Electron kinetics in pulsed plasmas

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Seminar Modern Problems of Plasma Physics
3 July 2020 (remote talk), EP5 - RUB

Electron kinetics in pulsed plasmas

Motivation

Increasing interest in non-equilibrium LTPs created by pulsed discharges, for different technological applications

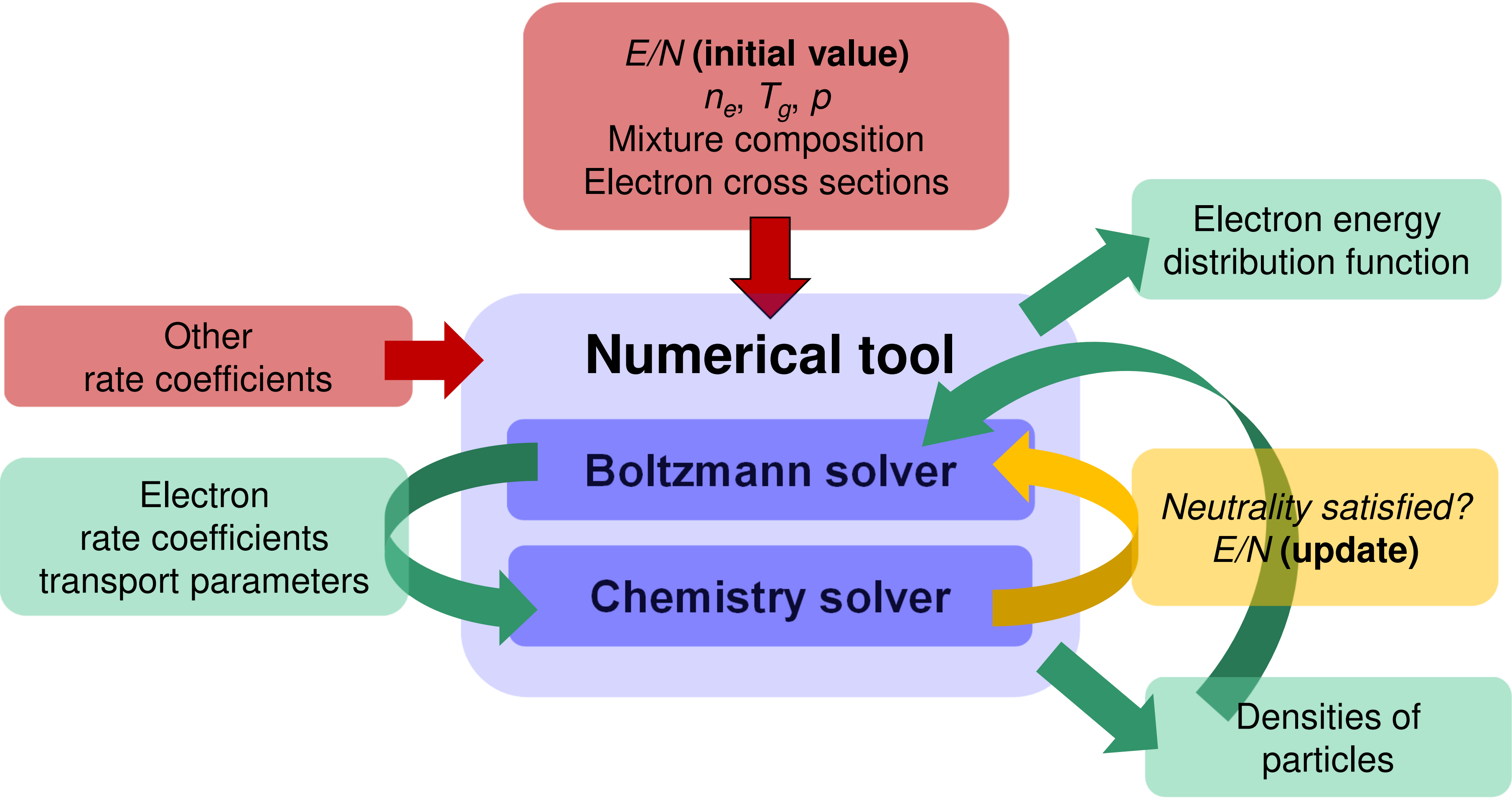
- nanosecond pulsed discharges for plasma-assisted ignition and combustion [Starikovskaia (2006), Samukawa et al (2012), Popov (2016)]
- plasma chemical-conversion, involving dry reforming, plasma pyrolysis and management of CO_2 [Adamovich et al (2017)]

The voltage applied to gases at intermediate-to-high pressures, during the nanosecond to microsecond time-scale typical of breakdown, greatly affects the plasma parameters and composition

- **N_2** [Colonna et al (2015)]
- **Air** [Tholin and Bourdon (2013); Rusterholtz et al; Xu et al (2014); Simek and Bonaventura (2018); Janda et al (2018)]
- **N_2-O_2** [Lepikhin et al (2018)]; **N_2-H_2** [Colonna et al (2020)]
- **H_2-air** [Kobayashi et al (2017)], **C_2H_4-air** [Burnette et al (2016)], **HC-air** [Aleksandrov et al (2014)]
- **CO_2** [Mei et al (2015); Moss et al (2017)]; **CH_4** [Zhang (2018)]; **CH_4-CO_2** [Scapinello et al (2016)]

Electron kinetics in pulsed plasmas

Modelling: possible workflow for global models



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

Other
rate coefficients

Electron
rate coefficients
transport parameters

Numerical tool

Boltzmann solver

Chemistry solver

Electron energy
distribution function

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

Densities of
particles

Electron kinetics in pulsed plasmas

Modelling: self-consistency (also in time)

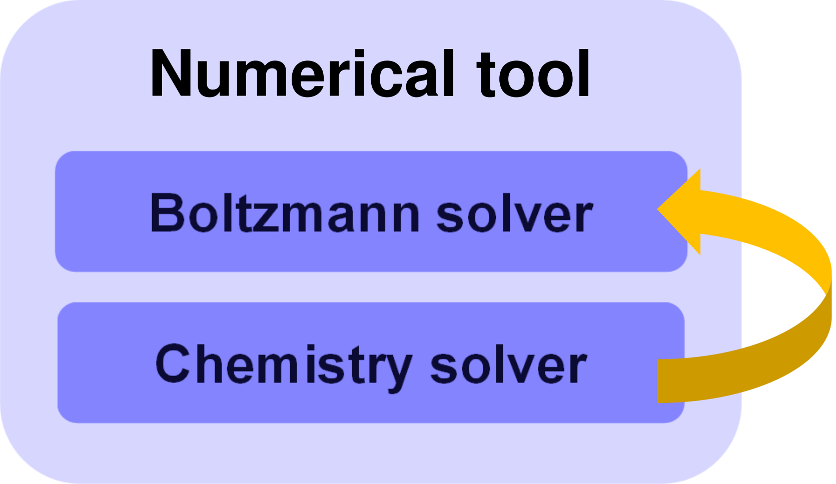
Efforts to analyze the electron kinetics as a function of time

- **homogeneous plasmas excited by time-varying sinusoidal electric-fields** [Fourier-development of 2-term electron Boltzmann equation (EBE)]
    - influence of e-V in N_2 and H_2 [Loureiro (1993)]
    - time-evolution of Ar excited states in HF plasmas [Sá et al (1994)]
- **discharges and afterglows** [solving the time-dependent EBE]
    - time-evolution of the EEDF in N_2 post-discharge [Guerra et al (2001)]
    - + coupling with heavy-particles balance equations (including VDF) in N_2, N_2-H_2 and CO_2, discharges and post-discharges [Guerra et al (2003); Colonna et al (2015, 2020); Pietanza (2020)]
- **electron diffusion in time-dependent *ExB* fields** [Monte Carlo simulations] [Raspopovic et al (2000); White et al (2008)]
- **time or the space-time analyses of electron relaxation** [2-term / multi-term EBE and Monte Carlo simulations]
    - in argon plasmas [Loffhagen et al (2002); Trunec et al (2006)]
    - argon-fluorine decaying plasmas [Dyatko et al (2005)]
    - nanosecond breakdown in atmospheric air [Hoder et al (2016)]

Seminal works of Capitelli and co-workers [Gorse et al (1985,1987,1988)]

Electron kinetics in pulsed plasmas

BUT…



Numerical tool

Boltzmann solver

Chemistry solver

time description coupling
assuming approximations

- using effective source terms for the electron-impact creation of excited species
  [Carbone et al (2016)]
- considering a quasi-stationary description for electrons by solving a time-independent form of the EBE for chosen values of *E/N*
  [Simek and Bonaventura (2018), Wang et al (2018), Heijkers et al (2019)]

Limitations in publicly available tools for solving the EBE ?

