Kinetics and Boltzmann models

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/
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
- Intense Lasers
- Advanced Training
- High performance computing

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Key research activities

- Experimental Physics
- Theory & Modeling
- Plasma Engineering & Systems Integration

Awarded “Outstanding”
(11/300 R&D units - 2014 evaluation procedure managed by ESF)
Modelling of low-temperature plasmas
Goal: understand and predict

• Understand

• Predict

• Propose

• Tailor / Optimize

Courtesy: Nor-Call Products
Modelling of low-temperature plasmas
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

electrons
heavy-species
Modelling of low-temperature plasmas
Modelling approaches

- Statistical models
- Kinetic models
- Fluid models
- Global (hybrid) models

Andrew Gibson
Mark Kushner
Kinetics and Boltzmann models (electron kinetics)

Outline

- Electron kinetic modelling
  - The electron Boltzmann equation
  - Input data
  - Workflow for Boltzmann-Chemistry modelling

- Examples of tools

- Examples of results (argon and nitrogen)
  - Influence of the reduced electric field
  - Swarm analysis
  - Influence of e-vibrational and e-rotational mechanisms

- Final remarks and questions
Electron kinetic modelling

Key references

• Foundations of modelling of nonequilibrium low-temperature plasmas
  L. L. Alves, A. Bogaerts, V. Guerra, and M. M. Turner
  Plasma Sources Sci. Technol. 27 (2018) 023002

• Electron kinetics in atomic and molecular plasmas
  C. M. Ferreira and J. Loureiro

• Kinetics and Spectroscopy of Low Temperature Plasmas
  J. Loureiro and J. Amorim
  Springer International Publishing, 2016

• Plasma Physics, Volumes 1 and 2
  Jean-Loup Delcroix

• Motions of Ions and Electrons
  W. P. Allis,
Electron kinetic modelling

The electron Boltzmann equation
**Electron kinetic modelling**

The “master” kinetic equation

- Inclusion of an energy description
- Definition of boundary conditions
- Complete problem: 6D ⇒ long run times

\[
\frac{\partial F}{\partial t} + \vec{v} \cdot \nabla F + \frac{\vec{X}}{m} \cdot \frac{\partial F}{\partial \vec{v}} = \left( \frac{\partial F}{\partial t} \right)_c
\]

\( F(\vec{r}, \vec{v}, t) \) is the **distribution function**, representing the number of particles per unit volume in phase space \((\vec{r}, \vec{v})\), at time \( t \).
Electron kinetic modelling
The electron Boltzmann equation

\[ \frac{\partial F}{\partial t} + \vec{u} \cdot \nabla F + \frac{\vec{X}}{m} \cdot \frac{\partial F}{\partial \vec{v}} = \left( \frac{\partial F}{\partial t} \right)_c \]

Rate of \( F \)
in configuration spacein timein velocity spacedue to collisions

Force acting upon particles

➢ The total electric field acting on electrons

\[ \vec{E} = \vec{E}_s(\vec{r}) + \vec{E}_p \exp(j \omega t) \]

dc space-charge fieldhf field at frequency \( \omega \)
Charge separation at the boundaries
The space-charge sheath
Charge separation at the boundaries
The space-charge sheath

Space-charge field, $E_s$
Charge separation at the boundaries
The space-charge sheath

Space-charge field, $E_s$
Charge separation at the boundaries
The space-charge sheath

The electron Boltzmann equation

Working conditions

- **Disregard** the space-charge electric field acting on electrons

\[ \vec{E} = \vec{E}_s(r) + \vec{E}_p \exp(j\omega t) \]

- dc space-charge field
- hf field at frequency \( \omega \)

- No external magnetic field

- The electron distribution function \( F \) is expanded
  - in spherical harmonics in velocity space
  - in Fourier series in time

\[ F = \sum_l \sum_p F^l_p P_l(\cos \theta) \exp(jp\omega t) \]
The electron Boltzmann equation
The small anisotropy / two-term approximation

Conditions...

