
UMa | Universidade da Madeira
Staff: 160 people (90+ PhDs)

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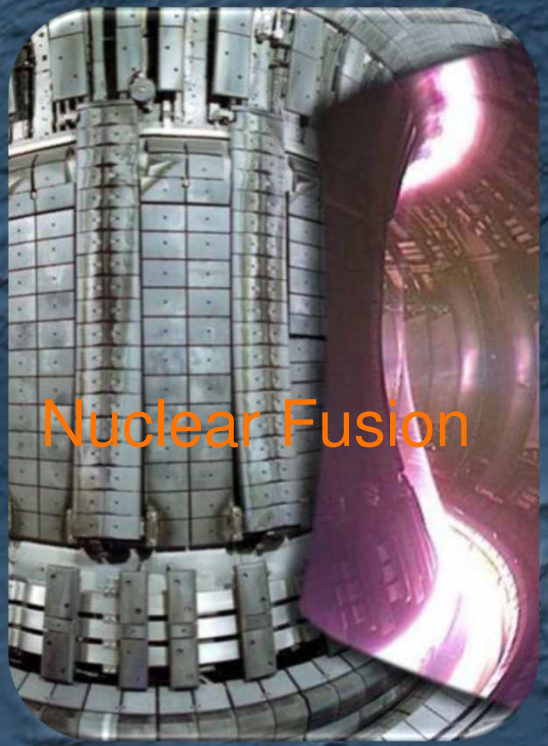
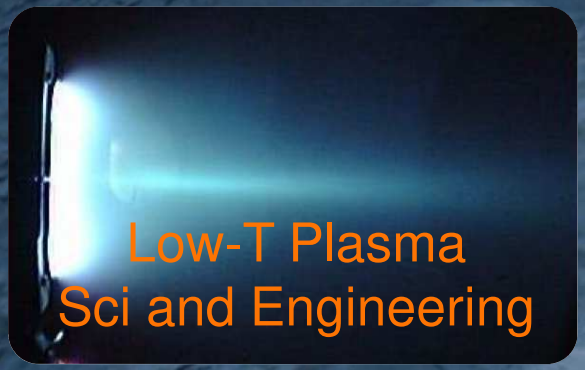
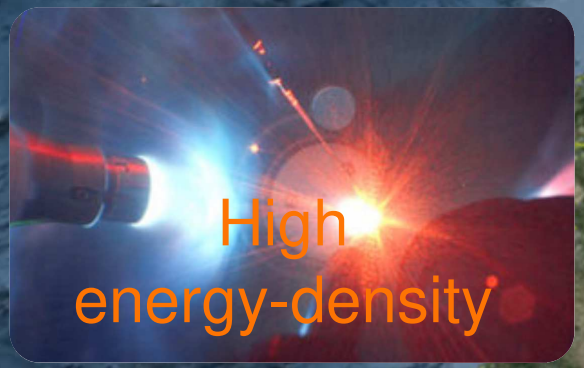
Key research activities







Plasma Chemistry

Key for developing plasma-driven applications

(e.g. material processing, plasma medicine, environmental control, energy storage, etc)

Focus on

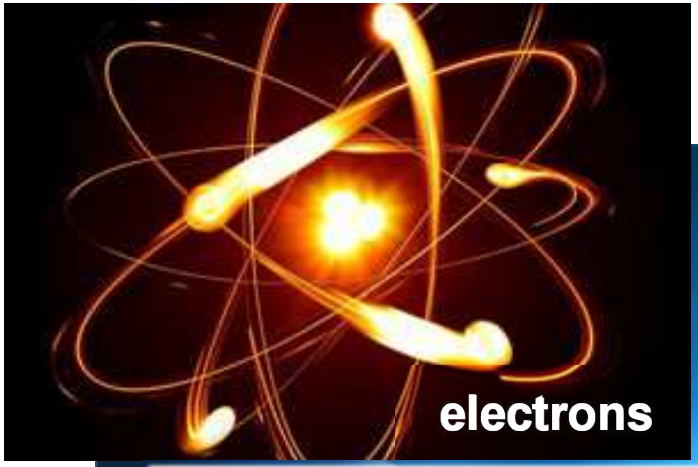
- plasma-enhanced production of reactive species
- analysis of chemical reaction pathways
- transfer of energy between the different species

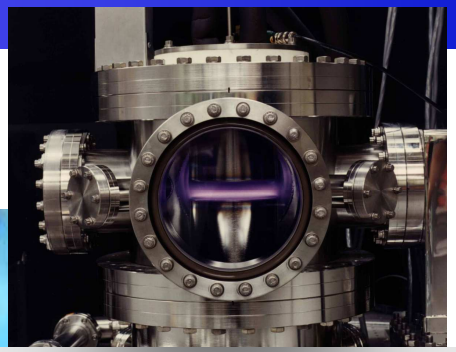
Modelling can be challenging

- various type of particles (charged and neutral, in several excited states)
- intrinsically in non-equilibrium with each other
- undergoing a large number of reactions
- involving collisional, radiative and electrostatic interactions

Plasma Chemistry

Species and interactions





Interaction with surface

Rotational interactions

Vibrational interactions

Dissociation

Electronic interactions

Fragmentation

Ionization / recombination

Attachment / detachment

Charge / excitation transfer

Association / dissociation

Recombination

Radiative transitions

heavy-species

Plasma Chemistry
Choice of models

Global models (most popular choice)

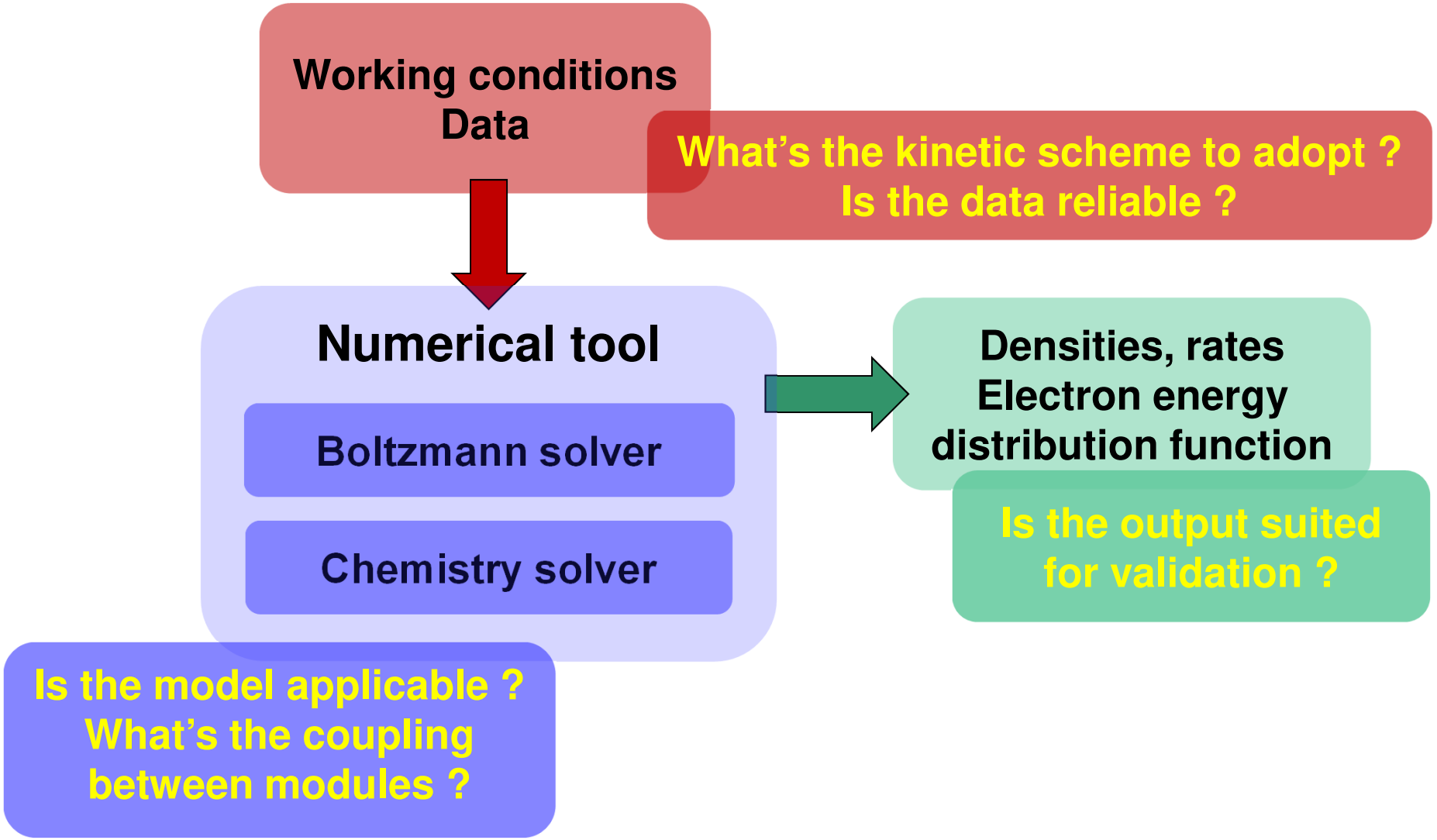
- allow describing the detailed plasma chemistry
  in complex gas mixtures

- adopt a spatially average description,
  hence involving little computational effort

- should involve the coupled solution of
  Chemistry solver (to solve the “kinetic scheme”)
  Boltzmann solver (to describe the “electron kinetics”)

Plasma Chemistry

Numerical tools / workflow



Outline

- **Global models for plasma chemistry**

  Introduction / formulation

- **Numerical tools**

  GlobalKin / ZDPlasKin / PLASIMO / LoKI / PumpKin & Boltzmann solvers

- **Implementation: success cases and open issues**

  Success cases for: N_2 / O_2 / N_2-O_2

  Open issues on: charge particle transport; Boltzmann-Chemistry coupling

- **Final remarks**

Global models for plasma chemistry

Global models for plasma chemistry

The Chemistry solver

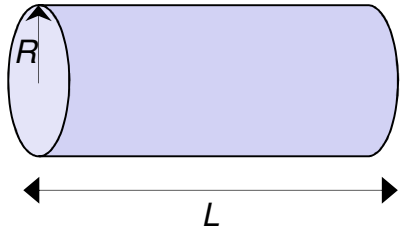
Global models solve the spatial-average rate balance equations of the various gas/plasma *k*-species

[L.L. Alves *et al*, Plasma Sources Sci. Technol. **27** 023002 (2018)]

Define *j*-reactions for the gain / loss of species A_k / $A_{k'}$

$$a_{kj}^{(1)} A_k \xrightarrow{k_j} a_{kj}^{(2)} A_{k'}$$

Kinetic scheme



$$\frac{dn_k}{dt} = S_k^{\text{chem}} + S_k^{\text{transp}}$$

Chemistry solver

The resulting system of non-linear algebraic equations is to be solved using time-dependent or stationary stiff-algorithms

Global models for plasma chemistry

The "chemistry" source-term

$$\frac{dn_k}{dt} = S_k^{\text{chem}} + S_k^{\text{transp}}$$

$$S_k^{\text{chem}} = \sum_j \left\{ \left[a_{kj}^{(2)} - a_{kj}^{(1)} \right] k_j \Pi_l n_l^{a_{kj}^{(1)}} \right\}$$

$$k_j = \begin{cases} \left(\frac{2}{m_e}\right)^2 \int_0^\infty u \sigma_j(u) f(u) du \ , & \text{for e-collisions} \\ \alpha T^\beta \exp\left[-\frac{T_{\text{ref}}}{T}\right] \ , & \text{for h-collisions} \end{cases}$$