- ELENDIF, BOLOS, METHES, Magboltz (DC electric fields)
- BOLSIG+, EEDF, LoKI (DC and HF electric fields)
- MultiBoltz (multi-harmonic model for intense microwave and THz fields)

Outline

Analysis of the electron kinetics under *E(t)* pulses

- **Formulation(s) adopted in solving the EBE**

  time-dependent formulation

  quasi-stationary approach

- **Results in dry air (80%N_2 : 20%O_2)**

  step-fields ($\tau_{on} \rightarrow \infty$) with different $\tau_{rise} \sim 0 - 1\ \mu s$

  typical discharge pulses at limited τ_{on} and $\tau_{rise} \sim$ ns, μs

  [stationary neutral gaseous background: no coupling with chemistry model]

- **Final remarks**

The LisbOn KInetics Boltzmann solver (LoKI-B)

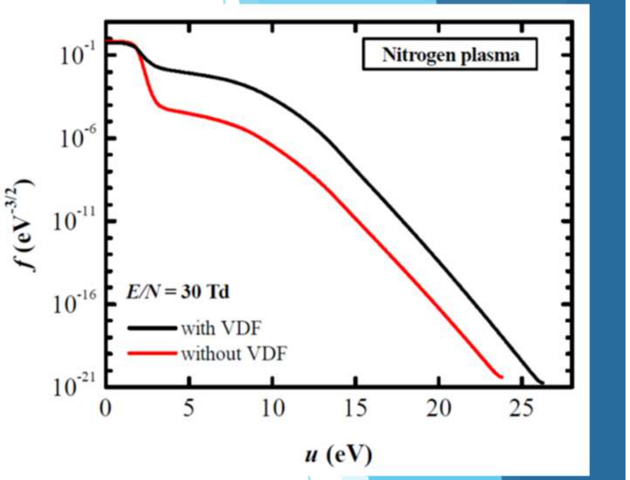
(developed under MATLAB®)

OPEN SOURCE

LoKI-B

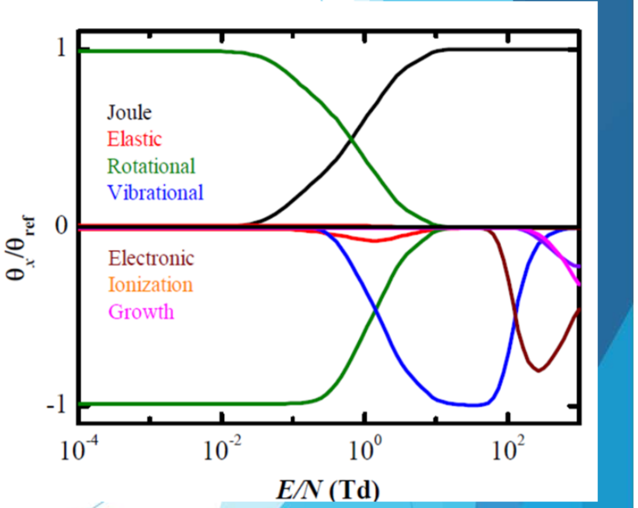
https://github.com/IST-Lisbon/LoKI

- solves the ~~time and space independent form of the~~ time-dependent 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

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Formulation(s) adopted

2-term approximation for the EBE

- homogeneous (space-independent) description
- variation of the electron density due to non-conservative binary events (ionization and attachment)
- steady-state form for the anisotropic equation

$$\mathcal{F}(\vec{v},t) \simeq n_e(t)\left\{F^0(v,t) + \vec{F}^1(v,t)\cdot\frac{\vec{v}}{v}\right\}$$

$$F^0(v,t)4\pi v^2 dv = f(u,t)\sqrt{u}du \; ; \; \int_0^\infty f(u,t)\sqrt{u}du = 1$$

… the EEDF

$$F^1(v,t)4\pi v^2 dv = f^1(u,t)\sqrt{u}du$$

$$\frac{\partial n_e(t)}{\partial t} = \langle\nu_{\text{eff}}\rangle(t)\, n_e(t)$$

$$\langle\nu_{\text{eff}}\rangle(t) \equiv \langle\nu_{\text{ion}}\rangle(t) - \langle\nu_{\text{att}}\rangle(t)$$

$$\langle\nu_x\rangle(t) = \sqrt{\frac{2e}{m_e}}\sum_i N_i \int_0^\infty u\sigma_{i,x}(u) f(u,t)du$$

Formulation(s) adopted

Time-dependent electron Boltzmann equation

$$\frac{1}{N}\sqrt{\frac{m_e}{2e}}\sqrt{u}\frac{\partial f(u,t)}{\partial t}+\sqrt{\frac{m_e}{2eu}}\frac{\langle\nu_{\text{eff}}\rangle(t)}{N}uf(u,t)+\frac{1}{N}\sqrt{\frac{m_e}{2e}}\frac{\partial G(u,t)}{\partial u}=S(u,t)$$

$$f^1(u,t)=-\frac{(E(t)/N)}{\Omega_c(u,t)}\frac{\partial f(u,t)}{\partial u}$$

… steady-state form

The characteristic evolution time of the EEDF is much larger than the characteristic evolution time of the anisotropic component

$$\tau\simeq\frac{1}{\sum_k \frac{m_e}{M_k}\nu_{k,c}^{\text{el}}}\gg\frac{1}{\sum_k \nu_{k,c}^{\text{el}}}$$

$G(u,t)$ … *upflux* function (e.g., ohmic heating, elastic, rotational, Coulomb **continuous** operators)

$S(u,t)$ … inelastic / superelastic collision **discrete** operator

$$\Omega_c(u,t)\equiv\sigma_c(u)+\sqrt{m_e/(2eu)}(\langle\nu_{\text{eff}}\rangle(t)/N)$$

