How relevant is charge-particle transport in global models?

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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")

Transport in global models

The (average) rate balance equation for particle s

$$\frac{\partial n_s}{\partial t} \simeq S_s - \nu_{\mathrm{transp}_s} n_s$$

Average loss-frequency due to transport

?

$$\frac{1}{V}\int_{\vec{r}} \vec{\nabla} \cdot \vec{\Gamma}_s \, d^3r$$

Focus on charged-particle transport: how relevant in global models ?

Formulating charged-particle transport

Defining charged-particle fluxes: challenges

- various working conditions
  - single-/multi- ion scenarios
  - electropositive (EP) / electronegative (EN) plasmas
  - low-pressure (LP) / high-pressure (HP)

- spatial-averaged (algebraic) description
  - simplifications
  - resort to spatially-resolved simulations
    - to define abacuses for ν_{transp_s}

Outline

- **Transport models in global models**

  Ambipolar-based models

  h-factor models

- **Simulations and results**

  DC oxygen plasma

    at low-to-intermediate pressures

  MW helium plasma

    at low-to-intermediate + atmospheric pressure

- **Final remarks**

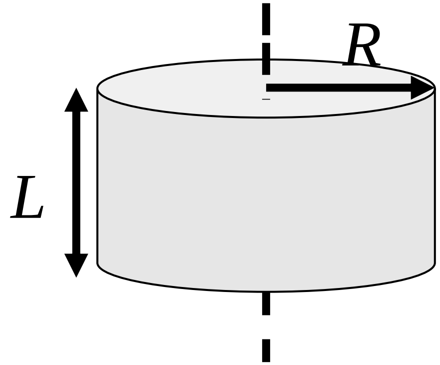
Alves and Tejero-del-Caz, PSST (accepted, 2023)

Transport models in global models

Ambipolar-based transport models

The (ambipolar) flux for ion species *i*

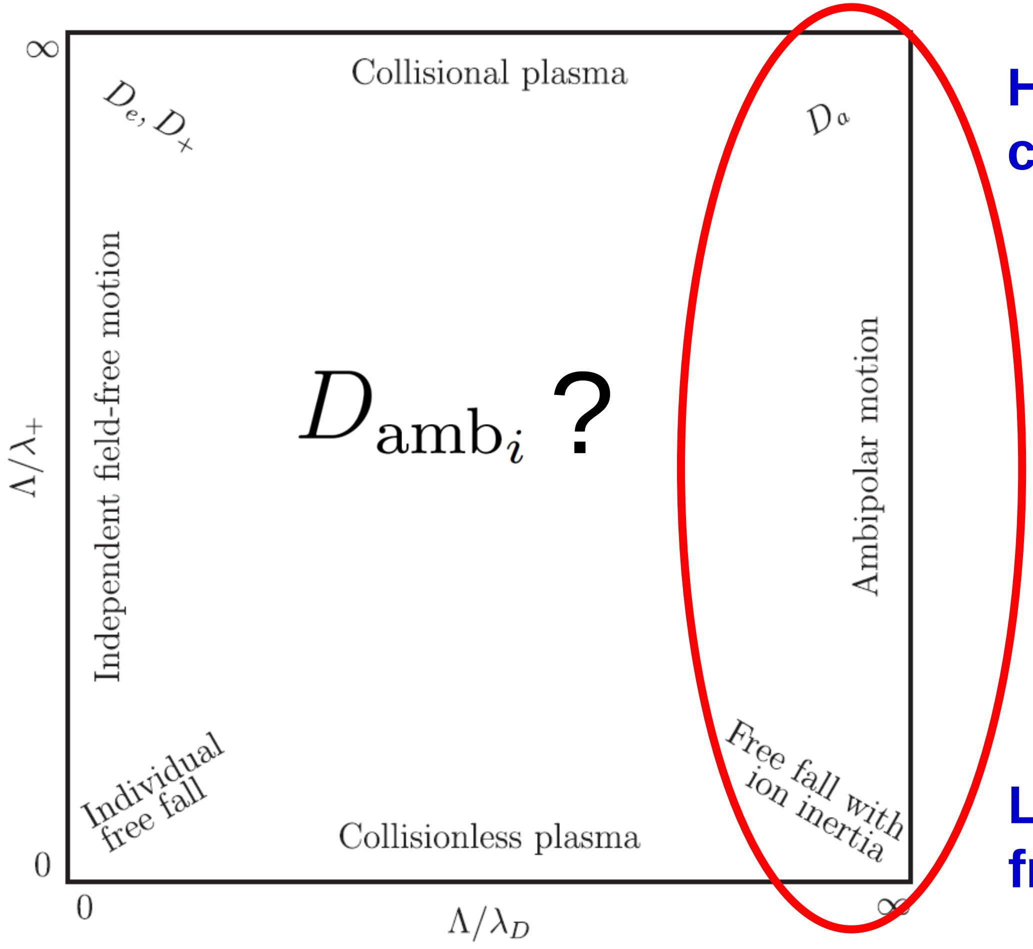
$$\vec{\Gamma}_i = -D_{\mathrm{amb}_i} \vec{\nabla} n_i$$



$$\begin{cases} \nu^{\mathrm{amb}}_{\mathrm{transp}_i} = \dfrac{\boxed{D_{\mathrm{amb}_i}}}{\Lambda^2} \\ \Lambda^2 = \left[\left(\dfrac{\pi}{L}\right)^2 + \left(\dfrac{2.405}{R}\right)^2\right]^{-1} \end{cases}$$

Effective ambipolar diffusion model

unified theory for dense plasmas



Coche *et al.*, JPD (2016)
Phelps, *J. Res. NIST* (1990)