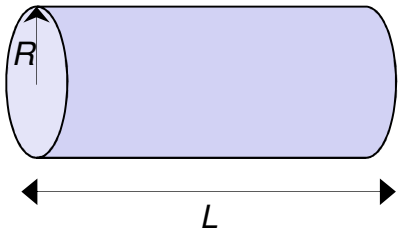
Elementary data

Electron energy distribution function

Global models for plasma chemistry

The "transport" term

$$\frac{dn_k}{dt} = S_k^{\text{chem}} + S_k^{\text{transp}}$$



$$S_k^{\text{transp}} = \begin{cases} \sum_j a_{kj}^{(2)} \frac{n_j}{\tau_j} - \frac{n_k}{\tau_k} \ , & \text{for neutral species} \\ -\frac{D_{sk}}{\Lambda^2} n_k \ , & \text{for charged species} \end{cases}$$

$$\tau_k = \frac{\Lambda^2}{D_k} + \frac{1 - \gamma_k/2}{\gamma_k \langle v_k \rangle} \frac{2RL}{L+R}$$

$$\Lambda^2 = \left[\left(\frac{\pi}{L}\right)^2 + \left(\frac{2.405}{R}\right)^2 \right]^{-1}$$

Elementary data

Electron kinetics

Global models for plasma chemistry

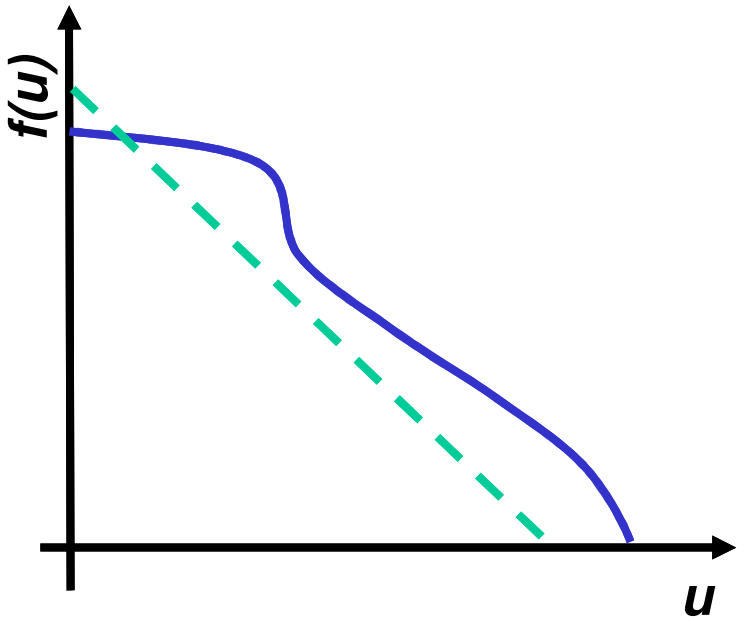
The Boltzmann solver

Electron kinetics

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \vec{\nabla} f - \frac{e\vec{E}}{m_e} \cdot \frac{\partial f}{\partial \vec{v}} = \left(\frac{\partial f}{\partial t} \right)_{\text{coll}}$$

Boltzmann solver (in LTPs)

- **Two-term approximation (most popular approach)**
- Multi-term development
- Density-gradient expansion
- Monte-Carlo approach
- …



The non-equilibrium features of the eedf can significantly change (> 20-30%) the values of the electron parameters

Global models for plasma chemistry

Closure of the model

Self-consistent calculation of the plasma maintenance characteristic, considering the input working conditions (*E/N*, *V*, *I*, n_e, …)

[L.L. Alves *et al*, Plasma Sources Sci. Technol. **27** 023002 (2018)]

The *local mean energy approximation* (LEA)

$$\cancel{\frac{\partial(\varepsilon n_e)}{\partial t}} = \Theta_{\text{field}} n_e - \cancel{\Theta_{\text{transp}} n_e} - \Theta_{\text{el}} n_e \pm \sum_j R_{j,\text{sup/inel}} \Delta V_j$$

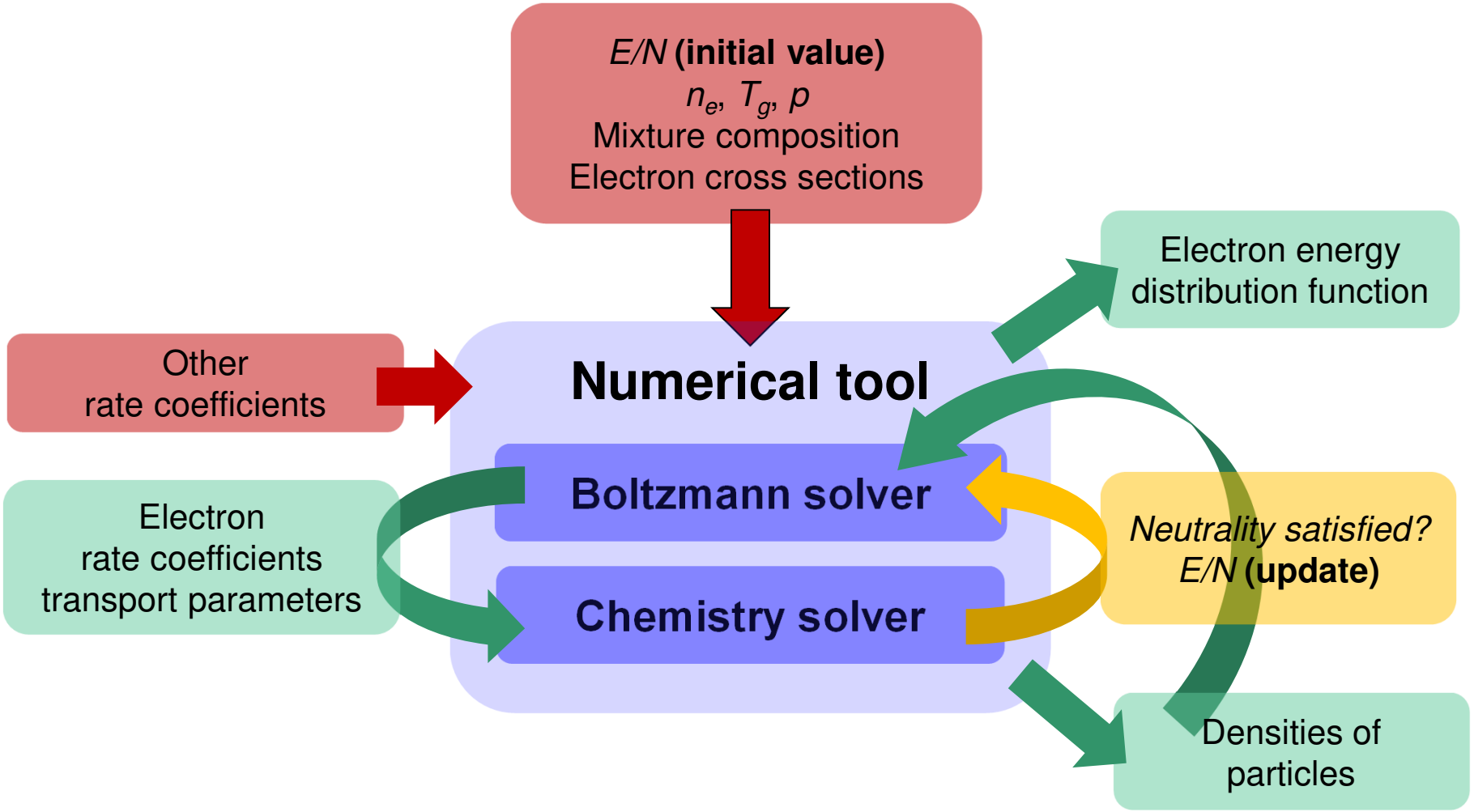
The *local field approximation* (LFA)

(often replaced by direct solution to the electron Boltzmann equation)

The decision should depend on the working conditions (e.g. low/high pressure) and should be clearly announced with every model.

Global models for plasma chemistry

Possible workflow



Global models for plasma chemistry
Applicability

Global models…
- are spatially averaged models
- focus on plasma chemistry

When to use ?
- homogeneous plasmas (dc / mw)
- intermediate to high pressures ($p > 10$ Pa $\rightarrow \lambda_i < 1$ cm)
- dense plasmas ($n_e > 10^{-16}$ m^{-3} $\rightarrow \lambda_D < 100$ μm)

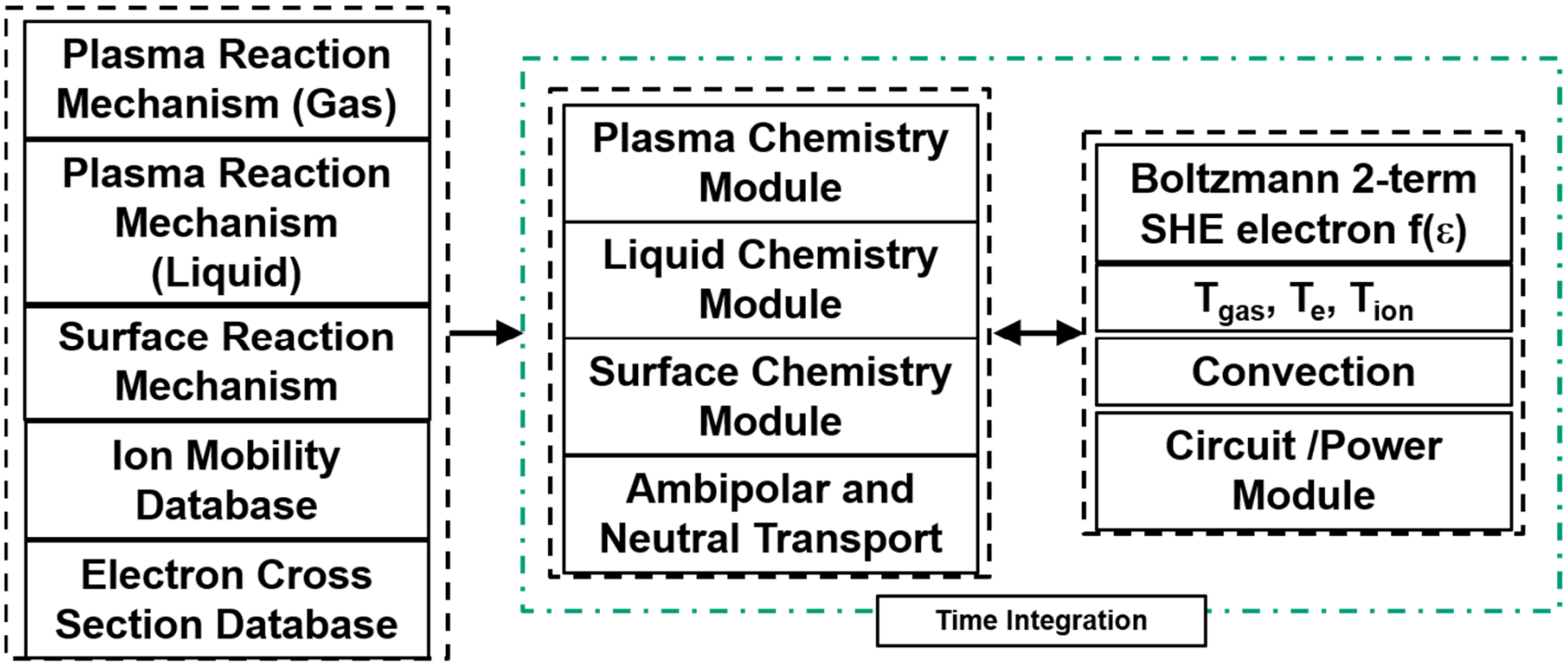
Space / time analysis ?
- dn_k/dt, by properly accounting for the time evolution of the plasma reactivity
- dn_k/dz, in surface-wave reactors, with local solution and resorting to dn_e/dz
- $dn_k/dz = dn_k/dt\ v_{flow}$, for plug-flow reactors (relate to gas residence time)

The global modelling of plasmas with strong space-time features (e.g. ccp, filamentary plasmas) should preferably follow different approaches

Numerical tools
(examples of Chemistry solvers)

GlobalKIN

- ***GlobalKIN*: 0-dimensional, multi-zone global model for plasma kinetics, and plasma-liquid-surface chemistry.**
- **Rate coefficients from 2-term SHE for Boltzmann Eq. with E/N provided by circuit model or power waveform.**
- **T_e, T_{ion} T_{gas} coupled to ambipolar, neutral and convective transport.**



[R. Dorai and M.J. Kushner, J. Phys. D **36** 1075 (2003)]
[D.S. Stafford and M.J. Kushner, J. Appl. Phys. **96** 2451 (2004)]
[J.J. Munro and J. Tennyson, J. Vac Sci. Technol. A **26** 865 (2008)]

