Global Models

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Global Models

- Predict spatially averaged quantities (density, temperature)
- Advantages:
  1. Finds relations between key parameters
  2. Negligible computational cost
- Disadvantages:
  1. No spatial information
  2. Shaky assumptions $\Rightarrow$ limited accuracy

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Lieberman and Lichtenberg [1994, 2005] supply much relevant background information for this lecture, which may be found easier to digest in smaller packages such as Lee and Lieberman [1995], Ashida et al. [1995], Lieberman and Ashida [1996].

Plan

1. General principles: Energy and Particle Balance
2. Example: Discharge in argon, with comparison with PIC
3. Example: Discharge with chemistry—argon with an excited state.
4. Example: Uncertainty in Complex Chemistry Models
5. Complications: Surface chemistry

Basics: Reaction Rates

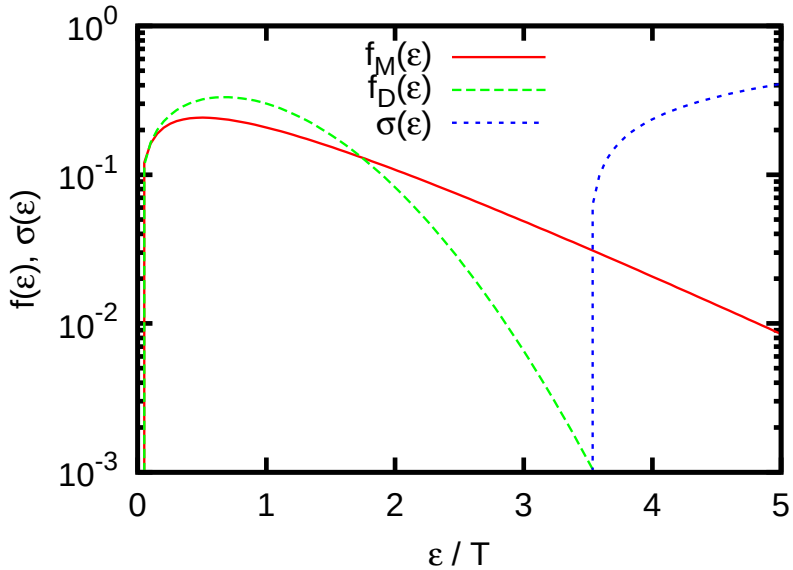
- Rate constants characterize chemistry.
- For electron energy distribution $f(\varepsilon)$ and collision cross section $\sigma(\varepsilon)$:

$$k = \int_0^\infty v(\varepsilon)\sigma(\varepsilon)f(\varepsilon)d\varepsilon$$

where

$$1 = \int_0^\infty f(\varepsilon)d\varepsilon$$

- Often, k *very* sensitive to $f(\varepsilon)$ and $\sigma(\varepsilon)$



Basics: Conservation Principles

- Particle balance $\Rightarrow$ Electron temperature, T_e
- Power balance $\Rightarrow$ Plasma density, n_0

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Basics: Conservation Principles

- Particle balance ⇒ Electron temperature, T_e
- Power balance ⇒ Plasma density, n_0

A common strategy (not discussed in this lecture) is to couple a global model with an external procedure for computing the electron energy distribution function, such as a Boltzmann equation solver.

Basics: Particle Balance

- Volume ionization balanced by wall recombination:

$$\int_V k_i \, n_e \, N \, dV = \int_S \mathbf{\Gamma} \cdot \mathbf{dS}.$$

Where:

1. $\mathbf{\Gamma}$ the charged particle flux
2. k_i the ionization rate
3. N the neutral gas density

Basics: Particle Balance

Assumptions about the volume ionization term:

1. Electron temperature (T_e) uniform $\Rightarrow$ k_i uniform
2. Volume of integration is the chamber volume

Hence:

$$\int_V k_i \, n_e \, N \, dV = V \, \bar{n}_e \, k_i(T_e) \, N \qquad (\text{defines } \bar{n}_e)$$

Basics: Particle Balance

Assumptions about the surface recombination term:

1. Bohm condition is satisfied at the sheath edge, $\Gamma = n_s u_B$
2. Surface of integration is the chamber wall, area A.
3. Ratio of $\bar{n}_e$ to n_s is h (to be discussed).

