Kinetics and Boltzmann models

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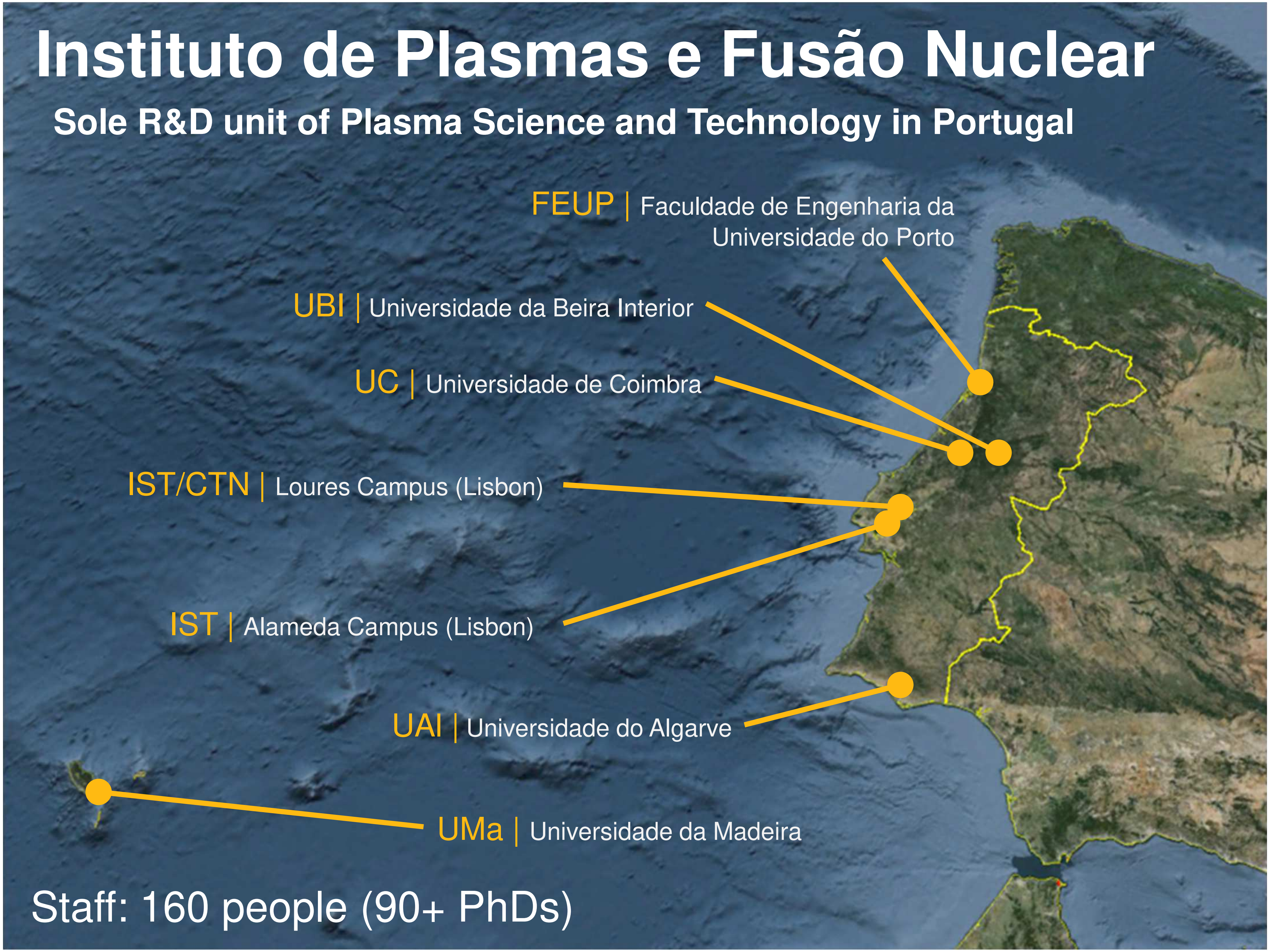
https://www.ipfn.tecnico.ulisboa.pt/nprime/

ISPC 24
24th International Symposium on Plasma Chemistry
Naples (Italy) June 9-14, 2019

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)

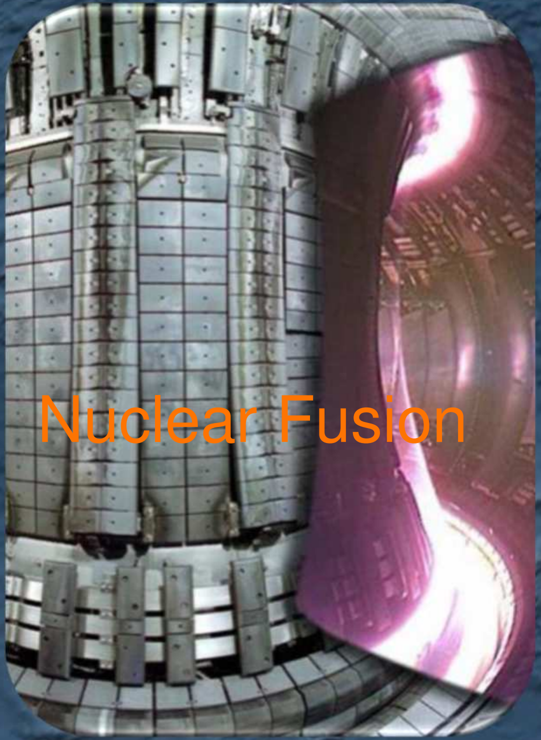
UAl | Universidade do Algarve

UMa | Universidade da Madeira

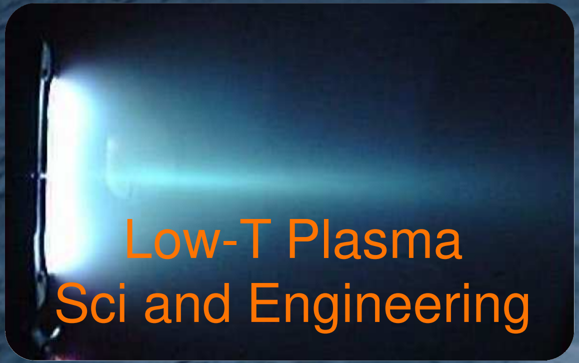
Staff: 160 people (90+ PhDs)

Instituto de Plasmas e Fusão Nuclear

Key research activities



Nuclear Fusion



Low-T Plasma
Sci and Engineering

Intense Lasers

APPLAuSE PhD Program
Advanced Program in Plasma Science and Engineering

Advanced Training

Fellowships available
Call opening: November 7, 2016
www.ipfn.ist.utl.pt/applause

High performance
computing

Instituto de Plasmas e Fusão Nuclear

Key research activities

Experimental Physics

Theory & Modeling

Society

Plasma Engineering & Systems Integration

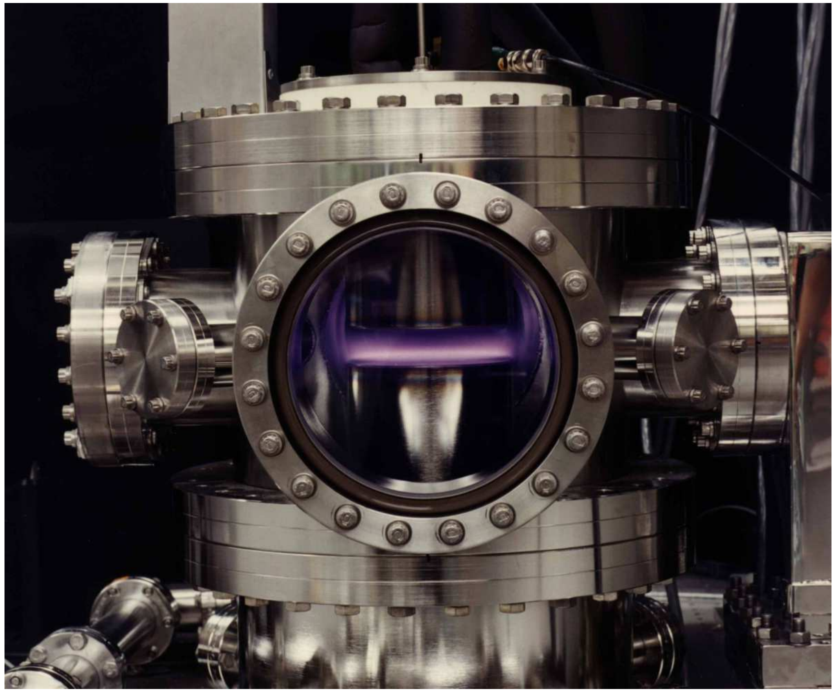
Awarded “Outstanding”

(11/300 R&D units - 2014 evaluation procedure managed by ESF)

Modelling of low-temperature plasmas

Goal: understand and predict

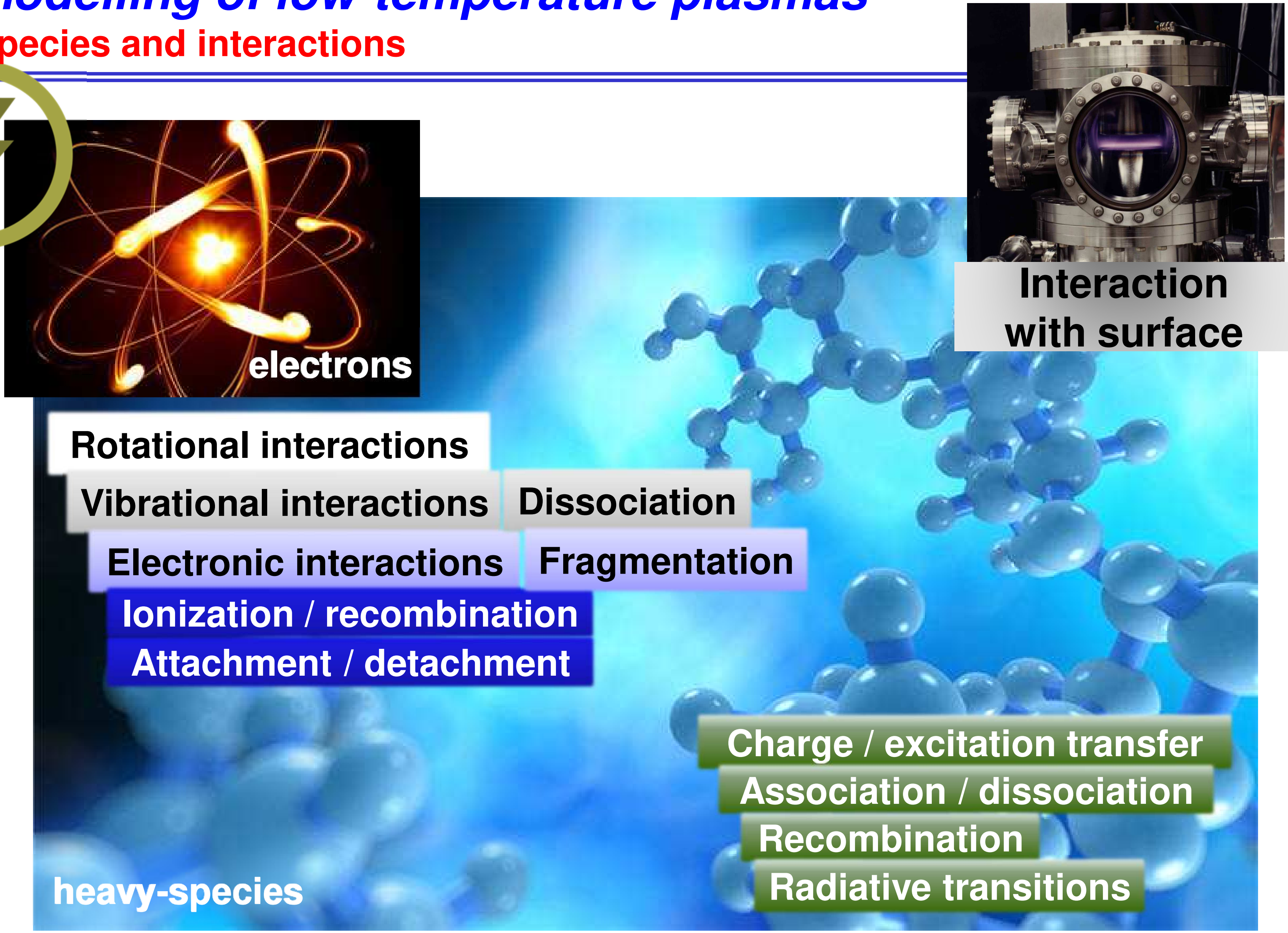
- Understand
- Predict
- Propose
- Tailor / Optimize



Courtesy: Nor-Call Products

Modelling of low-temperature plasmas

Species and interactions



Interaction with surface

Rotational interactions

Vibrational interactions

Dissociation

Electronic interactions

Fragmentation

Ionization / recombination

Attachment / detachment

Charge / excitation transfer

Association / dissociation

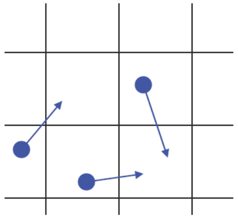
Recombination

Radiative transitions

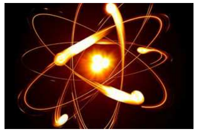
Modelling of low-temperature plasmas

Modelling approaches

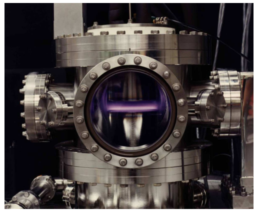
- **Statistical models**



- **Kinetic models**

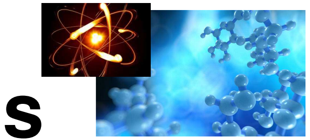


- **Fluid models**



Andrew Gibson

- **Global (hybrid) models**



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
  Plasma Sources Sci. Technol. 9 (2000) 528–540

- **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
  J. Wiley, 1965 / 1968

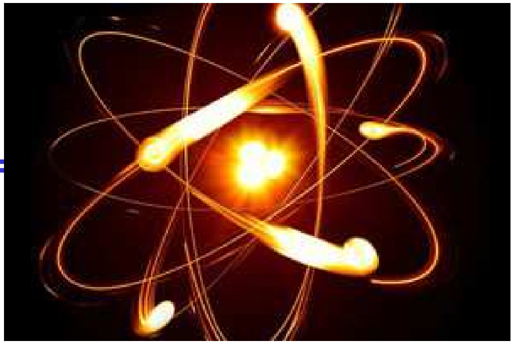
- **Motions of Ions and Electrons**
  W. P. Allis,
  Handbuch der Physik, vol. 21, 1956, S. Flugge, Springer-Verlag – Berlin

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

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

F(**r**,**v**,*t*) is the **distribution function,** representing the number of particles per unit volume in phase space (**r**,**v**), at time *t*.