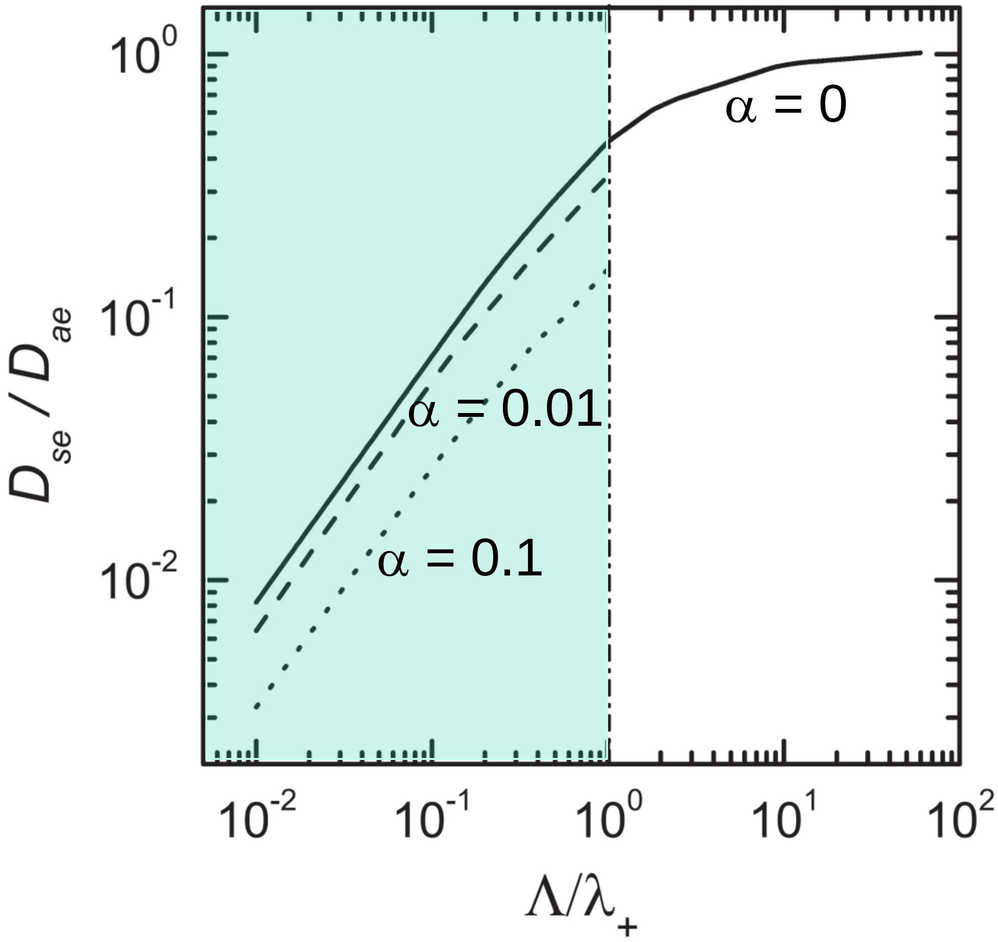
High-pressure:
classical ambipolar diffusion

Dense plasmas

$$\frac{\Lambda}{\lambda_D} \gg 1$$

Low-pressure:
free-fall limit

The effective ambipolar diffusion coefficient



Coche *et al.*, JPD (2016)

Theory valid for

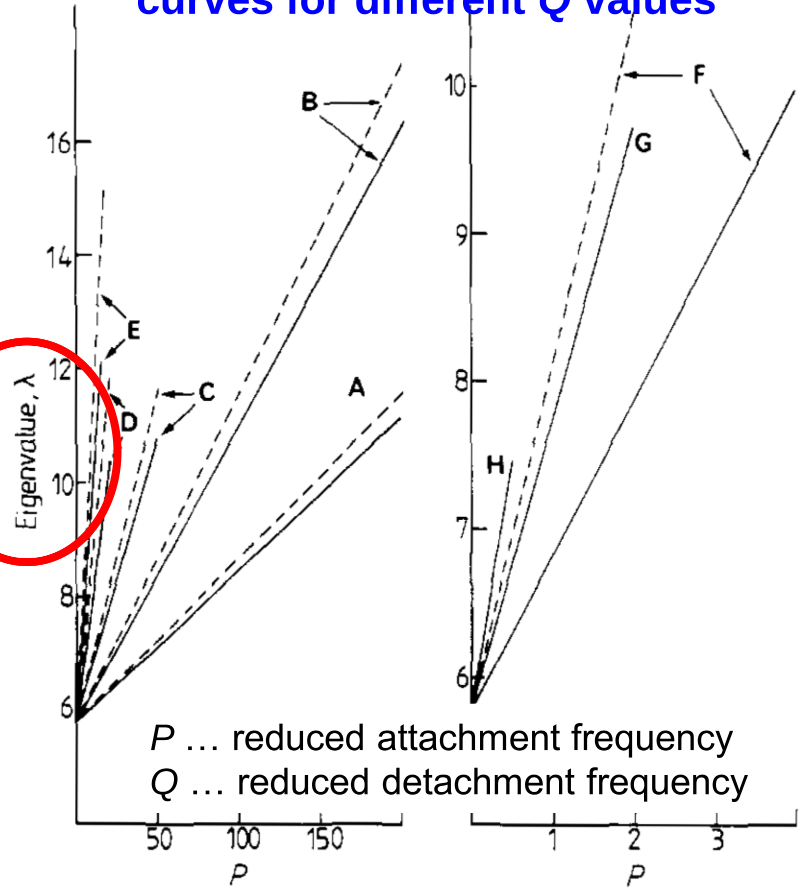
- Multiple positive ions
  with similar transport parameters
  with similar density profiles

$$\vec{\nabla} n_i / n_i \simeq \vec{\nabla} n_j / n_j$$

- In EP plasmas
  for all pressures

- In EN plasmas
  for low pressure
  for single negative ion
  with low density ($\alpha < 0.1$)

The eigenvalue diffusion length model



curves for different *Q* values

P … reduced attachment frequency
Q … reduced detachment frequency

Ferreira *et al.*, JPD (1988)
Guerra and Loureiro, PSST (1999)

Theory valid for

- Description of radial transport
- Multiple positive ions with similar creation/destruction rates
- Single negative ion
- Ion creation/destruction due to
  ionization / recombination
  attachment / detachment
  charge transfer

$$\nu_{\mathrm{transp}_i}^{\mathrm{eigen}} = \frac{D_{a_i}}{\Lambda_{\mathrm{eigen}}^2}$$

$$\Lambda_{\mathrm{eigen}} \equiv R\sqrt{\frac{1+\alpha}{\lambda_{\mathrm{eigen}}}}$$

The Quantemol Global Model (QGM)