Hence:

$$\int_S \mathbf{\Gamma} \cdot \mathbf{dS} = A\, u_B\, n_s = A\, u_B\, \bar{n}_e\, h$$

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Basics: Particle Balance

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The Bohm condition for a single positive ion is (see Bohm [1949], Riemann [1991])

$$u_B = \sqrt{k_B T_e} M_i,$$

for ion mass M_i. When there are several positive ions, what should be assumed is controversial. A reasonable and convenient assumption is that each ion reaches its own Bohm speed.

Basics: Particle Balance

Hence:

$$A\, u_B(T_e)\, \bar{n}_e\, h(T_e) = V\, \bar{n}_e\, k_i(T_e)\, N$$

or

$$A\, u_B(T_e)\, h(T_e) = V\, k_i(T_e)\, N$$

the **Plasma Balance Equation**, determines T_e.
[Historical note: This result was known to Francis (1957) and perhaps even Langmuir (1920s)]
We can find T_e either analytically or by trivial numerics.

Global Models

Basics: Particle Balance

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For historical references, see Tonks and Langmuir [1929], Langmuir [1929], Francis [1956a,b], Franklin [1976]. The language and concepts employed are not always easily related to modern discussions.

Basics: Particle Balance

Expressions for h, in terms of ion mean free path λ_i:

1. Langmuir regime, planar: $h = n_s/n_0 = 0.5$
2. Langmuir regime, cylindrical: $h = 0.4$
3. Intermediate regime, planar: $h = 0.86\,(3 + L/2\lambda_i)^{-1/2}$
4. Intermediate regime, cylindrical: $h = 0.80\,(4 + R/2\lambda_i)^{-1/2}$
5. High pressure, planar: $h = \left[1 + \left(\frac{L}{\pi}\frac{u_B}{D_a}\right)^2\right]^{-1/2}$

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These results are described in Lieberman and Lichtenberg [1994], but did not originate there. See Godyak [1986]. Some of the ideas go back as far as Schottky [1924].

Examples: Discharge in Argon

Example: Discharge in a cylindrical chamber

$$A\, u_B(T_e)\, h(T_e) = V\, k_i(T_e)\, N$$

$$u_B(T_e)\left(2\pi R^2 h_L + 2\pi R L h_R\right) = k_i(T_e) N \pi R^2 L$$

Examples: Discharge in Argon

This can be written:

$$N d_{eff}\, k_i(T_e) = u_B(T_e)$$

where

$$N d_{eff} = \frac{\pi R^2 L N}{2\pi R^2 h_L + 2\pi R L h_R}$$

$\Rightarrow$ T_e is a function of the single scaling parameter $N d_{eff}$ (recall h_R and h_L are functions of N).

Examples: Discharge in Argon

Cautions

- We need $d_{eff} \gg \lambda_D$, otherwise A and V cannot be calculated from the chamber dimensions.
  Usually not a problem, except in special cases, *e.g.*, low current positive columns.
- Typically, the electron distribution function is not Maxwellian.
  Almost always a problem.

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  Almost always a problem.

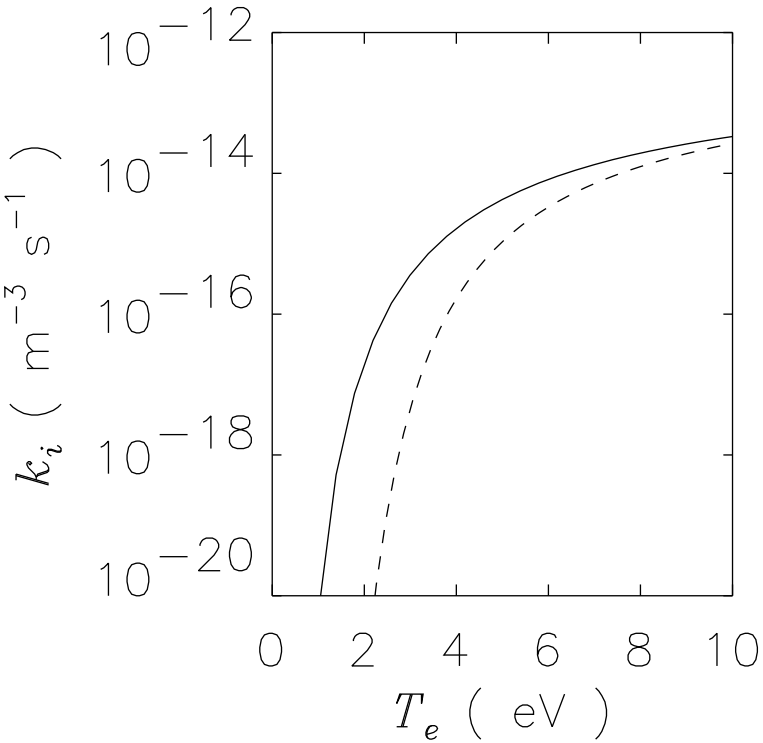
Maxwellian and Druyvesteyn distribution functions are solutions of the Boltzmann equation for constant elastic collision frequency and constant mean free path, respectively, see Cherrington [1979], Raizer [1991]. A Maxwellian is also a solution when electron-electron collisions are important. None of these conditions is routinely satisfied in low-pressure plasmas, so one should not expect either of these distribution functions to appear. They are assumed here for analytical convenience, and because there is often some resemblance between one of these functions and the real distribution function. Much more exotic distribution functions sometimes occur, *e.g.* with bumps, holes or super-thermal tails (see Godyak and Piejak [1990], Turner and Hopkins [1992]).