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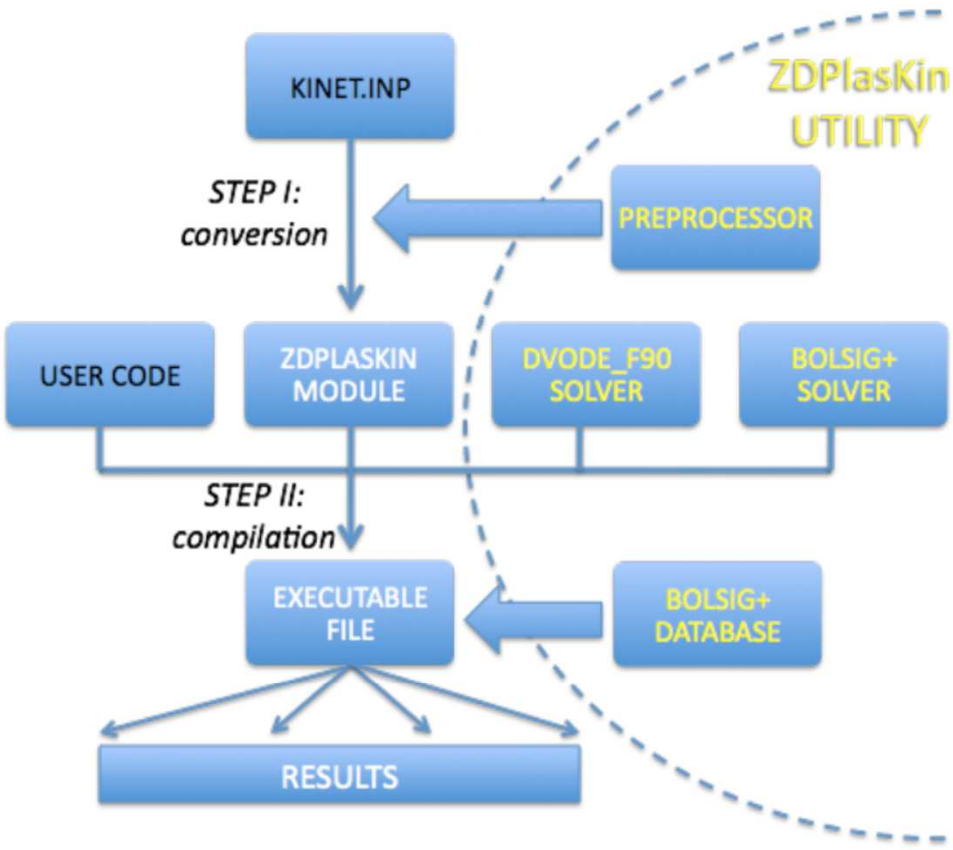
ZDPLASKIN

Zero-Dimensional PLASma KINetics solver



- In a **first step** a pre-processor is used to translate a list of species, reactions and corresponding rate constants in a simple user-friendly text format into a FORTRAN 90 module.

- This automatically generated module contains the definition of the problem, an interface to the **DVODE_F90** ODE solver and a set of supplementary routines. It includes as well an automated link to **BOLSIG+**, a Boltzmann equation solver based on the two-term approximation, which provides the electron transport rates and the rates of electron-neutral collisions.

- In a **second step**, execution of the code yields the time evolution of the species densities and the reaction rates.

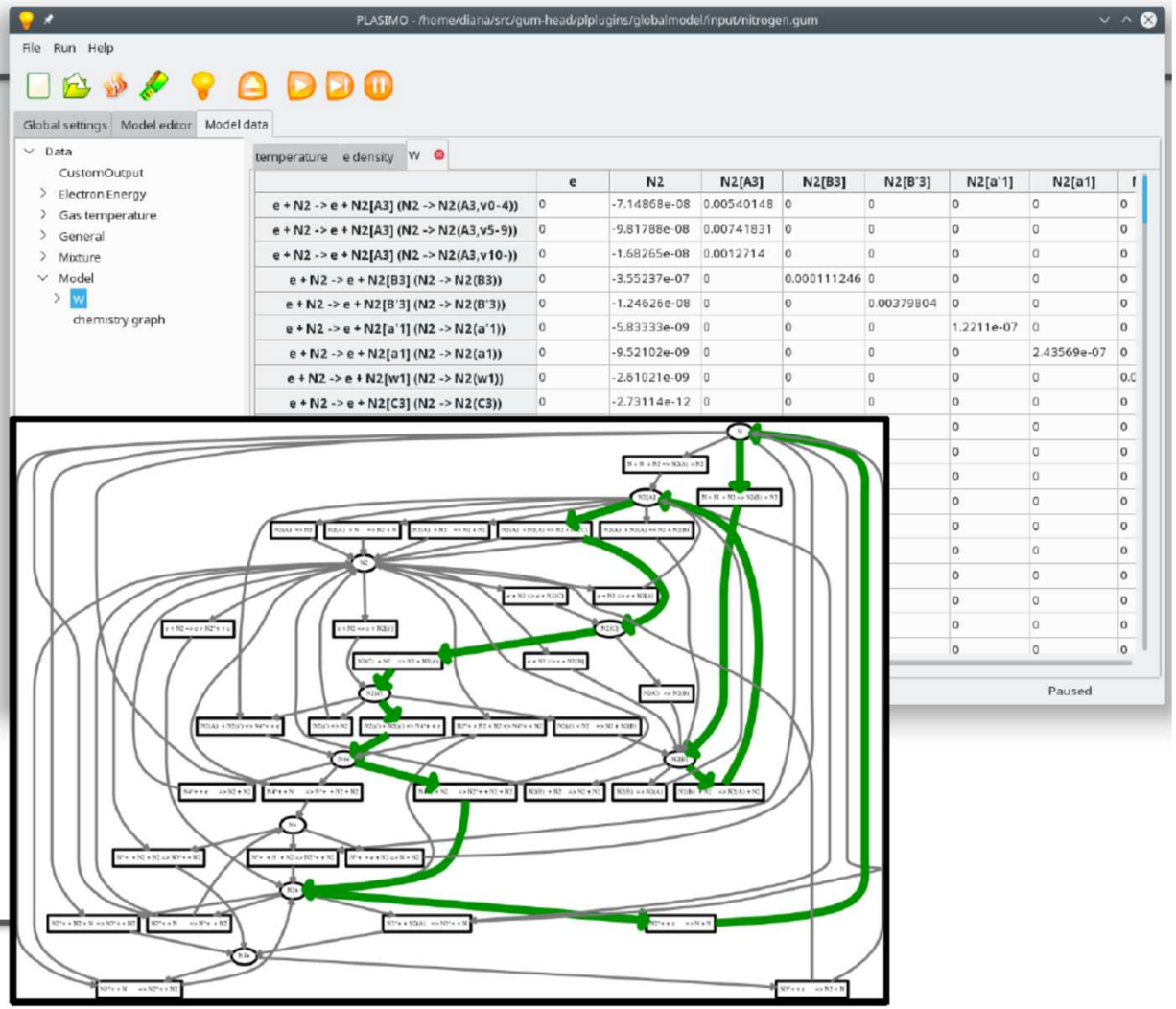
Sergey Pancheshnyi *et al*
http://zdplaskin.laplace.univtlse.fr (2008)

PLASIMO: Plasma simulation and modeling

Jan van Dijk and Diana Mihailova
[J. van Dijk *et al*, J. Phys. D **42** 194012 (2009)]

Output data analysis

- *Reaction analysis:*
  The contribution of each reaction to the production or destruction of each species
- *Pathway analysis:*
  Information about the significant pathways depending on user-specified criterion
- *Time scale analysis:*
  Generation of "Intrinsic Low Dimensional Manifolds (ILDMs)"
- *Principal Component Analysis (PCA)*



TU/e Plasma Matters.

The LisbOn KInetics (LoKI) simulation tool

(developed under MATLAB®)

LoKI-B

OPEN SOURCE

https://github.com/IST-Lisbon/LoKI

- solves the time and space independent form of the two-term electron Boltzmann equation
- includes e-e collisions, CAR operator, and growth models for the electron density.

LoKI-C

- solves the system of 0D rate balance equations for the heavy particles.
- includes modules to describe the collisional, radiative and transport mechanisms controlling the creation / destruction of species

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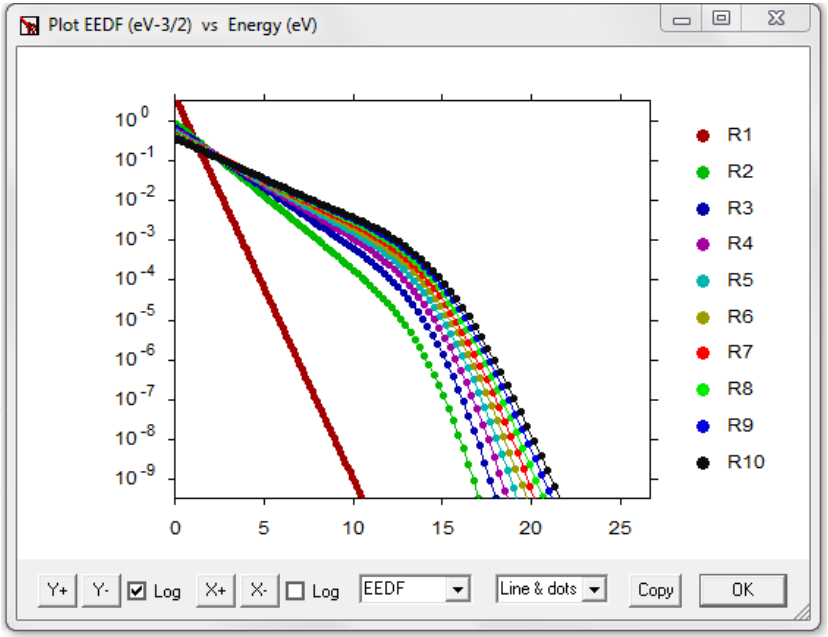
[Antonio Tejero-del-Caz, Luís L. Alves *et al* Plasma Sources Sci. Technol. **28** 043001 (2019)]

Numerical tools
(examples of Boltzmann solvers)

BOLSIG+

Electron Boltzmann equation solver

ABOUT HOW TO USE MANUAL DOWNLOAD COPYRIGHT



About

BOLSIG+ is a free and user-friendly computer program for the numerical solution of the Boltzmann equation for electrons in weakly ionized gases in uniform electric fields, conditions which occur in swarm experiments and in various types of gas discharges and collisional low-temperature plasmas. Under these conditions the electron distribution function is non-Maxwellian and determined by an equilibrium between electric acceleration and momentum and energy losses in collisions with neutral gas particles.

The main utility of BOLSIG+ is to obtain electron transport coefficients and collision rate coefficients from more fundamental cross section data, which can then be used as input for fluid models.

