Numerical simulation tools for plasma chemistry

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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

- Low-T Plasma Sci and Engineering
- Nuclear Fusion
- High energy-density
- Advanced Training
- High performance computing
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

- Rotational interactions
- Vibrational interactions
- Electronic interactions
- Ionization / recombination
- Attachment / detachment
- Dissociation
- Fragmentation
- Charge / excitation transfer
- Association / dissociation
- Recombination
- Radiative transitions

Interaction with surface

heavy-species

electrons
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

Working conditions
Data

What’s the kinetic scheme to adopt? Is the data reliable?

Numerical tool
Boltzmann solver
Chemistry solver

Densities, rates
Electron energy
distribution function

Is the output suited for validation?

Is the model applicable? What’s the coupling between modules?
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: N₂ / O₂ / N₂-O₂
  Open issues on: charge particle transport; Boltzmann-Chemistry coupling

• **Final remarks**
Global models for plasma chemistry
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 $A_k / A_{k'}$:

\[
\begin{align*}
& a_{k,j}^{(1)} A_k \xrightarrow{k_j} a_{k,j}^{(2)} A_{k'}
& \text{Kinetic scheme}
\end{align*}
\]

\[
\frac{dn_k}{dt} = S_{k}^{\text{chem}} + S_{k}^{\text{transp}}
\]

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

\[ \frac{dn_k}{dt} = S_{k}^{\text{chem}} + S_{k}^{\text{transp}} \]

\[ S_{k}^{\text{chem}} = \sum_j \left\{ \left[ a_{k,j}^{(2)} - a_{k,j}^{(1)} \right] k_{ij} \Pi_l n_l^{a_{k,j}^{(1)}} \right\} \]

\[ k_{ij} = \begin{cases} \left( \frac{2}{m_e} \right)^2 \int_{0}^{\infty} u \sigma_{j}(u) f(u) du, & \text{for e-collisions} \\ \alpha T^\beta \exp \left[ -\frac{T_{\text{ref}}}{T} \right], & \text{for h-collisions} \end{cases} \]

Elementary data

Electron energy distribution function
Global models for plasma chemistry

The "transport" term

\[
\frac{dn_k}{dt} = S_{k}^{\text{chem}} + S_{k}^{\text{transp}}
\]

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

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

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

Elementary data

Electron kinetics
Global models for plasma chemistry

The Boltzmann solver

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

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)

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

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

Numerical tool

- **E/N (initial value)**
  - $n_e$, $T_g$, $p$
  - Mixture composition
  - Electron cross sections

- **Electron energy distribution function**
- **Neutrality satisfied?**
  - $E/N$ (update)
- **Densities of particles**

Boltzmann solver

Chemistry solver

Other rate coefficients

Electron rate coefficients

Transport parameters
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 ($p > 10 \text{ Pa} \rightarrow \lambda_i < 1 \text{ cm}$)
- dense plasmas ($n_e > 10^{-16} \text{ m}^{-3} \rightarrow \lambda_D < 100 \mu\text{m}$)

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 $dn_e/dz$
- $dn_k/dz = dn_k/dt v_{\text{flow}}$, 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.
- $T_e, T_{\text{ion}}, T_{\text{gas}}$ coupled to ambipolar, neutral and convective transport.

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Institute for Plasma Science & Engr.
• 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.
PLASIMO: Plasma simulation and modeling

Jan van Dijk and Diana Mihailova

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)
The LisbOn Kinetics (LoKI) simulation tool
(developed under MATLAB®)

LoKI-B
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

[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

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.

http://www.bolsig.laplace.univ-tlse.fr/
Other (recent) Boltzmann solvers

- **EEDF** (N A Dyatko *et al*)
  

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

- **METHES** (M Rabie CM Franck) – *open source*
  MATLAB® Monte Carlo collision code
  [www.lxcat.net/download/METHES](http://www.lxcat.net/download/METHES)

- **Magboltz** (S Biagi) – *open source*
  Fortran with hardcoded data, using multi-term expansion + Monte Carlo algorithm

- **MultiBolt** (J Stephens) – *open source*
  MATLAB® for multi-term expansion and multi-harmonic model
  [https://gitlab.com/LXCatThirdParty/MultiBolt](https://gitlab.com/LXCatThirdParty/MultiBolt)
Data : electron scattering cross sections
The LXCat open-access website

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

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
“Reaction mechanisms”
sets of reactions and rate coefficients validated against benchmark experiments

Oxidation of methane

green line – calc., GRI-Mech 3.0
crosses – calc., Chemked

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?