Ion losses at the wall due to ambipolar transport and thermal losses

$$\nu_{\mathrm{transp}_i}^{\mathrm{QGM}} \simeq \frac{1}{\nu_{\mathrm{amb}_i}^{-1} + \nu_{\mathrm{th}_i}^{-1}}$$

$$= \frac{A}{V}\frac{\Gamma_{\mathrm{wall}_i}}{n_i} = \frac{A}{V}\frac{D_{a_+}\gamma_{r_i}}{\Lambda\gamma_{r_i} + \frac{4D_{a_+}}{v_{\mathrm{th}_i}}}$$

Tennyson *et al.*, PSST (2022)

$$\frac{1}{V}\int_{\vec{r}} \vec{\nabla}\cdot\vec{\Gamma}_i \, d^3r = \frac{A}{V}\Gamma_{\mathrm{wall}_i}$$

The Quantemol Global Model (QGM)

the ambipolar diffusion coefficient

$$D_{a+} \simeq D_+ \frac{1 + (T_e/T_+)(1 + 2\alpha)}{1 + \alpha(T_e/T_+)}$$

$$\begin{aligned} D_+ &\equiv \frac{\sum_i D_i n_i}{\sum_i n_i} \\ D_i &= \frac{\pi}{8} \lambda_i v_{\mathrm{th}_i} \\ \frac{1}{\lambda_i} &= \sum_j n_j \sigma_{ij} \end{aligned}$$

Hard-sphere model / LJ parameters
Rutherford scattering

Theory valid for

- Multiple positive and negative ions with similar density profiles

  $$\vec{\nabla} n_i / n_i \simeq \vec{\nabla} n_j / n_j$$

- Electron and negative ions in Boltzmann equilibrium with the space-charge potential

- Moderate eletronegativities and low ion mobilities

  $$\alpha < 1 \ ; \ \mu_{+,-}/\mu_e \ll 1$$

Tennyson *et al.*, PSST (2022)
Stoffels *et al.*, Contribs. Plasma Phys. (1995)
Rogoff JPD (1985)

h-factors transport models

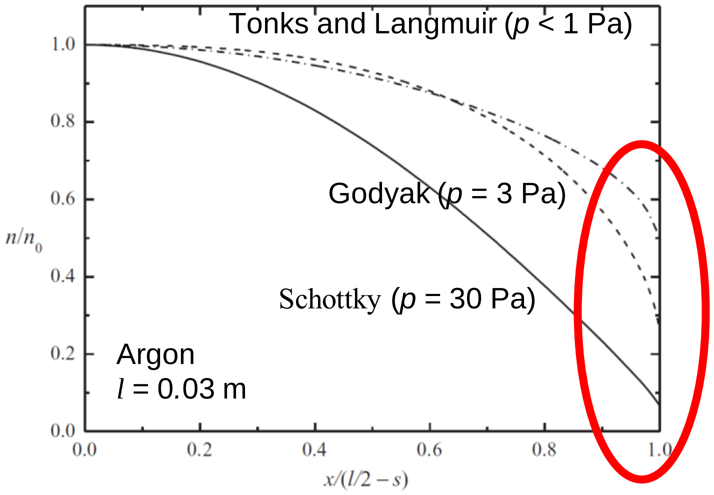
The flux for ion species *i* at the sheath edge

$$\Gamma_{i_{\mathrm{sh}}} = n_{i_{\mathrm{sh}}} u_{\mathrm{B}}$$

$$\begin{aligned} \nu^{\mathrm{h-fact}}_{\mathrm{transp}_i} &\simeq \frac{\Gamma_{i_{\mathrm{sh,axial}}} A_L + \Gamma_{i_{\mathrm{sh,radial}}} A_R}{n_{e_0} V} \\ &= 2u_{\mathrm{B}} \left(\frac{h_{L_i}}{L} + \frac{h_{R_i}}{R} \right) \end{aligned}$$

The h-factors

$$h_{L_i} \equiv \frac{n_{i_{\mathrm{sh}},\mathrm{axial}}}{n_{e0}} \; ; \; h_{R_i} \equiv \frac{n_{i_{\mathrm{sh}},\mathrm{radial}}}{n_{e0}}$$

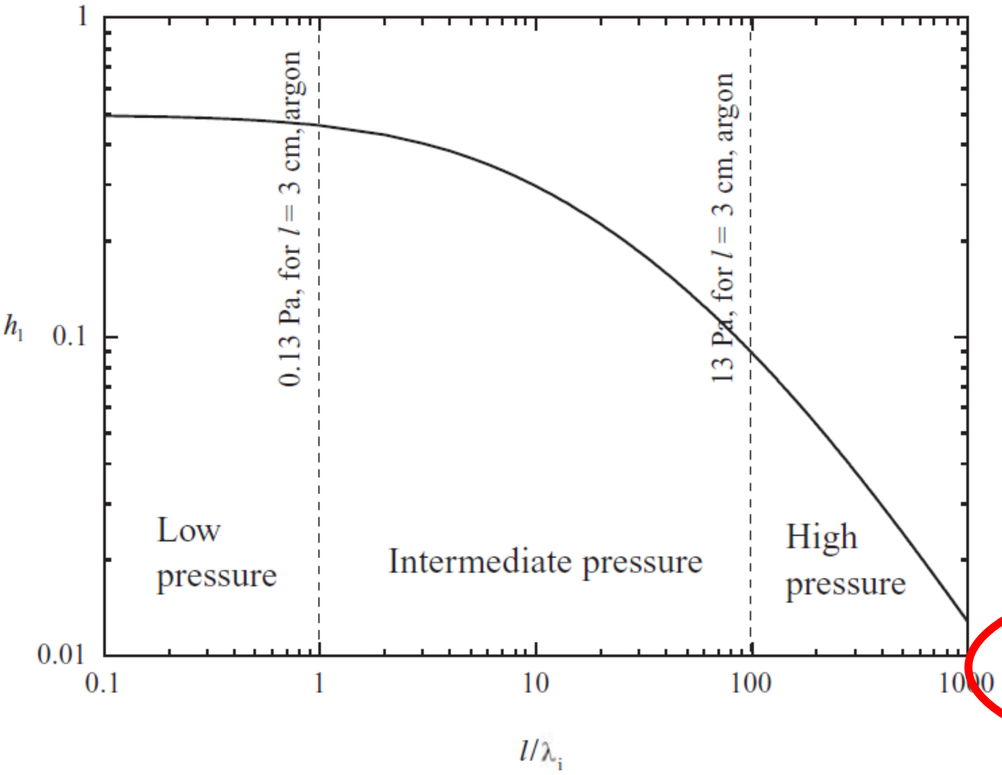


Chabert and Braithwaite (2011)

h-factors transport models

the h-factors

Heuristic expressions *stitching together* the various electronegativity / pressure regions



