Global modelling of non-equilibrium LTPs

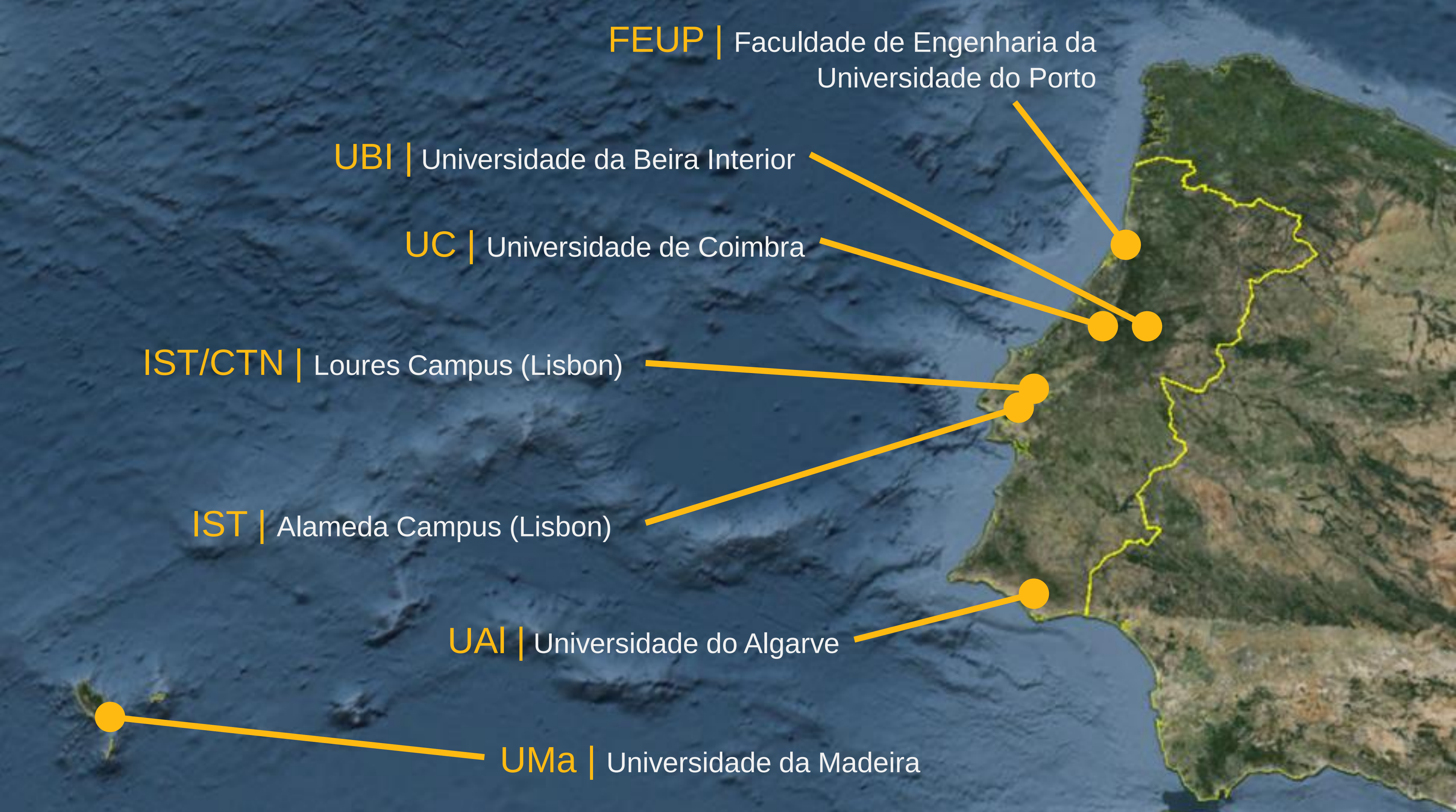
L.L. Alves
llalves@tecnico.ulisboa.pt

Instituto de Plasmas e Fusão Nuclear
Instituto Superior Técnico, Universidade de Lisboa
Lisboa, Portugal
http://www.ipfn.ist.utl.pt
https://www.ipfn.tecnico.ulisboa.pt/nprime/

Europhysics Conference on Atomic and Molecular Physics of Ionized Gases
9-13 July 2024, Brno, Czech Republic

Instituto de Plasmas e Fusão Nuclear

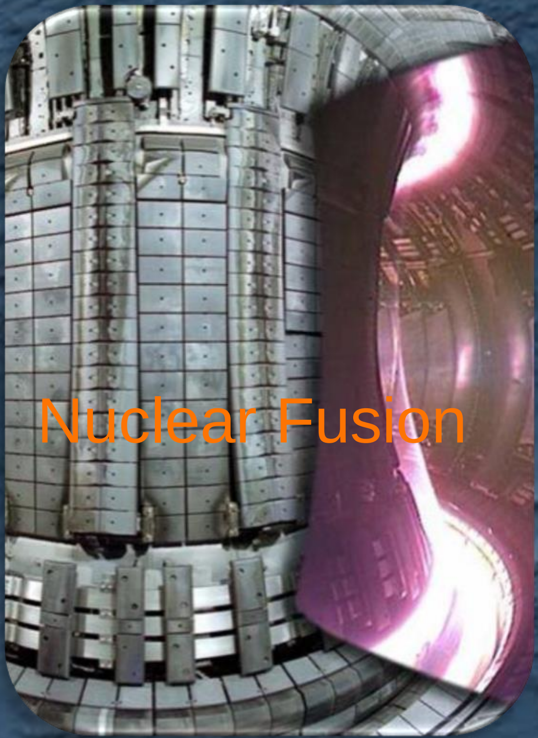
Sole R&D unit of Plasma Science and Technology in Portugal

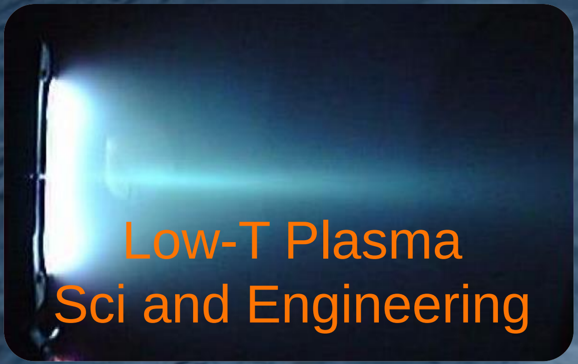


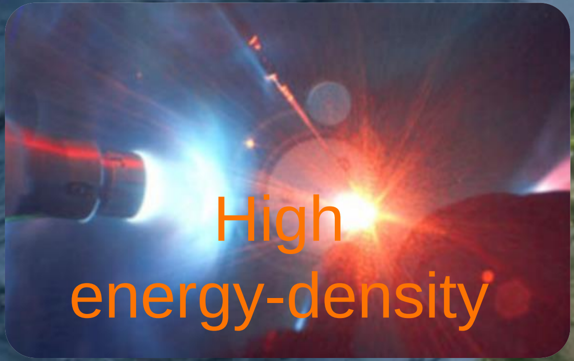
Staff: 160 people (90+ PhDs)

Instituto de Plasmas e Fusão Nuclear

Key research activities







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N-PRiME (reactive plasmas) group

Kinetic shock-tube to simulate entry plasmas, designed to reach shock-speeds in excess of 12km/s.

Platform for single-step synthesis of multi 2D-materials: free-standing graphene, N-graphene and nanocomposites.

Modelling activities

Fundamental component in any research domain

- **complementing** and/or aiding experimental diagnostics
- providing **predictions** on the behavior of significant quantities (especially when experimental access is limited)
- contributing to a deeper **understanding** of the field‘s fundamental knowledge

LTP models prove particularly valuable and challenging given the inherent complexity of the medium

- often characterized by **different material phases**
- **composed** by charged particles and by neutral species in different excited states
- intrinsically in **non-equilibrium**

I Adamovich *et al.* 2022 *J. Phys. D: Appl. Phys.* **55** 373001

Global models

Popular choice to study plasma chemistry

Adopt a **spatial averaged description**,
hence involving little computational effort

- allow describing in detail the plasma chemistry
  in complex gas mixtures
- should include transport effects
  especially at low to intermediate pressures

Usually involve the coupled solution of

Chemistry solver (to solve the "plasma chemistry")

Boltzmann solver (to describe the "electron kinetics")

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

L L Alves *et al.* 2018 *Plasma Sources Sci. Technol.* **27** 023002

Solution of global models

Example of codes used in the LTP community

- **ZDPlasKin** (freeware code)
  S Pancheshnyi *et al.* 2008 ZDPlasKin (www.zdplaskin.laplace.univ-tlse.fr)

- **GlobalKin** (available upon request)
  A M Lietz and M J Kushner 2016 *J. Phys. D: Appl. Phys.* **49** 425204
  D S Stafford and M J Kushner 2004 *J. Appl. Phys.* **96** 2451

- **Quantemol-P** (commercial application extending GlobalKin)
  J J Munro and J Tennyson 2008 *J. Vac. Sci. Technol. A* **26** 865

- **PLASIMO** (commercial software containing global model)
  J van Dijk *et al.* 2009 *J. Phys. D: Appl. Phys.* **42** 194012

- **LisbOn KInetics (LoKI-B+C)** (to be released as open-source)
  nprime.tecnico.ulisboa.pt/loki/
  A Tejero-Del-Caz *et al.*, *Plasma Sources Sci. Technol.* **28** (2019) 043001
  V Guerra *et al.*, *Plasma Sources Sci. Technol.* **28** (2019) 073001

Outline

- **The LisbOn KInetics (LoKI-B+C) tool**
  - Description
  - Chemistry model
  - Workflow
- **LoKI-B+C input / output**
  - Connection to LXCat
  - Formats for I/O
- **Results, validation, uncertainties**
  - Oxygen plasma model
  - N_2-H_2 plasma model
- **Final remarks**