Electron kinetic modelling

The electron Boltzmann equation

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

Rate of *F*

in time

in configuration space

in velocity space

due to collisions

Force acting upon particles

- The total electric field acting on electrons

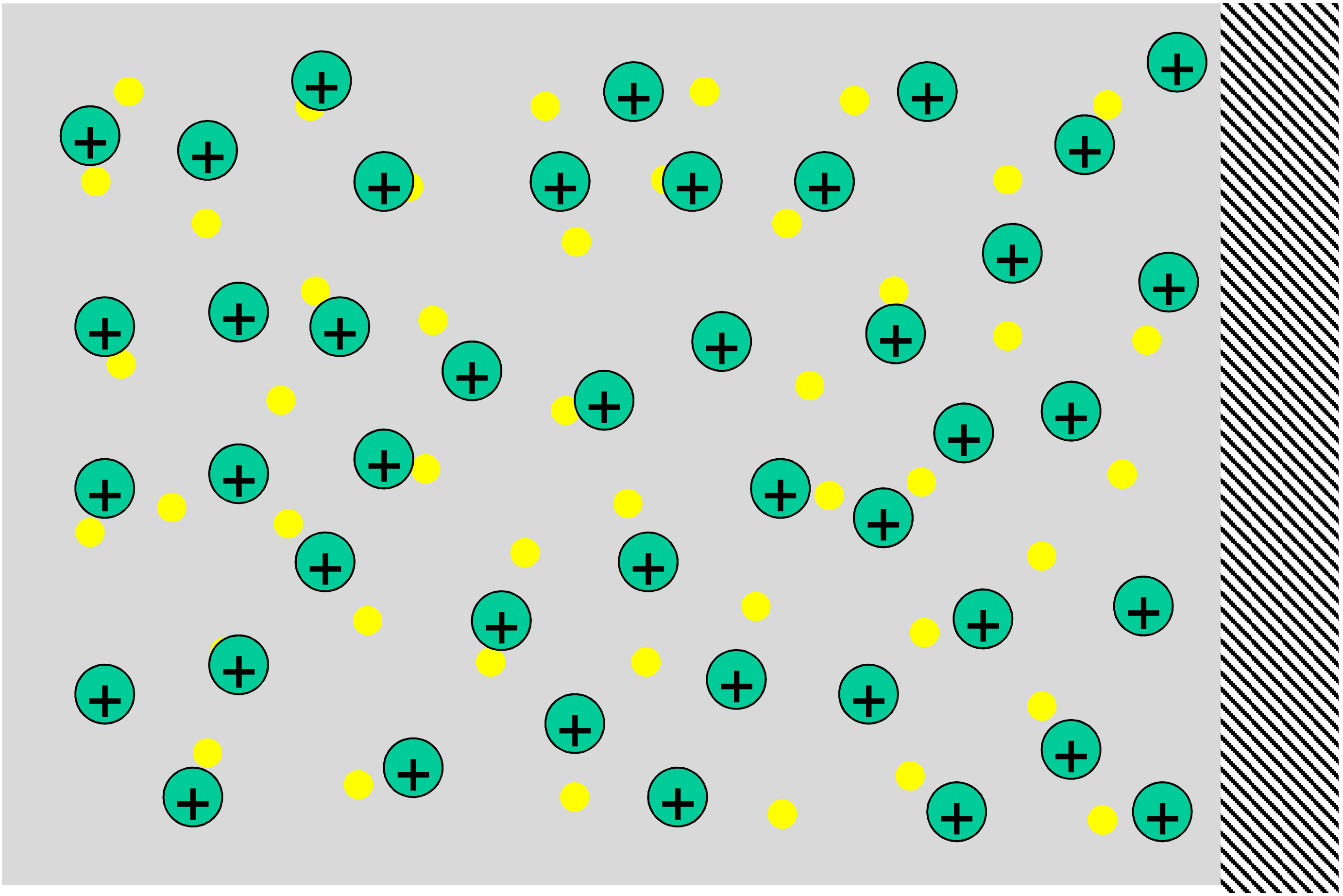
$$\vec{E} = \vec{E}_s(\vec{r}) + \vec{E}_p \exp(j\omega t)$$