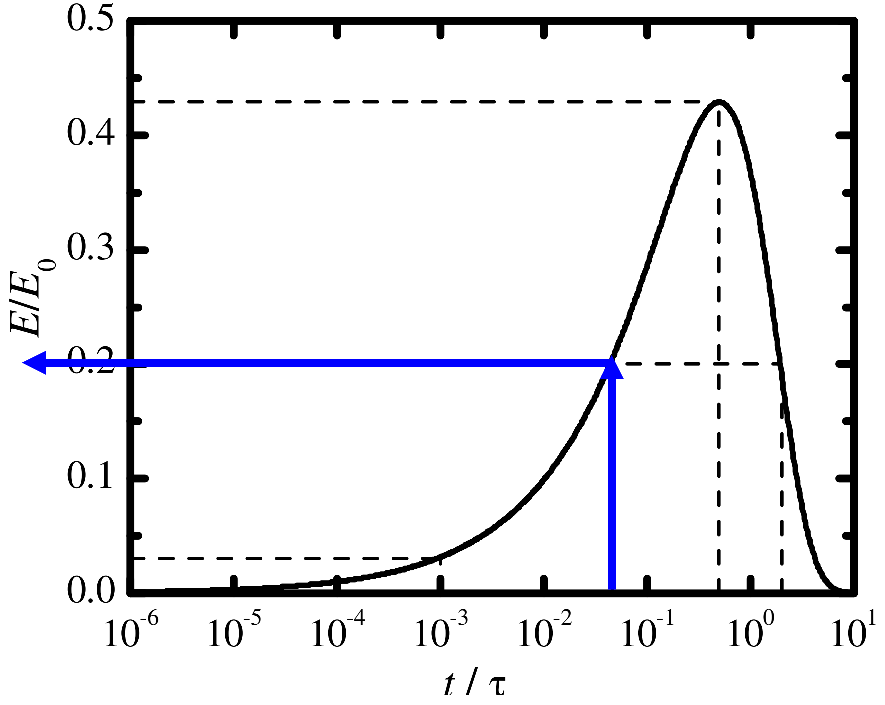
Formulation(s) adopted

Quasi-stationary electron Boltzmann equation

$$\cancel{\frac{1}{N}\sqrt{\frac{m_e}{2e}}\sqrt{u}\frac{\partial f(u,t)}{\partial t}} + \sqrt{\frac{m_e}{2eu}}\frac{\langle\nu_{\text{eff}}\rangle(\cancel{t})}{N}uf(u,\cancel{t}) + \frac{1}{N}\sqrt{\frac{m_e}{2e}}\frac{\partial G(u,\cancel{t})}{\partial u} = S(u,\cancel{t})$$

$$f^1(u,\cancel{t}) = -\frac{(E(\cancel{t})/N)}{\Omega_c(u,\cancel{t})}\frac{\partial f(u,\cancel{t})}{\partial u}$$

solution of the quasi-stationary EBE …



Results in dry air

Working conditions

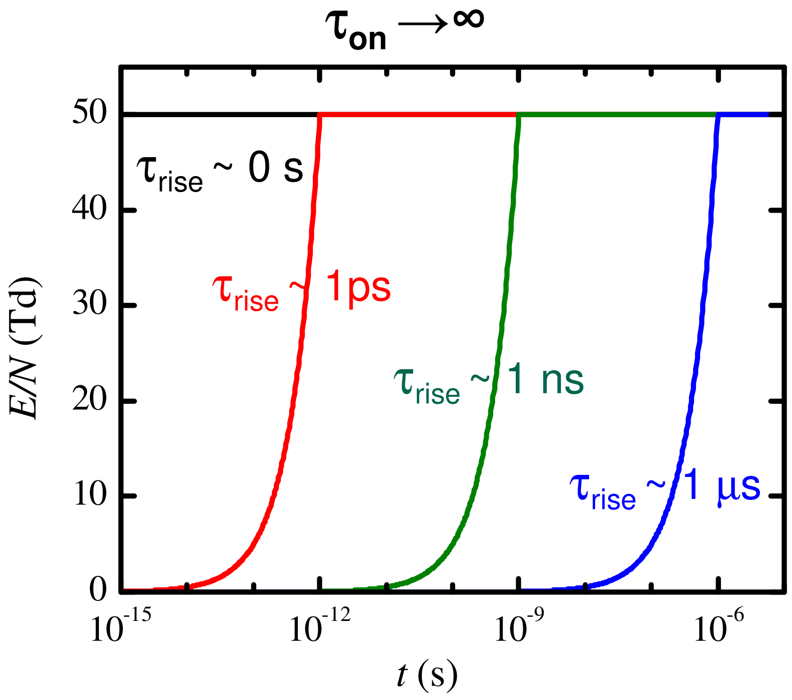
Dry air (80%N_2 : 20%O_2) @ $p = 10^5$ Pa and 133 Pa ; $T_g = 300$ K

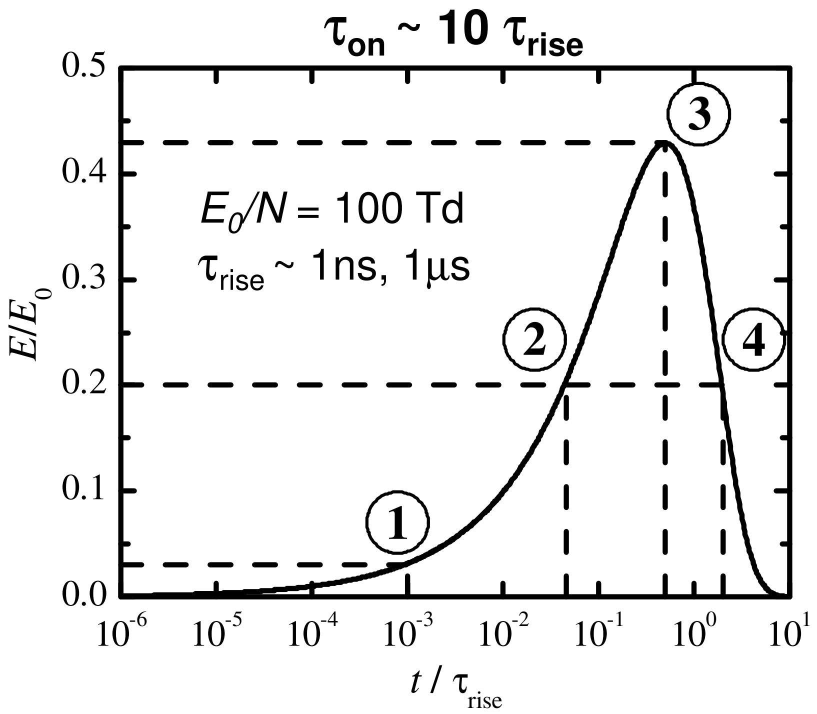
Initial condition : Maxwellian EEDF at 300 K

Assuming

- Boltzmann distributions at 300 K for the VDFs of $N_2(X,v=0-10)$ and $O_2(X,v=0-4)$
- the continuous approximation to describe rotational excitations / deexcitations

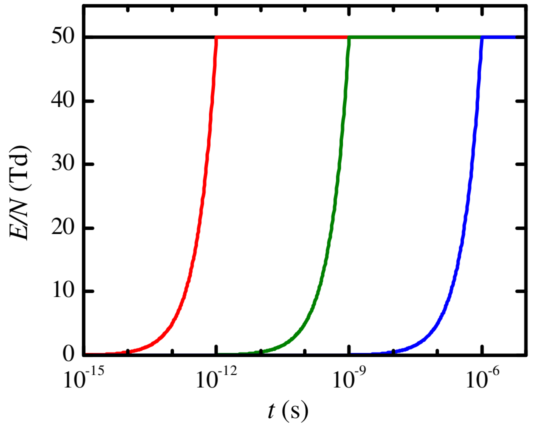
Electron-scattering cross sections published at the IST-Lisbon database with LXCat