The LoKI-B+C simulation tool

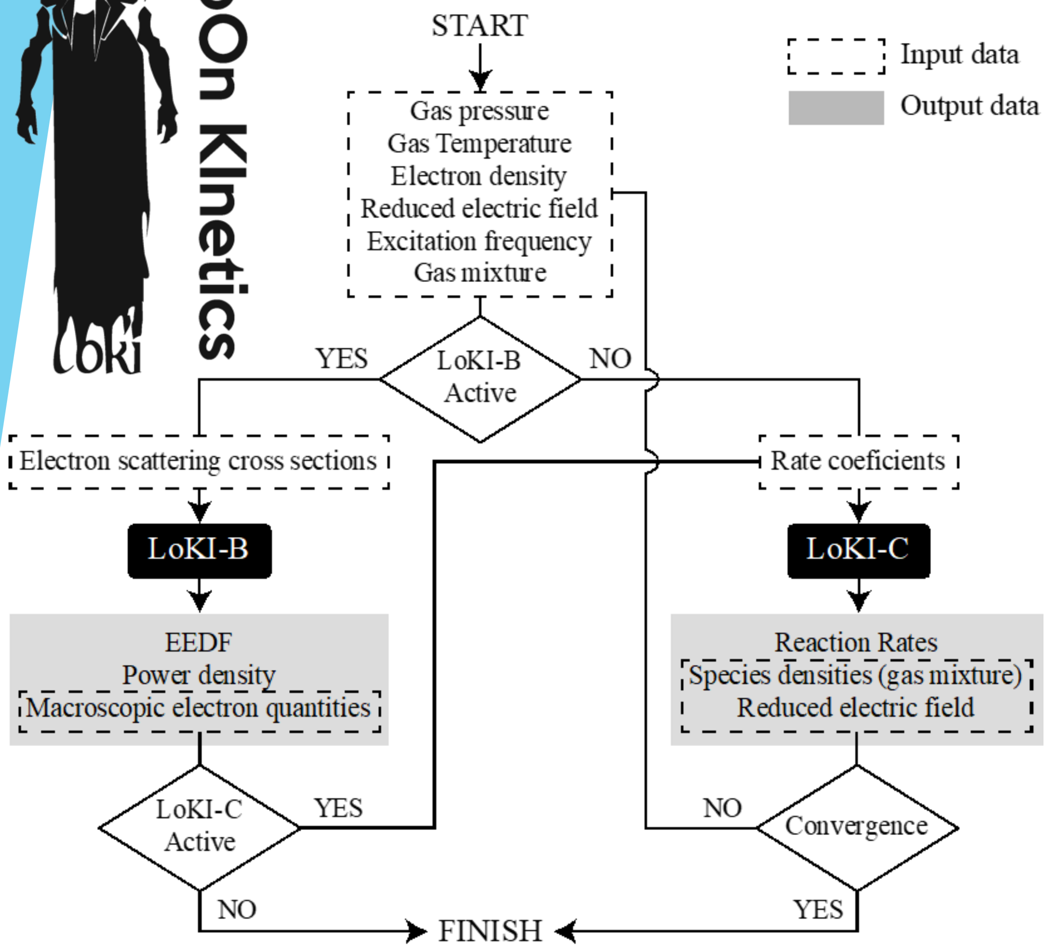
The LisbOn KInetics (LoKI-B+C) simulation tool

(developed under MATLAB®)

SEE POSTER P2-T6-51

OPEN SOURCE

LisbOn KInetics



LoKI-B

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

- solves the space independent form of the two-term electron Boltzmann equation, for DC/HF or time-dependent (non-oscillatory) electric fields.
- 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 of pure gases or gaseous mixtures.
- includes modules to describe

(i) the collisional, radiative and transport mechanisms controlling the creation / destruction of volume and surface species

(ii) the thermal heating of the neutral gas

loki@tecnico.ulisboa.pt

LoKI-B+C: main goal

LoKI-B+C has been developed to handle kinetic schemes

- in **any atomic / molecular** gas mixture
- describing collisional encounters between **any electron / neutral / ion species**
- considering targets in **any excited state (electronic, vibrational, rotational)**
- characterized by **any population** (eventually, user-prescribed)

LoKI-B considers first and second-kind electron collisions including anisotropic effects for elastic and rotational collisions

LoKI-B+C: description

Software features

- **Developed under Matlab®**
  to benefit from its matrix-based architecture
- **C++ version of LoKI-B** is under development **(to be integrated in PLASIMO)**
- Adopts flexible and upgradable object-oriented programming
- Follows an ontology that that privileges the separation between tool and data
- User and developer friendly (easy to use / maintain / upgrade)

History / status / roadmap

- First closed beta version of LoKI-B was **released early 2017**
- The Validation & Verification of the tool has been carried out
- First public release of LoKI-B: **March 2019**
- Current versions (November 2022)
  `LoKI-B_v2.2.0` (open source)
  `LoKI-C_v3.1.0` (internal release; **to become open source**)

LoKI-C: chemistry solver

The spatial-average particle balance equation: "chemistry" source-term

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

Kinetic scheme

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

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

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

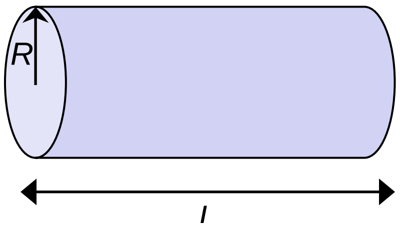
Electron energy distribution function

L L Alves *et al.* 2018 *Plasma Sources Sci. Technol.* **27** 023002

LoKI-C: chemistry solver

The spatial-average particle balance equation: "transport" term

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



$$S_k^{\mathrm{transp}} = \begin{cases} \sum_{j=\mathrm{transp}} a_{kj}^{(2)} \frac{n_l}{\tau_j} - \frac{n_k}{\tau_{\mathrm{transp}_k}} & \text{, for neutral species} \\ -\nu_k^{\mathrm{transp}} n_k & \text{, for charged species} \end{cases}$$

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

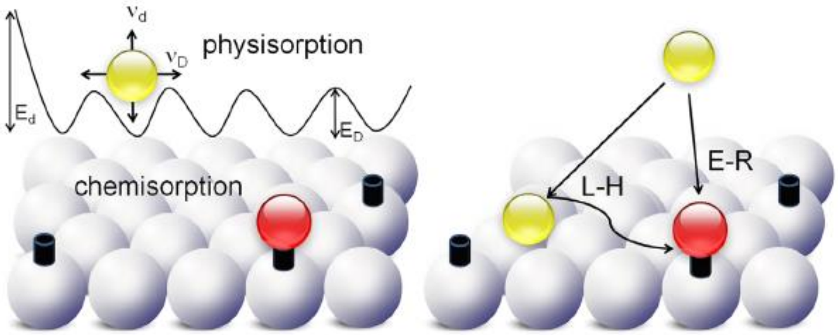
$$\Lambda^2 = \left[\left(\frac{\pi}{L}\right)^2 + \left(\frac{2.405}{R}\right)^2 \right]^{-1}$$

Electron kinetics

L L Alves *et al.* 2018 *Plasma Sources Sci. Technol.* **27** 023002

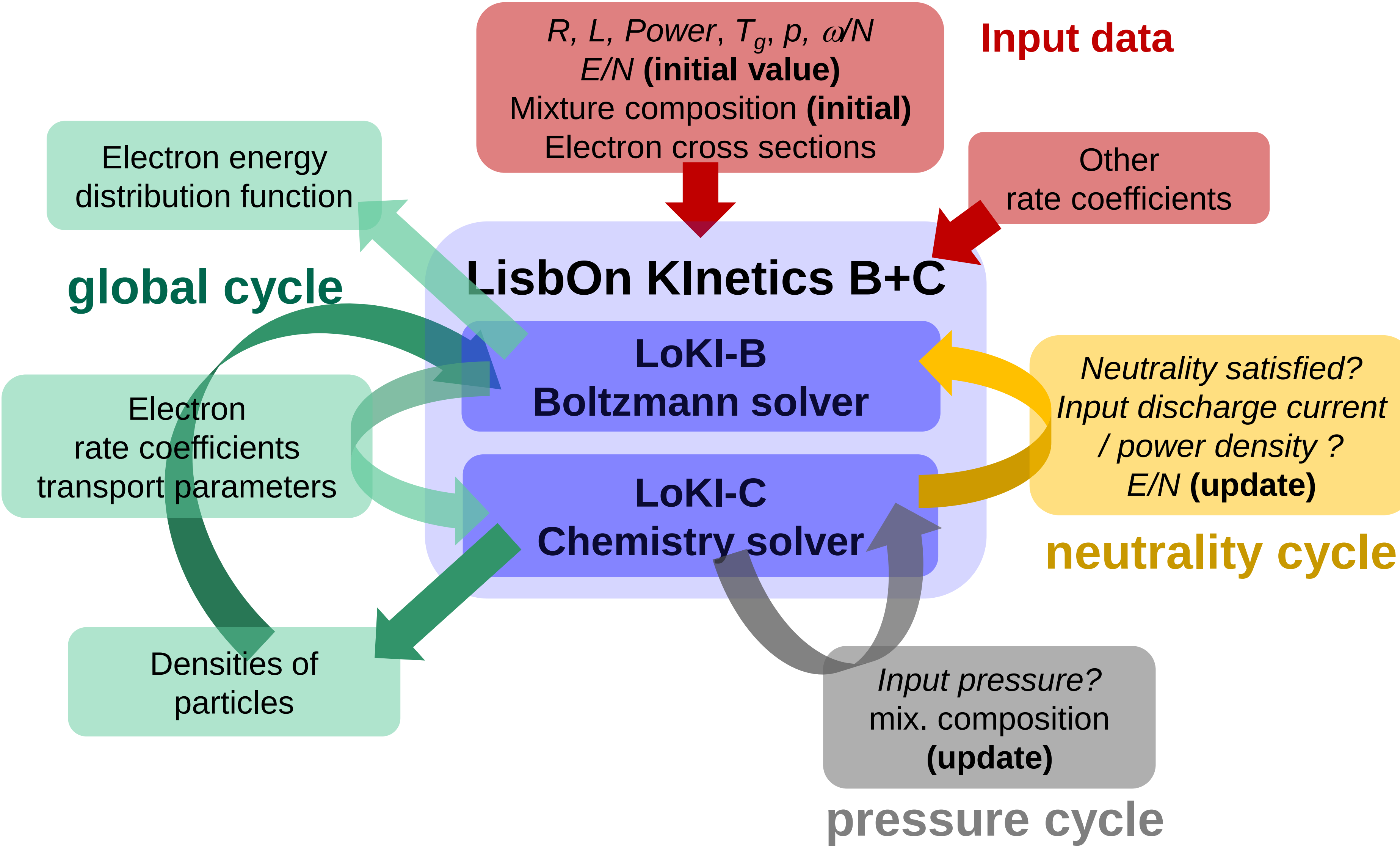
LoKI-C: model features

- Considers both volume and surface kinetic mechanisms
  The extension to a surface kinetics considers a mesoscopic description
  L. L. Alves et al. 2018 Plasma Sources Sci. Technol. **27** 023002
  D. Marinov et al. 2017 Plasma Process Polym. **14** 1600175