Chabert and Braithwaite (2011)

Theory valid for

- Multiple positive and negative ions
- Various electronegativity and pressure regimes
  - LP regime, with parabolic-profile EN core and two EP edges;
  - LP regime at high α, with one-region parabolic EN plasma;
  - HP regime at high α, with one-region flat-topped EN plasma.
- LP expressions dependent on

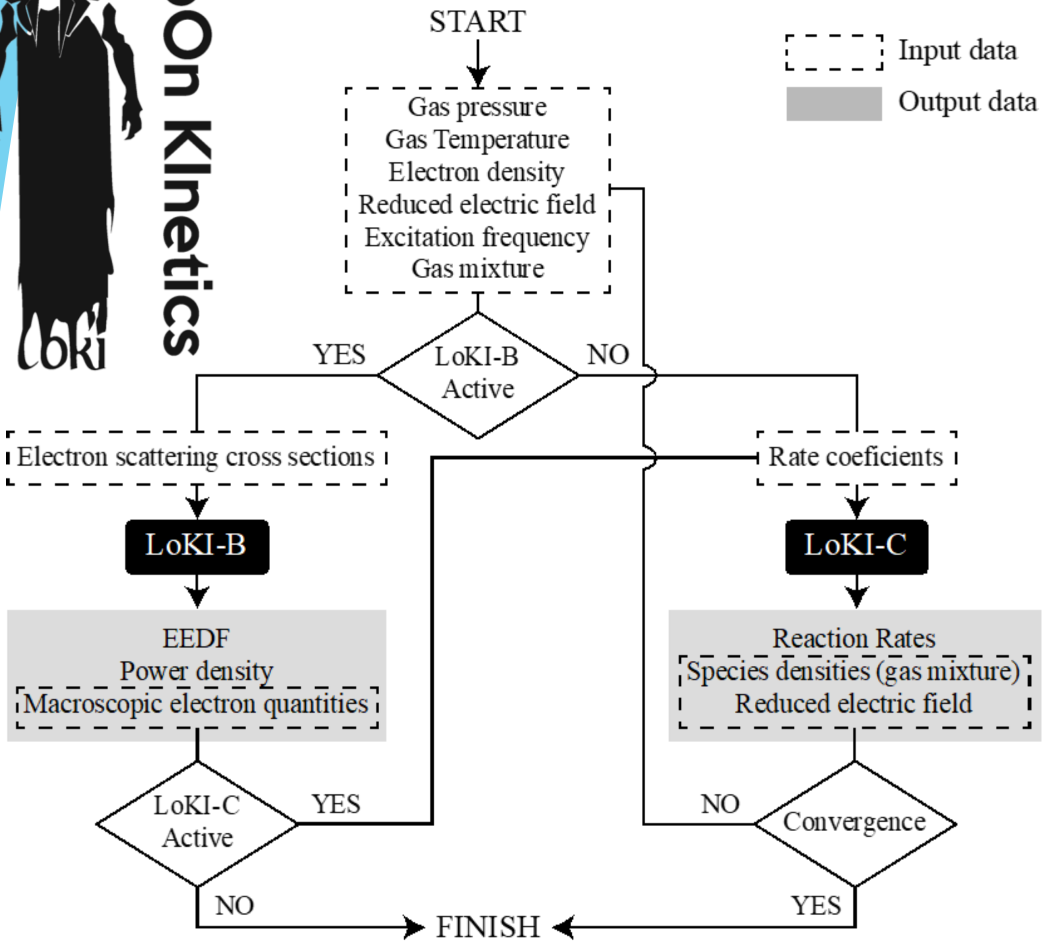
$$\lambda_i^{-1} \simeq \sum_j N\sigma_{ij}$$

Thorsteinsson and Gudmundsson, PSST (2010)
Chabert, PSST (2016)
Godyak (1986)
Lichtenberg *et al.*, JAP (1994)
Lee and Lieberman, JVST (1995)
Kim *et al.*, JVST (2006)

Simulations and results

The LisbOn KInetics (LoKI) simulation tool

(developed under MATLAB®)



OPEN SOURCE

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.
- includes modules to describe
  - (i) the collisional, radiative and transport mechanisms controlling the creation / destruction of species
  - (ii) the thermal heating of the neutral gas