[G.J.M. Hagelaar and L.C. Pitchford, Plasmas Sources Sci. Technol. **14** 722 (2005)]
http://www.bolsig.laplace.univ-tlse.fr/

Other (recent) Boltzmann solvers

- **EEDF** (N A Dyatko *et al*)
  http://lxcat.net/download/EEDFR (2015)

- **BOLOS** (A Luque) – **open source**
  Python library for two-term expansion, with algorithm similar to BOLSIG+
  https://github.com/aluque/bolos

- **METHES** (M Rabie CM Franck) – **open source**
  MATLAB® Monte Carlo collision code
  [M. Rabie and C.M. Franck, Comput. Phys. Comm. **203** 268 (2016)]
  www.lxcat.net/download/METHES

- **Magboltz** (S Biagi) – **open source**
  Fortran with hardcoded data, using multi-term expansion + Monte Carlo algorithm
  [S. F. Biagi, Nucl. Instrum. Methods Phys. Res. A **421** 234 (1999)]
  http://magboltz.web.cern.ch/magboltz/

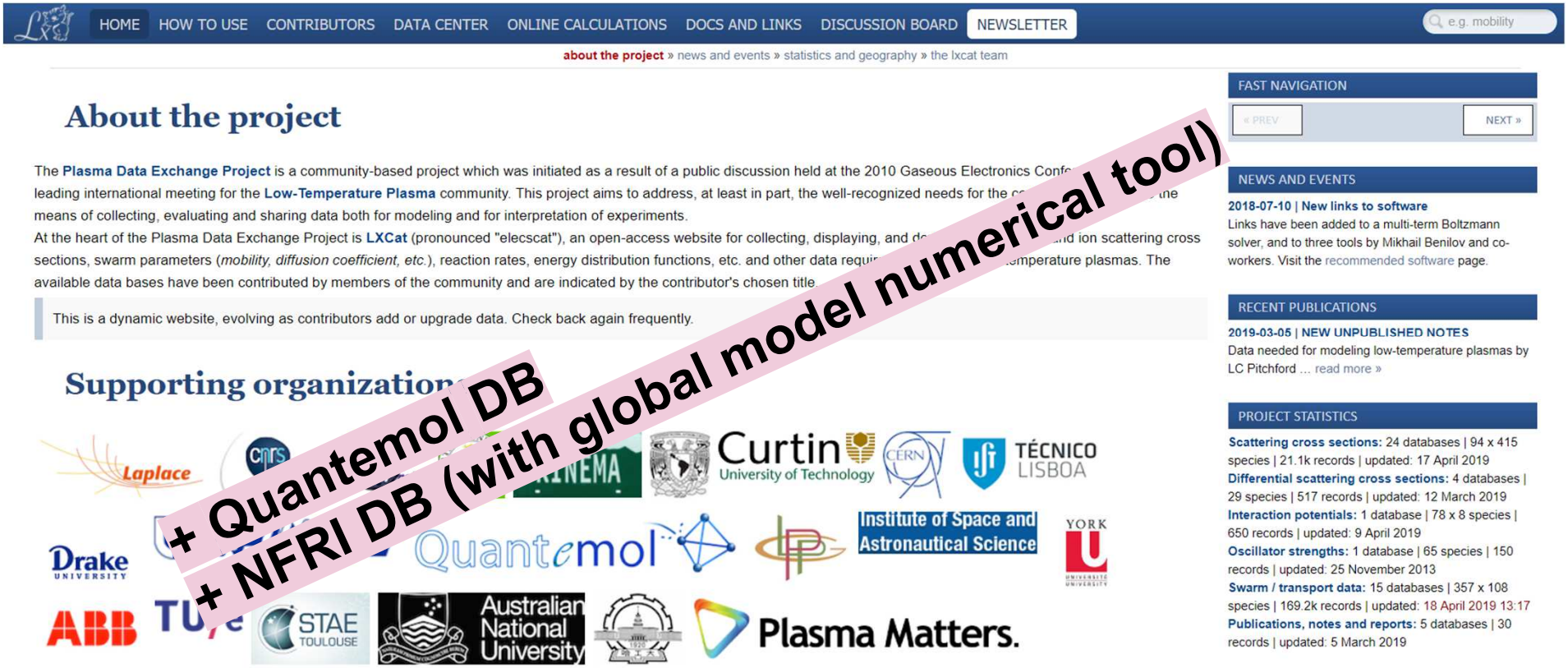
- **MultiBolt** (J Stephens) – **open source**
  MATLAB® for multi-term expansion and multi-harmonic model
  [J. Stephens, J. Phys. D: Appl. Phys. **51** 125203 (2018)]
  https://gitlab.com/LXCatThirdParty/MultiBolt

Data : electron scattering cross sections

The LXCat open-access website

[Monday, 2pm: E Carbonne et al – poster 011]

LXCat is an open-access website for collecting, displaying, and downloading **data required for modeling low-temperature plasmas**



Compatible with: BOLSIG+, LoKI-B, BOLOS, METHES, MultiBolt

[L.C. Pitchford et al, Plasma Process. Polym. 14 1600098 (2017)]

Choosing a numerical tool

Is the output independent of the numerical tool ?
(Unfortunately) No (for absolute results)**; Maybe** (for trends)

Possible reasons

- Absence of verification & benchmarking
  [round-robin exercises are needed]

- Differences in the data considered
  [hardcoded in some cases]

- Differences in the model formulation
  [**transport**, radiation, plasma-wall interaction, **coupling of Chemistry-Boltzmann solvers**, closure, …]

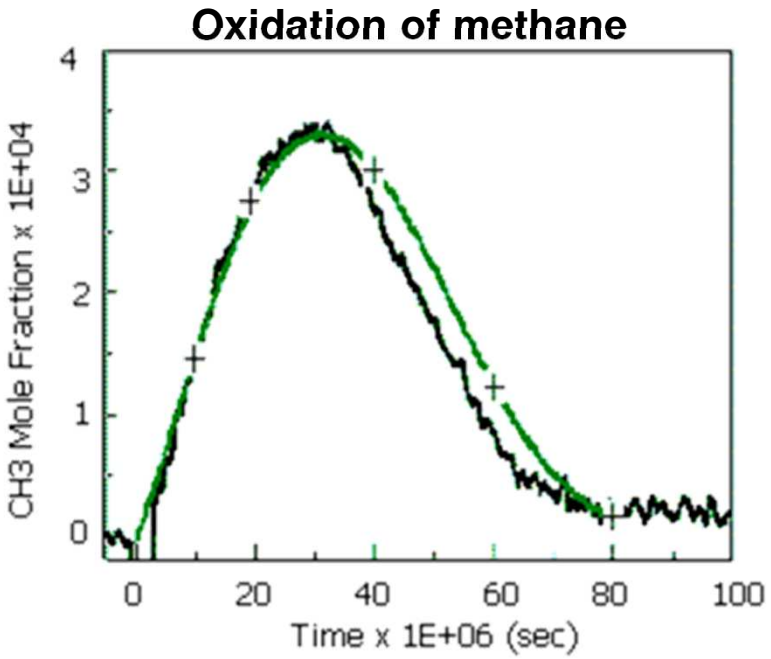
Key evolution: development of open-source codes

Choosing a kinetic scheme

Definition of reaction mechanisms

"Reaction mechanisms"

sets of reactions and rate coefficients validated against benchmark experiments



black line – exp., A.Y. Chang *et al*, 25th Symp Combustion (1994)
green line – calc., GRI-Mech 3.0
crosses – calc., Chemked

```
! GRI-Mech Version 3.0 7/30/99  CHEMKIN-II format
! See README30 file at anonymous FTP site unix.sri.com, directory gri;
! WorldWideWeb home page http://www.me.berkeley.edu/gri_mech/ or
! through http://www.gri.org , under 'Basic  Research',
! for additional information, contacts, and disclaimer
ELEMENTS
O  H  C  N  AR
END
SPECIES
H2       H        O        O2       OH       H2O      HO2      H2O2
C        CH       CH2      CH2(S)   CH3      CH4      CO       CO2
HCO      CH2O     CH2OH    CH3O     CH3OH    C2H      C2H2     C2H3
C2H4     C2H5     C2H6     HCCO     CH2CO    HCCOH    N        NH
NH2      NH3      NNH      NO       NO2      N2O      HNO      CN
HCN      H2CN     HCNN     HCNO     HOCN     HNCO     NCO      N2
AR       C3H7     C3H8     CH2CHO   CH3CHO
END
!THERMO
! Insert GRI-Mech thermodynamics here or use in default file
!END
REACTIONS
2O+M<=>O2+M                               1.200E+17   -1.000        .00
H2/ 2.40/ H2O/15.40/ CH4/ 2.00/ CO/ 1.75/ CO2/ 3.60/ C2H6/ 3.00/ AR/  .83/
O+H+M<=>OH+M                              5.000E+17   -1.000        .00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
O+H2<=>H+OH                               3.870E+04    2.700    6260.00
O+HO2<=>OH+O2                             2.000E+13     .000        .00
O+H2O2<=>OH+HO2                           9.630E+06    2.000    4000.00
O+CH<=>H+CO                               5.700E+13     .000        .00
O+CH2<=>H+HCO                             8.000E+13     .000        .00
O+CH2(S)<=>H2+CO                          1.500E+13     .000        .00
O+CH2(S)<=>H+HCO                          1.500E+13     .000        .00
O+CH3<=>H+CH2O                            5.060E+13     .000        .00
O+CH4<=>OH+CH3                            1.020E+09    1.500    8600.00
```

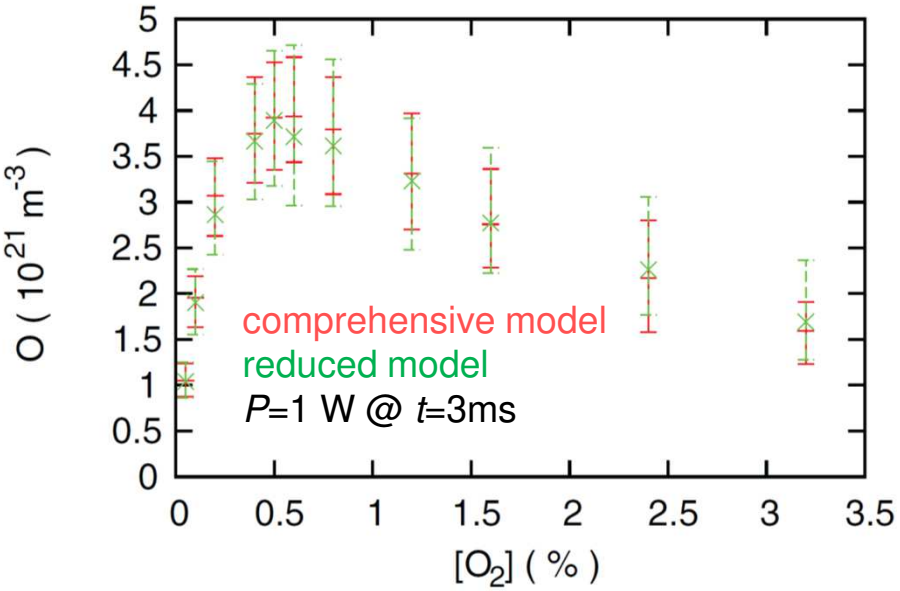
Bottlenecks: state-to-state excitations (e.g., between e-levels; for full v-manifold),
dissociation mechanisms, wall reactions, …

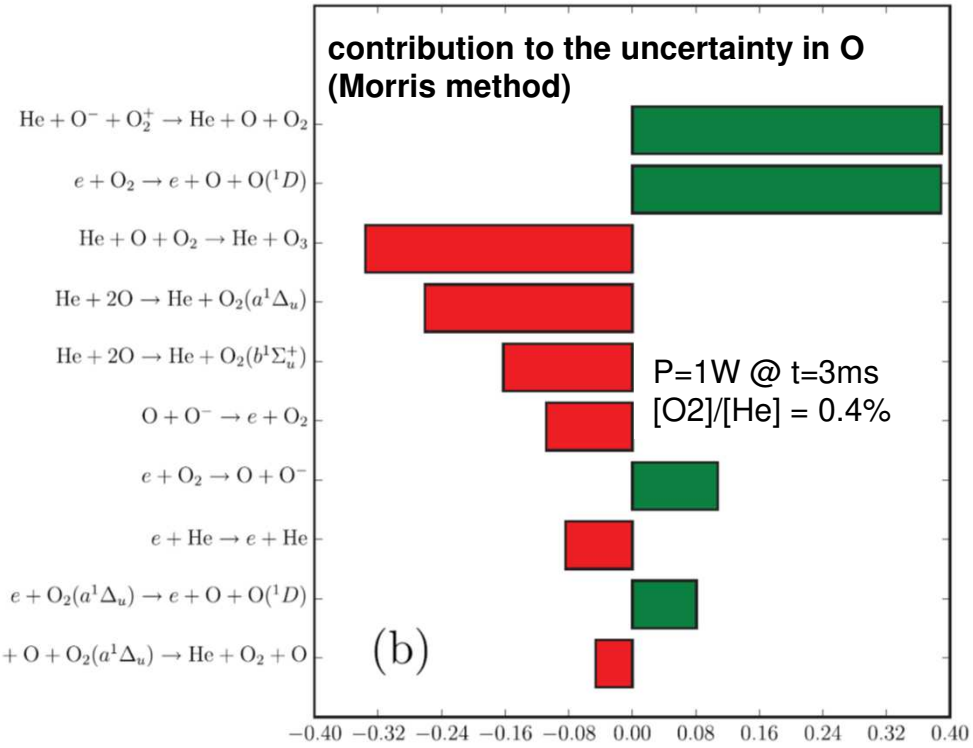
Key evolution: sharing of data and kinetic schemes

Definition of reaction mechanisms

Model reduction and screening

Accuracy: which reactions are meaningful for final predictions ?
Precision: which input most strongly affects model predictions ?