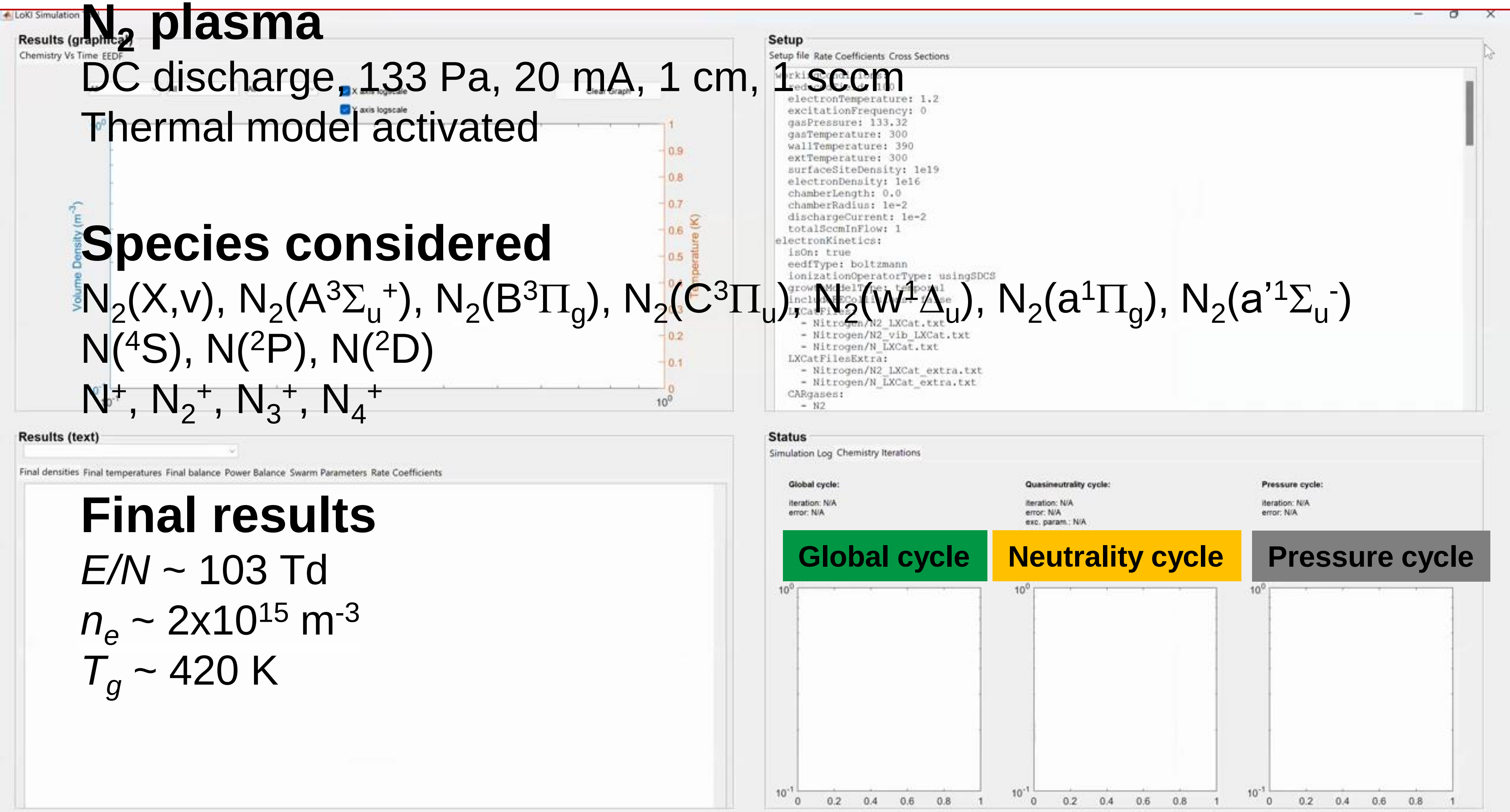


- Considers several transport models for charged / neutral species
- Includes many predefined functions to calculate rate coefficients
  e-collisions, h-collisions, radiative transitions, surface reactions with physical/chemical-adsorbed species, transport losses, …
- Includes gas thermal balance model
- Allows describing discharge and post-discharge scenarios

LoKI-B+C: workflow



LoKI-B+C: run testcase (speed 8x)



N_2 plasma

DC discharge, 133 Pa, 20 mA, 1 cm, 1 sccm

Thermal model activated

Species considered

$N_2(X,v)$, $N_2(A^3\Sigma_u^+)$, $N_2(B^3\Pi_g)$, $N_2(C^3\Pi_u)$, $N_2(w^1\Delta_u)$, $N_2(a^1\Pi_g)$, $N_2(a'^1\Sigma_u^-)$