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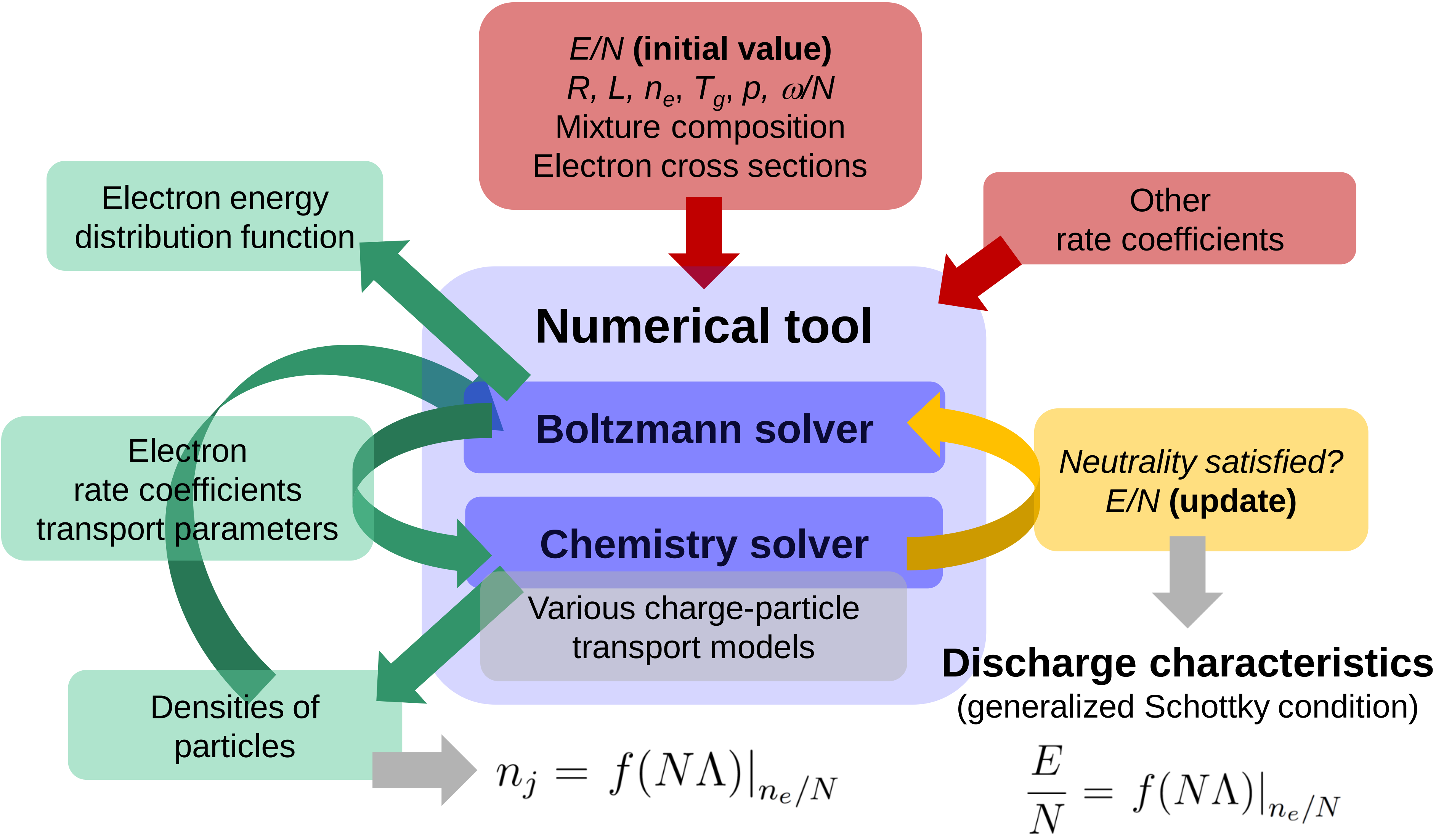
LoKI workflow



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

Other
rate coefficients

Electron energy
distribution function

Numerical tool

Boltzmann solver

Chemistry solver

Various charge-particle
transport models

Electron
rate coefficients
transport parameters

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

Densities of
particles

$$n_j = f(N\Lambda)|_{n_e/N}$$

Discharge characteristics
(generalized Schottky condition)

$$\frac{E}{N} = f(N\Lambda)|_{n_e/N}$$

Working conditions

Cylindrical DC glow discharge in oxygen

Dias *et al.*, PSST (2023); Booth *et al.*, PSST (2019, 2020, 2022)

R = 1 cm, L = 52.5 cm
p = 25 – 1300 Pa ; T_g ~ 320 – 580 K
I_{dc} = 10 – 40 mA ($n_e \sim 10^{15} - 8\times10^{15}$ m^{-3})

Reaction mechanism considering
$O_2(X,v=0\text{-}41)$, $O(^3P)$, $O_3(X)$, $O_2(a^1\Delta)$, $O_2(b^1\Sigma_g)$, $O_2(A^3\Sigma_u + C^3\Delta_u + c^1\Sigma_u)$, $O(^1D)$, O_3^*, O_2^+, O^+, O^-
Wall recombination probability $\gamma[O(^3P)] = f(p, T_g, I_{dc})$ from experiment

Cylindrical MW discharge in helium

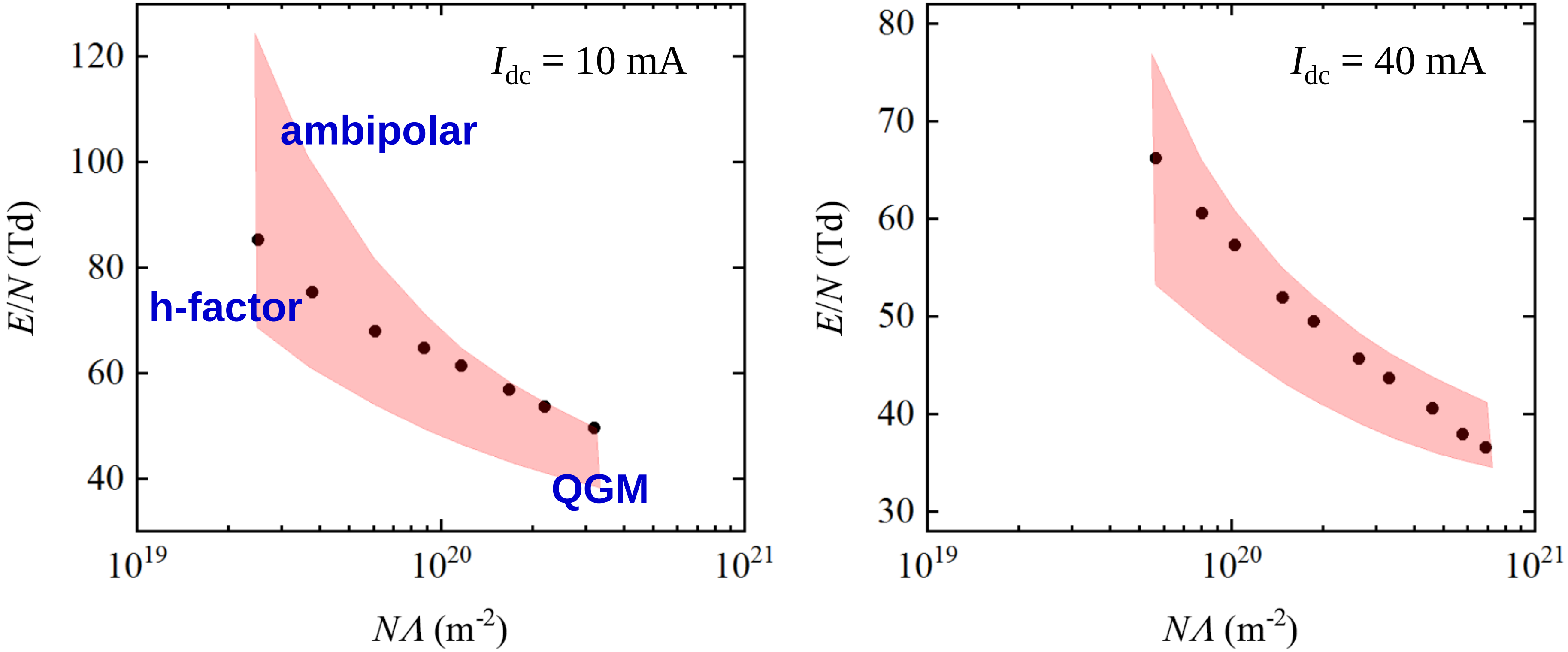
Alves *et al.*, JPD (1992); Santos *et al.*, PSST (2014); Alves and Tejero-del-Caz, PSST (accepted, 2023)