dc space-charge field

hf field at frequency ω

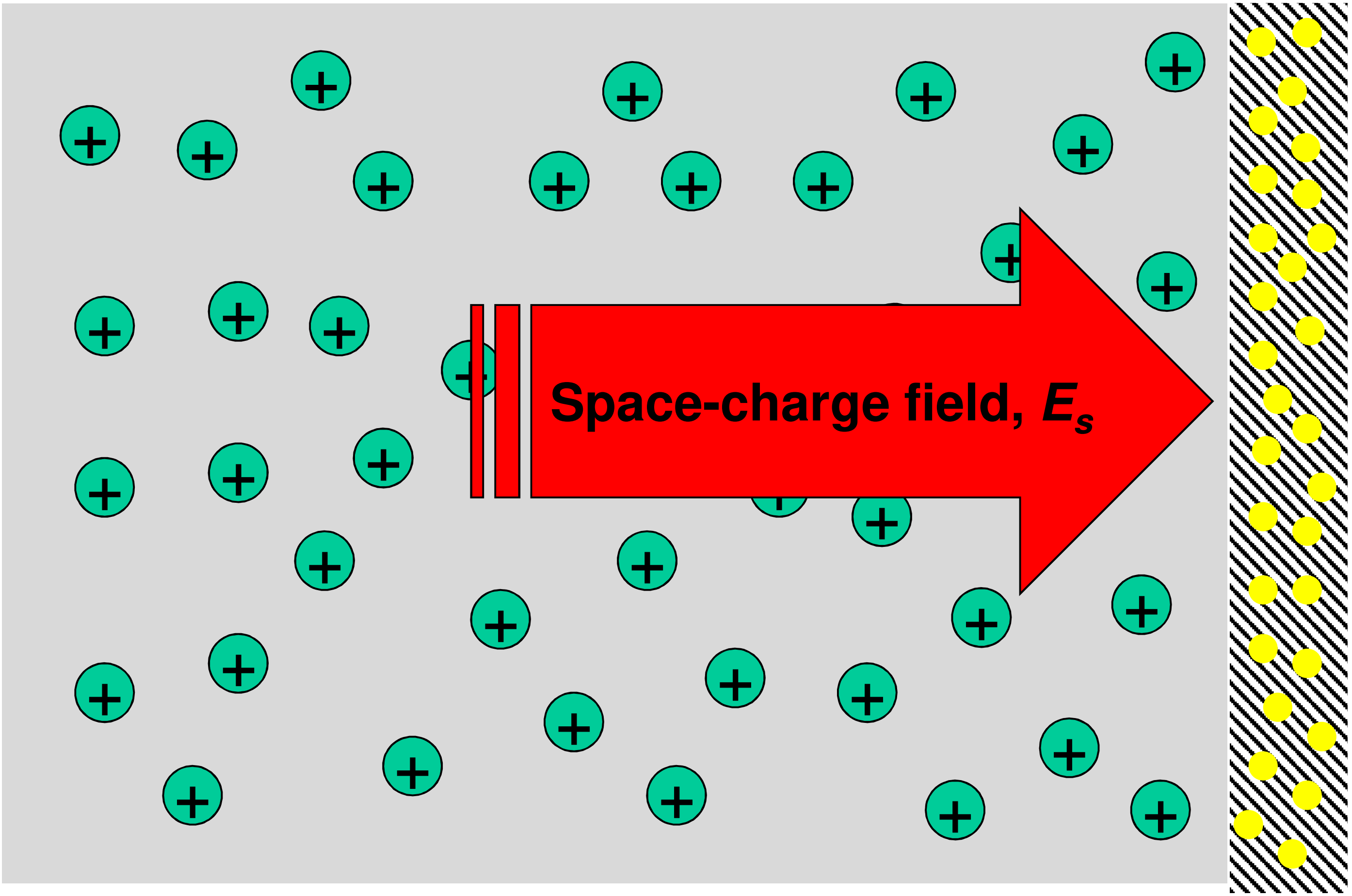
Charge separation at the boundaries

The space-charge sheath



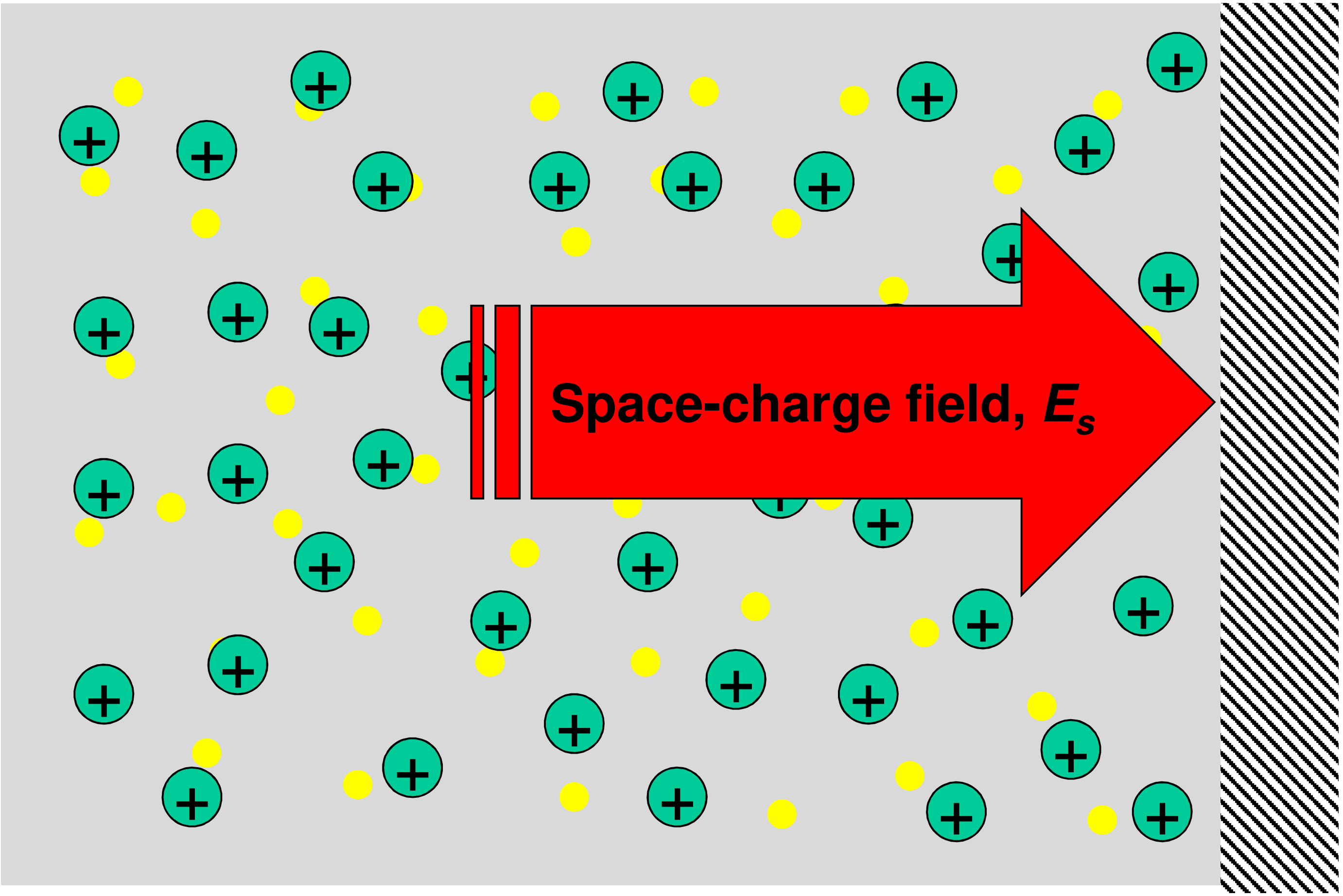
Charge separation at the boundaries

The space-charge sheath



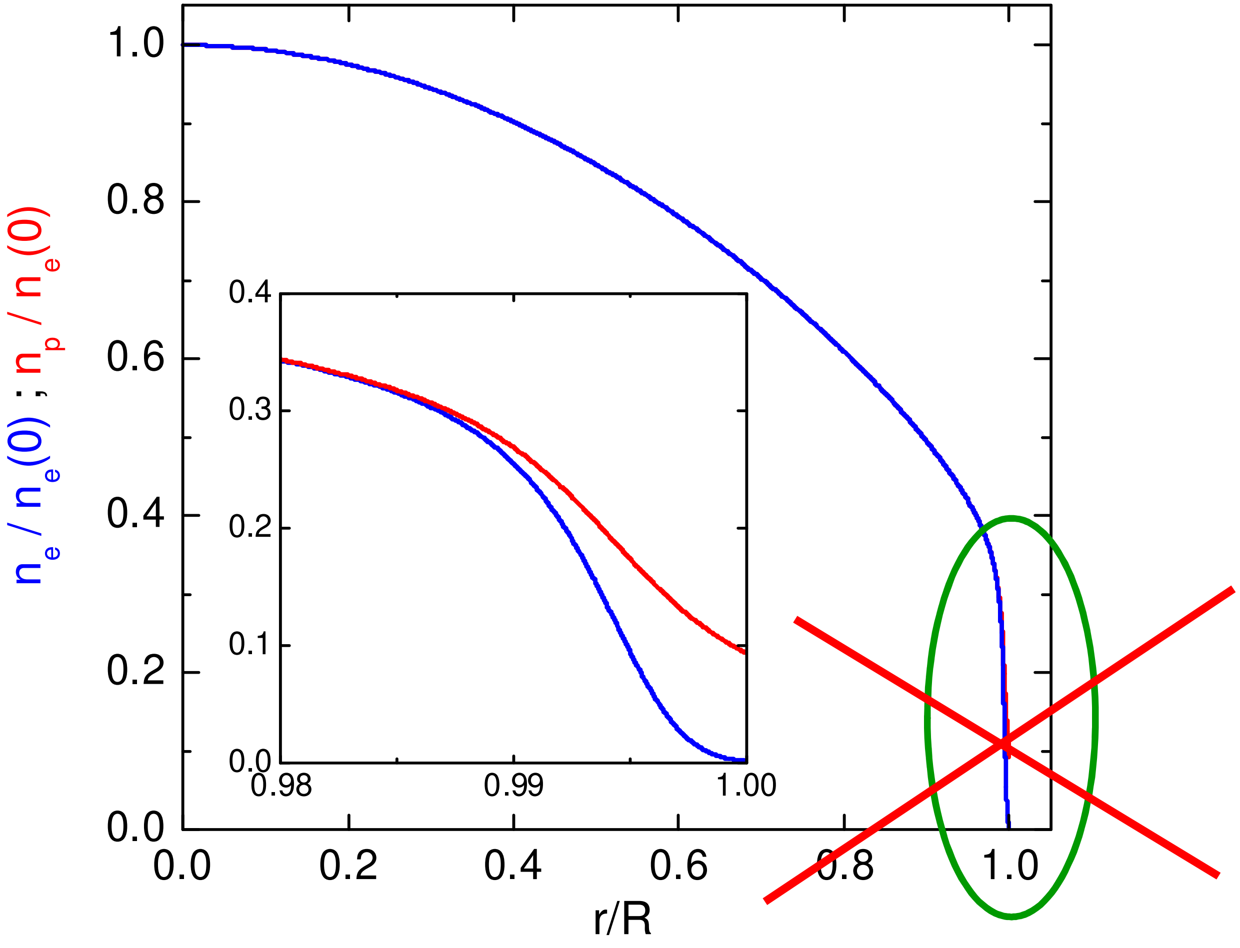
Charge separation at the boundaries

The space-charge sheath



Charge separation at the boundaries

The space-charge sheath



LL Alves, Plasmas Sources Sci. Technol. 16 557 (2007)

The electron Boltzmann equation

Working conditions

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

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

dc space-charge field   hf field at frequency ω

- No external magnetic field
- The electron distribution function F is expanded

  in spherical harmonics in velocity space

  in Fourier series in time

$$F = \sum_l \sum_p F_p^l \, P_l(\cos\theta) \exp(jp\omega t)$$

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, $\tau_e^{-1} \ll \omega$

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

Isotropic component
(energy relaxation)

Anisotropic components
(transport)

The homogeneous electron Boltzmann equation

Collision operators

- The isotropic equation

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

- The anisotropic equation

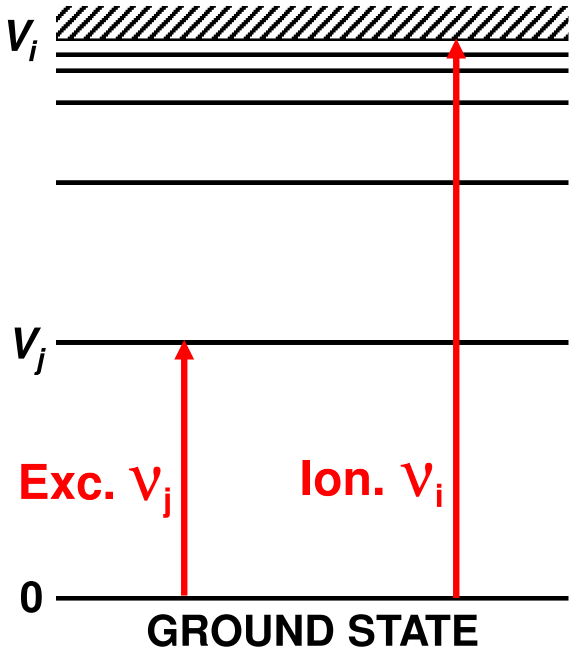
elastic collision operator

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

inelastic collision operator

The homogeneous electron Boltzmann equation

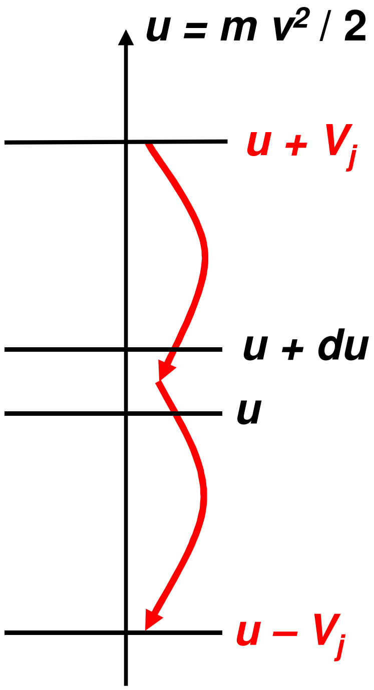
The inelastic collision operator



Entrance Exit

$$qF_0^0 - \left(\nu_x + \nu_i\right) F_0^0$$

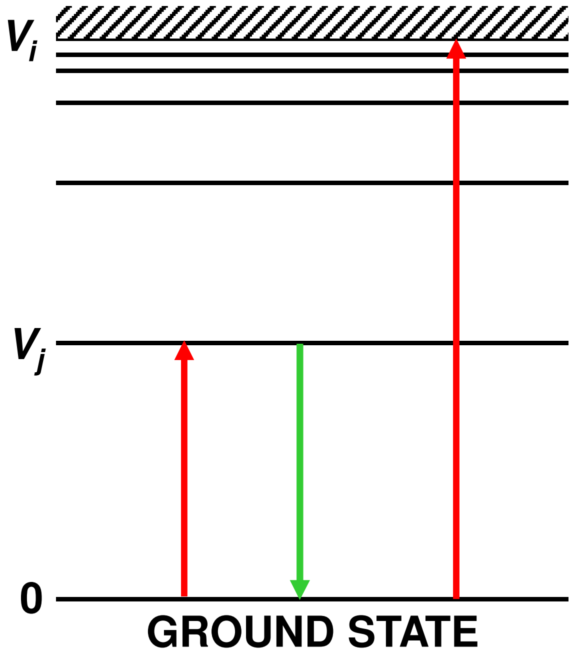
$$\nu_x = \sum_j \nu_j$$



INELASTIC

The homogeneous electron Boltzmann equation

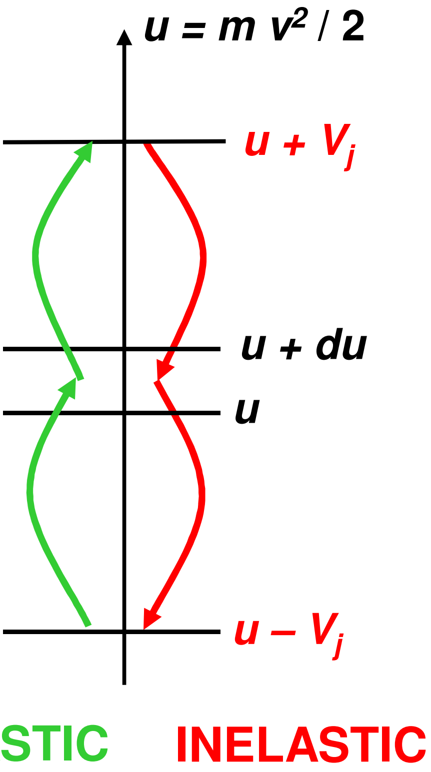
The inelastic / superelastic collision operator



Entrance Exit

$$qF_0^0 - \left(\nu_x + \nu_i\right) F_0^0$$

$$\nu_x = \sum_j \nu_j$$



The homogeneous electron Boltzmann equation

Input data: working parameters

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

$$\left(\nu_c + \jmath\omega\right)\vec{F}_1^1 = \frac{e\vec{E}_p}{m}\frac{\partial F_0^0}{\partial v}$$

$\frac{E_p}{N}, \frac{\omega}{N}$ ⇒ **Independent parameters**

The homogeneous electron Boltzmann equation

Input data: collisional data

$$u = mv^2/(2e)$$

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

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

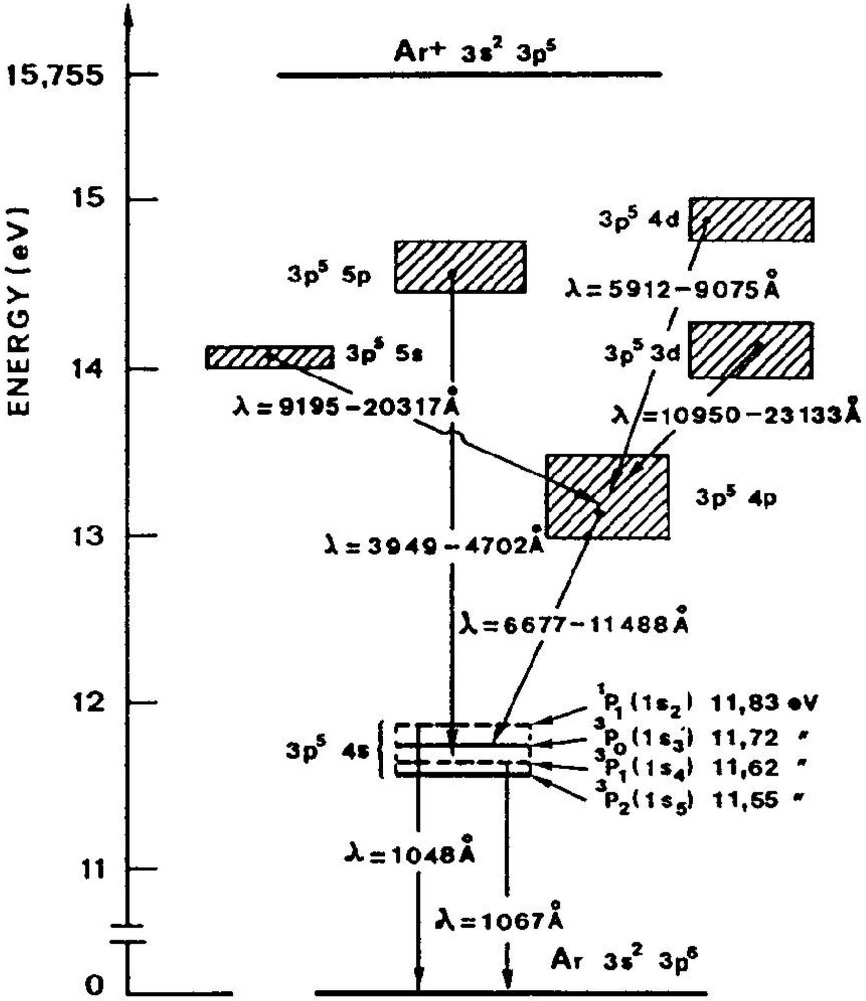
$$\nu_c = N\sigma_c\left(2eu/m\right)^{1/2} \qquad q,\nu = N_i\sigma_{ij}\left(2eu/m\right)^{1/2}$$