$N(^4S)$, $N(^2P)$, $N(^2D)$

N^+, N_2^+, N_3^+, N_4^+

Final results

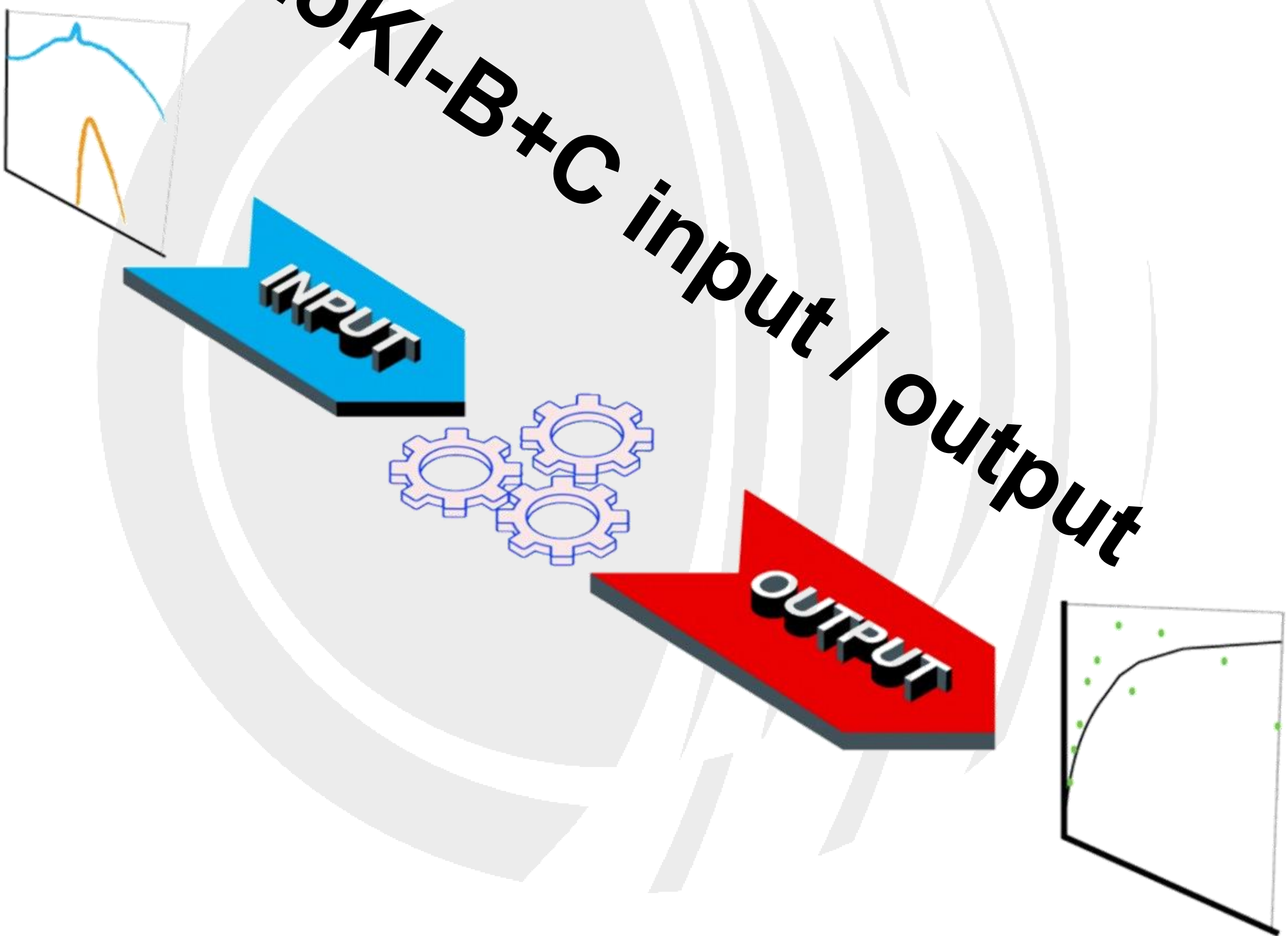
E/N ~ 103 Td

n_e ~ 2×10^{15} m^{-3}

T_g ~ 420 K

Global cycle | Neutrality cycle | Pressure cycle

LoKI-B+C input / output

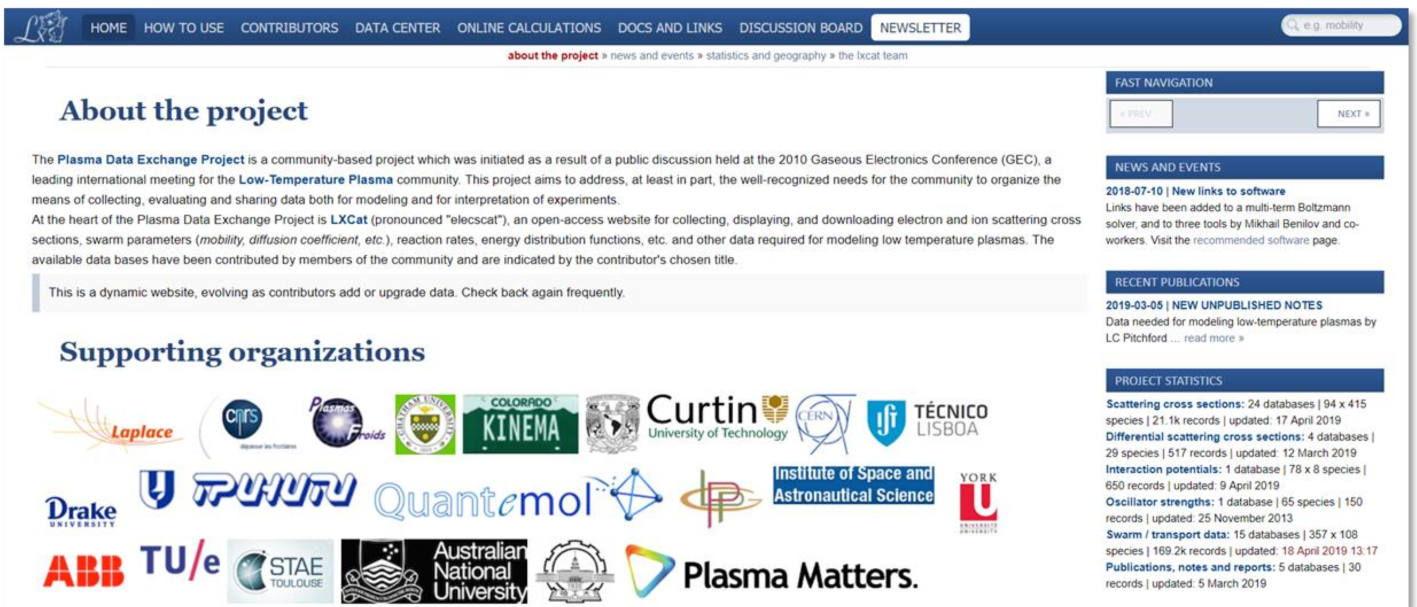


LoKI-B+C: input data

Input data refers to
general setup, **electron kinetics**, **chemical reactions**

LoKI-B+C follows a **clear ontology** for data handling

- it separates the tool from data
- it receives electron scattering cross sections, parsed adopting a format compliant with the **open-access website LXCat**



LoKI-B+C: input data (cont.)

Publishing data in a public database is advantageous for both users and developers

- to **separate tools and data (**enhancing **flexibility** of studies**)**
- to ensure the **open access** to data
- to promote using **validated** data (increasing **scientific rigor**)
- to encourage a **standardized classification and organization** of data

⇒ Publishing metadata is also essential

Currently, LoKI-B+C loads data and metadata using datafiles

⇒ Not ideal for guaranteeing data / metadata integrity

LoKI and LXCat 3.0 : the future

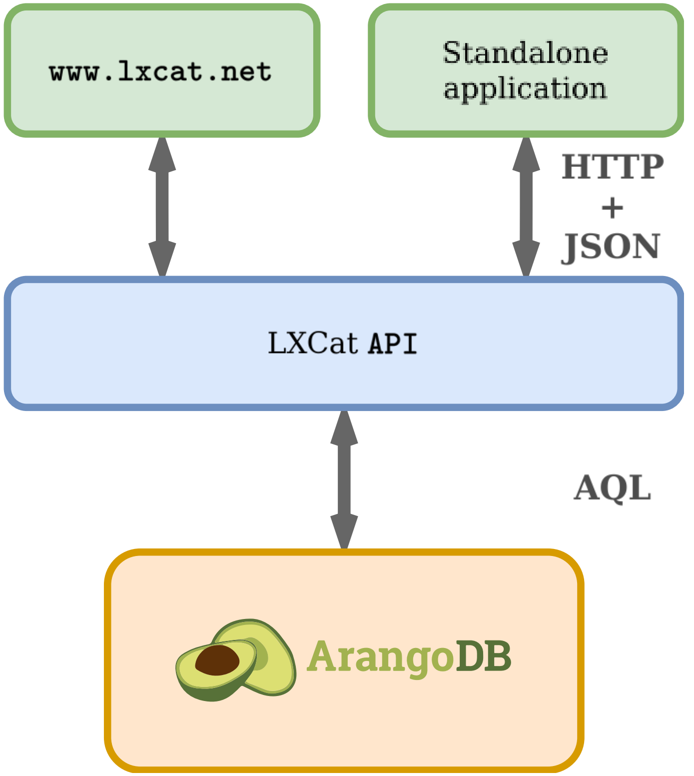
Courtesy D Boer and J van Dijk

LXCat 3.0 provides major improvements
to the way data is structured, annotated, stored, and accessed

- **LTP data** is encoded as **JSON** objects, whose structure is dictated by dedicated **schemas**
- Data accessibility is improved by providing an official **API**

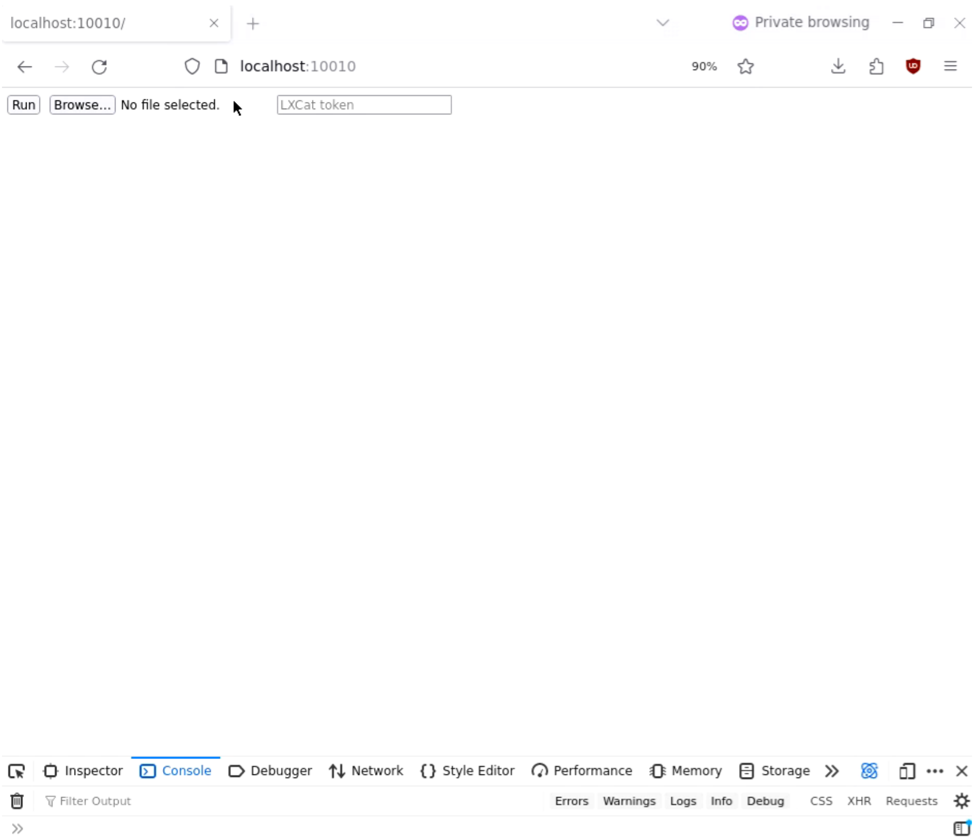
$$\mathrm{He}^{+}\left({}^{2}\mathrm{S}_{1/2}\right)$$

```json
{
  "particle": "He",
  "charge": 1,
  "type": "AtomLS",
  "electronic": {
    "config": [],
    "term": {
      "S": 0.5,
      "L": 0,
      "P": 1,
      "J": 0.5
    }
  }
}
```



LoKI and LXCat 3.0 : the future (cont.)

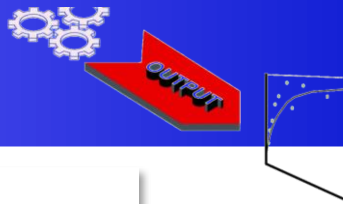
Courtesy D Boer and J van Dijk



LXCat 3.0 is open-source!