R = 0.3 cm << L
p = 50 – 5000 Pa and 10^5 Pa ; T_g ~ 1000 – 1800 K
$\omega/(2\pi)$ = 2.45 GHz ; $n_e \sim 5\times10^{17} - 2\times10^{19}$ m^{-3}

Reaction mechanism considering
$He(n^{2s+1}\ell)$, $n \leq 7$; He^+, He_2^+, He_2^*
Extensive revision of AI rate coefficients $He(1^1S) + He(n^{2s+1}\ell) \rightarrow e + He_2^+$

Results in oxygen

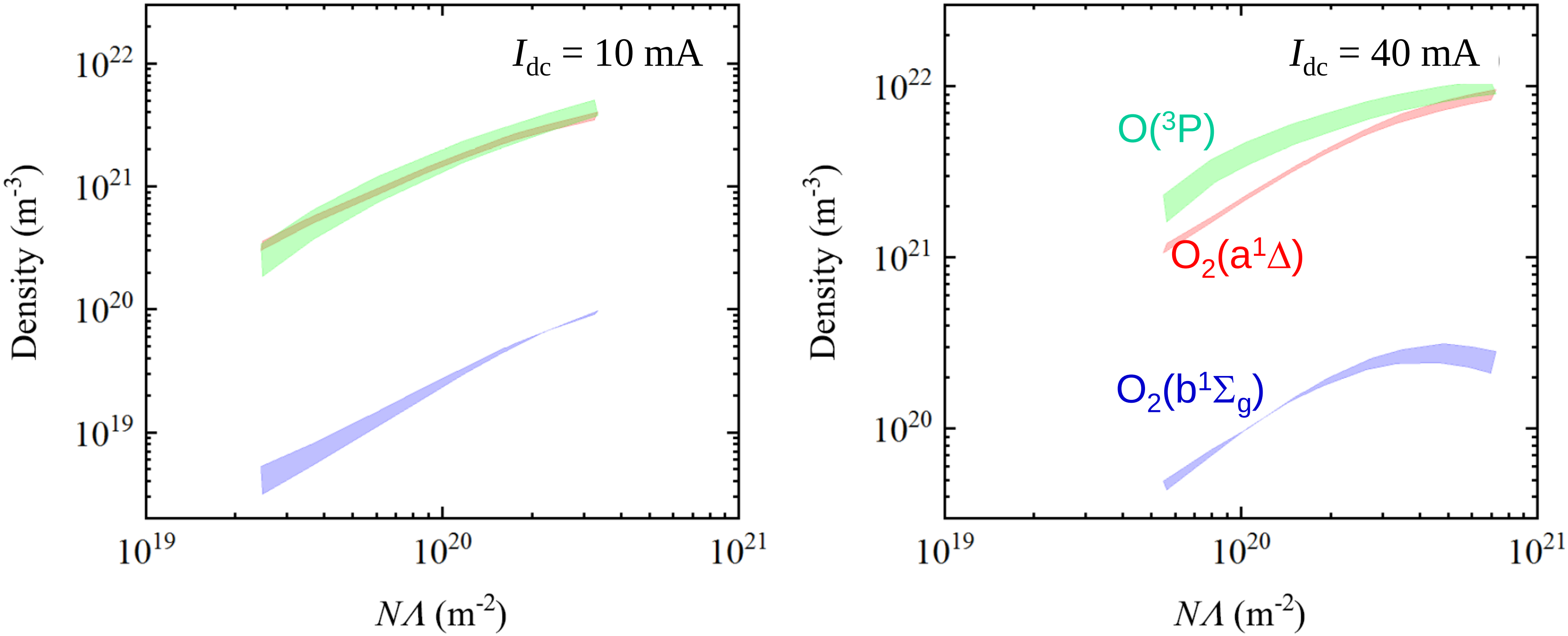
discharge characteristics



uncertainties of 20-60%
larger dispersion at low pressure and low discharge current