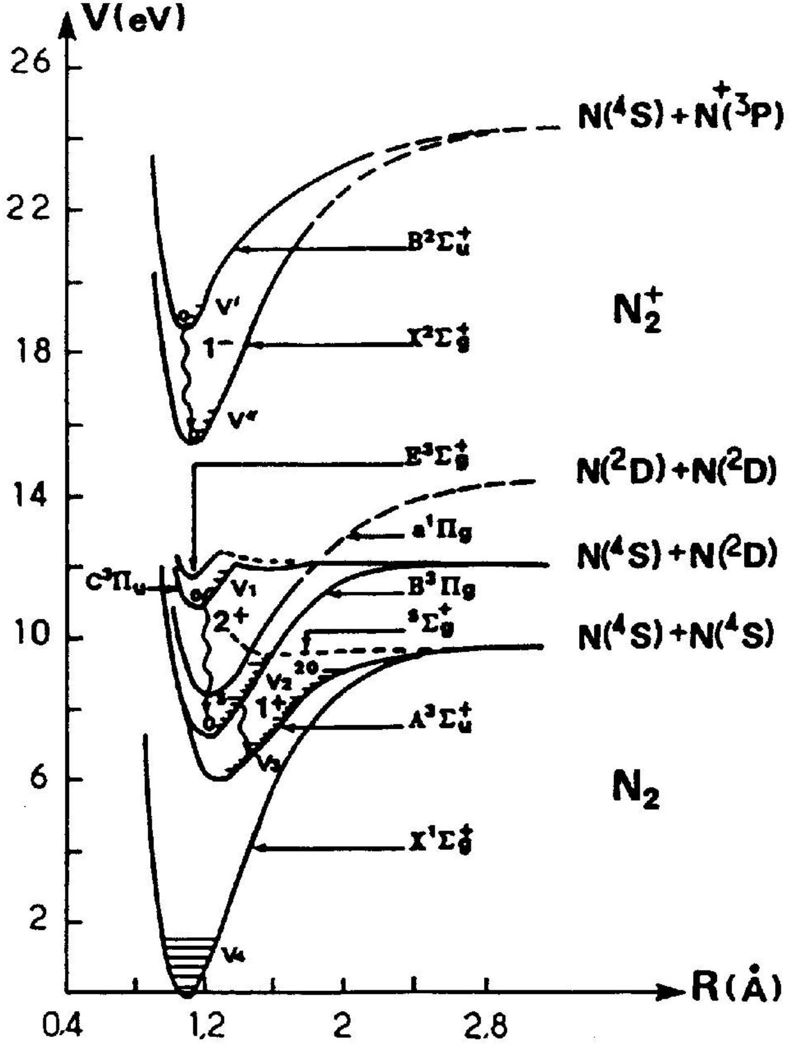
$N_{i=0} = N$ ⇒ **Gas density**

$N_{i\neq 0}$ ⇒ **Chemistry model (heavy-species kinetics)**

Input data

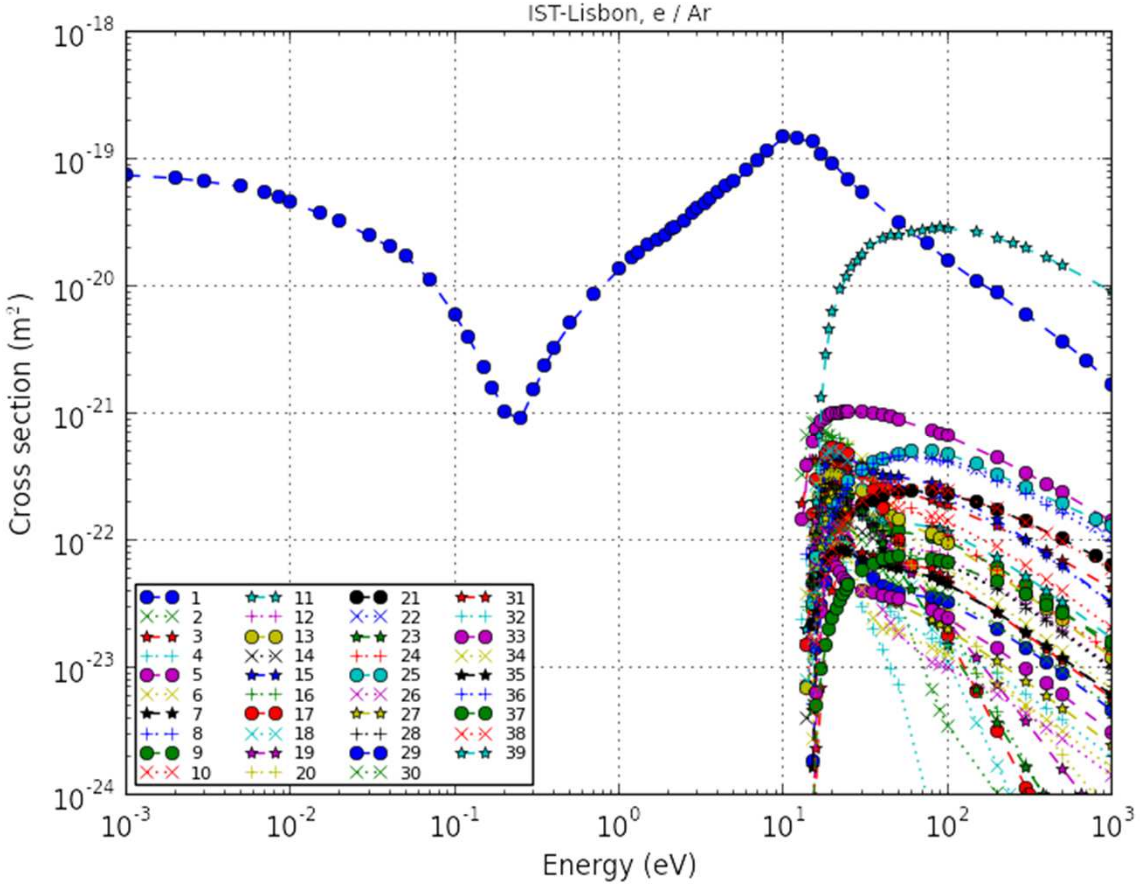
Excitation / ionization mechanisms





Input data

Electron-impact cross sections

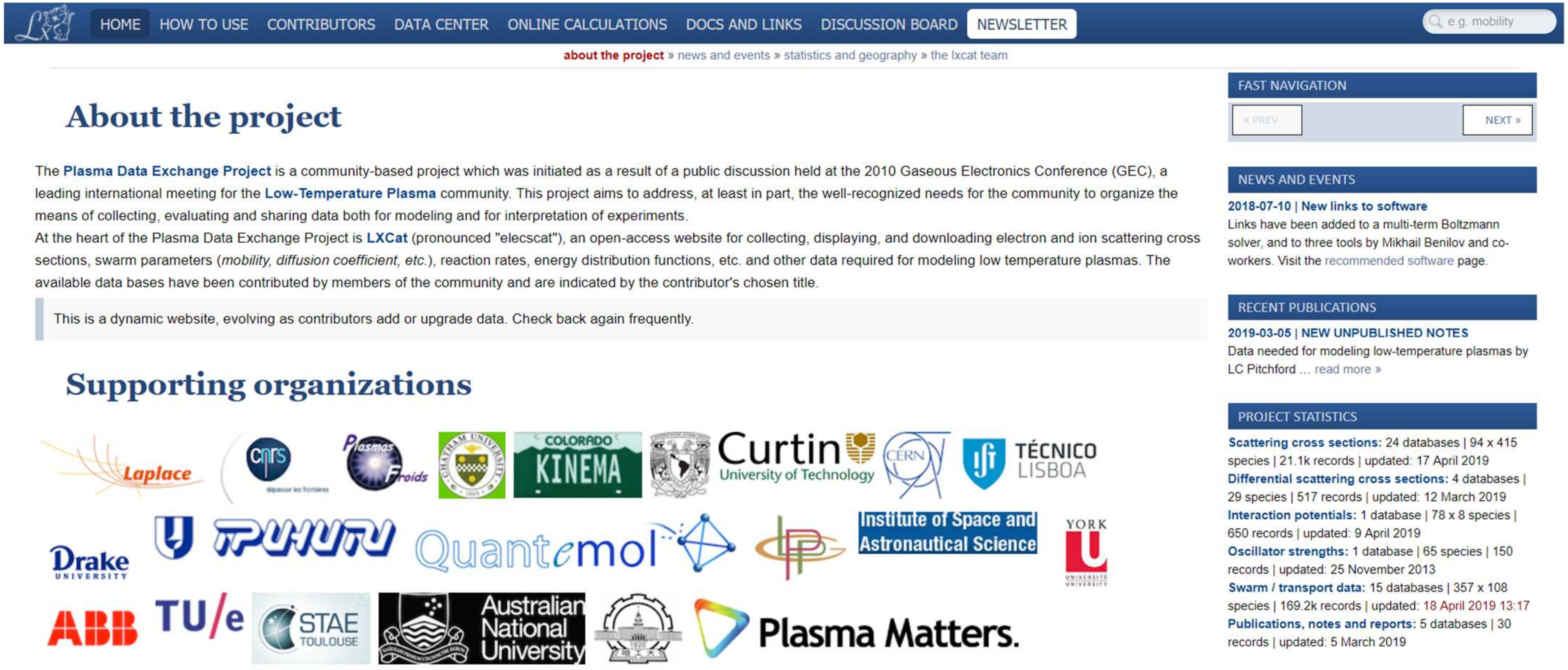


Data from…

- Bibliography
- Databases (e.g. LXCat: www.lxcat.net)

Input data

The LXCat open-access website



About the project

The **Plasma Data Exchange Project** is a community-based project which was initiated as a result of a public discussion held at the 2010 Gaseous Electronics Conference (GEC), a leading international meeting for the **Low-Temperature Plasma** community. This project aims to address, at least in part, the well-recognized needs for the community to organize the means of collecting, evaluating and sharing data both for modeling and for interpretation of experiments.

At the heart of the Plasma Data Exchange Project is **LXCat** (pronounced "elecscat"), an open-access website for collecting, displaying, and downloading electron and ion scattering cross sections, swarm parameters (*mobility, diffusion coefficient, etc.*), reaction rates, energy distribution functions, etc. and other data required for modeling low temperature plasmas. The available data bases have been contributed by members of the community and are indicated by the contributor's chosen title.

> This is a dynamic website, evolving as contributors add or upgrade data. Check back again frequently.

Supporting organizations

NEWS AND EVENTS

2018-07-10 | New links to software
Links have been added to a multi-term Boltzmann solver, and to three tools by Mikhail Benilov and co-workers. Visit the recommended software page.

RECENT PUBLICATIONS

2019-03-05 | NEW UNPUBLISHED NOTES
Data needed for modeling low-temperature plasmas by LC Pitchford ... read more »

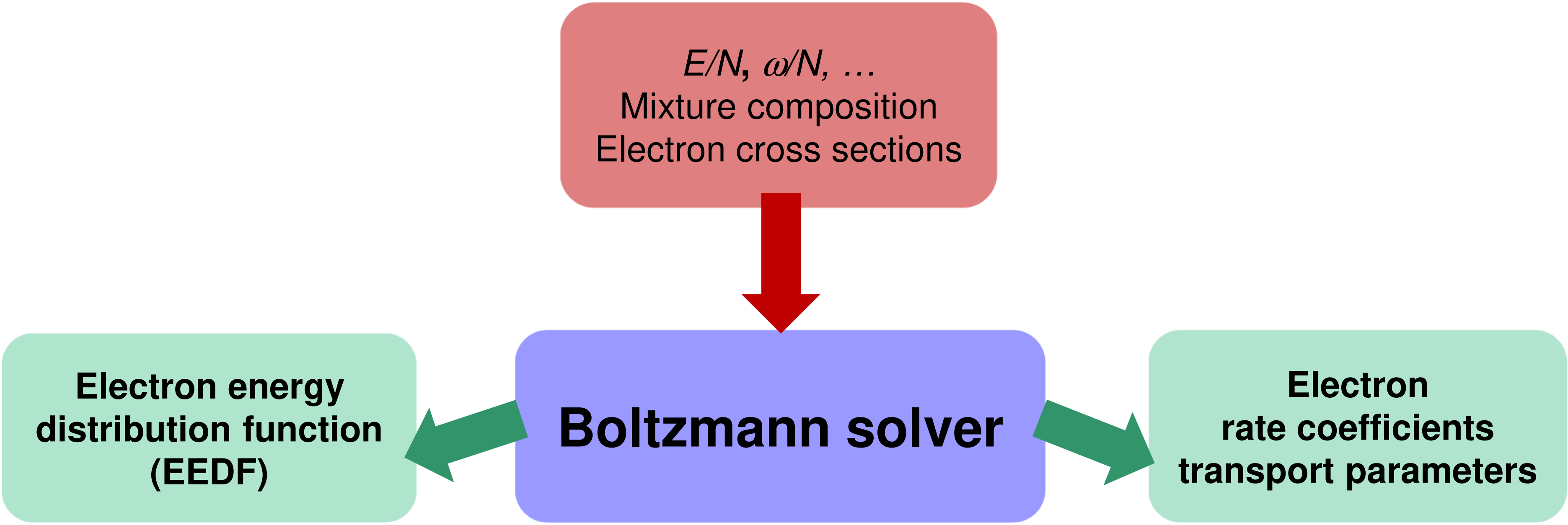
PROJECT STATISTICS

Scattering cross sections: 24 databases | 94 x 415 species | 21.1k records | updated: 17 April 2019
Differential scattering cross sections: 4 databases | 29 species | 517 records | updated: 12 March 2019
Interaction potentials: 1 database | 78 x 8 species | 650 records | updated: 9 April 2019
Oscillator strengths: 1 database | 65 species | 150 records | updated: 25 November 2013
Swarm / transport data: 15 databases | 357 x 108 species | 169.2k records | updated: 18 April 2019 13:17
Publications, notes and reports: 5 databases | 30 records | updated: 5 March 2019