Expansion to **chemistry data** is in the works

LoKI-B+C : structured output



Easier access for post-processing

N2

File Visualize Window Help

N2

HDF5 Dataset

Shape
(1, 20)

Type
Compound (4 fields)

1 HDF5 Attributes

Array Indexing: 0

	Species	Abs.Density	Population	Balance
0	N2(X,v=0)	1.33704506887e+22	0.577857829287	1.41600818822e-15
1	N2(X,v=1)	5.09219176159e+21	0.220079557988	-2.43324151123e-15
2	N2(X,v=2)	2.21756250252e+21	0.0958408870315	1.22969453867e-15
3	N2(X,v=3)	1.07192942423e+21	0.0463277435186	3.70387334856e-16
4	N2(X,v=4)	5.65011606513e+20	0.0244192501856	-1.36288675906e-15
5	N2(X,v=5)	3.1858761562e+20	0.0137690458075	6.42660277135e-15
6	N2(X,v=6)	1.94589525366e+20	0.00840996936815	-1.18523623834e-14
7	N2(X,v=7)	1.25422814476e+20	0.00542065162976	-4.11480395992e-16
8	N2(X,v=8)	8.38081202323e+19	0.00362210516023	3.72021612063e-16
9	N2(X,v=9)	5.6847386356e+19	0.00245688855561	5.37405199279e-16
10	N2(X,v=10)	3.76384892736e+19	0.00162669877147	2.35515844805e-15
11	N2(A3Su+)	3.34839675995e+18	0.00014471443995	-5.06118471362e-16
12	N2(B3Pg)	7.43169737197e+16	3.21190707125e-06	2.52097757727e-16
13	N2(C3Pu)	1.25791216135e+14	5.43657358992e-09	-1.52105771042e-16
14	N2(w1Du)	3.73402686209e+15	1.61380996592e-07	3.00707069184e-16
15	N2(a1Pg)	4.82946594109e+15	2.08724804445e-07	0.0
16	N2(a'1Su-)	4.86435737053e+17	2.10232777971e-05	-1.80962419131e-16
17	N2(X)	2.31340399349e+22	0.999830627304	0.0
18	N2(+,X)	1.09969468187e+15	4.75277308551e-08	3.37270382571e-16
19	N2(+,B2Su+)	33498734224.0	1.4477825986e-12	0.0

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Modelling results:
validation and uncertainties

Validity of model-type & tool

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 ($n_e > 10^{15} - 10^{16}$ 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

Validation

Kinetics schemes for plasma chemistry are meaningful only if **validated by comparing simulations with measurements**

A higher paradigm involves validating
reaction mechanisms against ***benchmark experiments***

- **reaction mechanism** is a set of experimentally validated reactions and corresponding rate coefficients
- **benchmark experiments** represent a significant ensemble of experimental data, intended (or suited) for model validation, obtained in well defined and reproducible conditions, using established diagnostics, and assessing multiple quantities

Validation of oxygen plasma model

Benchmark experiments

Plasmas produced by cylindrical DC glow discharges

- R = 1 cm; L = 52.5 cm
- p = 30 – 1000 Pa
- I_{dc} = 10 – 40 mA

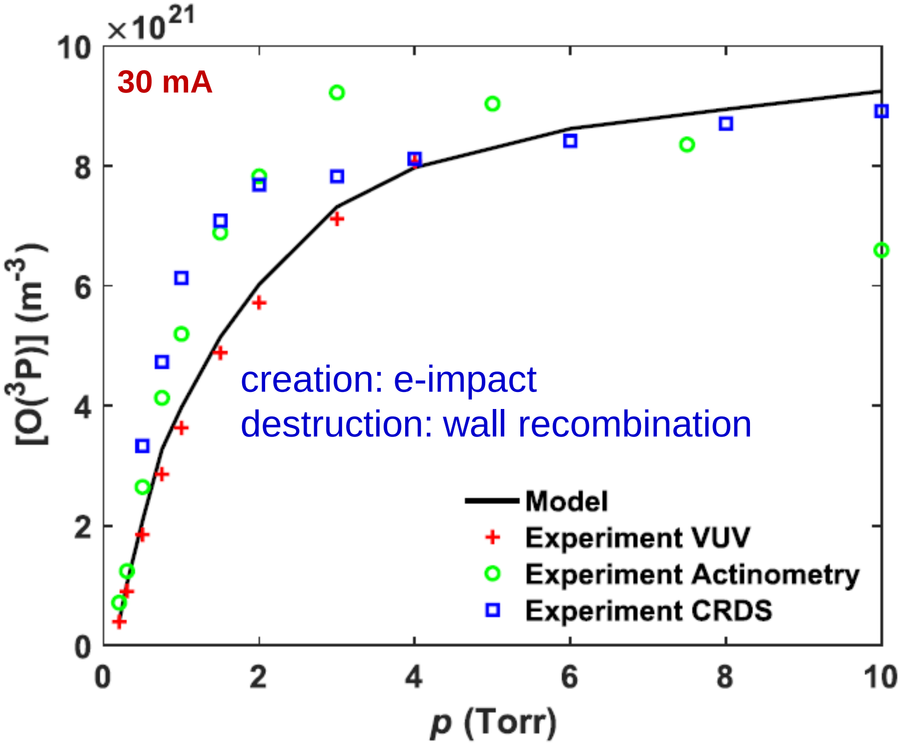
Measurements obtained from

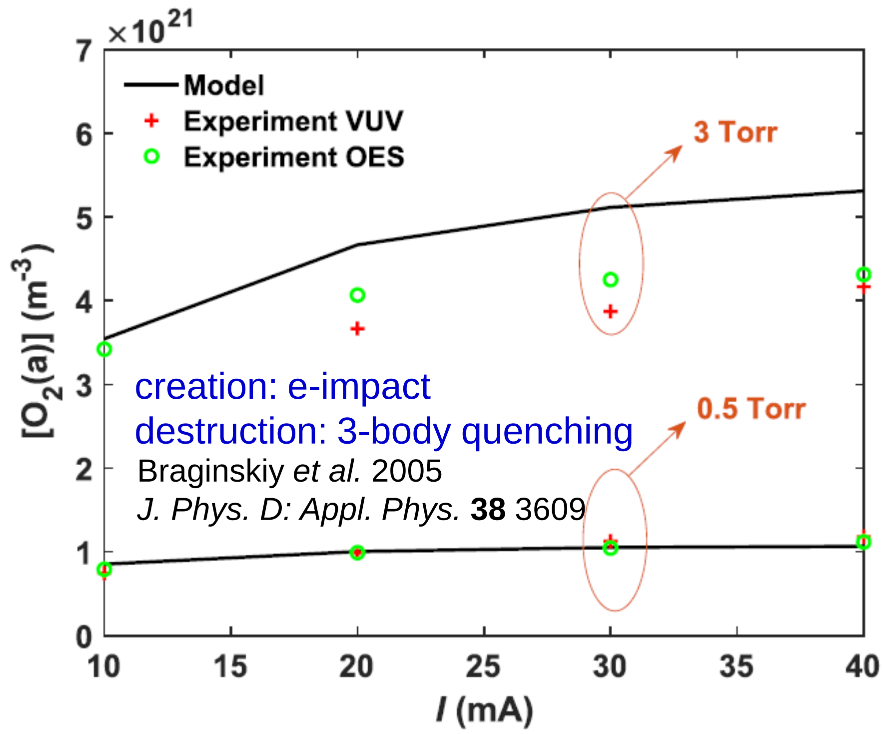
- probe for E/N
- radially averaged VUV; actinometry; on-axis CRDS
  for densities of species [$O_2(X^3\Delta_g^-)$, $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma_g^+)$ and $O(^3P)$]
- OES of $O_2(b^1\Sigma_g^+)$ and TALIF for T_g

Laboratoire de Physique des Plasmas (LPP), France
Lomonosov Moscow State University (MSU), Russia
T C Dias *et al.* 2023 *Plasma Sources Sci. Technol*. **32** 084003

Validation of oxygen plasma model

Simulation vs measurements

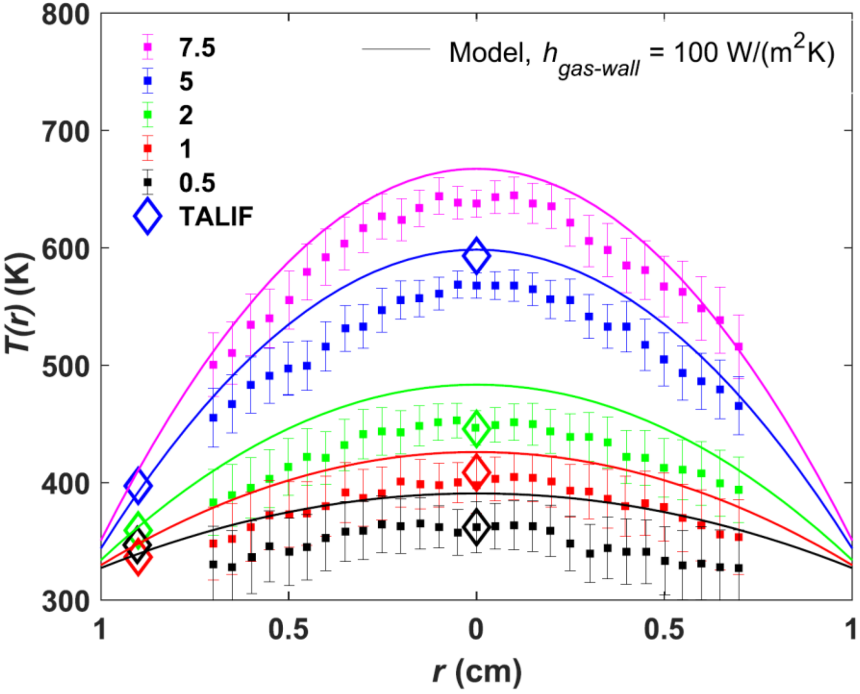


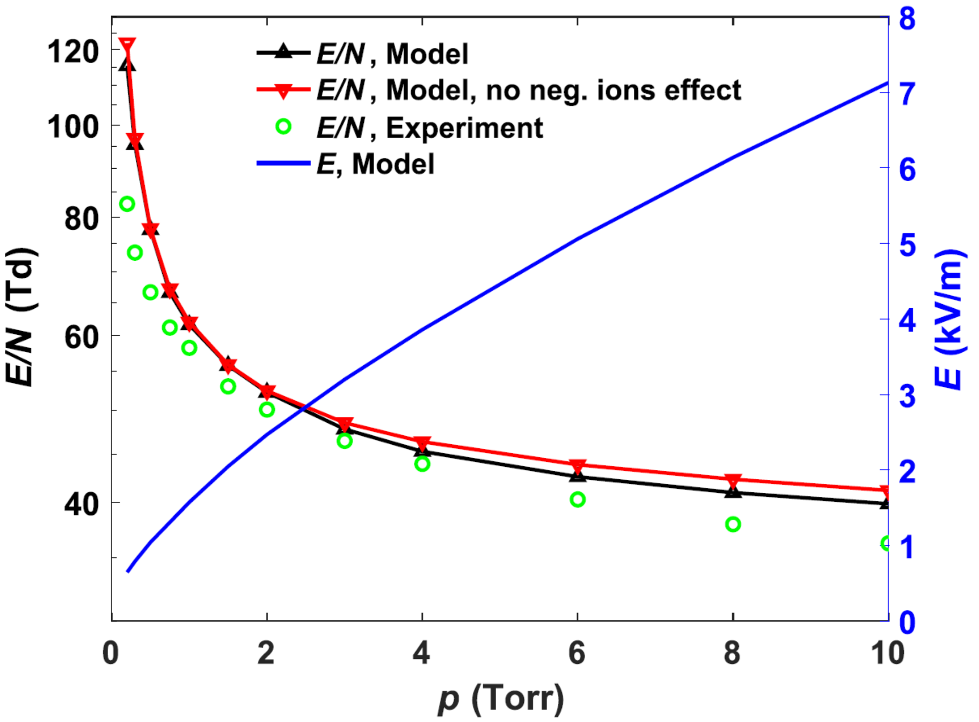


The scattering of measurements shows that model validation should focus on the **prediction of trends and orders of magnitude**

Validation of oxygen plasma model

Simulation vs measurements (cont.)