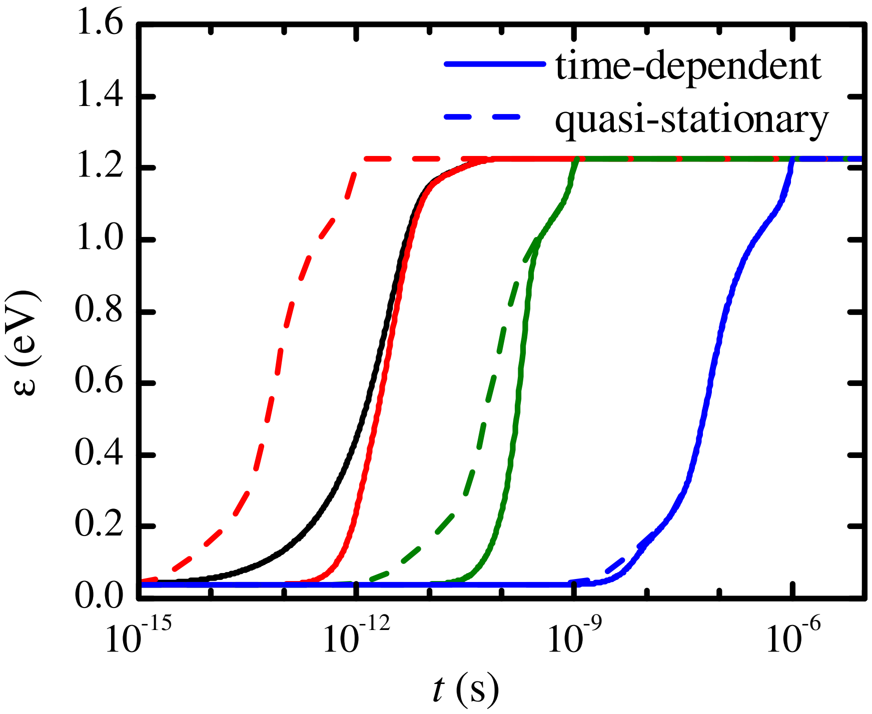


Results in dry air – step fields

The electron mean energy



$p = 10^5$ Pa



The natural response time of the electrons at atmospheric pressure is of the order of ~10ps

The quasi-stationary approach holds for

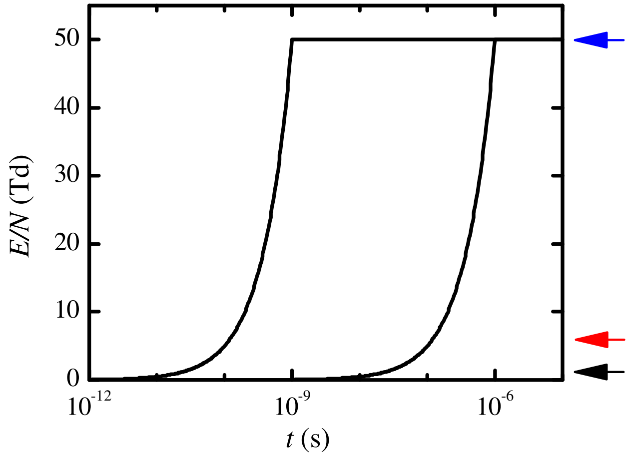
$$\tau_{\text{rise}} \gg \tau \simeq \frac{1}{\sum_k \frac{m_e}{M_k} \nu_{k,c}^{\text{el}}} \simeq \frac{2 \times 10^{18}}{N(\text{m}^{-3})}$$

At 1atm and room temperature

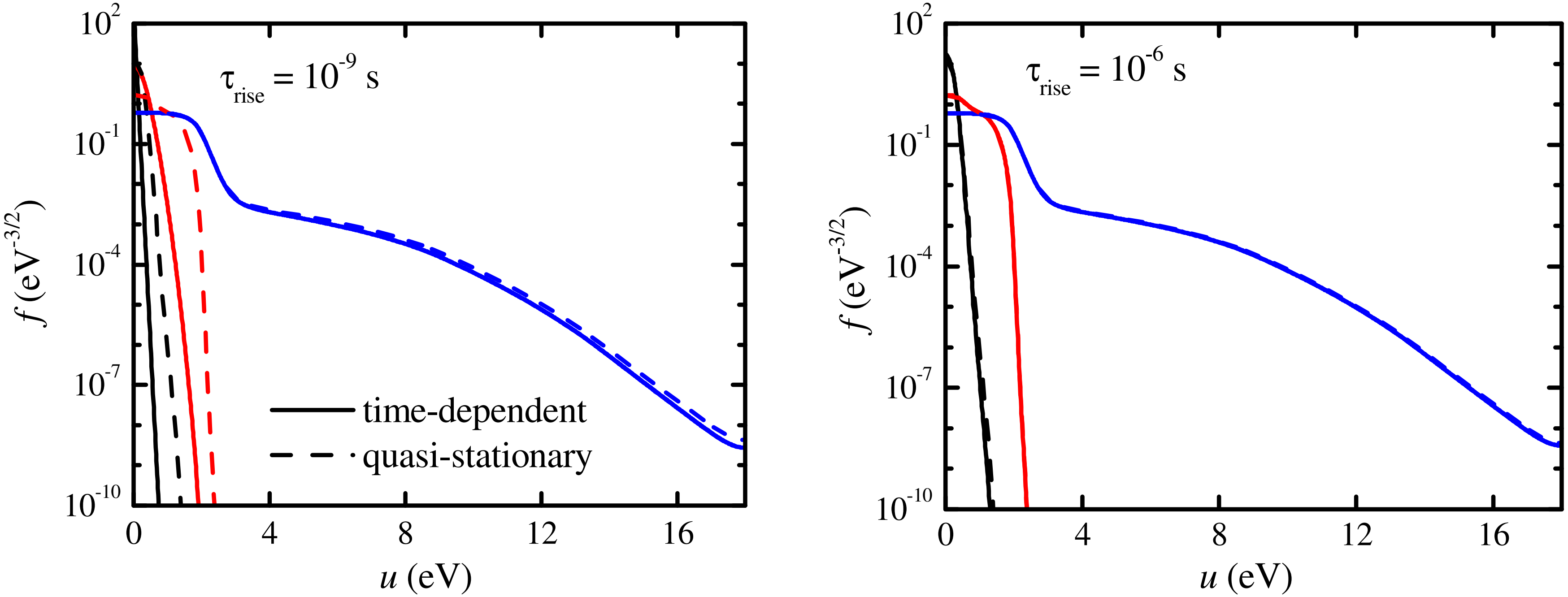
$$\tau_{\text{rise}} \gg 8 \times 10^{-8} \text{s}$$