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**Graph:**

- Comprehensive model vs. reduced model
- P = 1 W @ t = 3ms
- O(10^21 m^-3)

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**Equations:**

He + O^- + O_2^+ → He + O + O_2

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**Reference:**

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

[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)

\[ n_i(t = 0) \quad R_j \quad \text{input} \quad \text{Black box solver} \quad \text{output} \quad n_i(t = T) \quad \text{input} \quad \text{PumpKin solver} \quad \text{output} \quad \dot{i} \quad \dot{j} \]

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

\[ f = 13.56 \text{ MHz}; \ P < 500\text{W}; \ p = 1.33-10.67 \text{ Pa} \]

Implementation: success cases
Dry-air microwave micro-discharge at low pressure

\[ \gamma_{N_2} = 1.1 \times 10^{-3} \]
\[ \gamma_{N_2} = 0.02 \]

\[ f = 2.45 \text{ GHz}; \; P \sim 100 \text{ W}; \; p = 300 \text{ Pa}; \; R = 345 \mu\text{m} \]

\[ \gamma_{N_2} = 1.1 \times 10^{-3} \]
\[ \gamma_{N_2} = 0.02 \]

\[ 129 \text{ W} \]

\[ z (\text{cm}) \]

\[ T_{\text{vib}} (10^3 \text{ K}) \]

Implementation: success cases
Dry-air microwave micro-discharge at low pressure

Implementation: success cases
Nitrogen DC discharges (work in progress)

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

Points – experiment ($p = 60-300$ Pa; $T_g \sim 400-700$ 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

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

Implementation: open issues
Ambipolar transport of charged species – the effective diffusion coefficient

\[ S_{k}^{\text{transp}} = -\frac{D_{sk}}{\Lambda^2} n_k \]

\[ \alpha = \frac{n_-}{n_e} \]

\[ T_e \sim 10 \text{ eV} \]
\[ T_- = 1000 \text{ K} \]

[\text{P. Coche et al, J. Phys. D 49, 235207 (2016)}]
Implementation: open issues
Ambipolar transport of charged species – comparison between models

\[ \alpha = [O^-]/n_e \]

- Lieberman’s model
- Effective ambipolar diffusion (this work)
- Classic ambipolar diffusion

\( E/N (\text{Td}) \)

\( NR (\text{cm}^{-2}) \)

\( 10^{16} \quad 10^{17} \quad 10^{18} \quad 10^{19} \)

\( 200 \quad 160 \quad 120 \quad 80 \quad 40 \)

O\(_2\) discharges

Good agreement with Lieberman’s model

Further analysis in progress

[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)]
Time-dependent or quasi-stationary calculations
Growing interest in fast-pulsed nanoscale discharges

For quasi-stationary calculations

\[
\frac{1}{N} \frac{\partial f}{\partial t} \sim \frac{1}{N \tau_{\text{evol}}} \sim \frac{n_{\text{energy}}}{N}
\]

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

At low pressure (1 Torr)

\[t_{\text{exc}} \gg 10^{-5} \text{ s} \quad !\]

At atmospheric pressure (~10^3 Torr)

\[t_{\text{exc}} \gg 10^{-8} \text{ s} \quad \text{OK}\]
Implementation: open issues
Coupling between Boltzmann and Chemistry solvers

Electron kinetics calculations (with LoKI-B) in dry air (80% N₂ – 20% O₂)
Time evolution of the ionization rate coefficient for a **micro-second pulse**

**Quasi-stationary calculations, valid for…**

- **Low pressure:** $t_{\text{exc}} \gg 10^{-5}$ s
- **High pressure:** $t_{\text{exc}} \gg 10^{-8}$ s

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

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