Results in oxygen

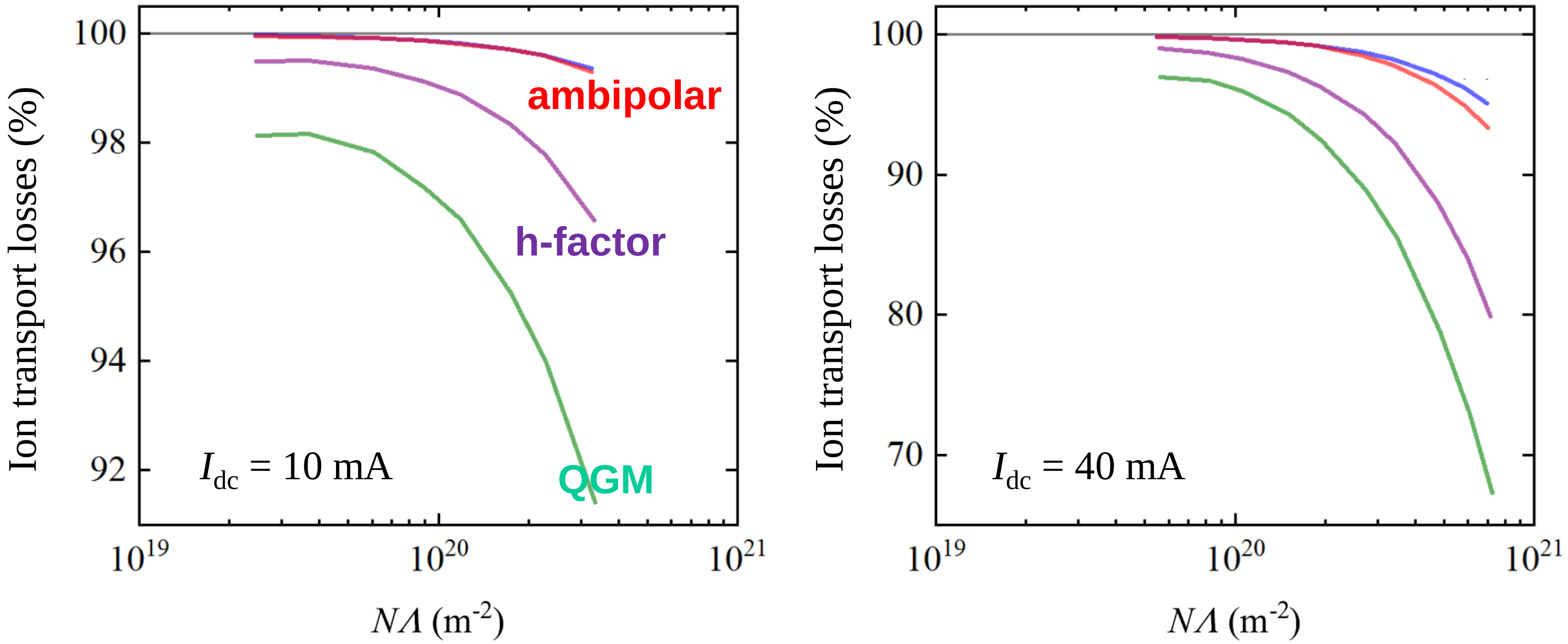
densities of main plasma species



uncertainties that can reach 60%
larger dispersion at low pressure and low discharge current

Results in oxygen

relevance of transport losses in the ion kinetics

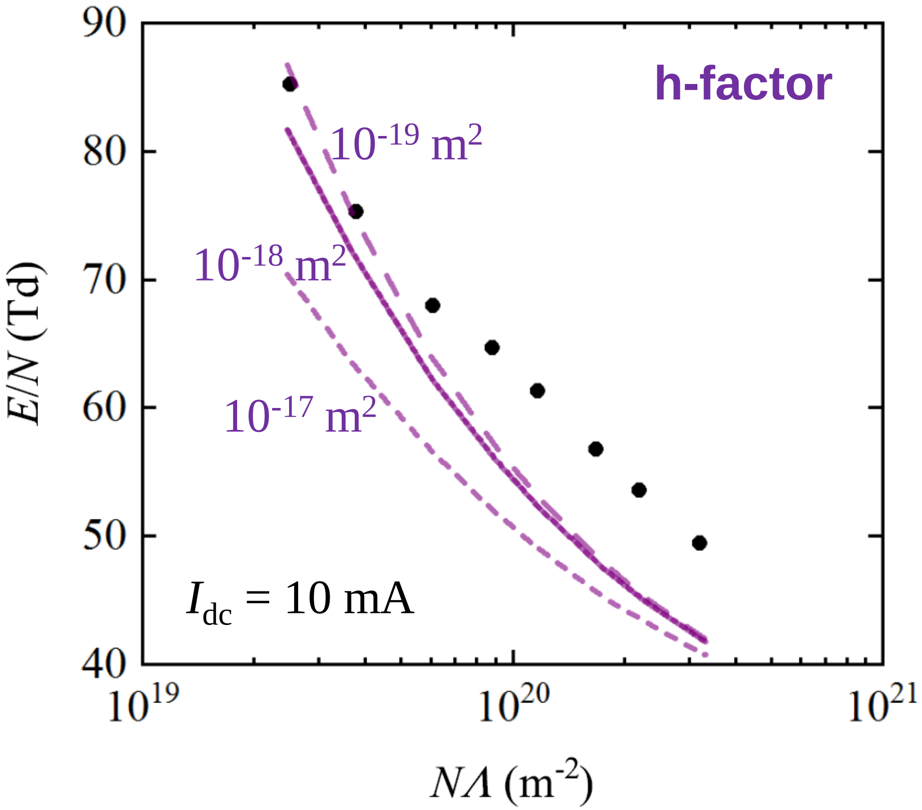


Transport accounts for > 70 – 90% of the total ion losses

- for O_2^+, transport is responsible for > 90% of destruction
- for O^+, charge-transfer $O^+ + O_2(X,v=0) \rightarrow O_2^+ + O(^3P)$ yields 40-95% destruction