Examples: Discharge in Argon

- We'll look at results for Maxwellian and Druyvesteyn distribution functions.
- A Maxwellian *might* occur in a dense, low pressure plasma.
- The assumptions for a Druyvesteyn are *most unlikely* to be satisfied in practice
- Qualitatively different distribution functions (bumps, holes, bi-Maxwellian) are not unlikely.

$\Rightarrow$ The purpose of these comparisons is to indicate sensitivity

Examples: Discharge in Argon

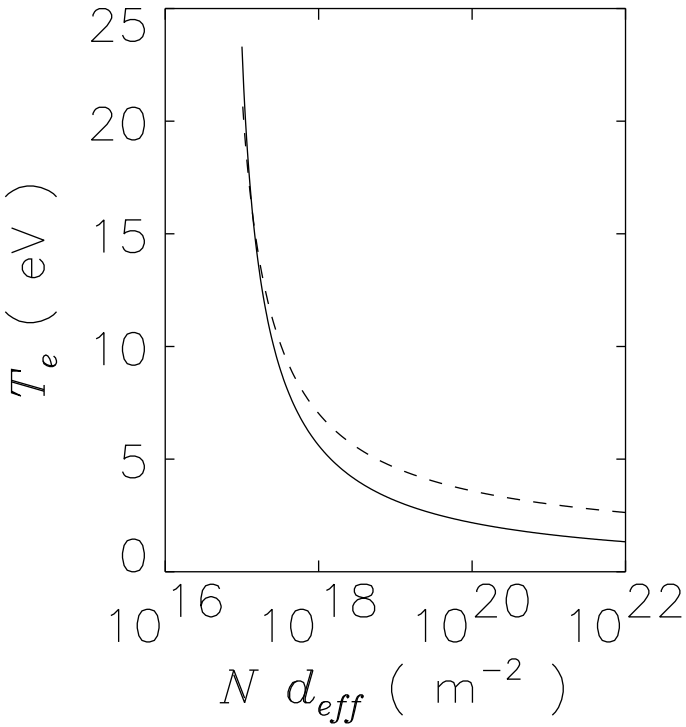


Ionization rate as a function of $T_e \equiv \frac{2}{3}\langle\epsilon\rangle$

Solid line - Maxwellian

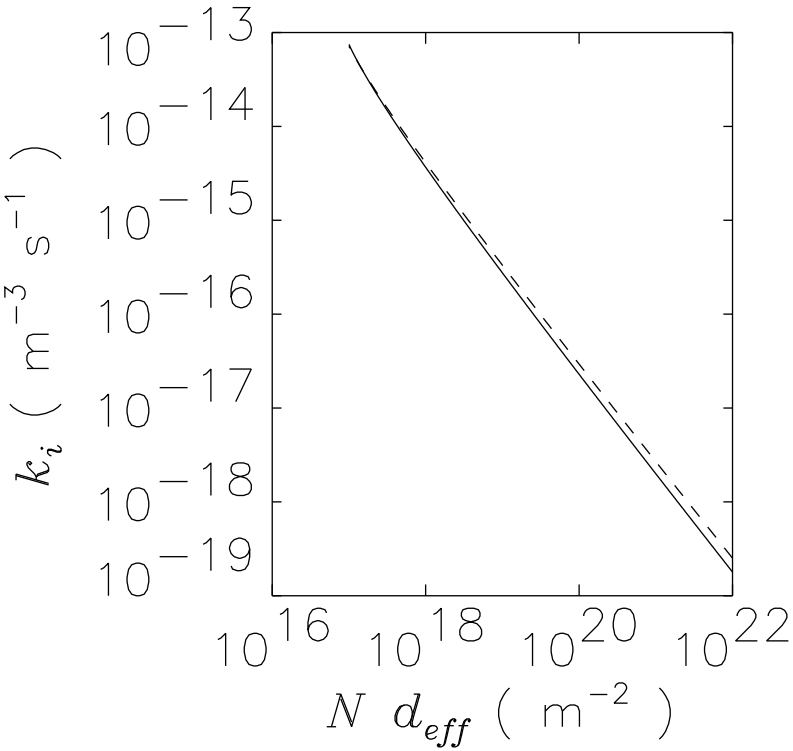
Dashed line - Druyvesteyn

Examples: Discharge in Argon



Particle balance equation solved for T_e in Ar
Solid line - Maxwellian electron distribution function
Dashed line - Druyvesteyn electron distribution function
Assuming $u_B^2 = \frac{2}{3}\frac{k_B\langle\epsilon\rangle}{m_i}$
(Typically $10^{18} < Nd_{eff} < 10^{20}$)

Examples: Discharge in Argon



Particle balance equation solved for k_i in Ar
Solid line - Maxwellian electron distribution function