Results in dry air – step fields

The electron energy distribution function

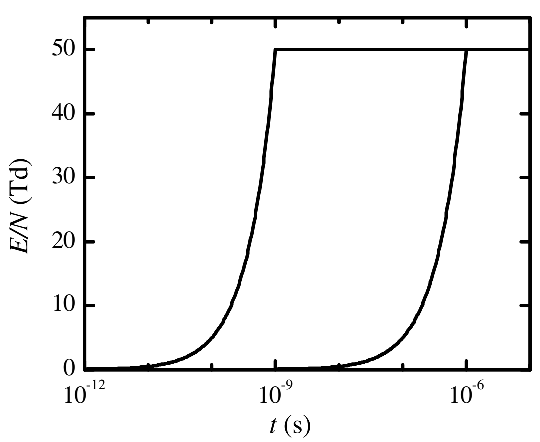


$p = 10^5$ Pa

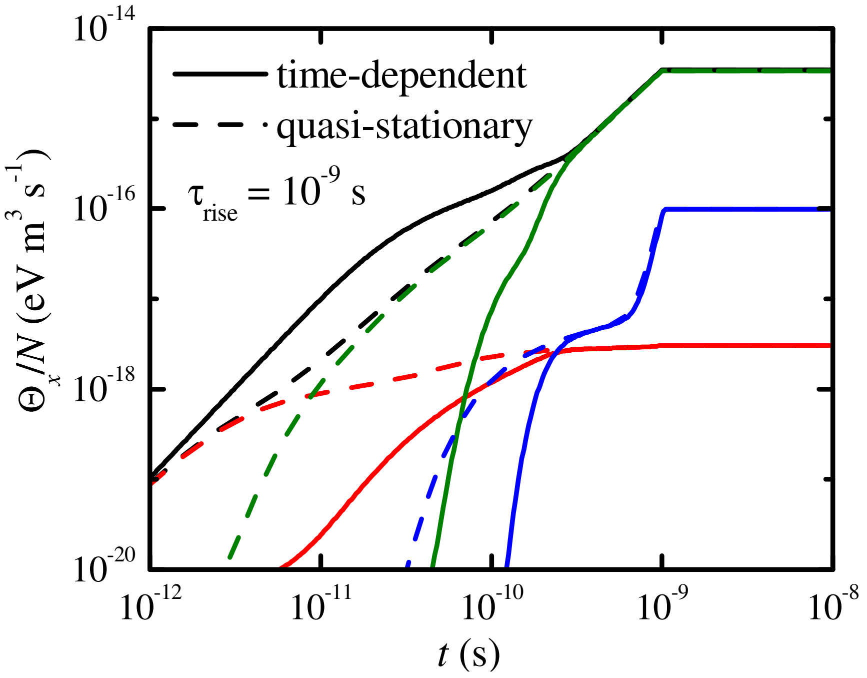


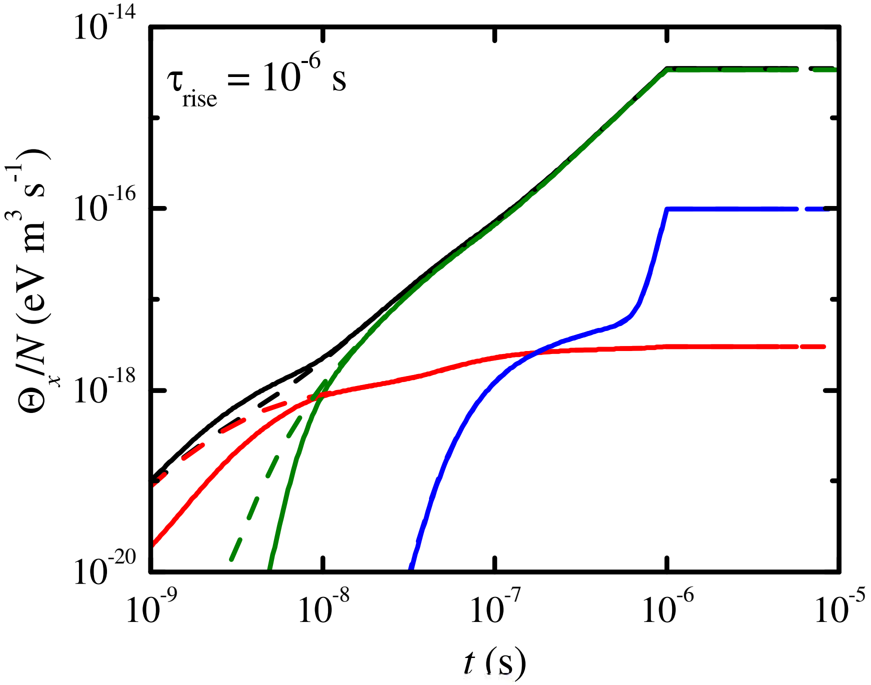
Results in dry air – step fields

The power balance per electron (at unit gas density)



$p = 10^5$ Pa

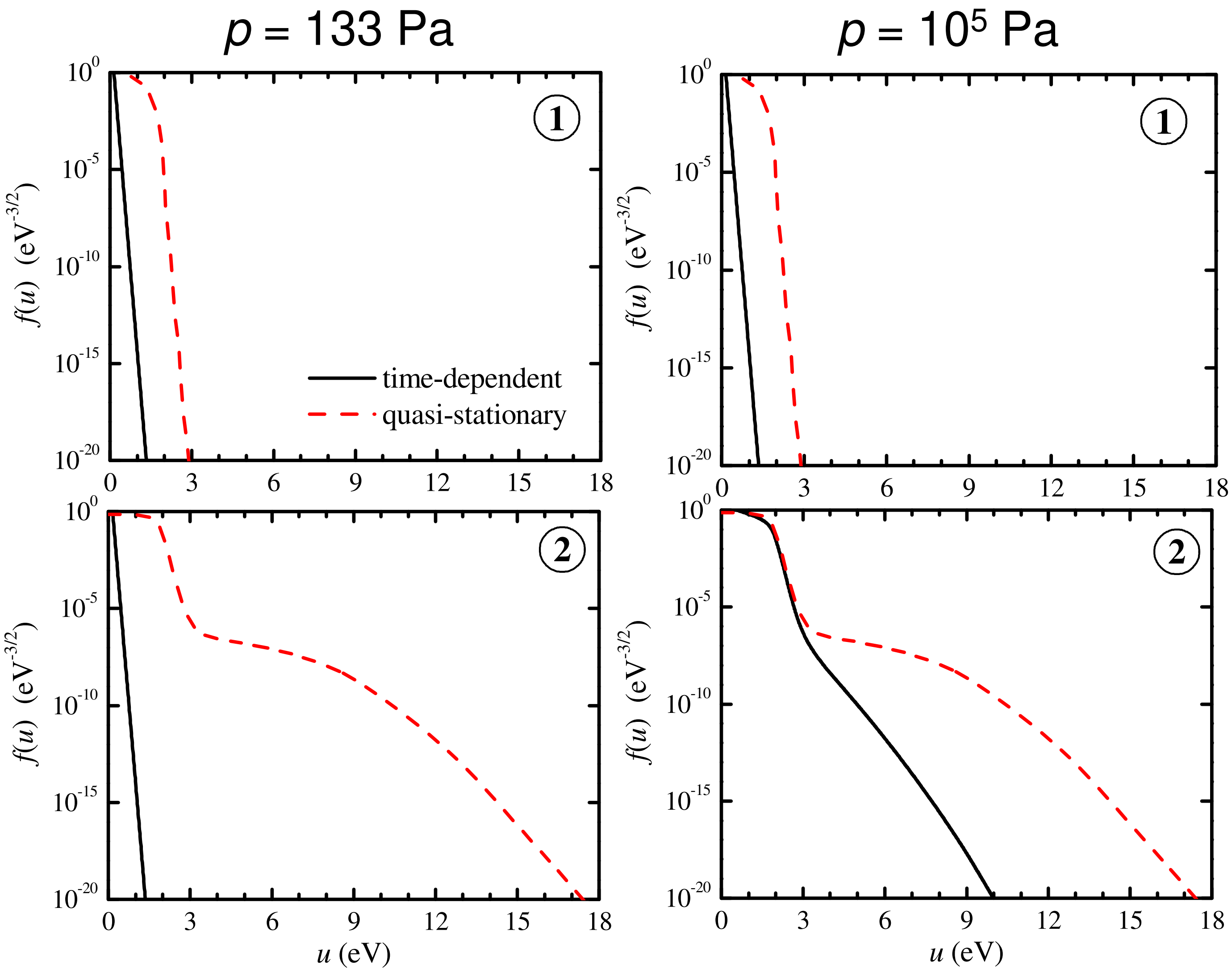


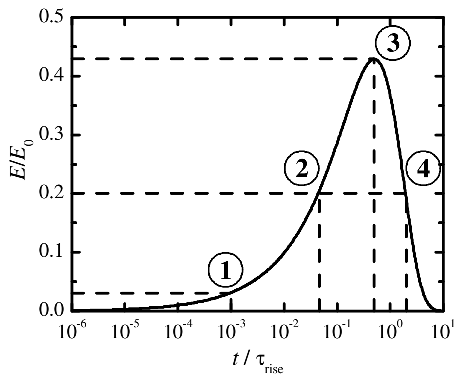


$$\frac{d\varepsilon(t)}{dt} = \Theta_{\mathrm{growth}} + \Theta_E - \Theta_{\mathrm{rot}} - \Theta_{\mathrm{vib}} - \Theta_{\mathrm{ele}}$$