- the electron mean free path is much smaller than any relevant dimension of the container, $\lambda_e \ll L$

- the energy gained from the electric field per collision by a representative electron is much smaller than the thermal energy of the electrons

- the oscillation amplitude of the electron motion under the action of the hf field is small as compared to $L$

- the characteristic frequency for the electron energy relaxation by collisions is much smaller than the oscillation frequency of the hf field, $\tau_e^{-1} \ll \omega$

$$F(f, v) \simeq F_0^0(f, v) + (\bar{v}/v) \cdot \left[ \bar{F}_0^1(f, v) + \bar{F}_1^1(f, v) \exp(j \omega t) \right]$$

Isotropic component (energy relaxation)  Anisotropic components (transport)
The homogeneous electron Boltzmann equation

Collision operators

- The isotropic equation

\[- \frac{1}{v^2} \frac{\partial}{\partial v} \left\{ \left( \frac{ev^2}{6m} \right) \text{Re} \left( \vec{E}_p \cdot \vec{F}_1 \right) + \frac{m}{M} \nu_c v^3 F_0^0 \right\} = (q - \nu_x - \nu_i) F_0^0\]

- The anisotropic equation

\[(\nu_c + j\omega) \vec{F}_1^1 = \frac{e\vec{E}_p}{m} \frac{\partial F_0^0}{\partial v}\]

Elastic collision operator

Inelastic collision operator
The homogeneous electron Boltzmann equation

The inelastic collision operator

\[ u = m \frac{v^2}{2} \]

\[ q F_0^0 - (\nu_x + \nu_i) F_0^0 \]

\[ \nu_x = \sum_j \nu_j \]

\[ u + V_j \]

\[ u + du \]

\[ u - V_j \]

INELASTIC
The homogeneous electron Boltzmann equation

The inelastic / superelastic collision operator

\[ u = m \frac{v^2}{2} \]

\[ qF_0^0 - (\nu_x + \nu_i) F_0^0 \]

\[ \nu_x = \sum_j \nu_j \]

Entrance

Exit

SUPERELASTIC

INELASTIC
The homogeneous electron Boltzmann equation

Input data: working parameters

\[- \frac{1}{v^2} \frac{\partial}{\partial v} \left\{ \left( \frac{e v^2}{6m} \right) \text{Re} \left( \overline{E_p} \cdot \overline{F_1^1} \right) + \frac{m}{M} \nu_c v^3 F_0^0 \right\} = (q - \nu_x - \nu_i) F_0^0 \]

\[(\nu_c + i\omega) \overline{F_1^1} = \frac{e \overline{E_p}}{m} \frac{\partial F_0^0}{\partial v} \]

\[\overline{E_p} \quad \omega \quad \frac{\nu_c}{N} \quad \frac{\nu_i}{N} \quad \Rightarrow \text{Independent parameters} \]
The homogeneous electron Boltzmann equation
Input data: collisional data

\[ u = \frac{mv^2}{(2e)} \]

\[ -\frac{1}{v^2} \frac{\partial}{\partial v} \left\{ \left( \frac{e v^2}{6m} \right) Re \left( \vec{E}_p \cdot \vec{F}_1^1 \right) + \frac{m}{M} \nu_c \bar{v}^3 F_0^0 \right\} = (q - \nu_x - \nu_z) F_0^0 \]

\[ \nu_c = N \sigma_c \left( \frac{2eu}{m} \right)^{1/2} \quad q, \nu = N_i \sigma_{ij} \left( \frac{2eu}{m} \right)^{1/2} \]

\[ N_{i=0} = N \quad \Rightarrow \text{Gas density} \]

\[ N_{i \neq 0} \quad \Rightarrow \text{Chemistry model (heavy-species kinetics)} \]
Input data
Excitation / ionization mechanisms
Input data
Electron-impact cross sections

Data from...
- Bibliography
- Databases (e.g. LXCat: www.lxcat.net)
Input data
The LXCat open-access website

**Workflow**

Electron Boltzmann kinetics

- $E/N$, $\omega/N$, …
- Mixture composition
- Electron cross sections

Electron energy distribution function (EEDF)

Boltzmann solver

Electron rate coefficients transport parameters

\[ C_{ij} = \int_0^\infty \sigma_{ij}(v) v \frac{F_0^0(v)}{n_e} 4\pi v^2 dv \]

\[ D_e N = \int_0^\infty \frac{v}{3\sigma_c(v)} \frac{F_0^0(v)}{n_e} 4\pi v^2 dv \]
**Electron parameters**

Example: the free-diffusion coefficient

\[
D_e N = \int_0^\infty \frac{v}{3\sigma_c(v)} \frac{F_0^0(v)}{n_e} 4\pi v^2 \, dv = \text{function}(E/N)
\]

1 Td ≡ 10^{-17} V cm^2

Ar @ IST-LISBON

www.lxcat.net
Workflow
Global (Boltzmann + Chemistry) modelling

- Electron energy distribution function
- Neutrality satisfied? $E/N$ (update)
- Densities of particles
- $E/N$ (initial value)
  - $\omega/N$, $n_e$, $T_g$, $p$
  - Mixture composition
  - Electron cross sections

Boltzmann solver

Chemistry solver

- Electron rate coefficients transport parameters
- Other rate coefficients
Examples of tools
Examples of tools
BOLSIG+

http://www.bolsig.laplace.univ-tlse.fr/

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.