[M.M. Turner, Plasma Sources Sci. Technol. **25** 015003 (2016)]

Definition of reaction mechanisms

Sensitivity analysis and reduction of kinetic schemes

The analysis is challenging

- it can be cumbersome
  due to the initial huge number of reactions and parameters

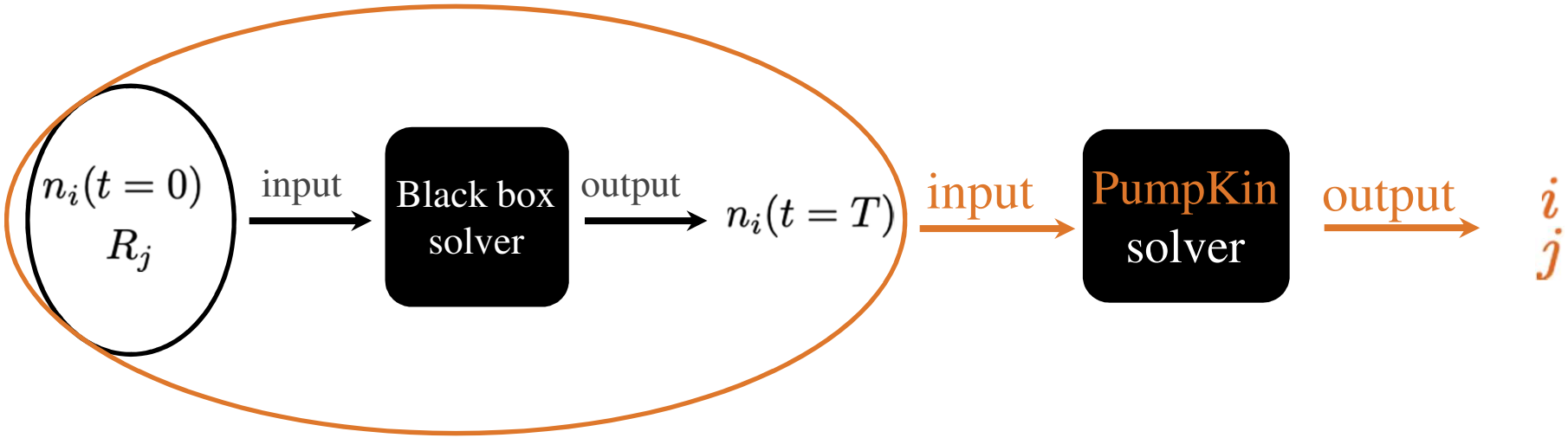
- results can depend on the approach followed
  (uncertainty analysis, stoichiometric analysis, PCA, physical intuition, …)

- misleading conclusions can be drawn

[K. Peerenboom *et al* Plasma Sources Sci. Technol. **24** 025004 (2015)]
[P. Bílek, A. Obrusník *et al*, Plasma Sources Sci. Technol. **27** 085012 and 085013 (2018)]
[A. Ayilaran *et al*, Plasma Sci. Technol. **21** 064006 (2019)]

PumpKin

(Pathway reduction method for plasma Kinetics)



Aram Markosyan

A.H. Markosyan et al Computer Physics Communications **185** 2697 (2014)

www.pumpkintool.org (2013)

Implementation
success cases

Implementation: success cases

Based on the LoKI suit

"Success" =

- Good description of key plasma quantities
  validation of kinetic schemes **(KIT)** by comparing calculations with experimental measurements

- Good performance of the **tool**
  including basic **verification**: benchmarks, conservation laws, …

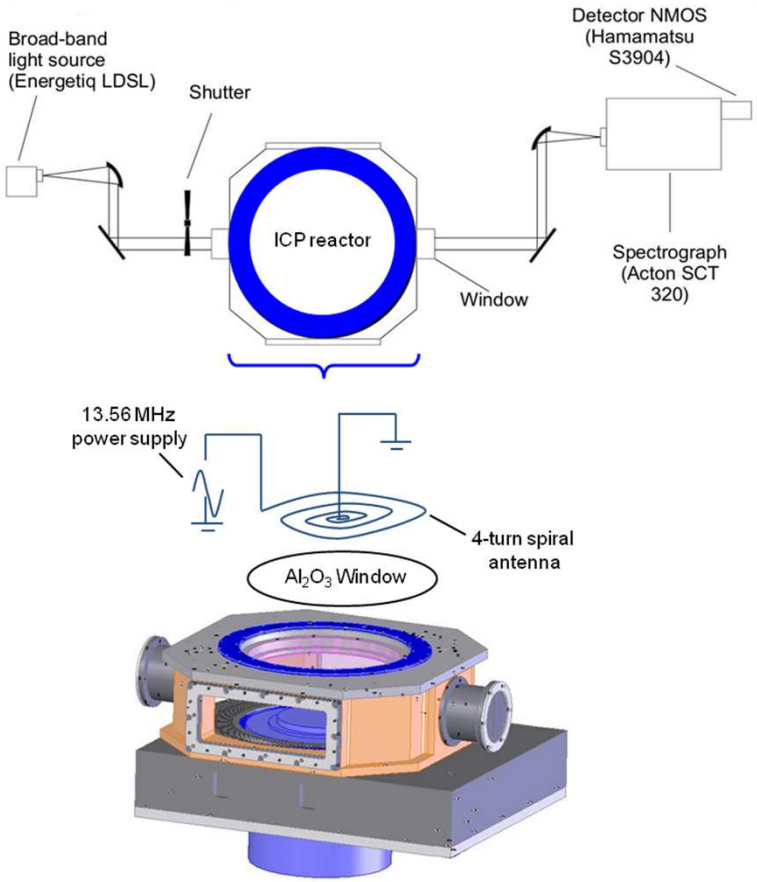
Examples for nitrogen, oxygen and dry air at various conditions

- New work
- Legacy checks
  (confirming previous validations / performing benchmarks with old tool)

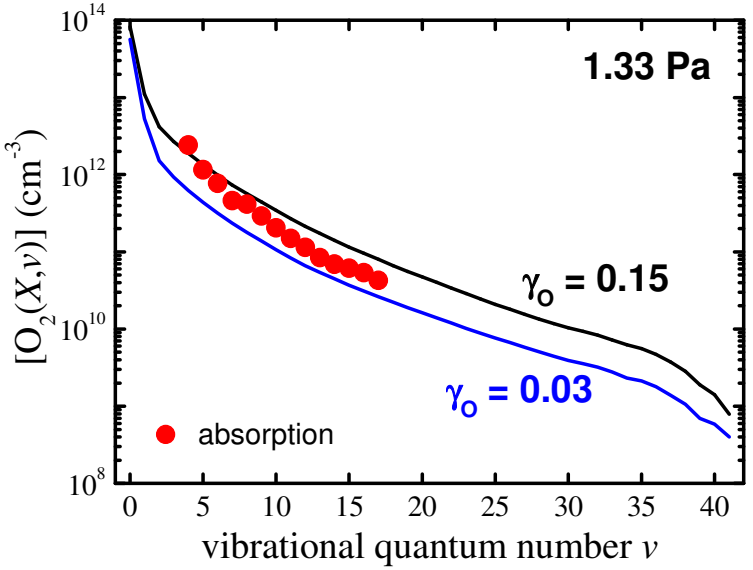
[V. Guerra *et al*, Plasma Sources Sci. Technol., in print (2019)]

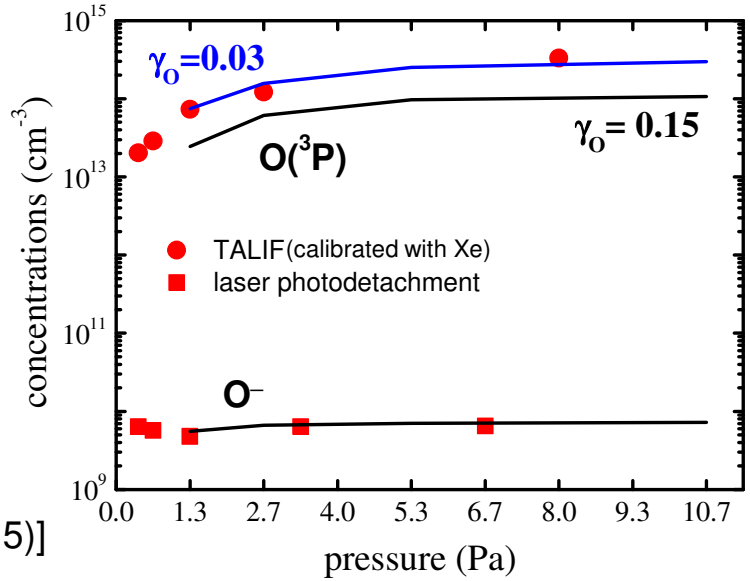
Implementation: success cases

Oxygen ICP at low pressure



f = 13.56 MHz; P < 500W; p = 1.33-10.67 Pa

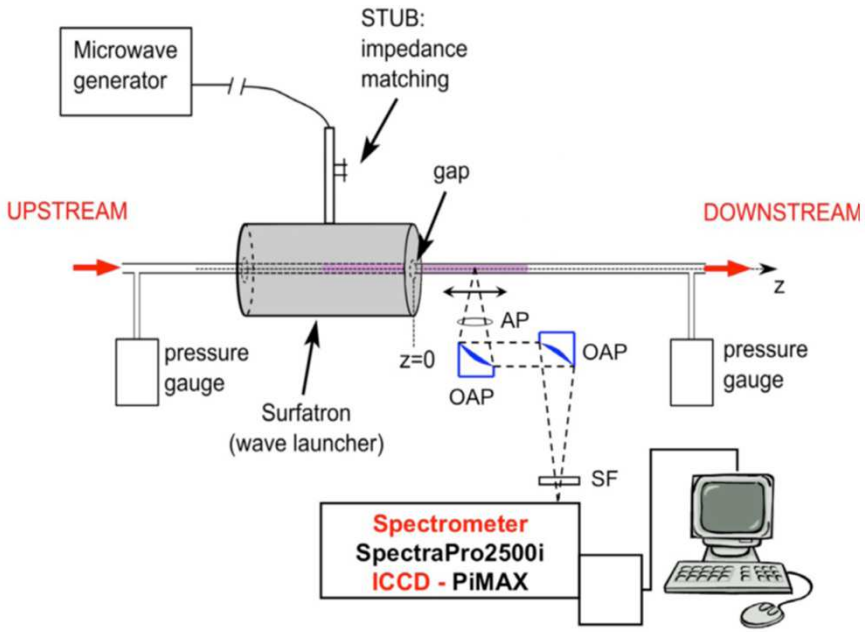




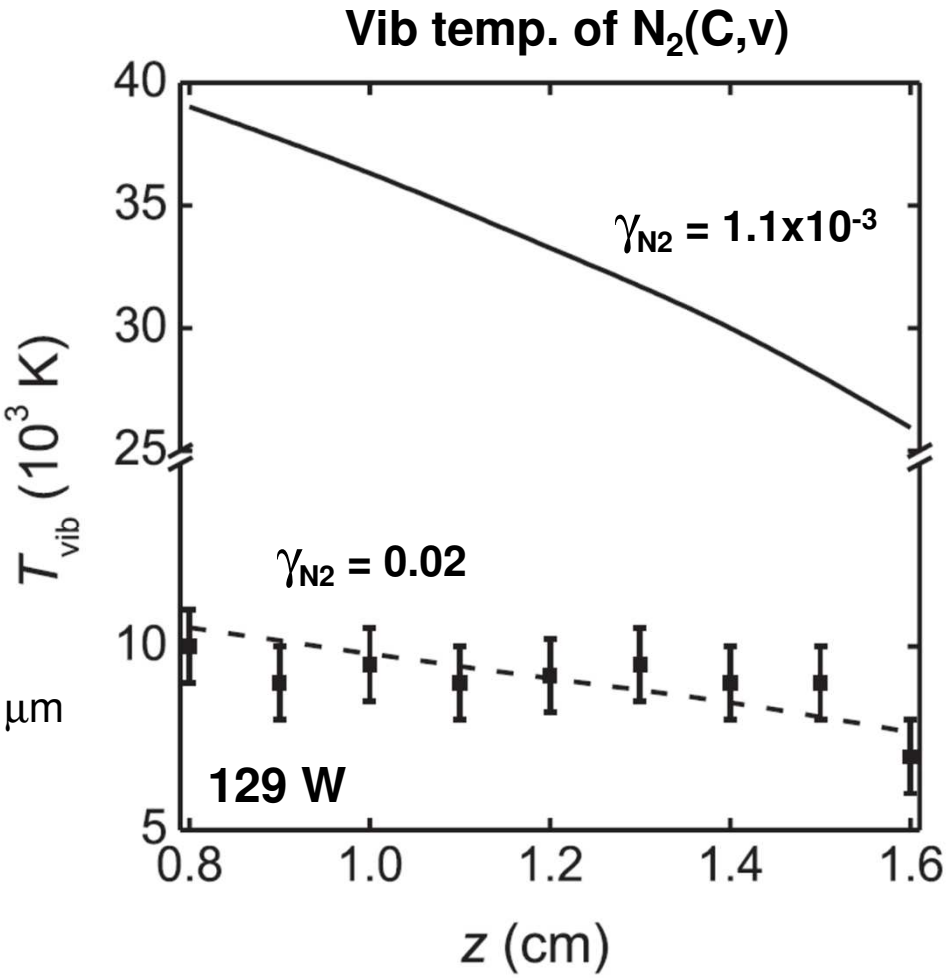
[J-P Booth *et al*, J. Phys. D **45** 195201 (2012)]
[M. Foucher *et al*, Plasma Sources Sci. Technol. **24** 042001 (2015)]