Predicting the experimental **gas temperature** and **maintenance reduced electric field** is key to model validation

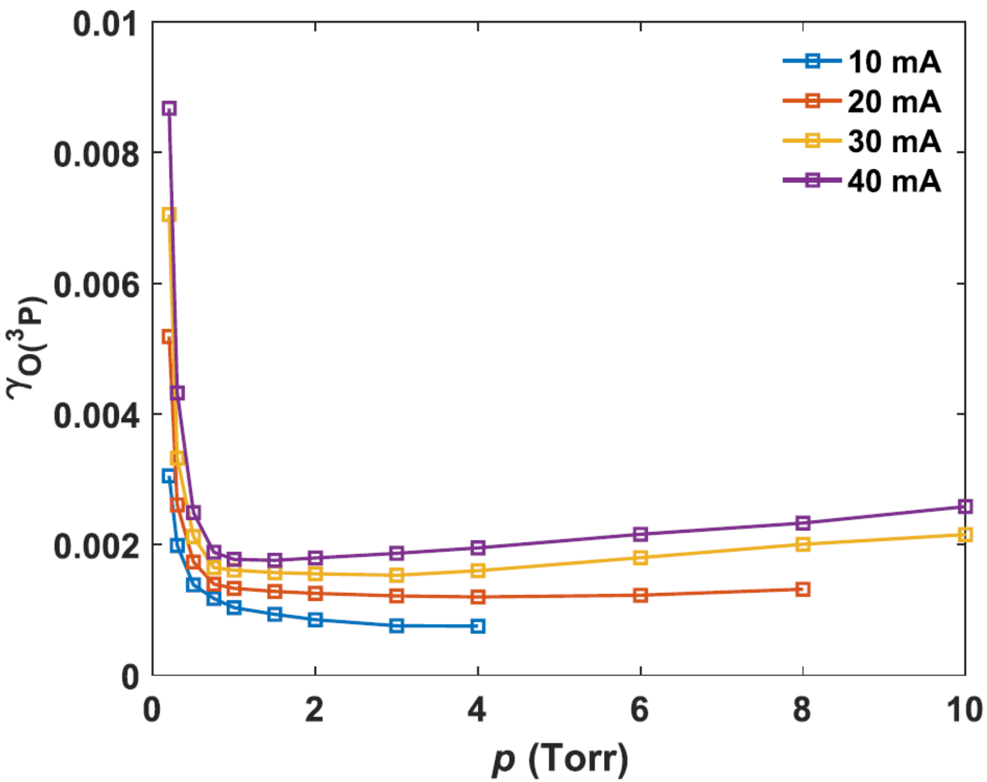
Validation of oxygen plasma model

Most relevant results

Main creation / destruction mechanisms

- electron-impact excitation/dissociation
- two- and three-body quenching
- wall recombination

O(^{3}P) wall-recombination probability



J-P Booth *et al.* 2020
Plasma Sources Sci. Technol. **29** 115009

Modelling uncertainties

Influence of transport models

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

$$S_k^{\text{transp}} = -\nu_k^{\text{transp}} n_k$$

$$\nu_k^{\text{amb}} = \frac{D_{\text{amb}_k}}{\Lambda^2}$$

P Coche *et al.* 2016 *J. Phys. D: Appl. Phys.* **49** 235207

$$\nu_k^{\text{QGM}} = \frac{1}{\left(\nu_k^{\text{amb}}\right)^{-1} + \left(\nu_k^{\text{th}}\right)^{-1}} = \frac{A}{V} \frac{D_{a_+}\gamma_{r_k}}{\Lambda\gamma_{r_k} + \frac{4D_{a_+}}{v_{\text{th}_k}}}$$

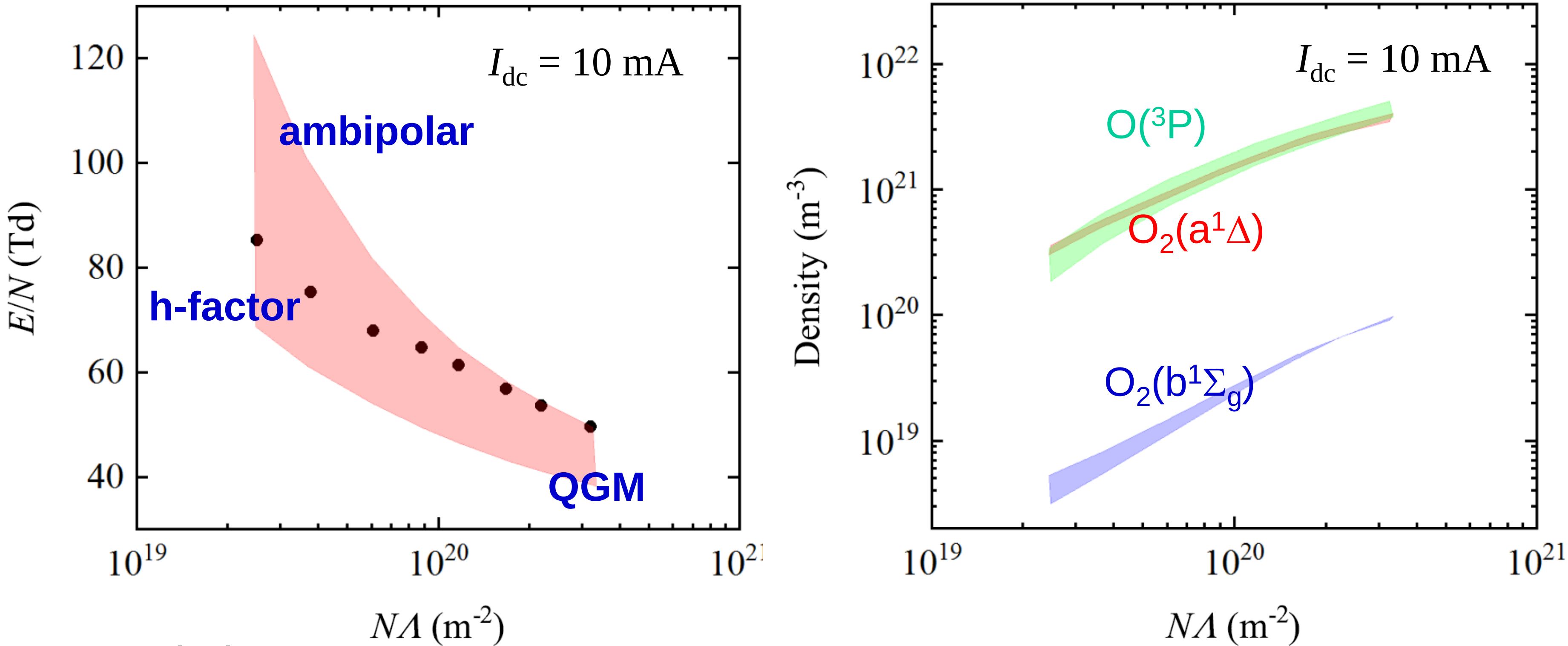
J Tennyson *et al.* 2022 *Plasma Sources Sci. Technol.* **31** 095020

$$\nu_k^{\text{h-fact}} = 2u_{\text{B}} \left(\frac{h_{L_k}}{L} + \frac{h_{R_k}}{R} \right)$$

P Chabert 2016 *Plasma Sources Sci. Technol.* **25** 025010

Modelling uncertainties

Influence of transport models in the description of oxygen plasmas



uncertainties

- of **20-60% in discharge characteristics**
- that can reach **60% in the densities** of the main species

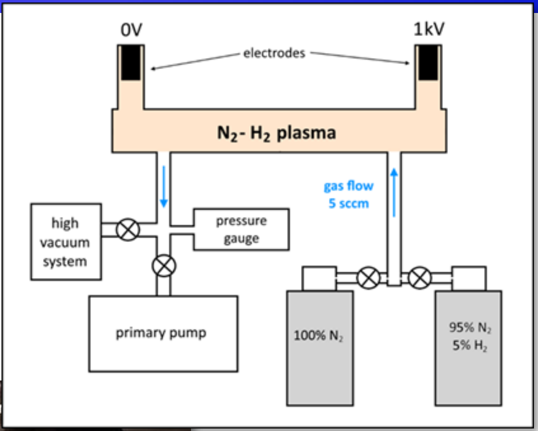
larger dispersion at low pressure and low discharge current