Dashed line - Druyvesteyn electron distribution function

$$0.6 < \frac{k_{i,Maxwellian}}{k_{i,Druyvestyen}} < 1.2$$

Basics: Power Balance

Assume power absorbed from circuit is a given, P_{abs}, then

$$P_{abs} = P_{loss} \equiv u_B \; A_{eff} \; \epsilon_T \; n_0$$

where:
A_{eff} accounts for the density at surfaces using h, *e.g.*, for the cylindrical example:

$$A_{eff} = 2\pi R^2 h_L + 2\pi RLh_R.$$

ϵ_T is the energy required to produced an electron-ion pair.

Basics: Power Balance

n_0 — maximum plasma density
$\bar{n}$ — volume average plasma density
Note that we fudge the difference, by assuming density drops "sharply" near the edge.
Causes error $O(1)$: Other errors are more significant.

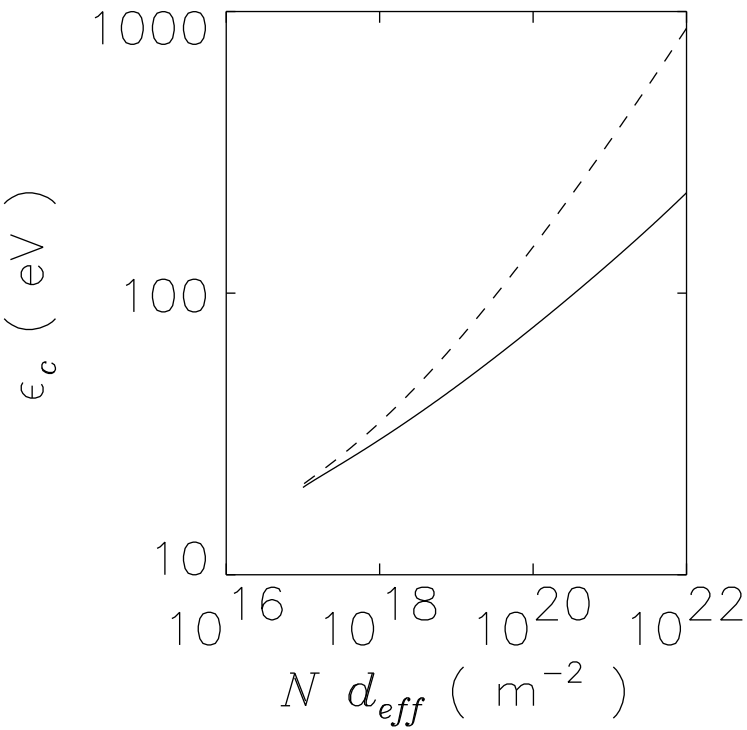
Basics: Power Balance

Contributions to ϵ_T:

Electron inelastic collisions	$\frac{1}{k_i}\sum_j \epsilon_j k_j N$
Electron elastic collisions	$\frac{1}{k_i}\frac{2m_e}{m_i} k_e N \frac{3}{2} k_B T_e$
Electron energy loss at surfaces	$2 k_B T_e$
Ion energy loss at surfaces	$e V_s + \frac{1}{2} k_B T_e$

where *e.g.* $eV_s = \frac{k_B T_e}{2} \ln\left(\frac{m_i}{2\pi m_e}\right)$ for a Bohm sheath.