Results in dry air – field pulse

The electron energy distribution function - I



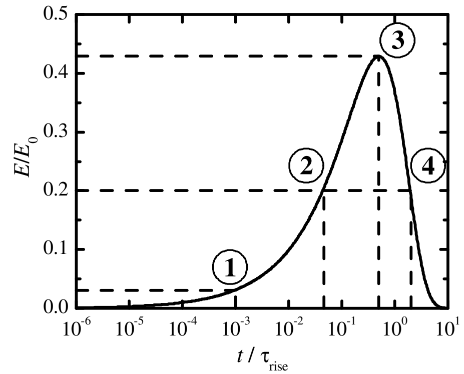


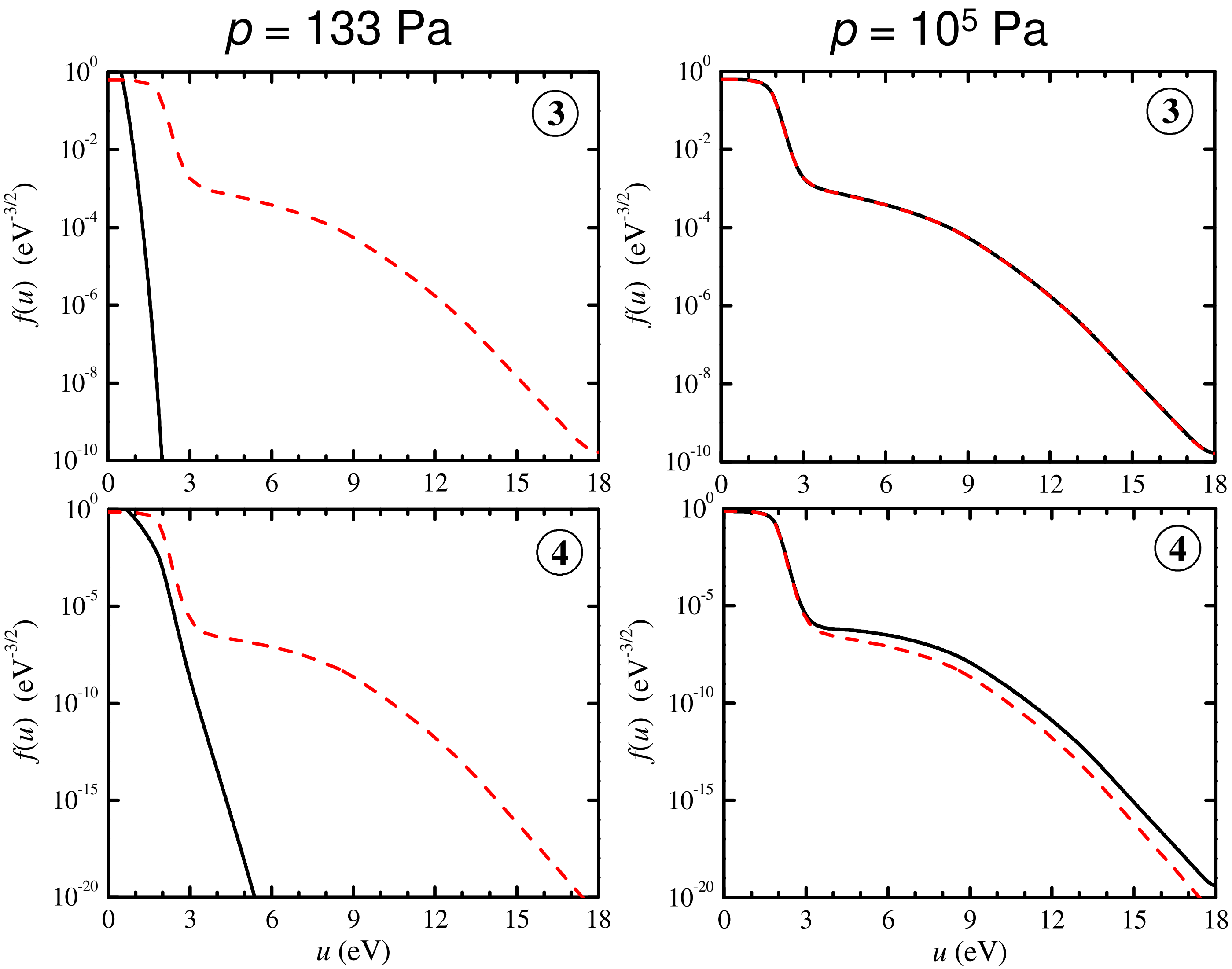
E_0/N = 100 Td

τ_{rise} ~ 10^{-9} s

Results in dry air – field pulse

The electron energy distribution function - II



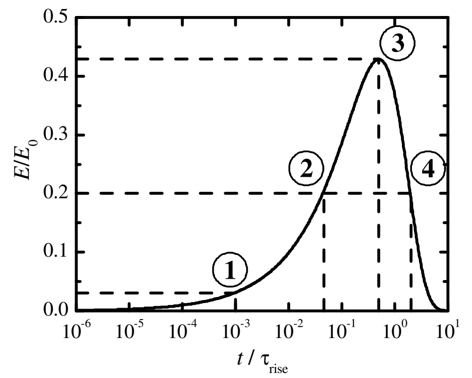


E_0/N = 100 Td

τ_{rise} ~ 10^{-9} s

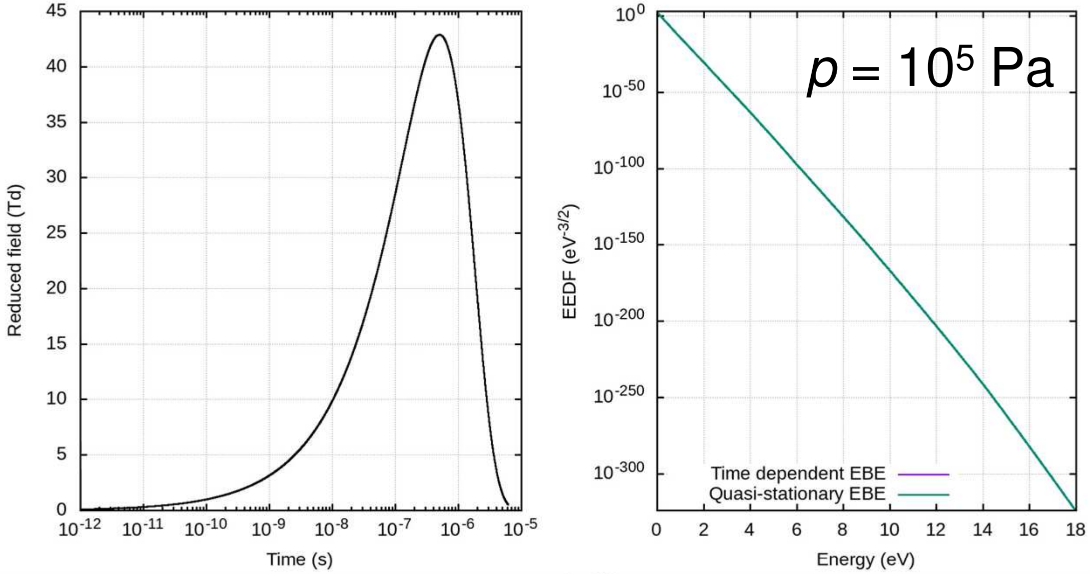
Results in dry air – field pulse

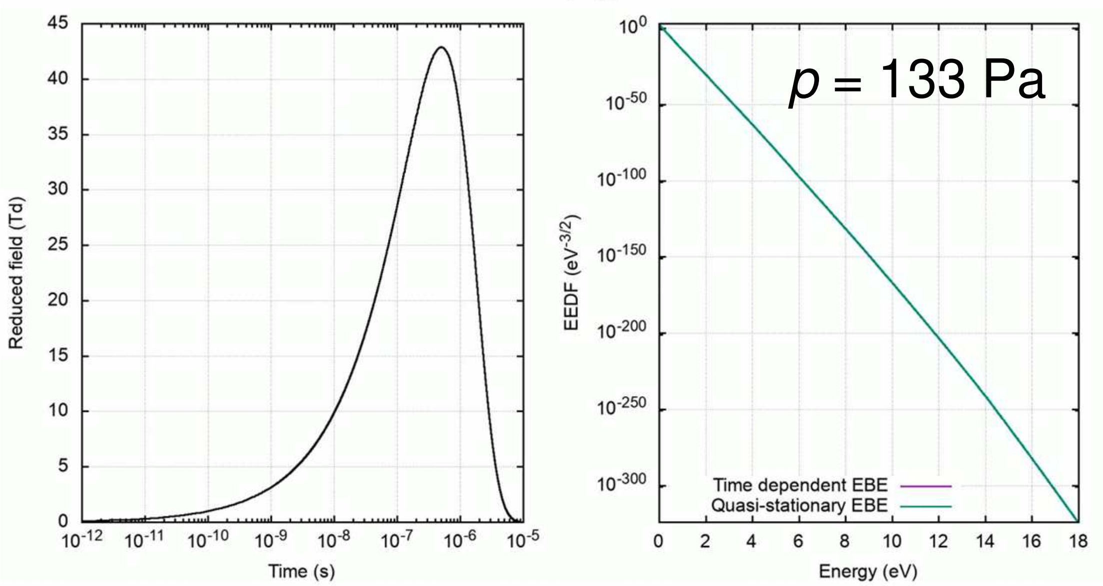
The electron energy distribution function - III



E_0/N = 100 Td

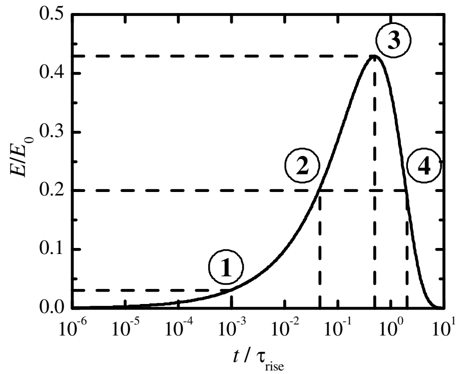
τ_{rise} ~ 10^{-6} s





Results in dry air – field pulse

Criterion for quasi-stationary simulations