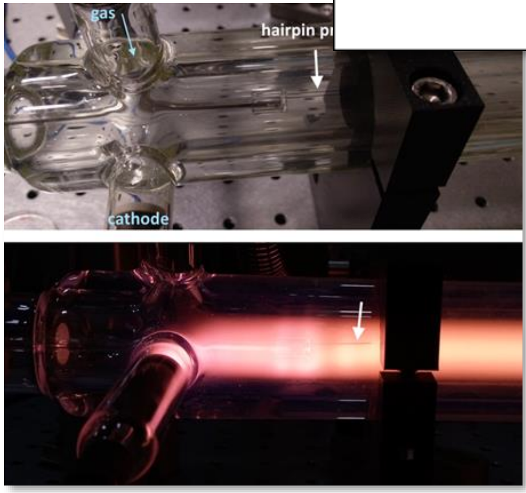
L L Alves and Tejero-del-Caz 2023 *Plasma Sources Sci. Technol.* **32** 054003

Validation of N_2-H_2 plasma model

Benchmark experiments

SEE POSTER P1-T6-51





Plasmas produced by cylindrical DC glow discharges

- R ~ 1 cm; L > 15 cm
- p = 30 – 400 Pa ; T_g ~ 300 – 600 K
- I_{dc} = 5 – 100 mA
- H_2 = 0 – 100%
- Q = 0 – 600 sccm
- Non- catalytic surface density 10^{20} m^{-2}

Measurements obtained from

- probe for *E/N*
- densities of NH_3 (FTIR absorption) and atomic H,N (LIF calibrated with VUV)
- fractional ion fluxes (mass spectrometry)

A Chatain *et al.* 2023 *Plasma Sources Sci. Technol.* **32** 035002

B Gordiets *et al.* 1998 *Plasma Sources Sci. Technol.* **7** 379–88

Validation of N_2-H_2 plasma model

Surface kinetics : mesoscopic description

$$N(4S) + F(v) \longrightarrow N(F)$$
$$N(F) \longrightarrow N(4S) + F(v)$$
$$H(1S) + F(v) \longrightarrow H(F)$$
$$H(F) \longrightarrow H(1S) + F(v)$$

$$N(4S) + S(v) \longrightarrow N(S)$$
$$N(F) + S(v) \longrightarrow N(S) + F(v)$$
$$N(4S) + N(S) \longrightarrow N_2(X, v=0) + S(v)$$
$$N(F) + N(S) \longrightarrow N_2(X, v=0) + S(v) + F(v)$$

$$H(1S) + S(v) \longrightarrow H(S)$$
$$H(F) + S(v) \longrightarrow H(S) + F(v)$$
$$H(1S) + H(S) \longrightarrow H_2(X, v=0) + S(v)$$
$$H(F) + H(S) \longrightarrow H_2(X, v=0) + S(v) + F(v)$$

$$N(4S) + H(S) \longrightarrow NH(S)$$
$$N(F) + H(S) \longrightarrow NH(S) + F(v)$$
$$H(1S) + N(S) \longrightarrow NH(S)$$
$$H(F) + N(S) \longrightarrow NH(S) + F(v)$$
$$NH(X) + S(v) \longrightarrow NH(S)$$

$$H(1S) + NH(S) \longrightarrow NH_2(S)$$
$$H(F) + NH(S) \longrightarrow NH_2(S) + F(v)$$
$$NH(X) + H(S) \longrightarrow NH_2(S)$$
$$NH_2(X) + S(v) \longrightarrow NH_2(S)$$

$$H(1S) + NH_2(S) \longrightarrow NH_3(X) + S(v)$$
$$H(F) + NH_2(S) \longrightarrow NH_3(X) + S(v) + F(v)$$
$$NH_2(X) + H(S) \longrightarrow NH_3(X) + S(v)$$
$$H_2(X, v=0) + NH(S) \longrightarrow NH_3(X) + S(v)$$

Physisorption/desorption is decoupled from the rest of the surface kinetics

The presence of H/N-atoms is key to trigger the surface kinetics

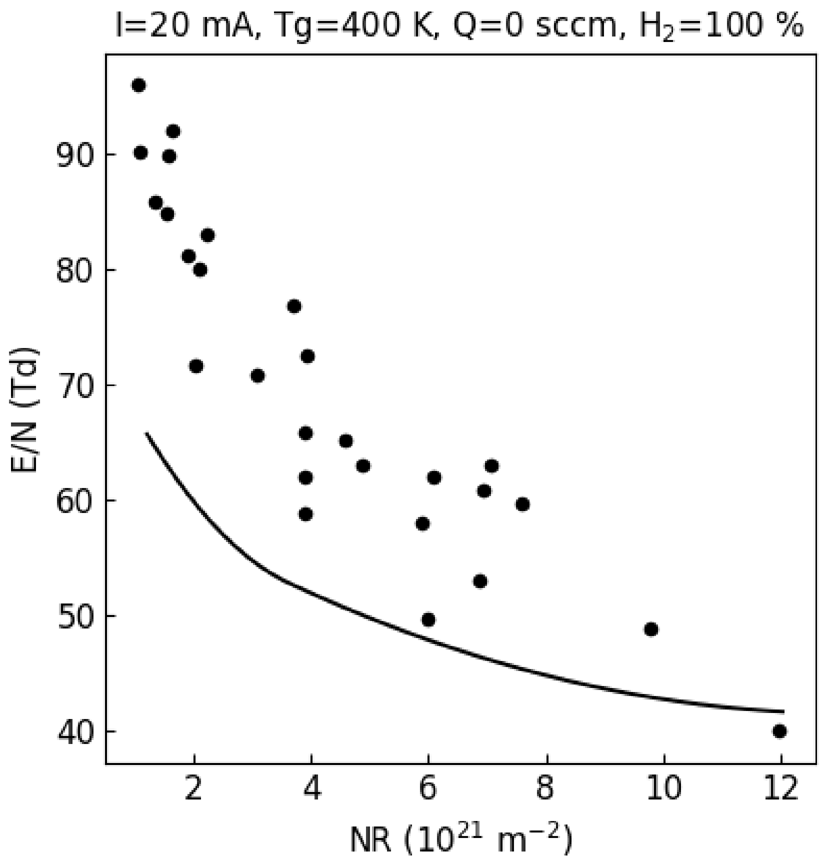
The chemical bonding of H/N-atoms on the surface creates NH and NH_2, as part of the pathway for NH_3

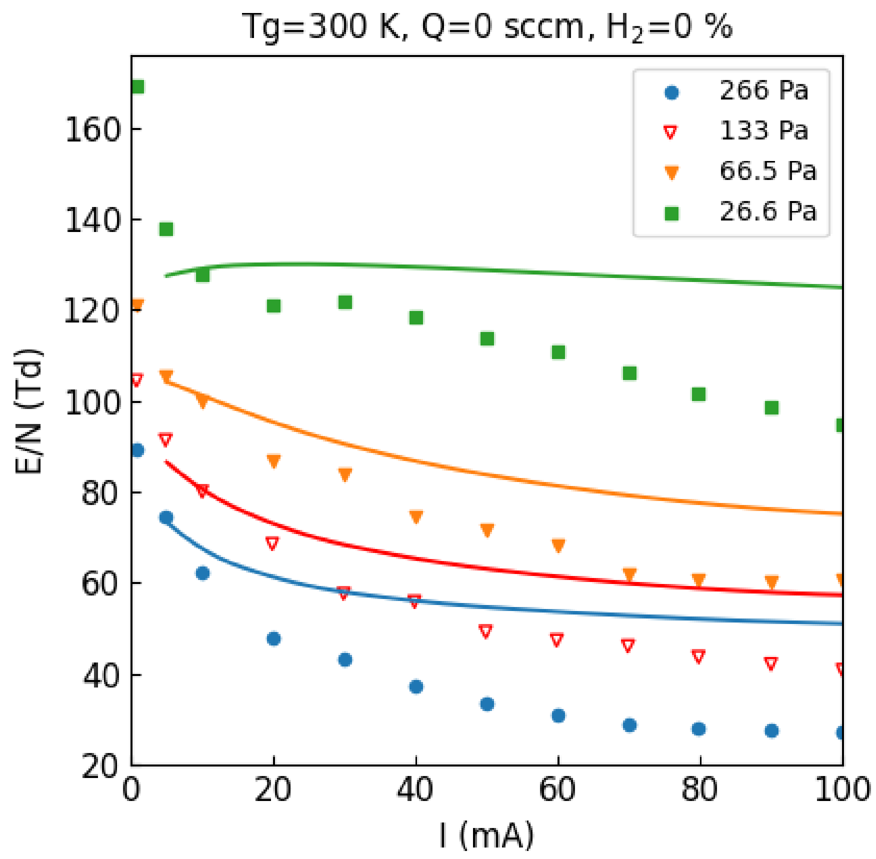
B Gordiets *et al.* 1998
Plasma Sources Sci. Technol. **7** 379–88