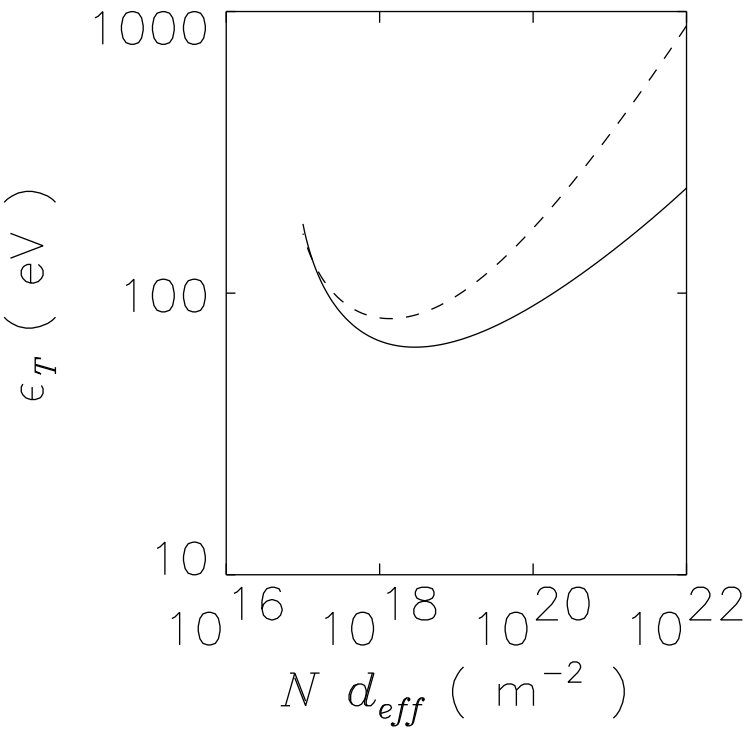
Examples: Discharge in Argon



ϵ_c (volume/collisional energy loses) in Ar
Solid line - Maxwellian electron distribution function
Dashed line - Druyvesteyn electron distribution function

$$0.2 < \frac{\epsilon_{c,Maxwellian}}{\epsilon_{c,Druyvestyen}} < 1.0$$

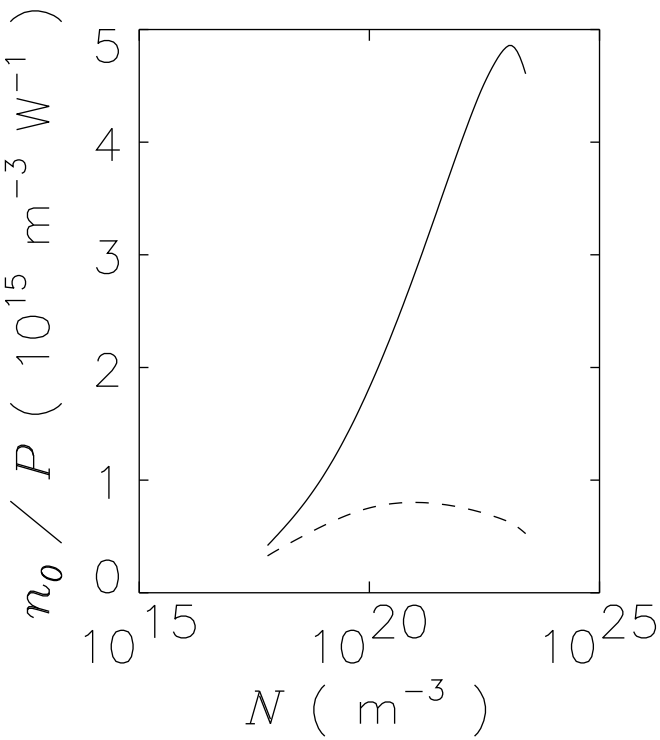
Examples: Discharge in Argon



ϵ_T (total energy losses,ϵ_c plus fluxes to walls) in Ar
Solid line - Maxwellian electron distribution function
Dashed line - Druyvesteyn electron distribution function

$$0.1 < \frac{\epsilon_{T,Maxwellian}}{\epsilon_{T,Druyvestyen}} < 1.2$$

Examples: Discharge in Argon



Example:
Cylinder $R = 0.1$ m, $L = 0.1$ m
Solid line - Maxwellian electron distribution function
Dashed line - Druyvesteyn electron distribution function