Implementation: success cases

Dry-air microwave micro-discharge at low pressure



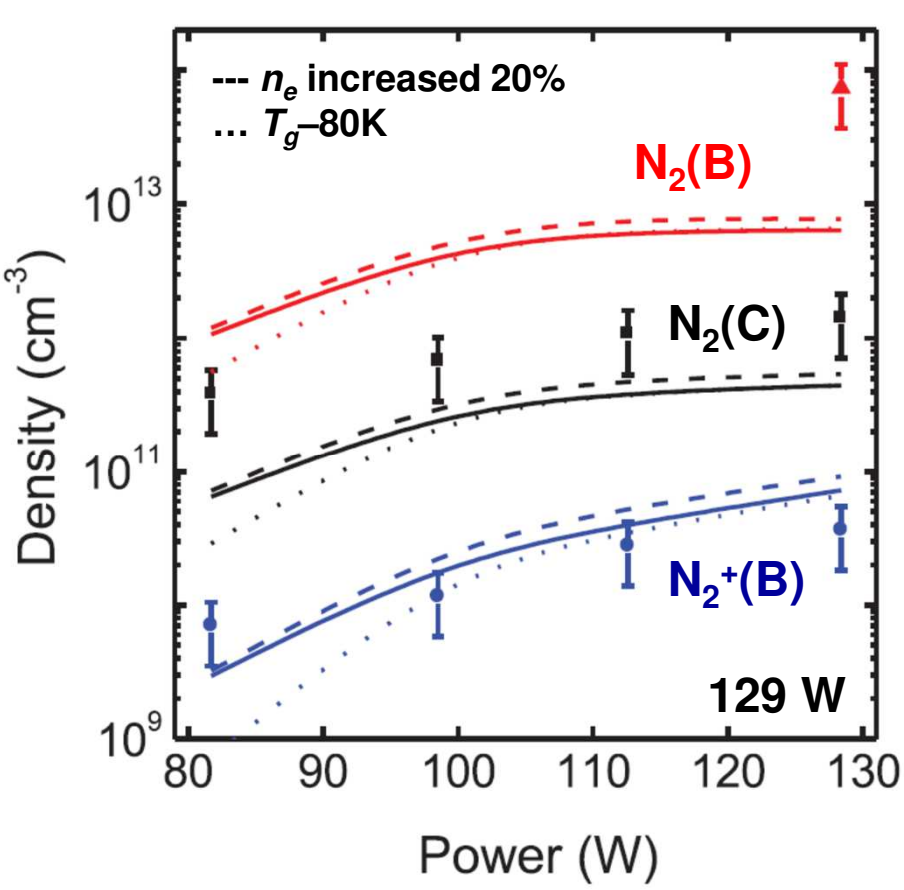
f = 2.45 GHz; P ~ 100 W; p = 300 Pa; R = 345 μm

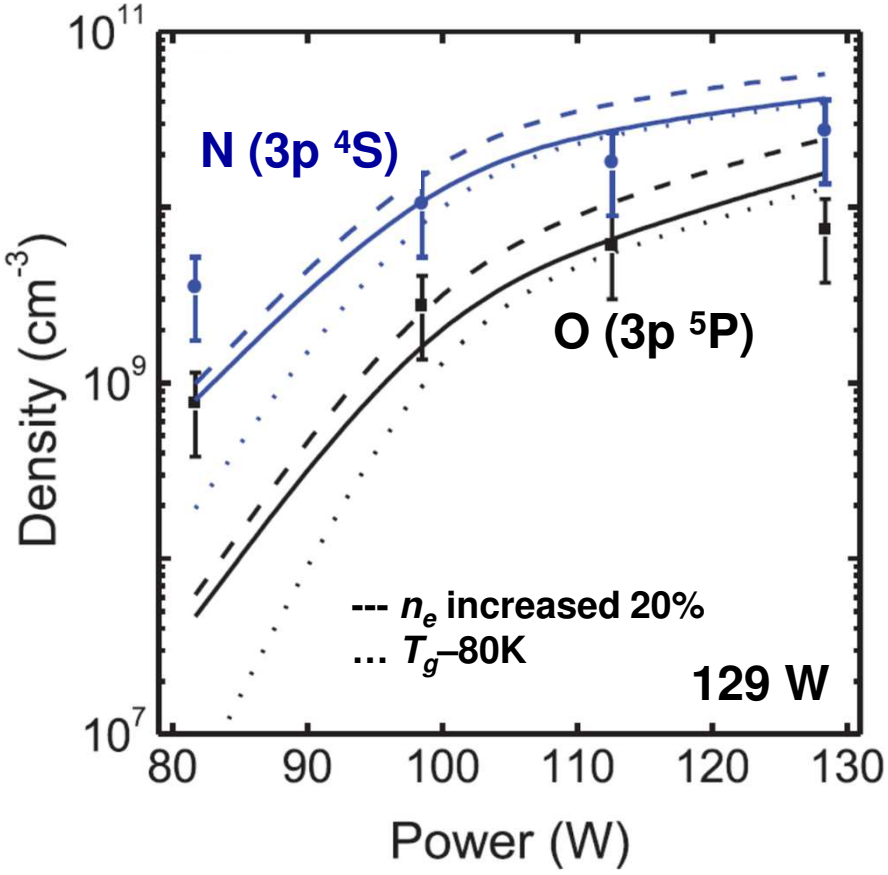


[G.D. Stancu *et al*, J. Phys. D **49** 435202 (2016)]

Implementation: success cases

Dry-air microwave micro-discharge at low pressure





[G.D. Stancu *et al*, J. Phys. D **49** 435202 (2016)]

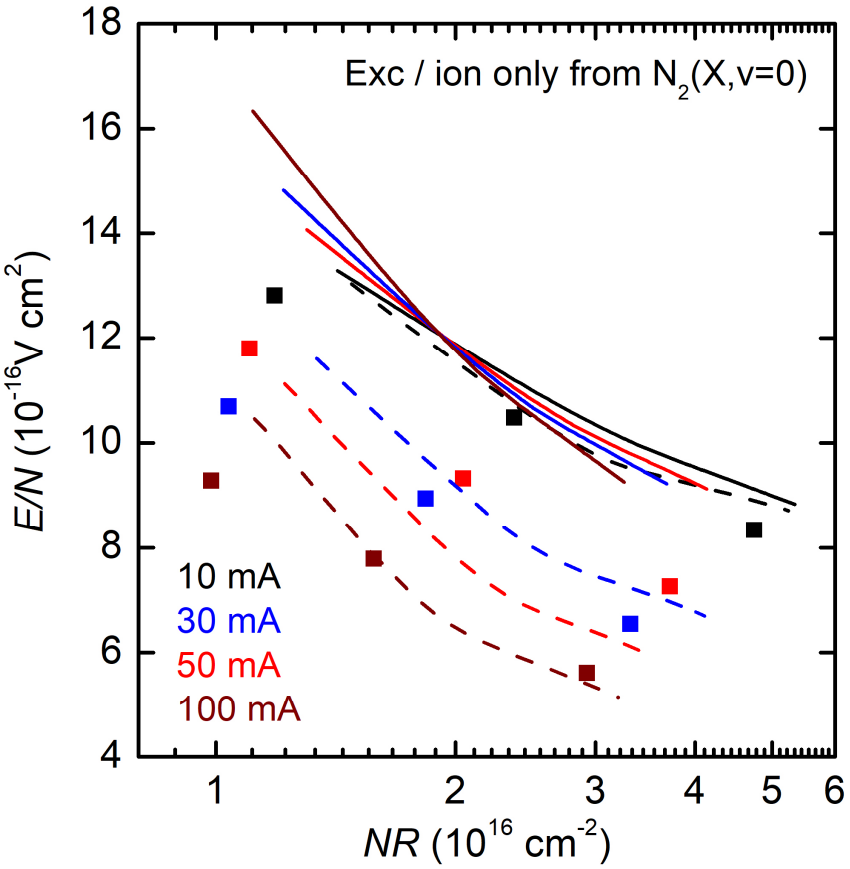
Implementation: success cases

Nitrogen DC discharges (work in progress)

[Tuesday, 2pm: A Tejero-Del-Caz et al – poster 023]

Dashed lines – previous calculations
[V. Guerra and J Loureiro, Plasma Sources Sci. Technol. **6** 361 (1997)]

Points – experiment (p = 60-300 Pa; T_g ~ 400-700 K; I = 5-100 mA)
[G. Cernogora, PhD Thesis, Université Paris-Sud (Orsay, France) (1980)]