The quasi-stationary approach holds for

$$\tau_{\mathrm{rise}} \gg \tau \simeq \frac{1}{\sum_k \frac{m_e}{M_k}\nu_{k,c}^{\mathrm{el}}} \simeq \frac{2\times 10^{18}}{N(\mathrm{m}^{-3})}$$

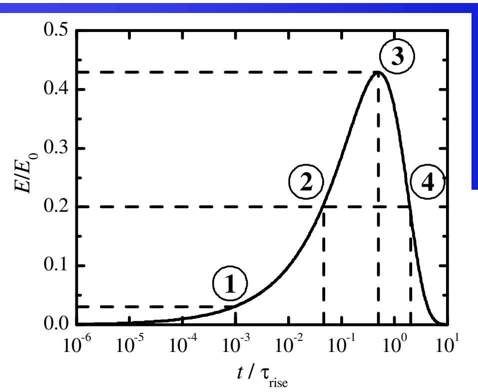
		p = 10^5 Pa and τ = 8×10^{-8} s	p = 133 Pa and τ = 6×10^{-5} s
τ_{rise}	10^{-9} s	Fail	Fail
τ_{fall}	10^{-8} s	Fail	Fail
τ_{rise}	10^{-6} s	OK	Fail
τ_{fall}	10^{-5} s	OK	Fail

At low pressure, there is no instantaneous collisional transfer of the E-field energy into the gas, hence the slow temporal increase of the electron mean (kinetic) energy

Results in dry air – field pulse

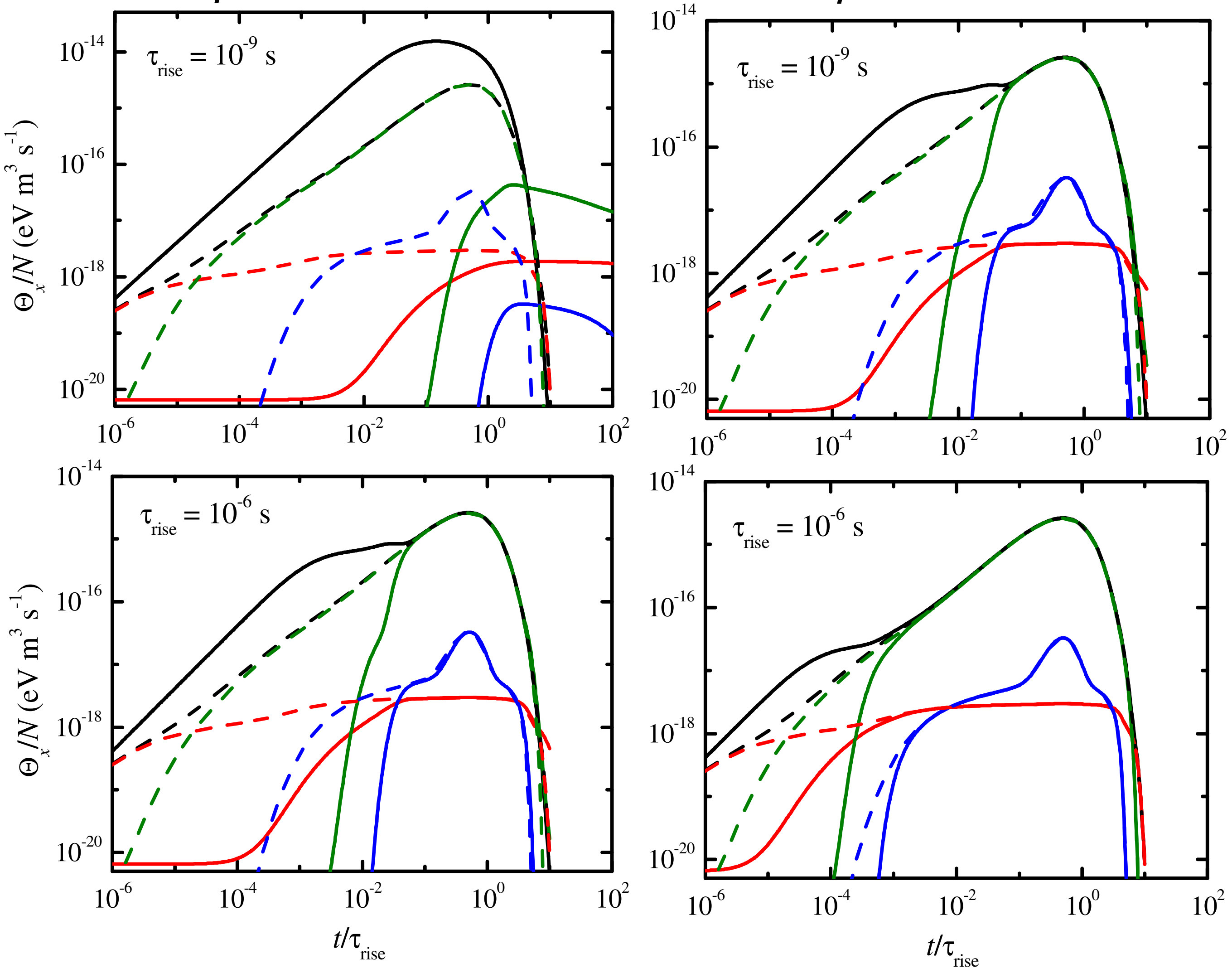
The power balance per electron (at unit gas density)