Pause

- Caution: when $\lambda_\epsilon < L$, the assumption that T_e is uniform is likely false.
- Caution: electron distribution function is likely not Maxwellian
- Caution: if electron distribution function is not Maxwellian, assumption that T_e is uniform is formally false.

Examples: Compare Global Model with PIC Simulation

PIC (Particle-in-cell) simulation: Highly accurate kinetic procedure, self consistent calculation of $f(\epsilon)$.

Gas	Argon
N	$1.8 \times 10^{20}\ \mathrm{m}^{-3}$, 20 mTorr, 1.5 Pa
d	4 cm (one dimensional Cartesian)

One space dimension, x, excited by given current driven by uniform electric field along z

$\Rightarrow$ Minimize global model errors.

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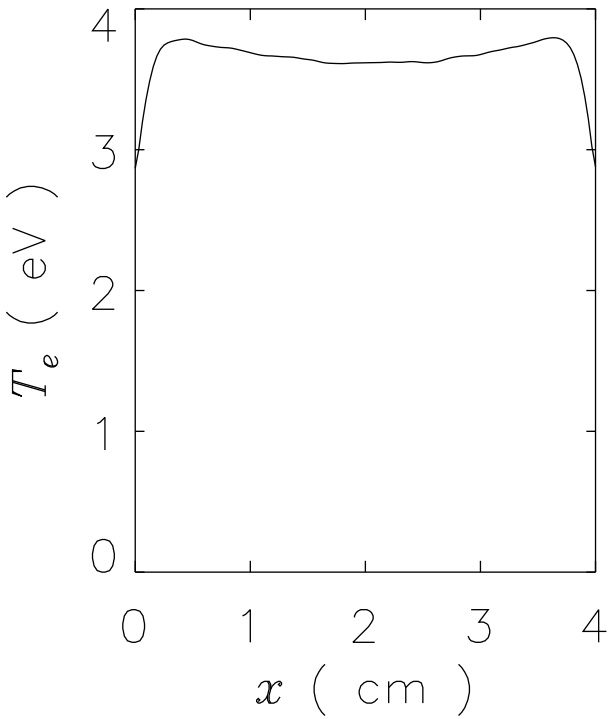
For more on the particle-in-cell technique, see Birdsall and Langdon [1991], Birdsall [1991], Hockney and Eastwood [1981], Donkó [2011]