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

Workflow

Electron Boltzmann kinetics

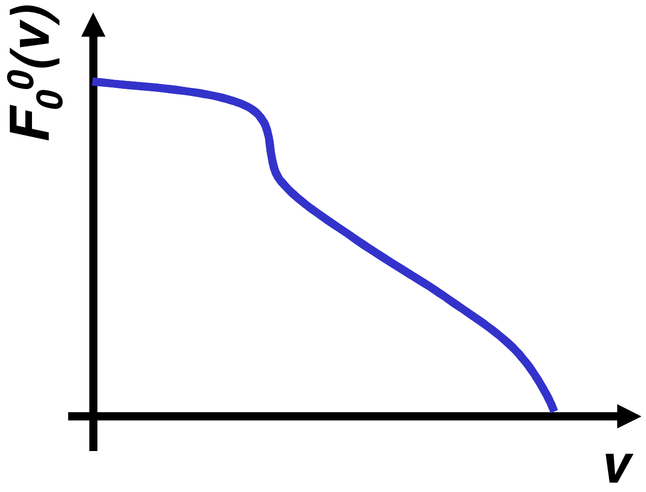


E/N, *ω/N*, …
Mixture composition
Electron cross sections

Boltzmann solver

Electron energy distribution function (EEDF)

Electron rate coefficients transport parameters



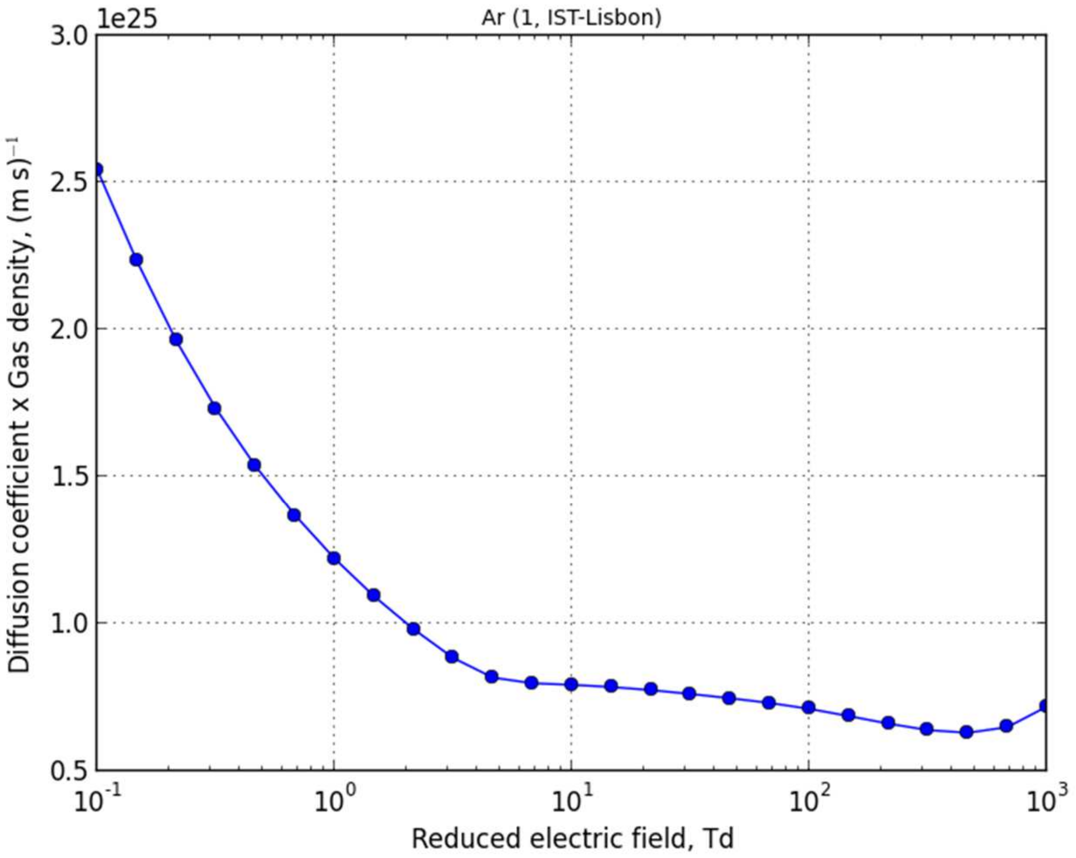
$$C_{ij} = \int_0^\infty \sigma_{ij}(v) v \frac{F_0^0(v)}{n_e} 4\pi v^2 dv$$

$$D_e N = \int_0^\infty \frac{v}{3\sigma_c(v)} \frac{F_0^0(v)}{n_e} 4\pi v^2 dv$$