Eley-Rideal and Langmuir-Hinshelwood are key mechanisms for NH_3 production

Validation of N_2-H_2 plasma model

Simulation vs measurements



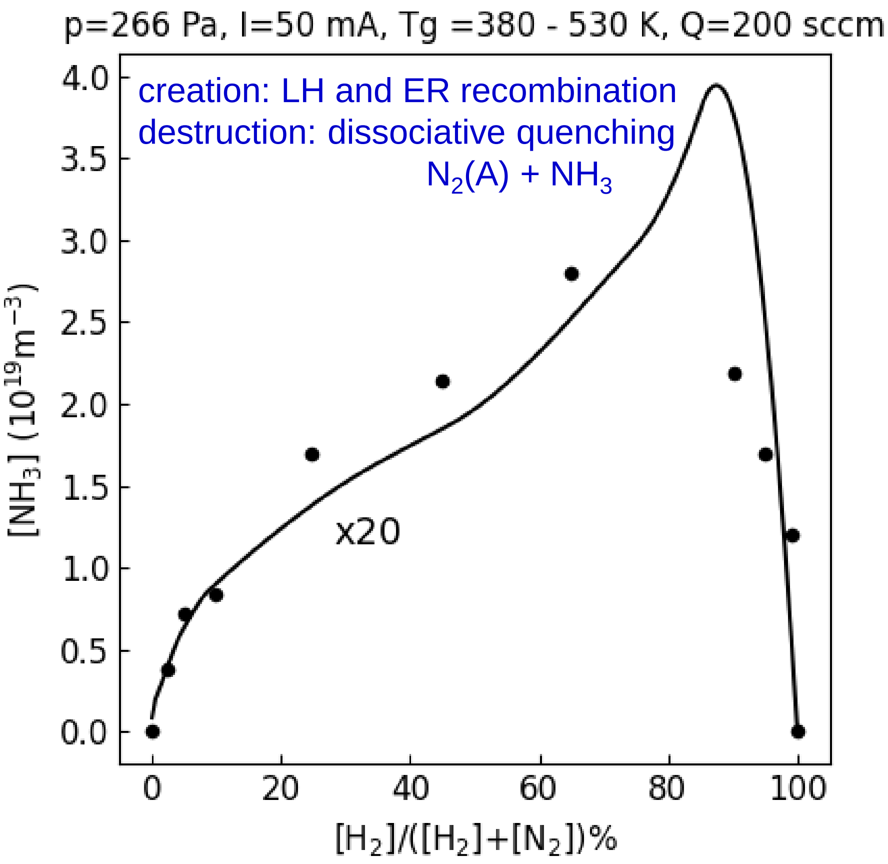


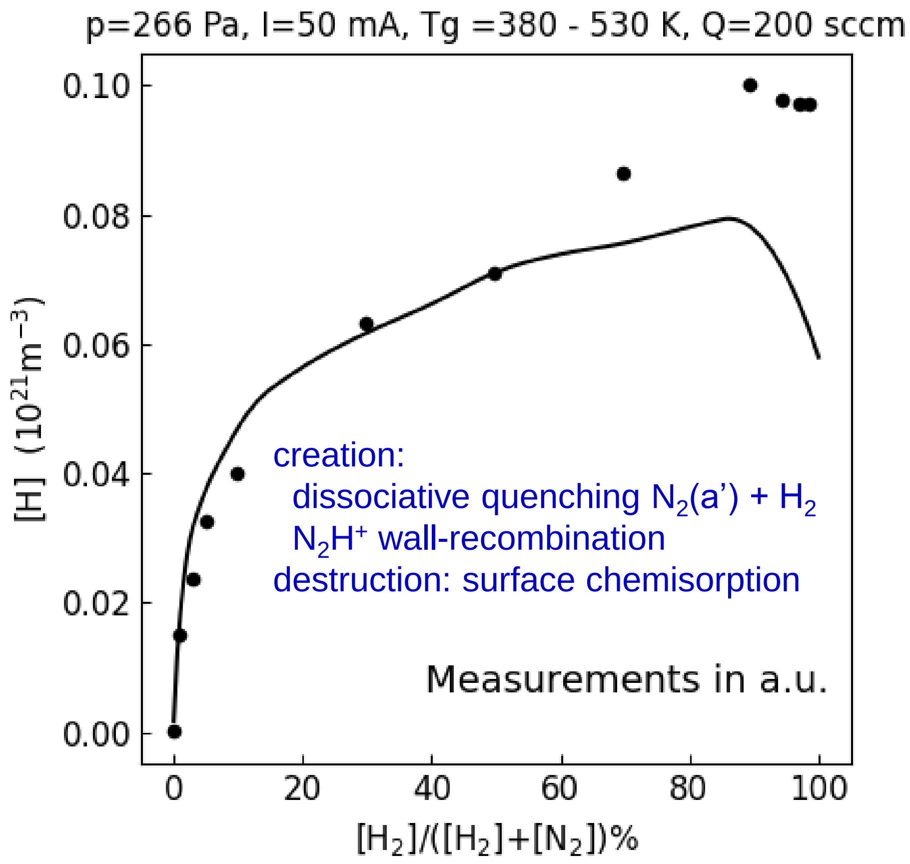
Improving the agreement for the discharge characteristics may require

- decreasing the rate coefficient for **production of H_3^+**
- increasing the rate coefficient for **production of N_2(A) and N_2(a')**

Validation of N_2-H_2 plasma model

Simulation vs measurements



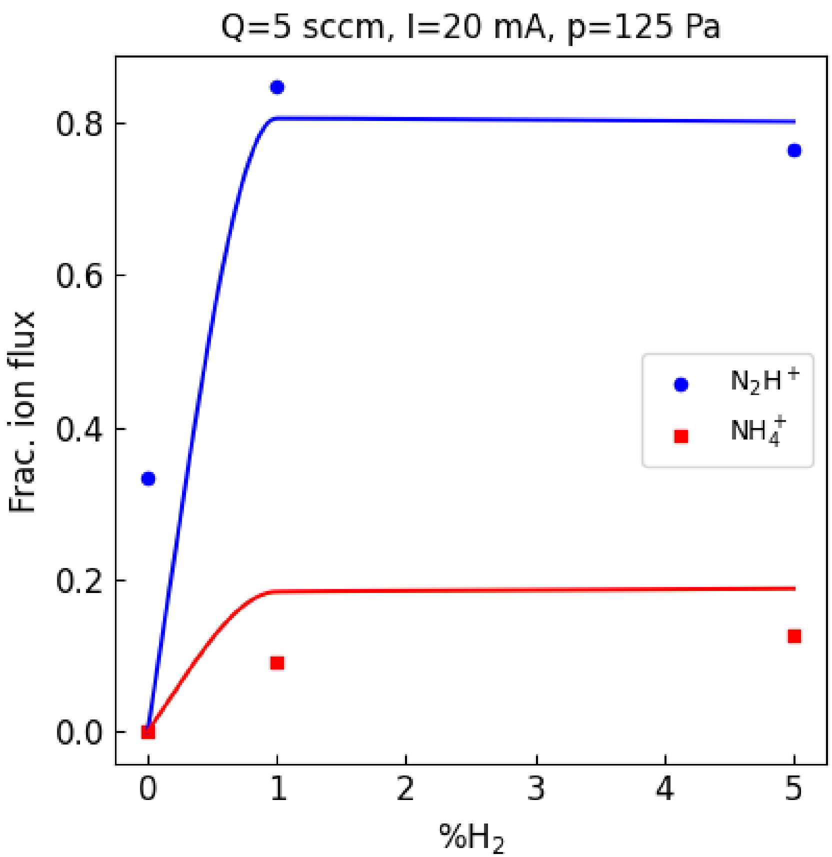


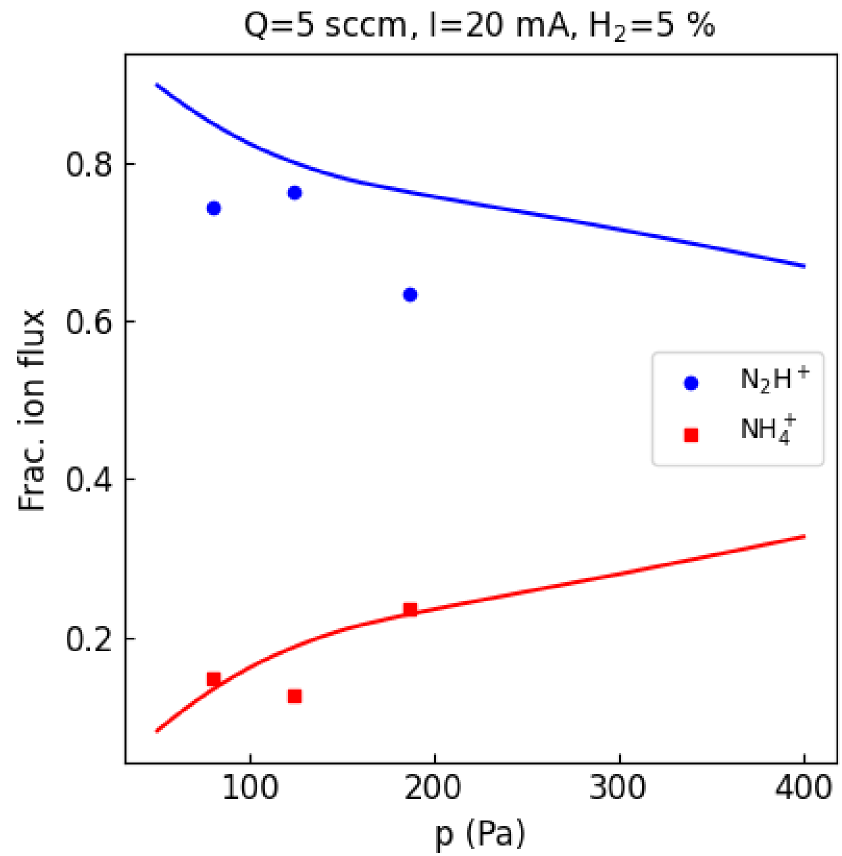
Large underestimation in the production of NH_3

Good predictions for $[H(^1S)]$ vs H_2%

Validation of N_2-H_2 plasma model

Simulation vs measurements





In N_2-H_2 discharges with H_2 = 10-90%

- the **most relevant ions** are N_2H^+ and NH_4^+
- **good predictions** for the fractional ion flux

Validation of N_2-H_2 plasma model

Main conclusions and future directions

Improve the predictions of discharge characteristics

- Check the kinetic mechanisms for H_3^+, $N_2(A)$ and N_2H+

Improve the predictions for $[NH_3]$

- Surface mechanisms are key in the model of N_2-H_2 plasmas
- Revise the mesoscopic surface model

Check the influence of gas temperature and flow

- Most rate coefficients for heavy-species are T_g-dependent
- The residence time affects the dissociation of species
- The presence of H (and N) atoms is key to control NH_3 production

Final remarks

The potential of modelling as a predictive tool can only be achieved after a validation process, by comparing modelling results with experimental measurements, a step that requires an intense **collaborative work within the community**

Sharing tools and data in open-access can make a decisive contribution

- to improve the quality of tools and data
- to improve the quality of model predictions
- to advance knowledge in LTP chemistry

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Information on LoKI

LoKI-B @ IST-Lisbon Github

Call for EoI to develop LoKI