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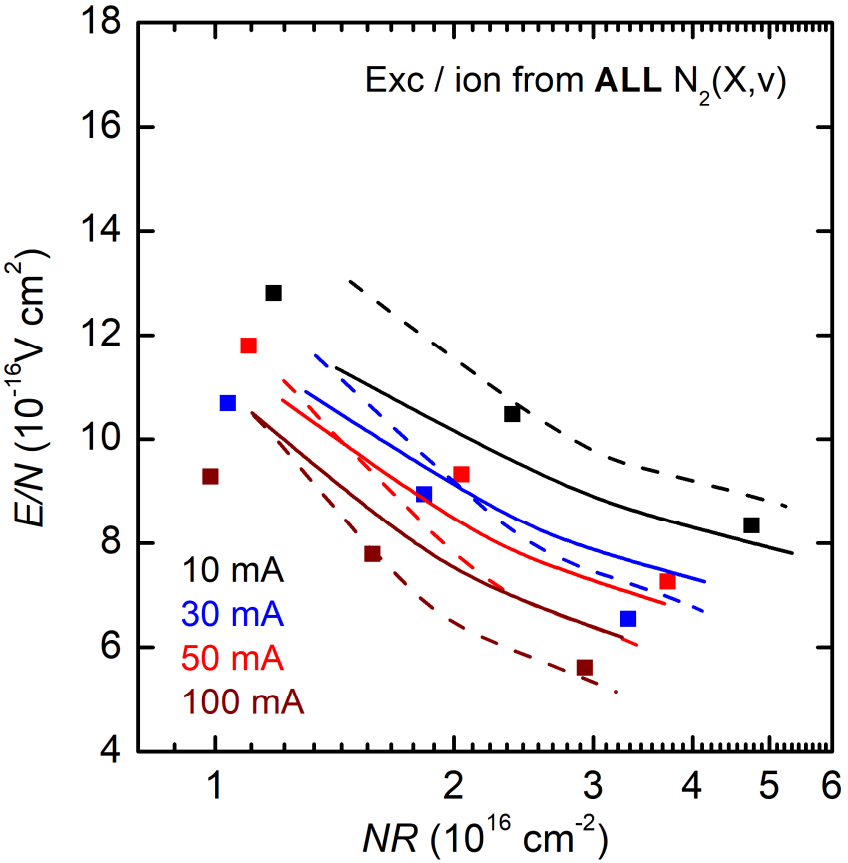
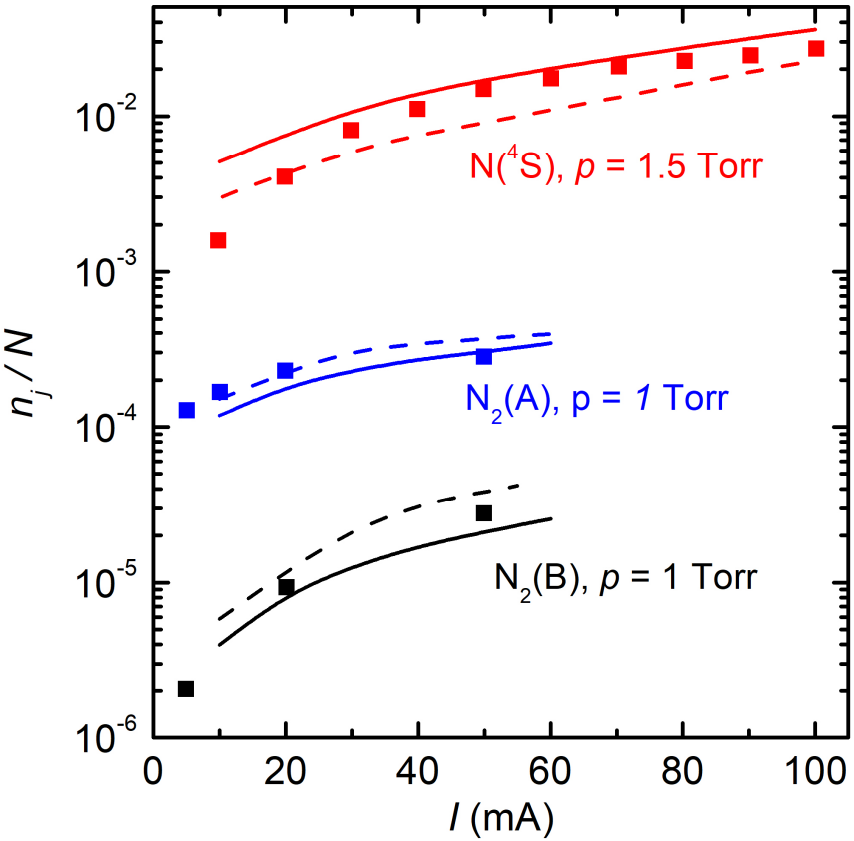
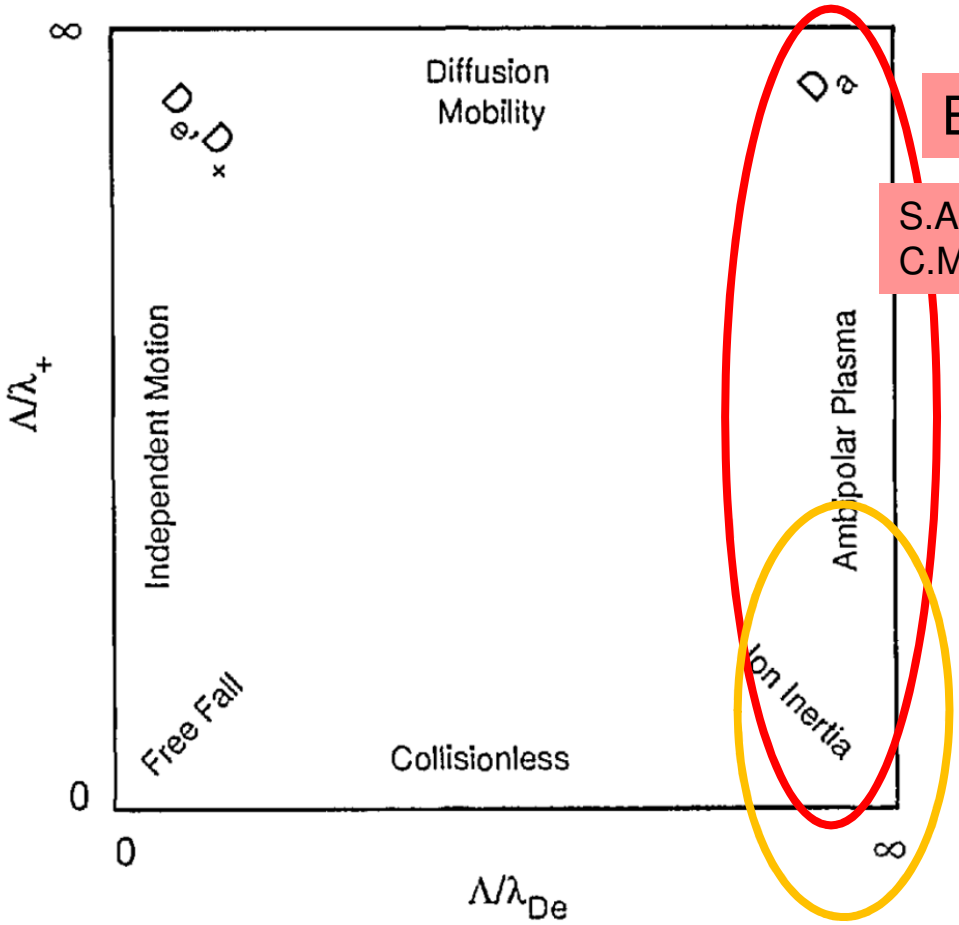




Implementation
open issues

Implementation: open issues

Ambipolar transport of charged species



Electrons and one positive ion species

S.A. Self and H.N. Ewald, Phys. Fluids **9** 2486 (1966)
C.M. Ferreira and A. Ricard, J. Appl. Phys. **54** 2261 (1983)

$$S_k^{\text{transp}} = -\frac{D_{sk}}{\Lambda^2} n_k$$

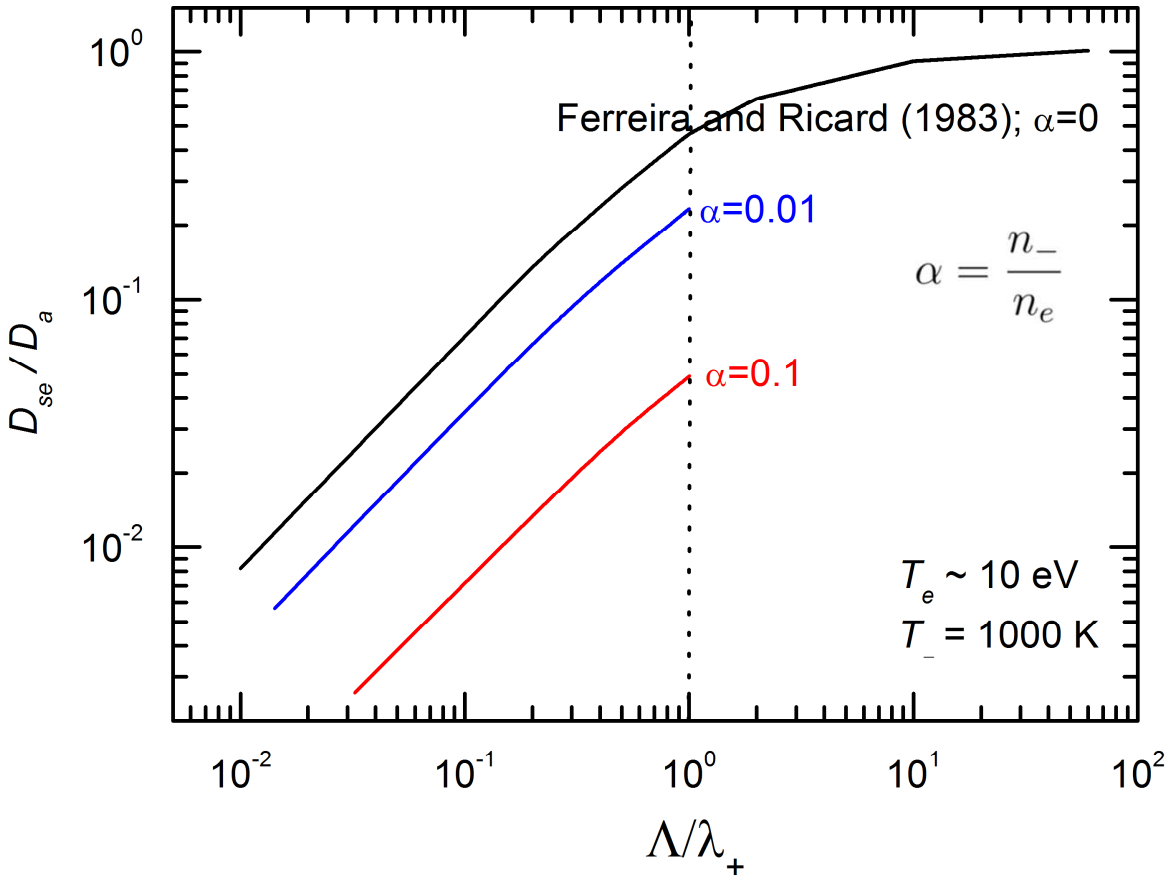
Electrons; multiple positive ions; one negative ion (at low density)

P. Coche *et al*, J. Phys. D **49**, 235207 (2016)

[A.V. Phelps, J. Res. Natl. Inst. Stand. Technol. **95** 407 (1990)]

Implementation: open issues

Ambipolar transport of charged species – the effective diffusion coefficient

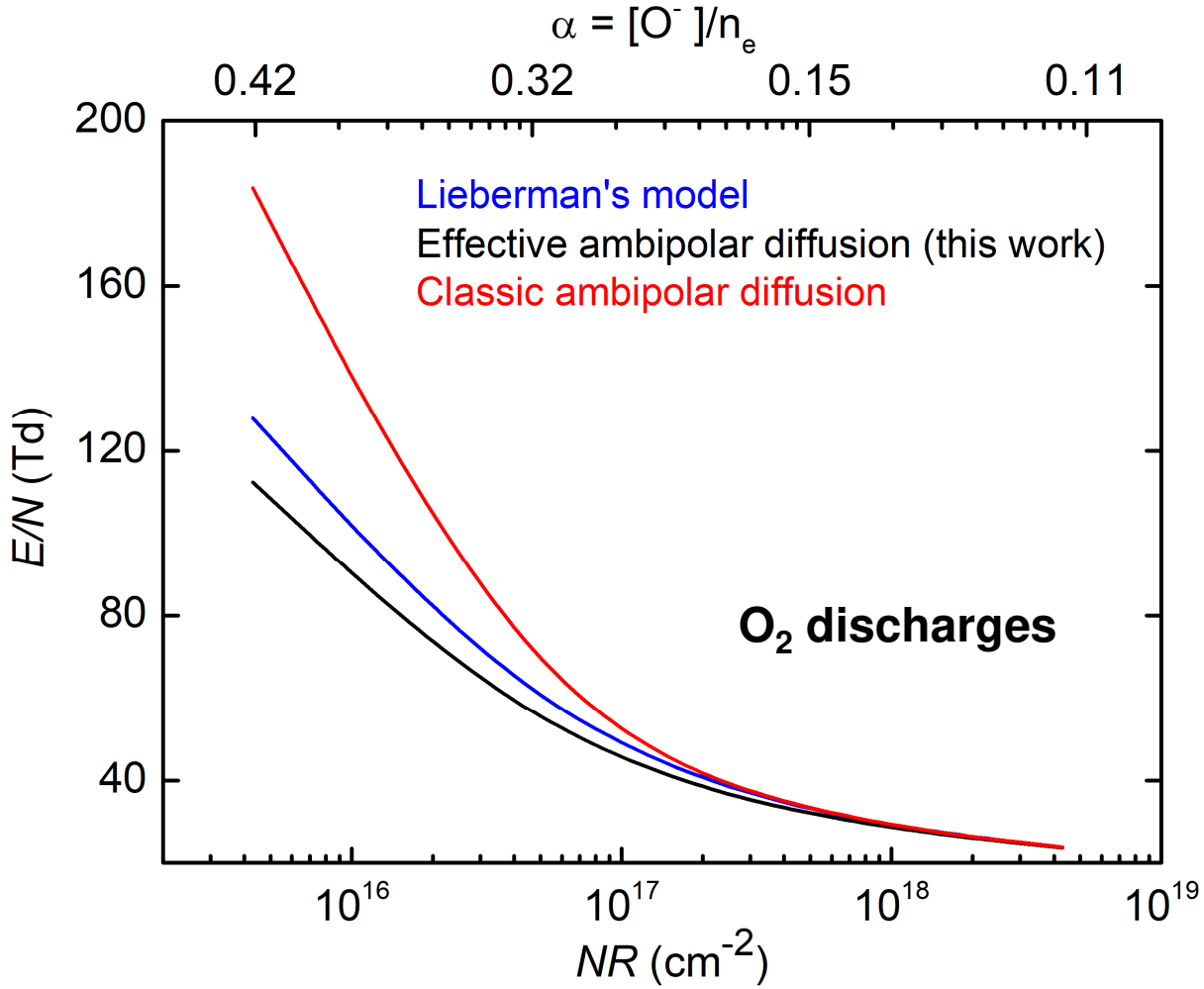


$$S_k^{\text{transp}} = -\frac{D_{sk}}{\Lambda^2} n_k$$

[P. Coche *et al*, J. Phys. D **49**, 235207 (2016)]