Electron parameters

Example: the free-diffusion coefficient

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



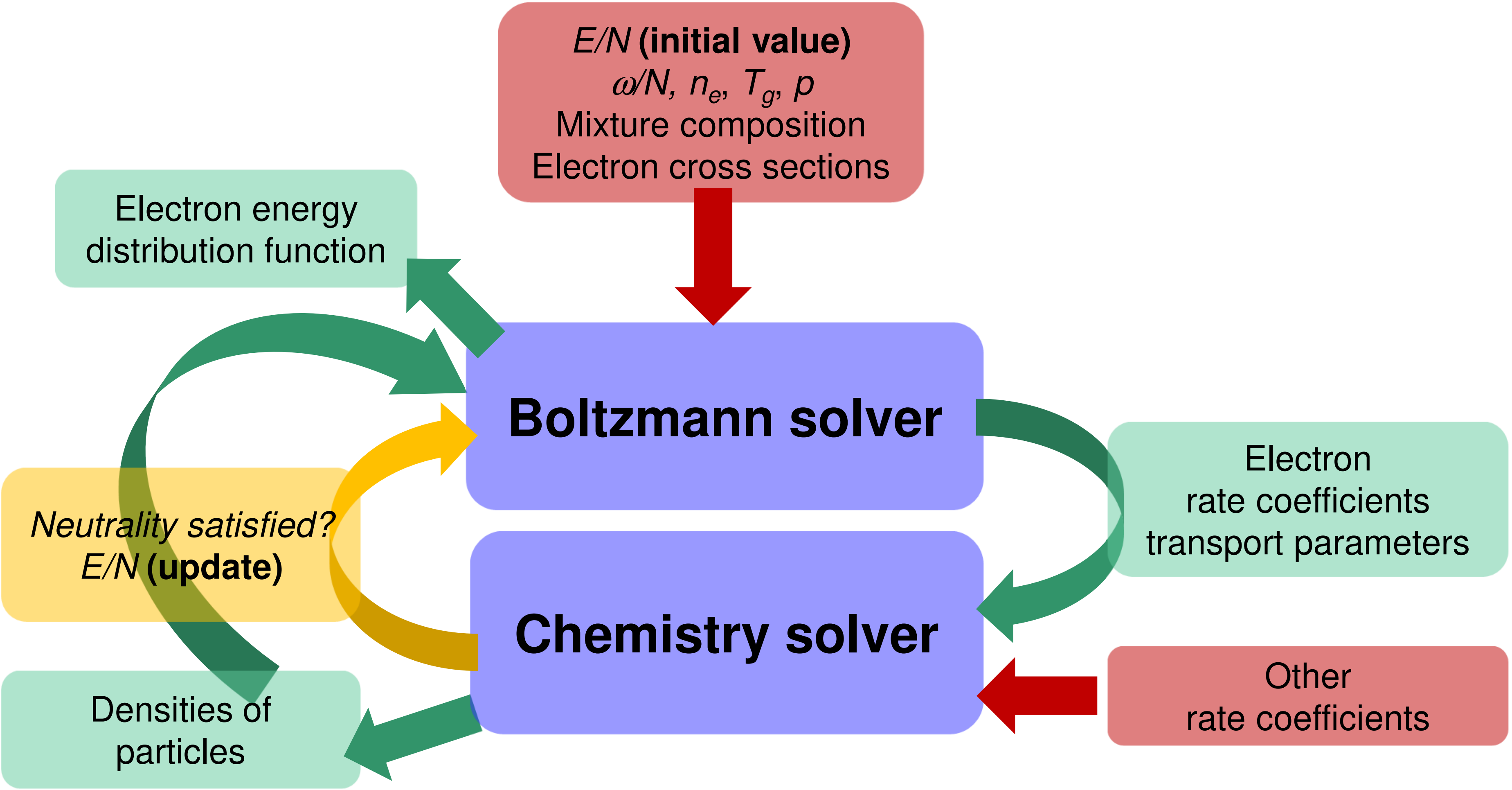
↓

1 Td ≡ 10^{-17} V cm^2

Ar @ IST-LISBON
www.lxcat.net

Workflow

Global (Boltzmann + Chemistry) modelling



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

Electron energy distribution function

Boltzmann solver

Electron
rate coefficients
transport parameters

Neutrality satisfied?
E/N **(update)**

Chemistry solver

Other
rate coefficients

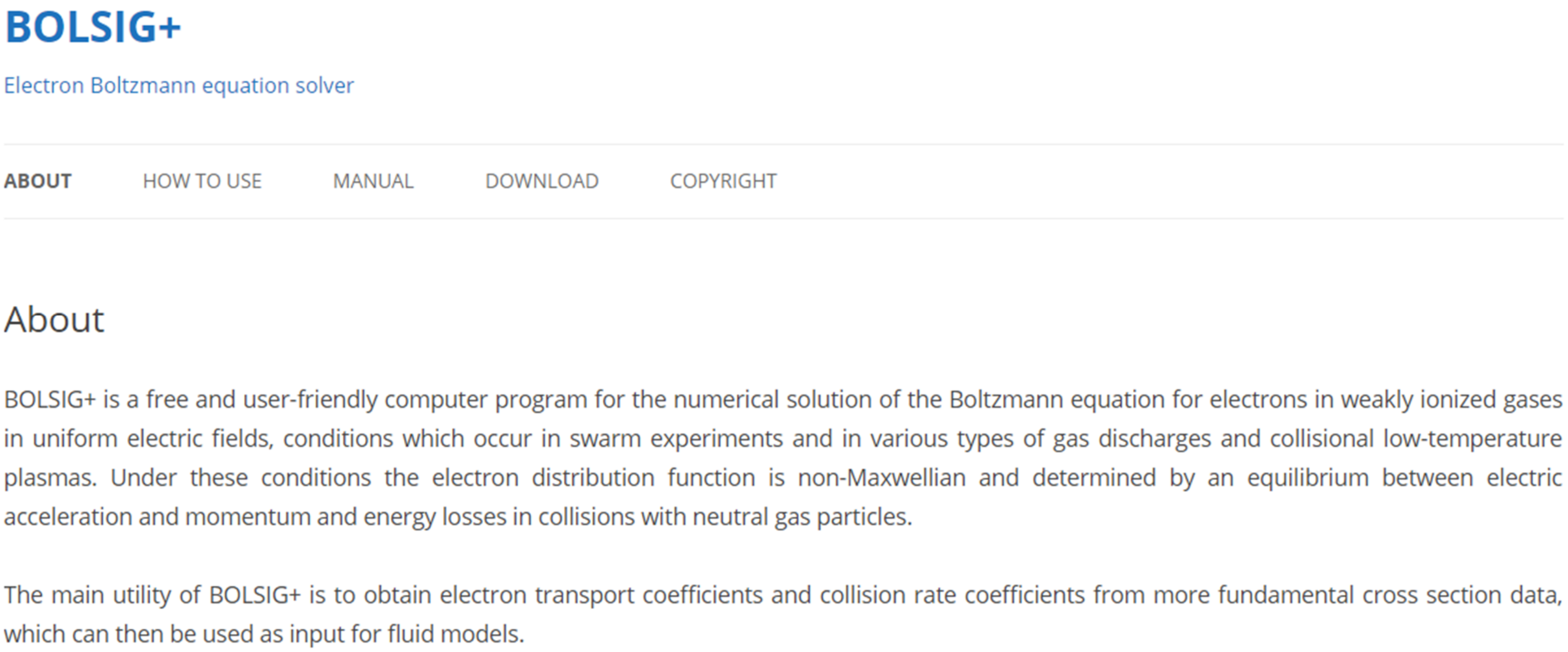
Densities of
particles

Examples of tools

Examples of tools

BOLSIG+

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



BOLSIG+

Electron Boltzmann equation solver

About

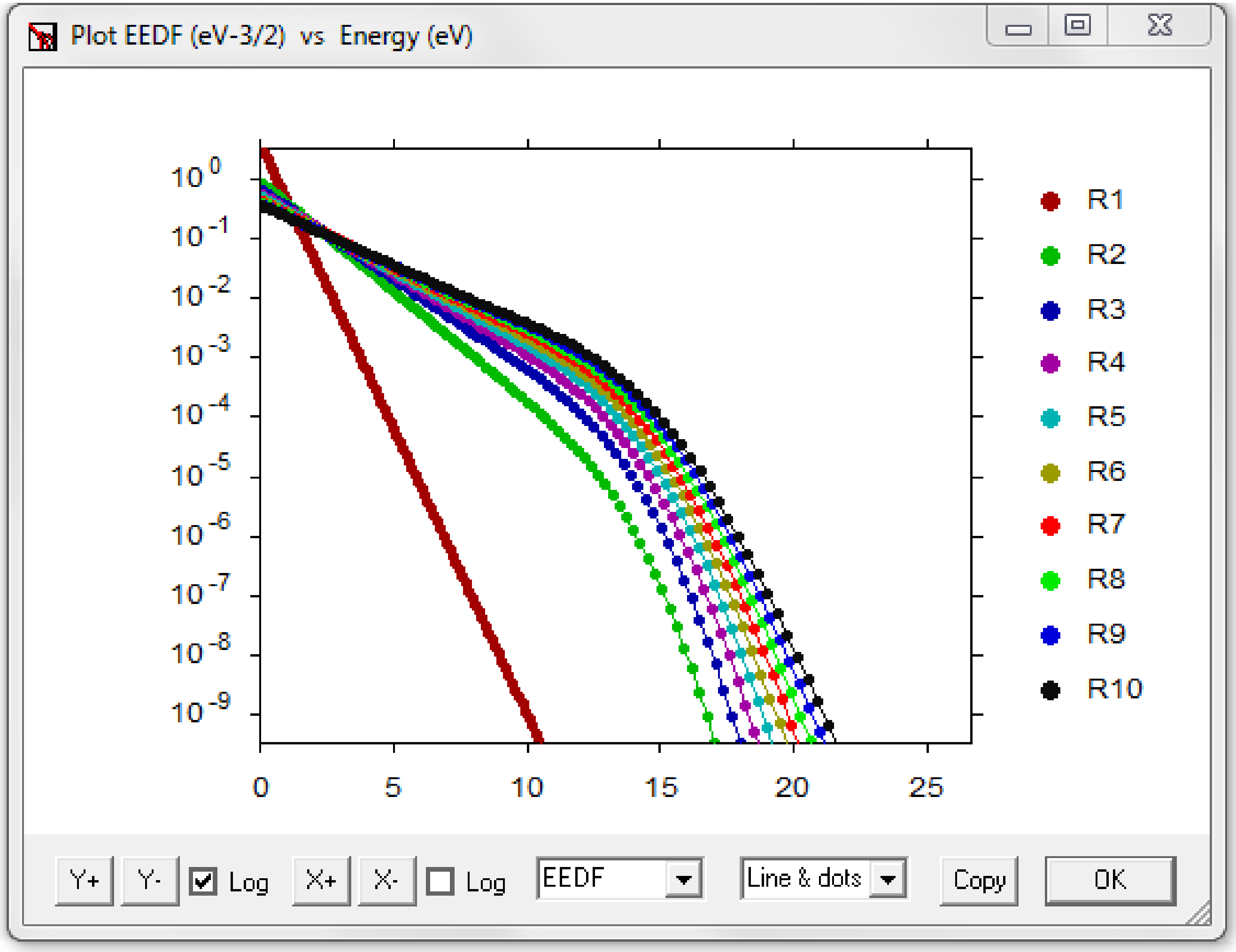
BOLSIG+ is a free and user-friendly computer program for the numerical solution of the Boltzmann equation for electrons in weakly ionized gases in uniform electric fields, conditions which occur in swarm experiments and in various types of gas discharges and collisional low-temperature plasmas. Under 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.

G.J.M. Hagelaar and L.C. Pitchford, Plasmas Sources Sci. Technol. 14 722 (2005)

BOLSIG+

The electron energy distribution function (EEDF)



The LisbOn KInetics Boltzmann solver (LoKI-B)

(developed under MATLAB®)

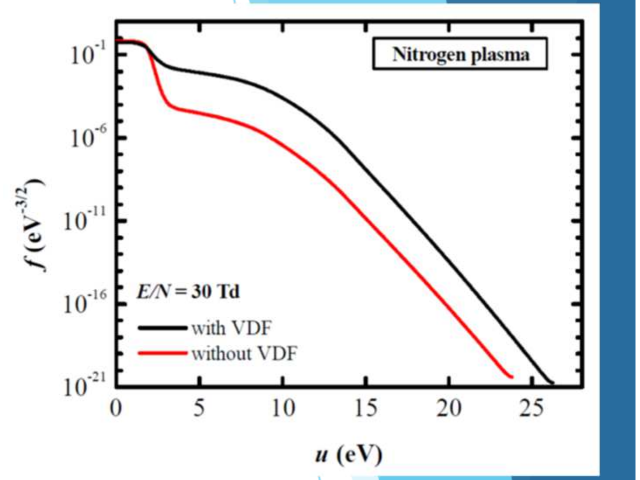
LisbOn KInetics

OPEN SOURCE

LoKI-B

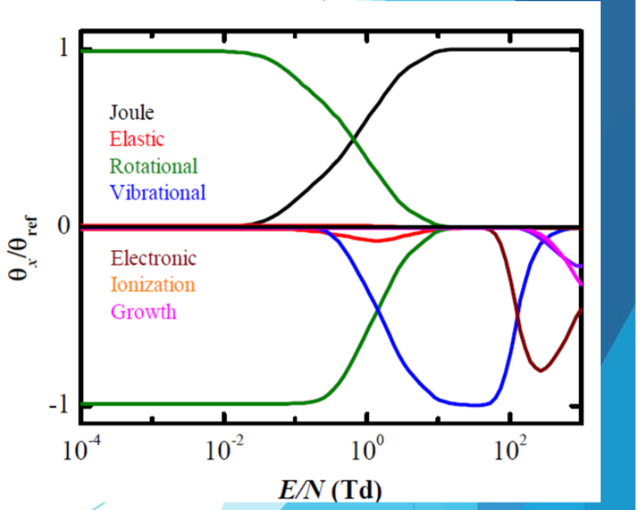
https://github.com/IST-Lisbon/LoKI

- 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

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

LisbOn KInetics

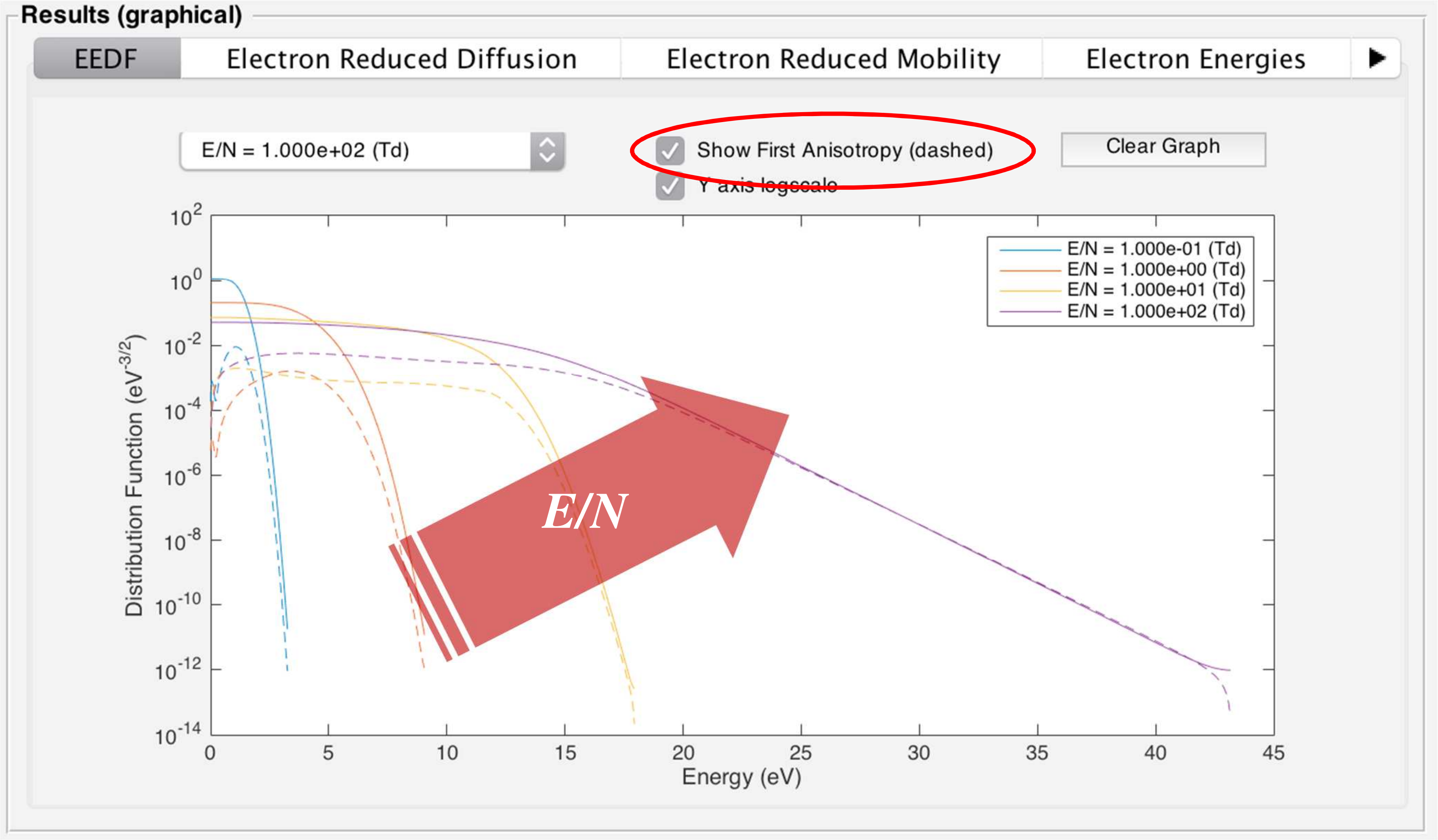
- **Install MATLAB®**
- **Get the code**
  https://github.com/IST-Lisbon/LoKI
- **Get the data**
  www.lxcat.net

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 (graphical)

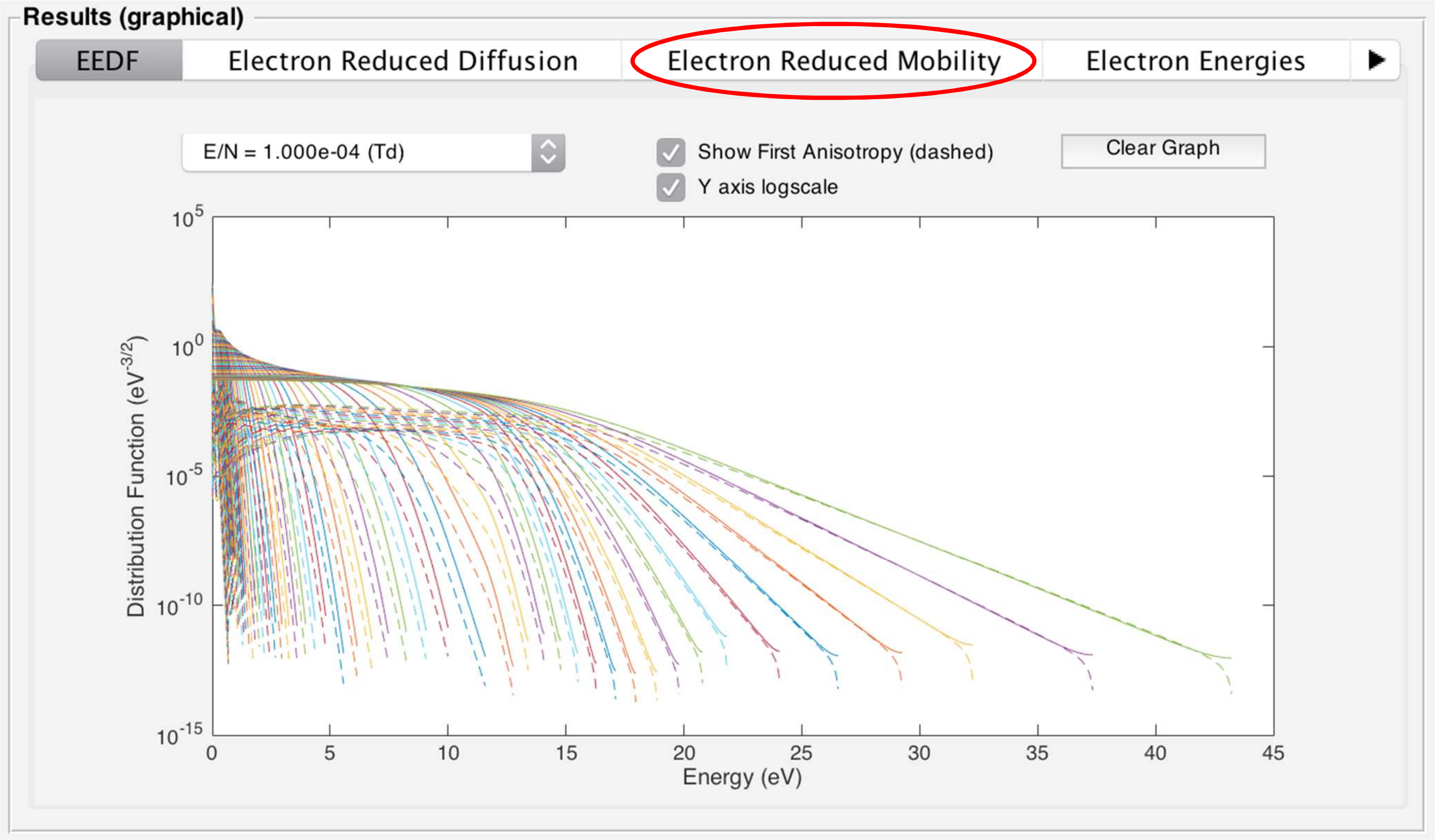
E/N = 1.000e+02 (Td)

☑ Show First Anisotropy (dashed)

☑ Y axis logscale

Results – "swarm analysis"