**BOLSIG+**

The electron energy distribution function (EEDF)
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.

The LisbOn Kinetics Boltzmann solver (LoKI-B) was developed as a response to the need of having an electron Boltzmann solver easily addressing the simulation of the electron kinetics in any complex gas mixture (of atomic / molecular species), describing first and second-kind electron collisions with any target state (electronic, vibrational and rotational), characterized by any user-prescribed population.

A. Tejero-del-Caz et al Plasma Sources Sci. Technol. 28 (2019) 043001

loki@tecnico.ulisboa.pt
LoKI-B

Examples of simulation

- Install MATLAB®
- Get the code
  https://github.com/IST-Lisbon/LoKI
- Get the data
  www.lxcat.net

Illustration for “swarm analysis” in nitrogen, including e-rotational mechanisms
Examples of results
Results – influence of the reduced electric field
Argon @ 0.1 Td ≤ E/N ≤ 100 Td and T_g = 300K
Results – “swarm analysis”
Argon @ $10^{-4}$ Td $\leq E/N \leq 100$ Td and $T_g = 300$K
Results – “swarm analysis”
Argon mobility as a function of $E/N$
**Results – “swarm analysis”**

Argon mobility as a function of $E/N$ – comparison with experimental data
**Results – “swarm analysis”**

Swarm adjustment of cross sections

Complete sets of cross sections are those describing the total transfer of momentum and energy between electrons and the gas.

Results – molecular gases
Argon vs Nitrogen

\[ \begin{align*}
\text{Ar}^+ \ 3s^2 \ 3p^5 & \quad \lambda = 5912 - 9075 \text{ Å} \\
3p^5 \ 4d & \quad \lambda = 9195 - 20317 \text{ Å} \\
3p^5 \ 4p & \quad \lambda = 1048 - 1067 \text{ Å} \\
3p^5 \ 5s & \quad \lambda = 3949 - 4702 \text{ Å} \\
3p^5 \ 5p & \quad \lambda = 6677 - 11488 \text{ Å}
\end{align*} \]
Results – influence of e-vibrational mechanisms
Nitrogen @ $E/N = 10$ Td and $T_g = 300$K
Results – influence of e-vibrational mechanisms

Nitrogen @ $E/N = 10$ Td and $T_g = 300K$
Results – influence of e-rotational mechanisms

Nitrogen – swarm analysis

\[ \mu N \left( \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{V}^{-1} \right) \]

\[ 10^{25} \]

\[ 10^{24} \]

\[ 10^{-4} \quad 10^{-2} \quad 10^{0} \quad 10^{2} \]

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

- With rotational mechanisms
- Without rotational mechanisms

- Frommhold 1960
- Pack and Phelps 1961
- Wagner and Raether 1962
- Lowke 1963 - 293K
- Errett 1951 (from Engelhardt et al 1964) - 293K

Final remarks
Final remarks
Word of caution – topics beyond this lecture

- This lecture was about electron kinetic modelling: solving the *two-term homogeneous time-independent* electron Boltzmann equation
  - there are other approaches to solve the EBE (multiterm expansion, Monte-Carlo, …)
  - the two-term approximation is valid only in the presence of *small anisotropies*
  - the homogeneous EBE cannot describe plasmas with relevant spatial features
  - the time-independent EBE should not be used to describe plasmas with relevant time-evolution features
Final remarks
Word of caution – topics beyond this lecture

• The quality of simulation results depends on the quality of the tool and data
  - if you are a developer…
    verify your tool (benchmark tests, asymptotic behaviours, …)
  - if you are a user …
    learn about the tool you are using (validity limits / operating options / input / output / …)
    read the documentation and send queries to the developers
  - workout your kinetic model
    do the bibliography; make educate choices when collecting data

• Validate modelling results, by comparing simulations with experiment
Acknowledgements

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