Examples: Compare Global Model with PIC Simulation



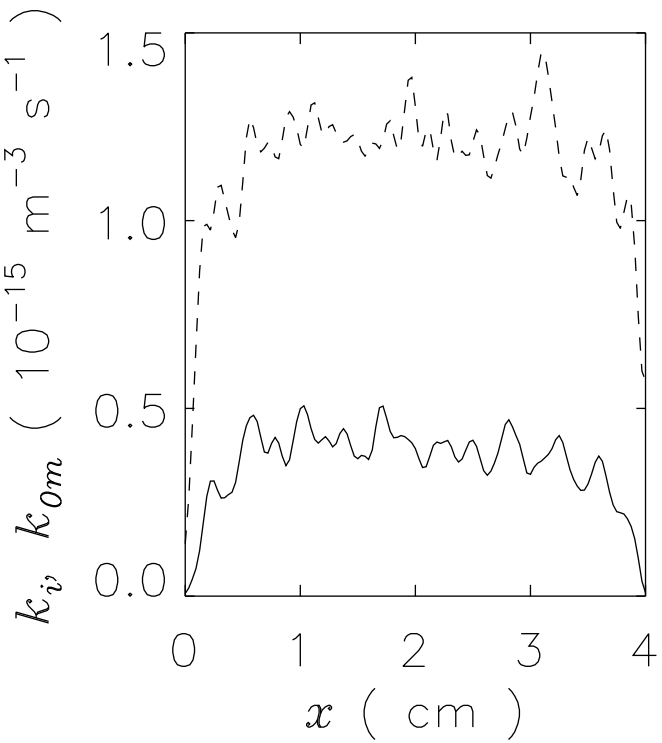
$$\frac{d}{\lambda_i} \sim 7$$

$$h = \frac{0.86}{\sqrt{3 + d/2\lambda_i}} = 0.32$$

$$Nd_{eff} = \frac{Nd}{2h} = 1.2 \times 10^{19}\ \mathrm{m}^{-2}$$

$$\Rightarrow T_e = 3.0\ \mathrm{eV}$$

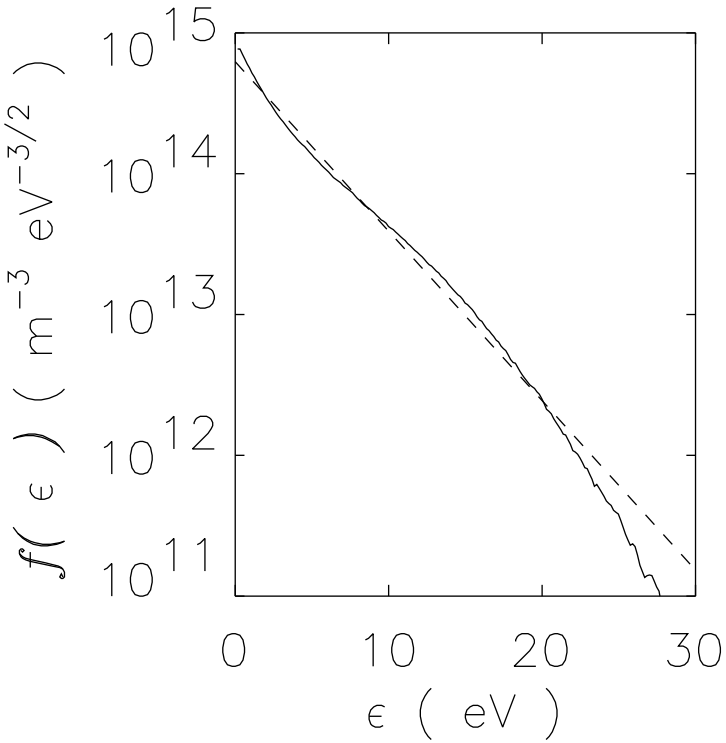
Examples: Compare Global Model with PIC Simulation



$$k_i(T_e = 3\,\mathrm{eV}) = 2.2\times10^{-16}\ \mathrm{m}^{-3}\ \mathrm{s}^{-1}$$

$$k_{0m}(T_e = 3\,\mathrm{eV}) = 6\times10^{-16}\ \mathrm{m}^{-3}\ \mathrm{s}^{-1}$$

Examples: Compare Global Model with PIC Simulation



Solid line — $f(\epsilon)$ from PIC calculation,

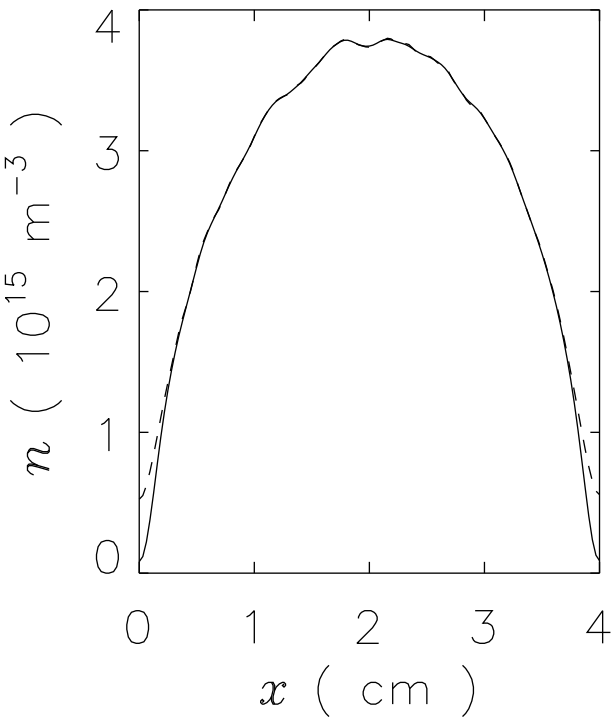
$$k_i = 4.1 \times 10^{-16}\ \mathrm{m}^{-3}\ \mathrm{s}^{-1}$$