Argon @ 10^{-4} Td ≤ E/N ≤ 100 Td and T_g = 300K



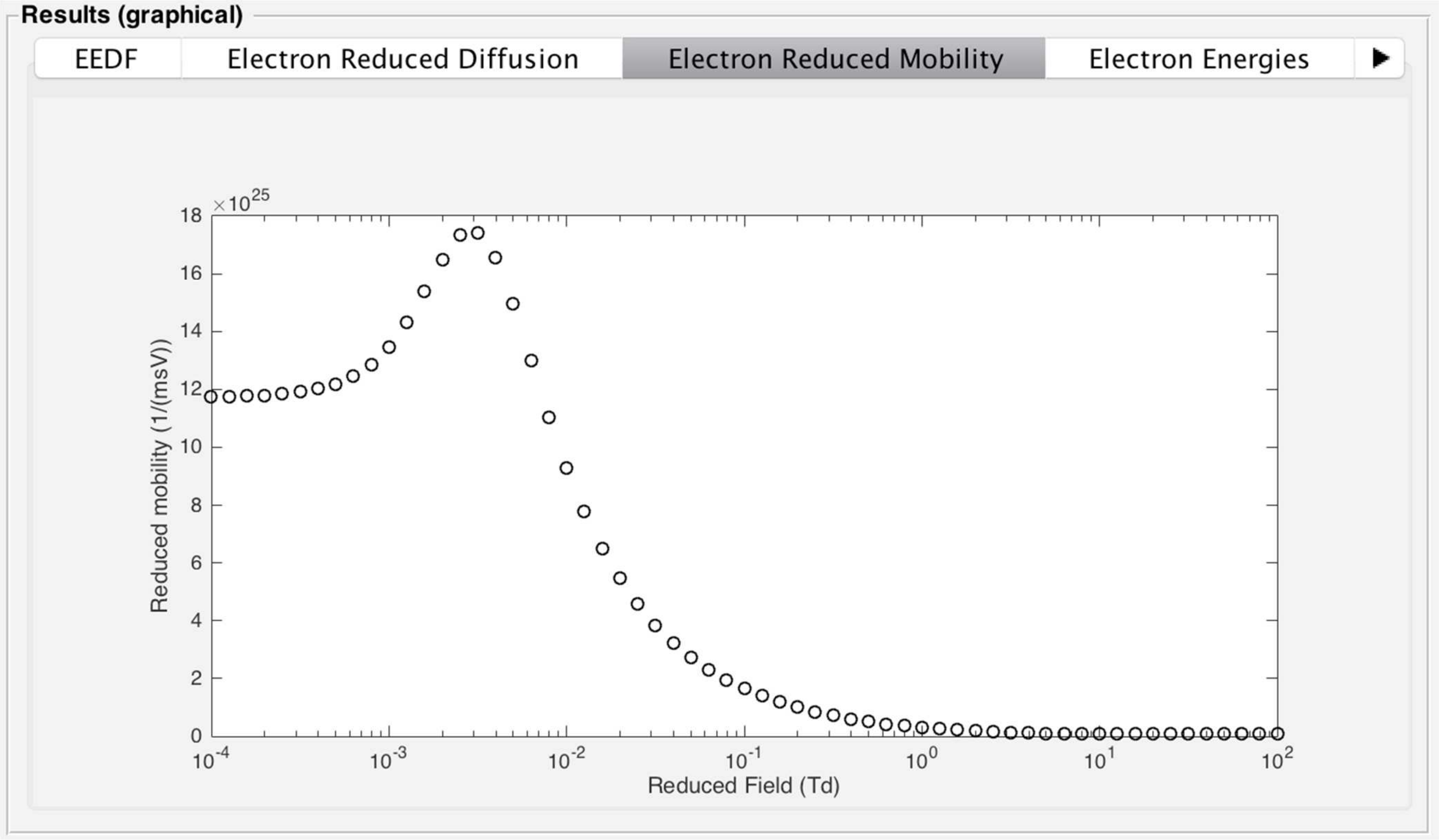
E/N = 1.000e-04 (Td)

☑ Show First Anisotropy (dashed)

☑ Y axis logscale

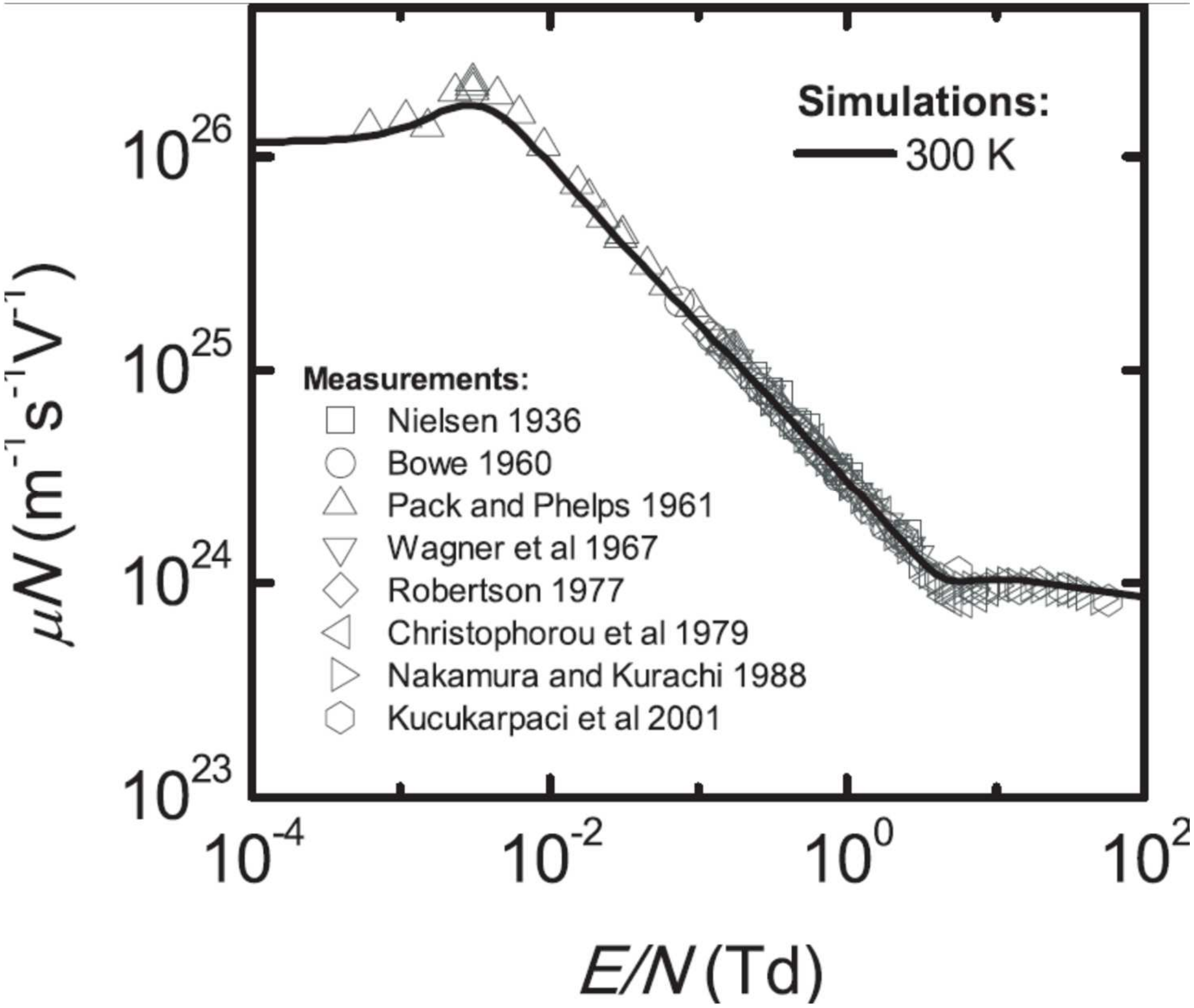
Results – “swarm analysis”

Argon mobility as a function of *E/N*



Results – "swarm analysis"

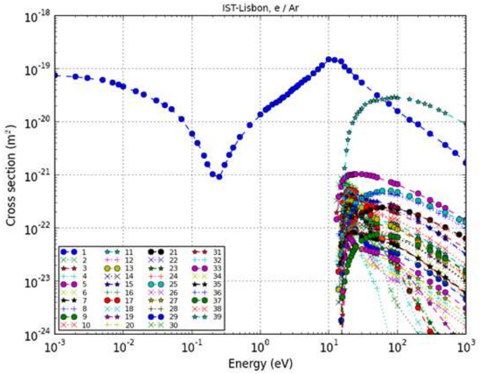
Argon mobility as a function of *E/N* – comparison with experimental data

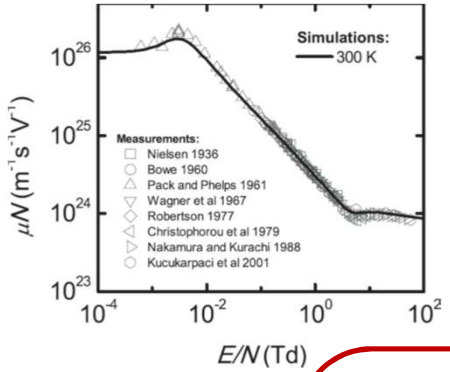


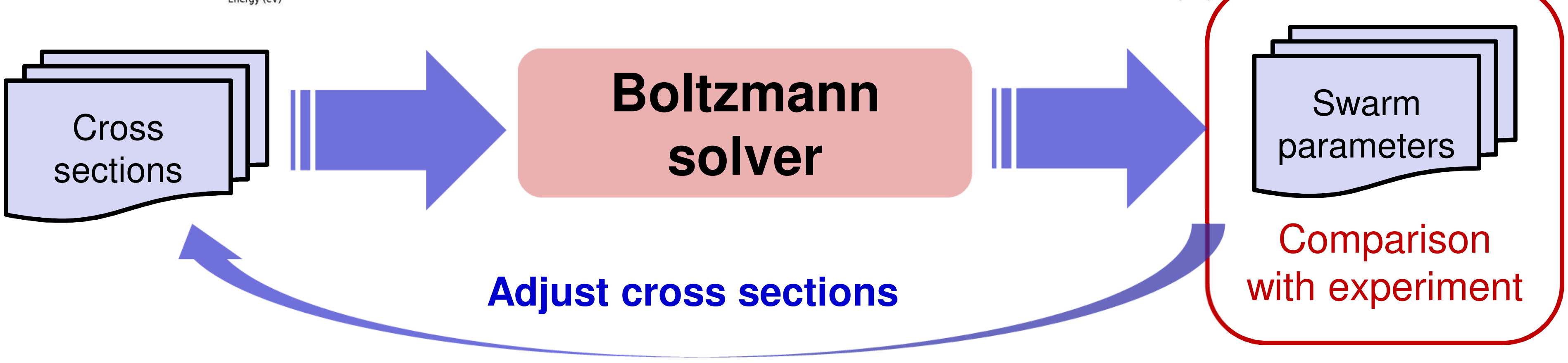
Results – "swarm analysis"