$$\frac{d\varepsilon(t)}{dt} = \Theta_{\mathrm{growth}} + \Theta_E - \Theta_{\mathrm{rot}} - \Theta_{\mathrm{vib}} - \Theta_{\mathrm{ele}}$$



p = 133 Pa

$p = 10^5$ Pa

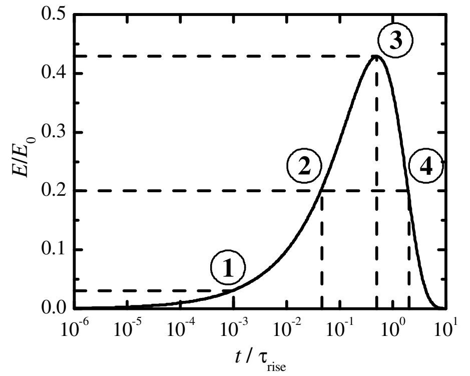


E_0/N = 100 Td

- time-dependent
- quasi-stationary

Results in dry air – field pulse

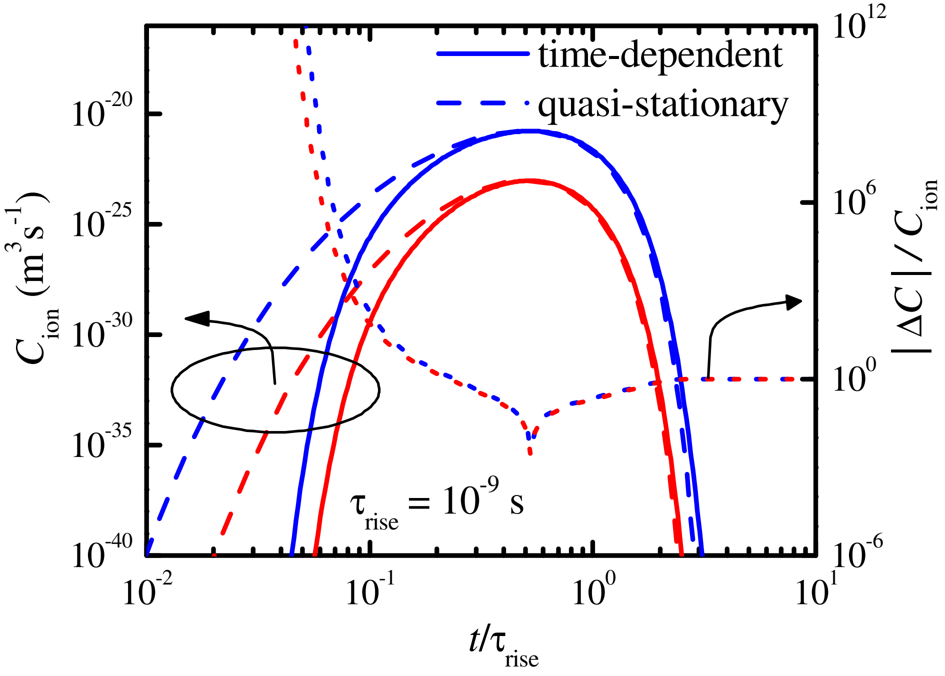
Ionization rate coefficients

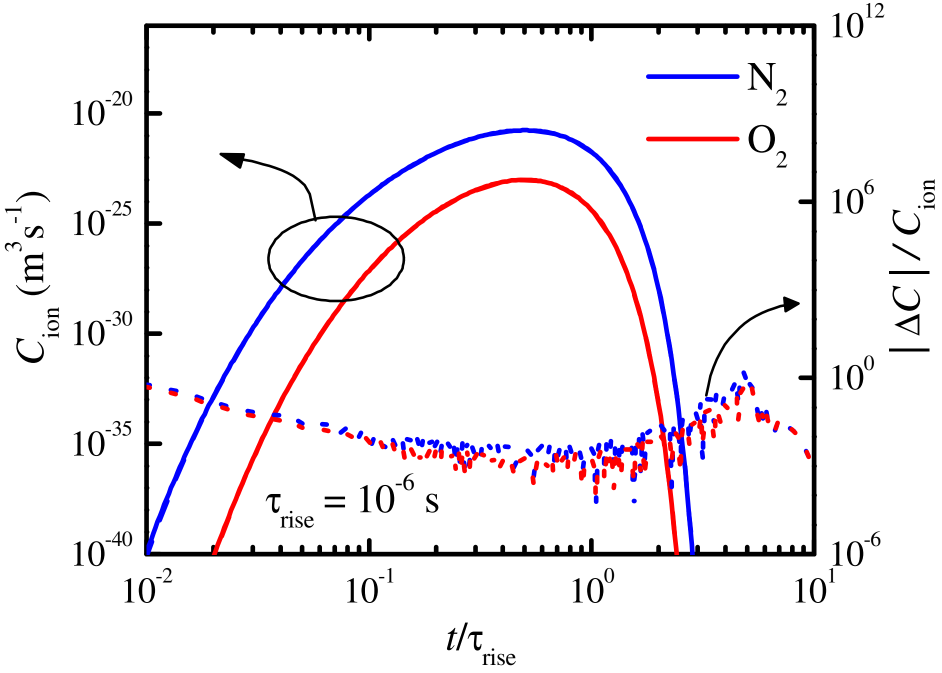


p = 10^5 Pa

τ ~ 8×10^{-8} s

E_0/N = 100 Td





Similar observations for other (excitation) rate coefficients

Final remarks

- **Analysis of the time evolution of the electron kinetics in dry-air plasmas**
  - excited by electric-field pulses (τ_{rise} ~ ns to μs; p = 133 Pa, 10^5 Pa)
  - applied to a stationary neutral gaseous background
  - adopting (i) time-dependent formulation; (ii) quasi-stationary approach

- **Two major approximations**
  - steady-state form for f^1 ($\tau_1 \sim 4\times10^{-13}$ s << τ @ atm. pressure)
    [potential uncertainties in the ps range]
  - space-independent form of the EBE
    [no description of local space-time transient phenomena]

- **Quasi-stationary description**
  - holds for high-collisionality and long rise-times
    [e.g. microsecond pulses at atmospheric pressure]
  - fails for fast risetimes
    [e.g. nanosecond pulses, irrespectively of the pressure]

Final remarks

- **Role of collisionality in evolution times**

  similar results obtained for

  long pulses / low pressures and short pulses / high pressures

  → optimization of the pulse duration, depending on the gas pressure,
  to maximize electron energy absorption

- **Inclusion of the effects of heavy-particle interactions (e.g., VVs & VTs)**
  - can alter modelling predictions (especially beyond the μs scale and/or in multi-pulse scenarios)
  - caused by deviations in electron rate coefficients at low pressures and/or short rise-times
  - correct approach: fully-coupled time-dependent Boltzmann-Chemistry calcs.

    → future work

Acknowledgements

People

Funding institution

FCT

Fundação para a Ciência e a Tecnologia

MINISTÉRIO DA CIÊNCIA, TECNOLOGIA E ENSINO SUPERIOR