Implementation: open issues

Ambipolar transport of charged species – comparison between models



Good agreement with Lieberman's model

Further analysis in progress

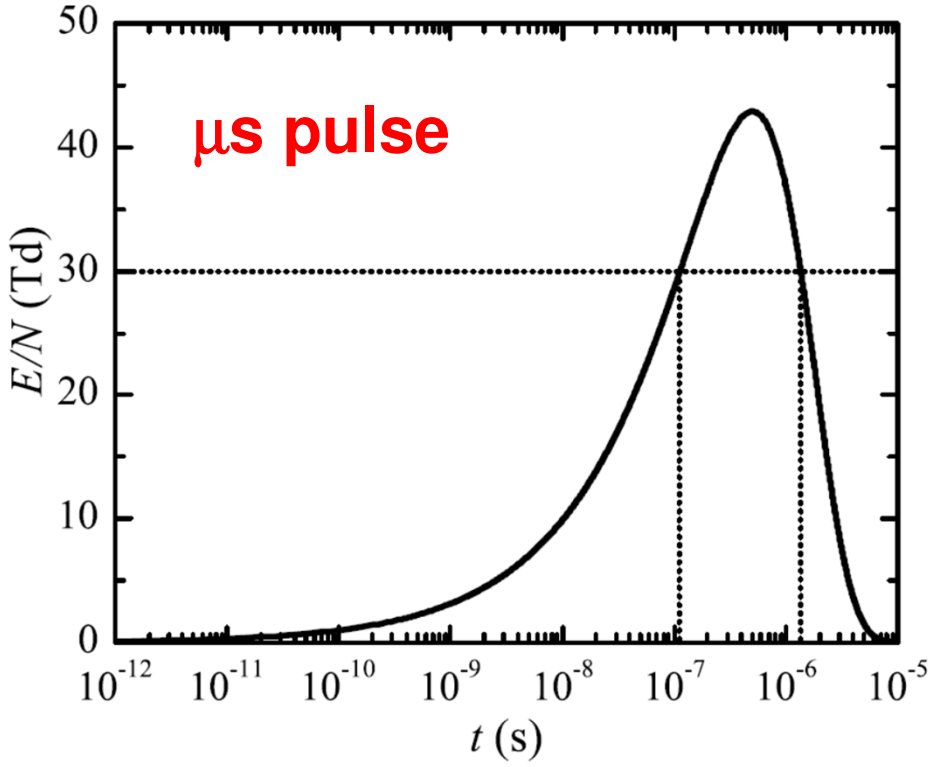
[C. Lee and M.A. Lieberman, J. Vac. Sci. Technol. **13** 368 (1995)]
[E.G. Thorsteinsson and J.T. Gudmundsson, Plasma Sources Sci. Technol. **19** 015001 and 055008 (2010)]
[P. Chabert, Plasma Sources Sci. Technol. **25** 025010 (2016)]

Implementation: open issues

Coupling between Boltzmann and Chemistry solvers : tracking time evolution

Time-dependent or quasi-stationary calculations

Growing interest in fast-pulsed nanoscale discharges



For quasi-stationary calculations

$$\frac{1}{Nf}\frac{\partial f}{\partial t} \sim \frac{1}{N\tau_{\text{evol}}} \sim \frac{\nu^{\text{energy}}}{N}$$

$$\Rightarrow \tau_{\text{evol}} \sim \frac{10^{11}}{N(\text{cm}^{-3})} \ll t_{\text{exc}}\,(\text{s})$$

At low pressure (1 Torr)

$$t_{\text{exc}} \gg 10^{-5}\ \text{s}$$ **!**

At atmospheric pressure (~10^3 Torr)

$$t_{\text{exc}} \gg 10^{-8}\ \text{s}$$ **OK**

Implementation: open issues

Coupling between Boltzmann and Chemistry solvers

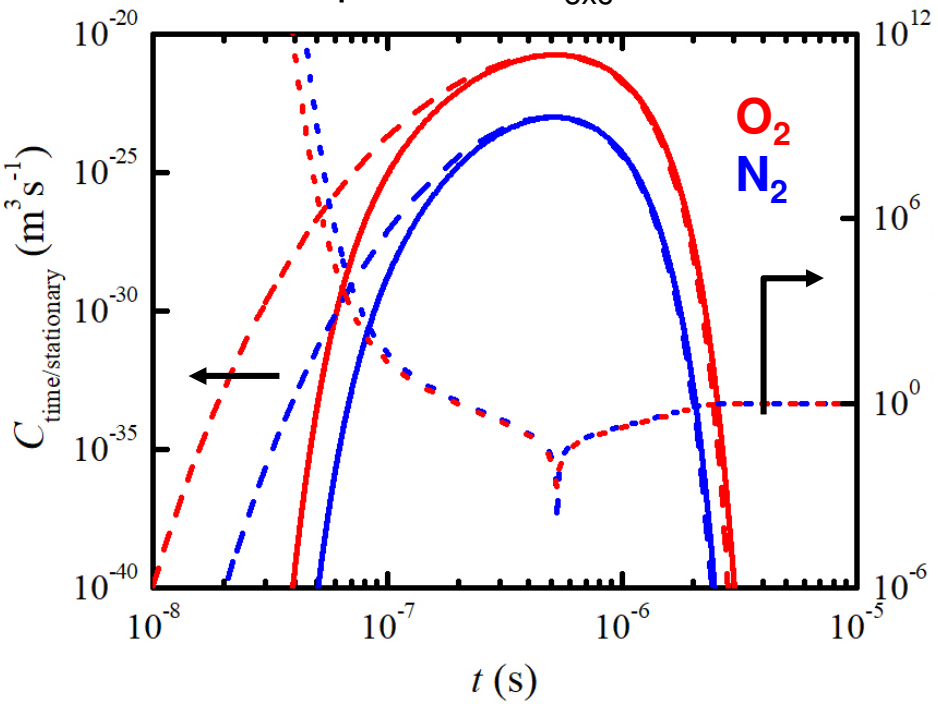
[Tuesday, 2pm
A Tejero-Del-Caz et al – poster 022]

Electron kinetics calculations (with LoKI-B) in dry air (80% N_2 – 20% O_2)

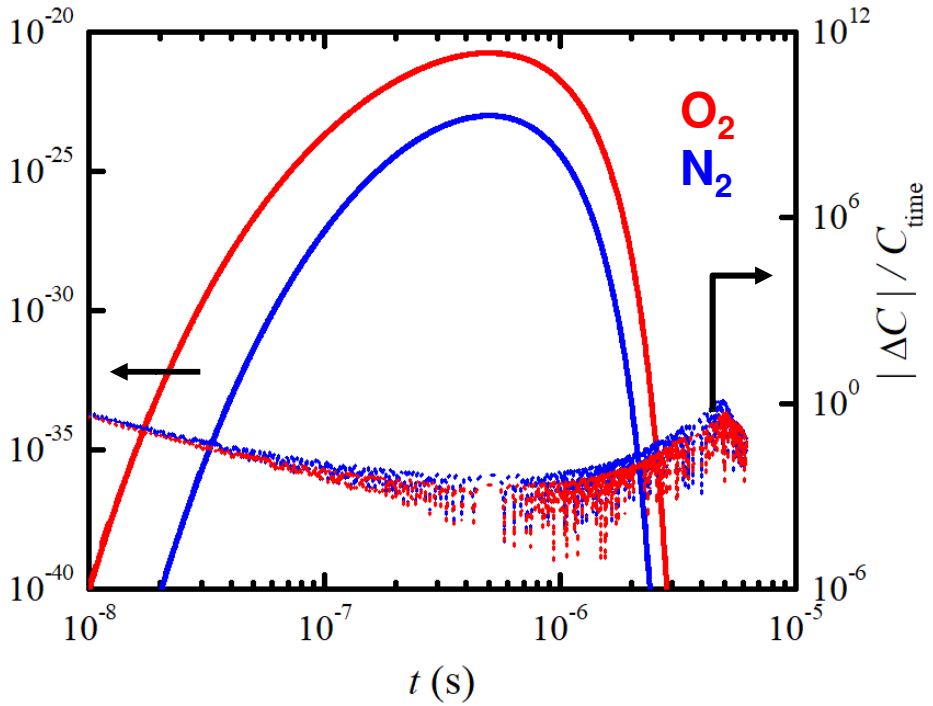
Time evolution of the ionization rate coefficient for a **micro-second pulse**

Quasi-stationary calculations, valid for…

Low pressure: t_{exc} » 10^{-5} s



High pressure: t_{exc} » 10^{-8} s



solid - time-dependent calc. ; dashed - quasi-stationary calc.

Final remarks

Final remarks

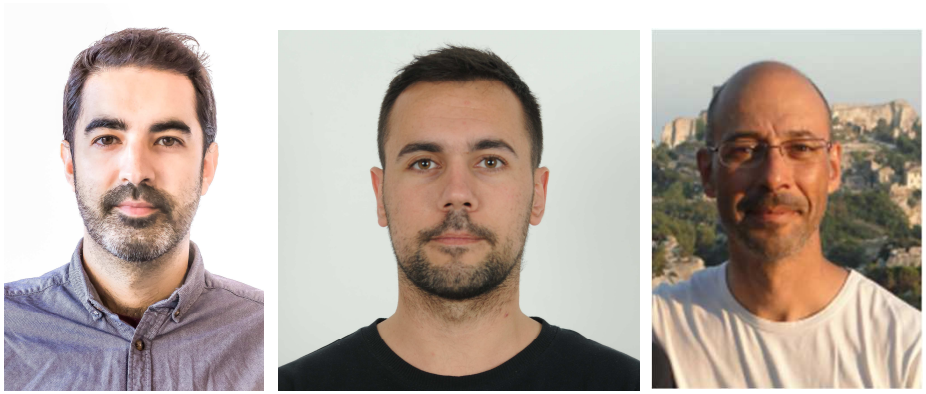
- **Simulation tools for plasma chemistry** are formidable aides for understanding and predicting the behaviour of LTPs
  (demonstrated by success cases for various complex gases and gas mixtures)

- The **improvement of the tools** needs
  - **verification procedures**
    e.g. based on crossed-benchmarking, round-robin exercises…
  - the **development of open-source codes**

- The **improvement of results** needs
  - the **definition of reaction mechanisms**
    scarce info on state-to-state reactions and wall reactions are bottlenecks
    reduction and screening of kinetics schemes could be beneficial
    the sharing of data in open-access web-platforms is key
  - **further analysis of the formulation**
    transport, coupling of modules, radiation, integrated plasma-surface modelling …
  - **validation procedures**, by comparing simulations with experiment
    collaboration with experimental teams is essential

Acknowledgements

The team



The funding institution

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