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







Cross sections

Boltzmann solver

Swarm parameters

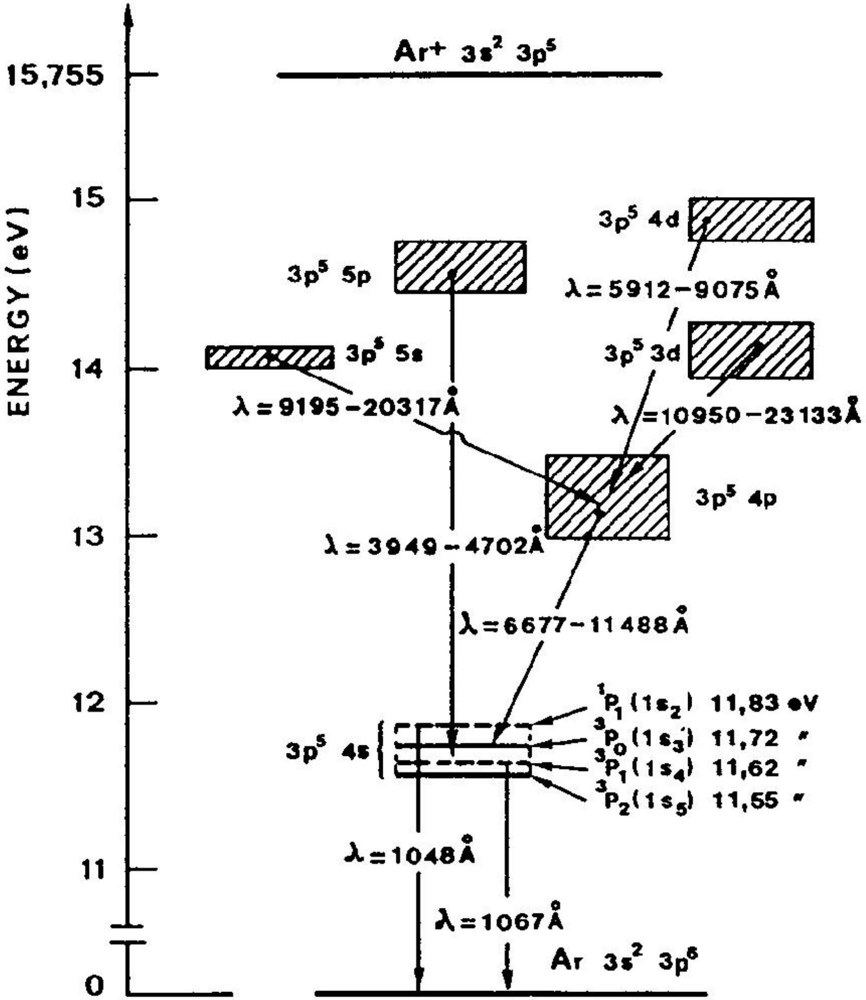
Comparison with experiment

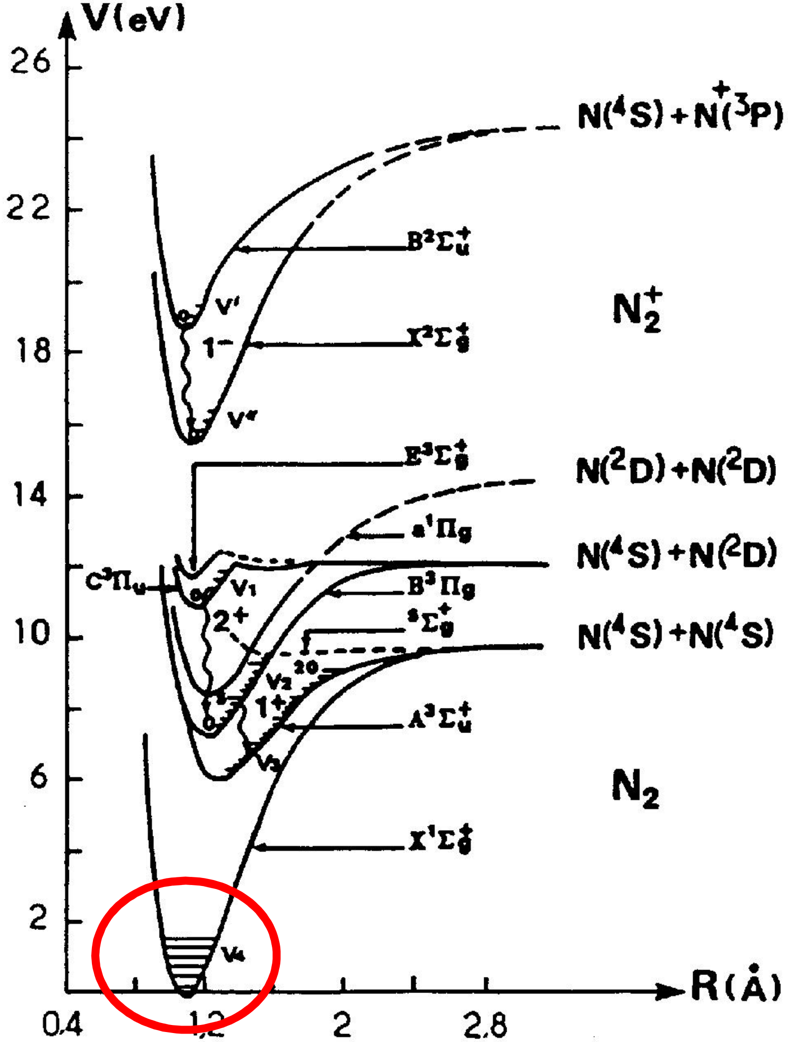
Adjust cross sections

L.C. Pitchford et al, J. Phys. D 46 334001 (2013)

Results – molecular gases

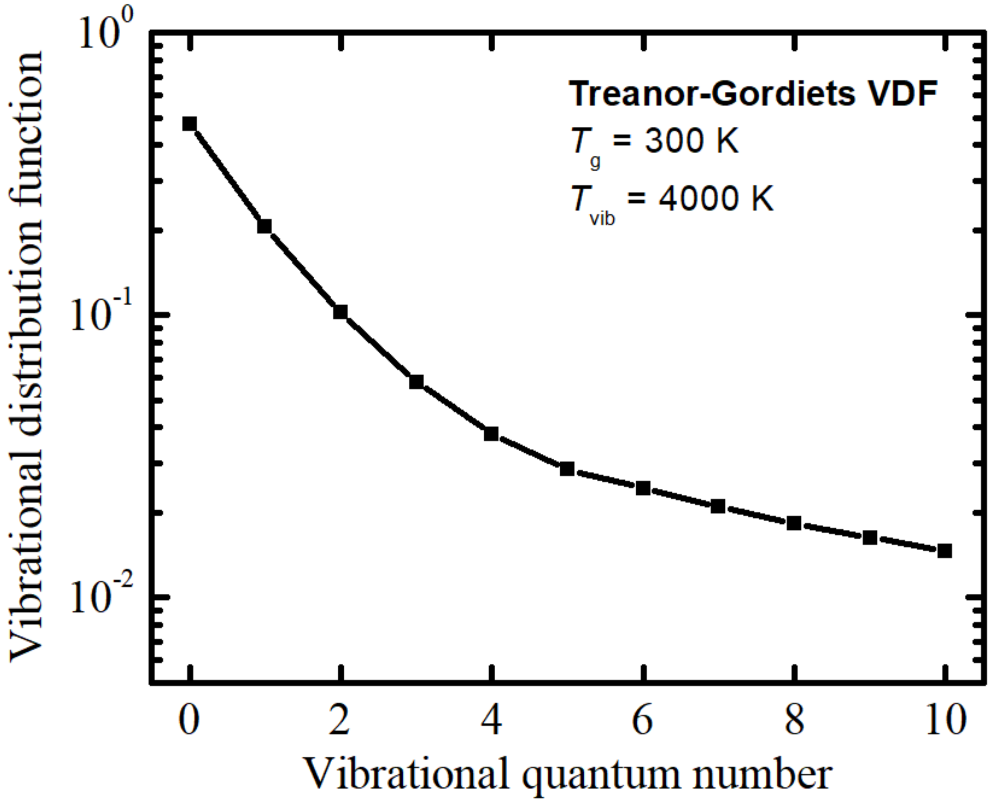
Argon vs Nitrogen





Results – influence of e-vibrational mechanisms

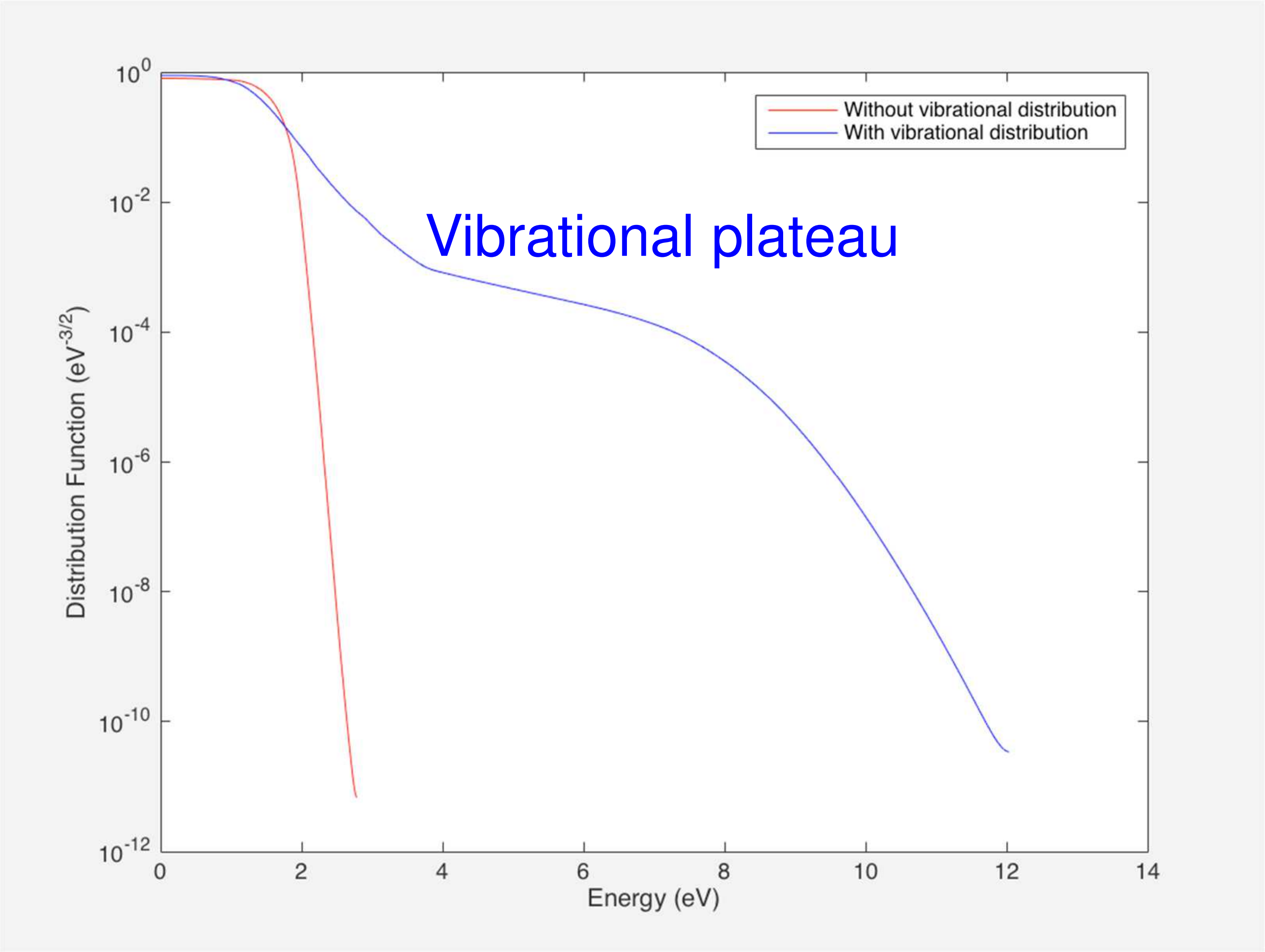
Nitrogen @ E/N = 10 Td and T_g = 300K



$$\xi_v = \begin{cases} \exp\left\{-v\left[\frac{E_1-E_0}{k_B T_{\text{vib}}} - (v-1)\frac{\Delta E}{k_B T_g}\right]\right\} & v \le v^\star \\ \xi_{v^\star}\frac{v^\star}{v} & v \ge v^\star \end{cases}$$

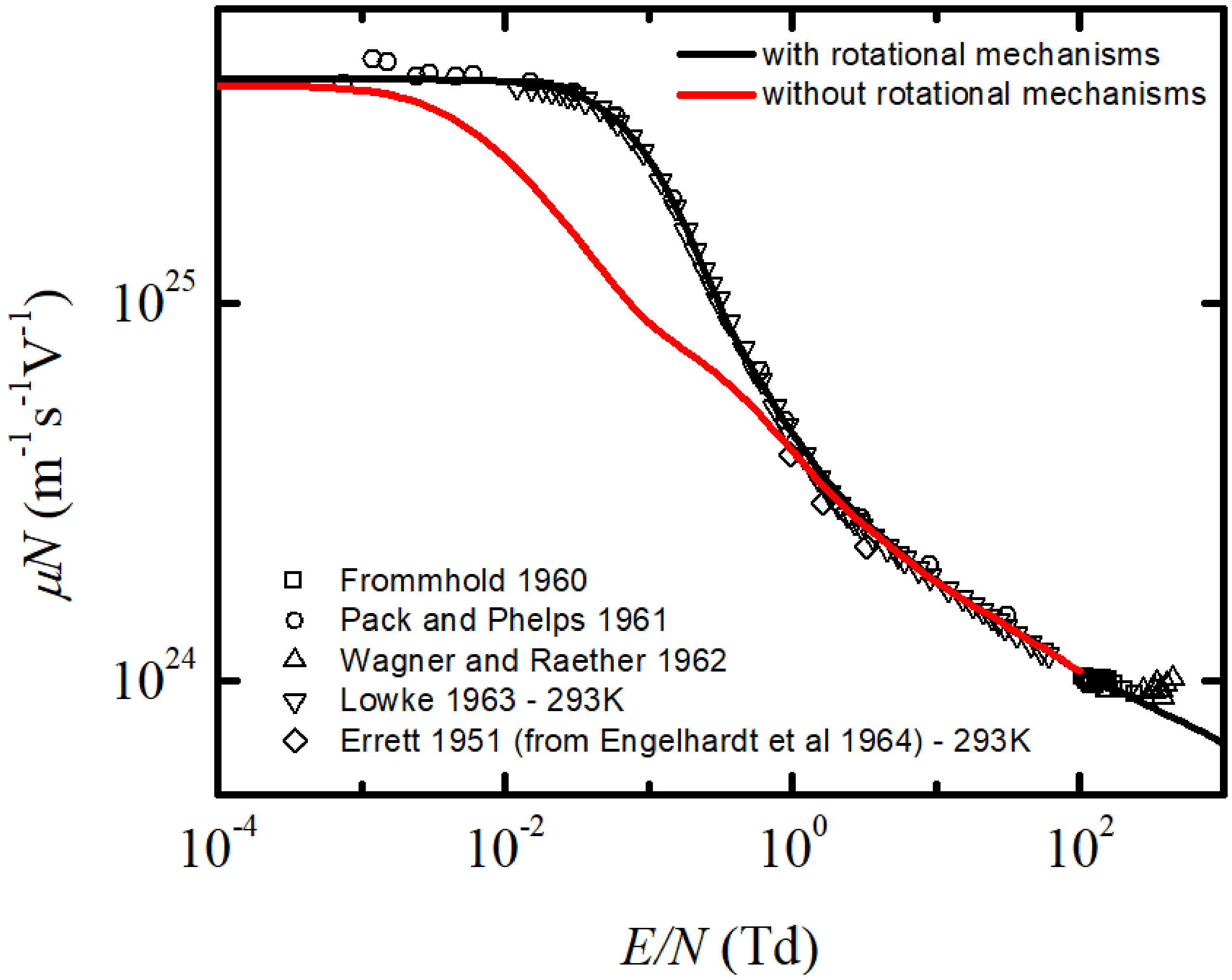
Results – influence of e-vibrational mechanisms

Nitrogen @ *E/N* = 10 Td and T_g = 300K



Results – influence of e-rotational mechanisms

Nitrogen – swarm analysis



MA Ridenti et al, Plasma Sources Sci. Technol. 24 035002 (2016)

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

Antonio Tejero-del-Caz

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