Results in oxygen

influence of elementary data: σ_{ij} in h-factor model



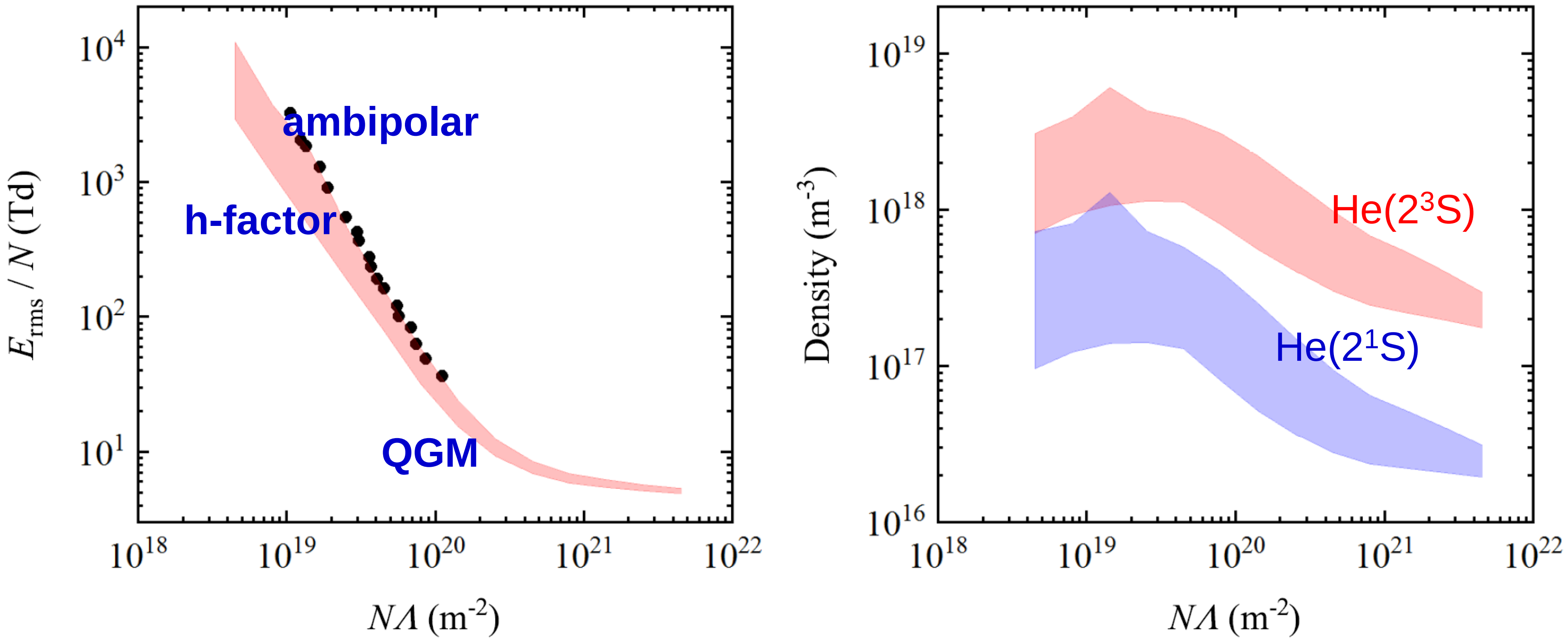
dispersion between 2 – 20%

the changes in the collisional cross section

- modify the LP terms only (dependent on λ_i)
- keep HP terms unchanged (dependent on D_i)

Results in helium

discharge characteristics and densities of main plasma species



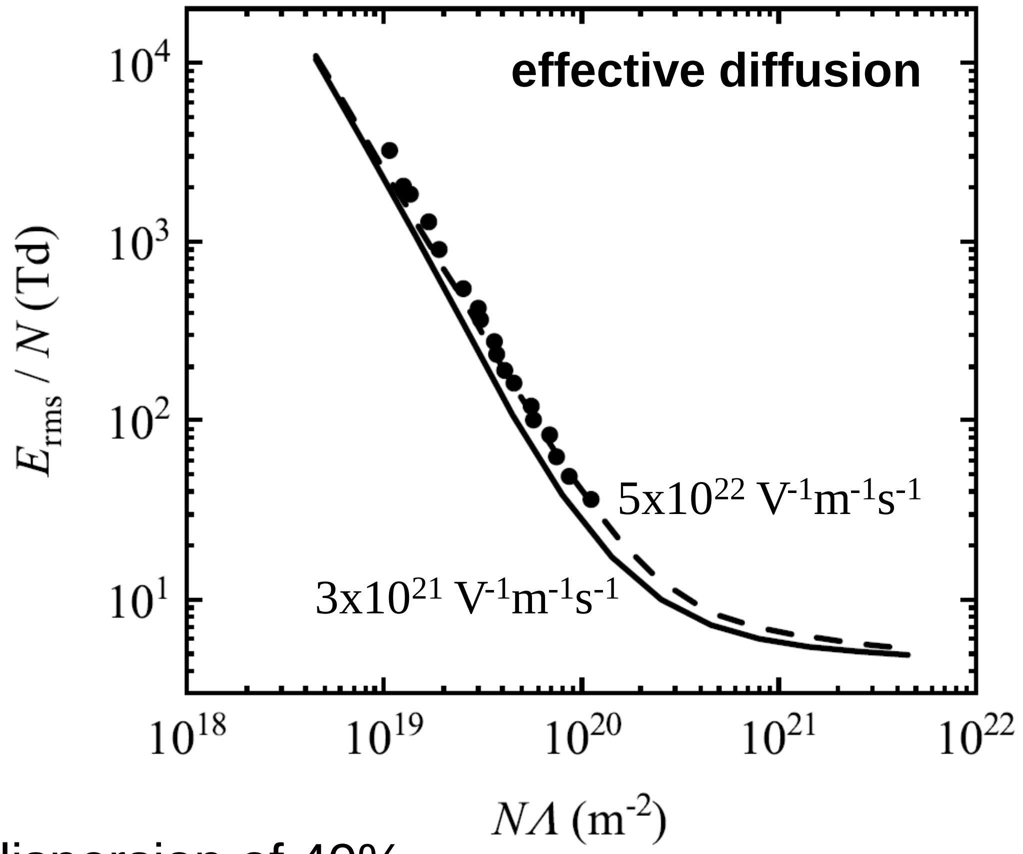
uncertainties of

- 8-115% for the discharge characteristics
- 50-150% for the densities of metastables

larger dispersion at low pressure

Results in helium

influence of elementary data: $\mu(He_2^+)N$ in effective diffusion model



The literature reports a dispersion > 25% in $\mu(He_2^+)N$

dispersion of 40%

the discharge characteristics become unchanged

- at LP, where transport becomes the dominant loss mechanism
- at HP, where transport losses are strongly reduced

Final remarks

- We have analyzed the influence of different charged-particle transport models on the global modeling of LTPs
- The models were applied to the description of
  - a DC discharge in oxygen, at p ~ 25 - 1300 Pa
  - a microwave discharge in helium, from p ~ 5 - 10^5 Pa
- The simulations reveal dispersions of
  - 5 – 120% for the discharge characteristics
  - 50 – 150% for the densities of the main plasma species
- Transport accounts for more than 50% of total charge losses

Charge-particle transport in global models is relevant

Final remarks

- **Transport phenomena should be considered and assessed in plasma chemistry studies** like any other kinetic mechanism, for example as part of the quantitative sensitivity analysis of a kinetic scheme

- To this date, **there is no general formulation** describing the transport of charged-particles in plasmas that can be used in global models for all types of plasmas and working conditions (this probably out of reach)

- The **choice of "suited" transport models** should consider the specific conditions considered (pressure, electronegativity, single-/multi-ions)

- Efforts should me made
  - to **translate accurate fluid/PIC-MCC simulation results into fitting / abacus formula** for transport loss-frequencies
  - to **express kinetic coefficients** (mobilities, diffusion coefficients, loss frequencies) as a **function of measured / calculated elementary data** (ion-scattering cross sections)

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