Dashed line — Maxwellian with same mean energy,

$$k_i = 5.1 \times 10^{-16}\ \mathrm{m}^{-3}\ \mathrm{s}^{-1}$$

Examples: Compare Global Model with PIC Simulation

Plasma density, solid line, n_e ; dashed line, n_+



$\mathcal{P}_{abs} = 91$ W m^{-2} from PIC

$\epsilon_T = 70$ eV

$$n_0 = \frac{P_{abs}}{A_{eff} u_B \epsilon_T} = \frac{\mathcal{P}_{abs}}{2 h u_B \epsilon_T}$$

$$= 4.5 \times 10^{15} \text{ m}^{-3}$$

Examples: Compare Global Model with PIC Simulation

Finally:

	Global Model	PIC (line average)	PIC (centre)
T_e	3.0 eV	3.6 eV	3.6 eV
n	$4.5 \times 10^{15}\ \mathrm{m}^{-3}$	$2.8 \times 10^{15}\ \mathrm{m}^{-3}$	$3.8 \times 10^{15}\ \mathrm{m}^{-3}$

Comment on Errors

Volume (Bohm surface chamber wall not identical)	~ 0.85
Profile (Line average and maximum density not identical)	~ 0.75
Non-Maxwellian $f(\epsilon)$	~ 0.8

Together overestimate ionization frequency by factor ~ 2

Examples: Discharge in Argon with Chemistry

To the model already discussed, add processes:

$$\begin{aligned} \mathrm{Ar} + e &\rightarrow \mathrm{Ar}^* + e \\ \mathrm{Ar}^* + e &\rightarrow \mathrm{Ar}^+ + 2e \\ \mathrm{Ar}^* &\rightarrow \mathrm{Ar} + h\nu \end{aligned}$$

Ar^* is a composite state.
Ar^* has a pressure dependent effective lifetime, because the radiation is trapped.

Examples: Discharge in Argon with Chemistry

Require:

- Balance particle equation for excited state:

$$k_{0m} N n_0 - k_{mi} n_m n_0 - \frac{n_m}{\tau_m} = 0$$

- Additional terms in particle balance, energy balance, *e.g.*,

$$A u_B h = V \left(k_i N + k_{mi} n_m \right)$$

  Particle and energy balance equations now couple.

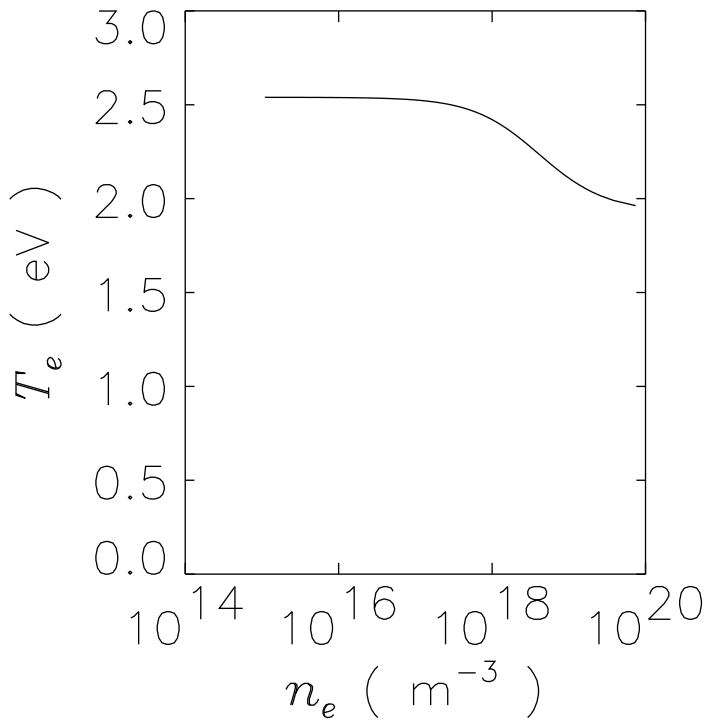
Examples: Discharge in Argon with Chemistry

Note:

$$
\begin{aligned}
n_m &= \frac{k_{0m} N n_0}{k_{mi} n_0 + 1/\tau_m} \\
&= \frac{k_{0m}}{k_{mi}} N, \qquad n_0 \gg 1/\tau_m k_{mi} \\
&= k_{0m} \tau_m N n_0, \qquad n_0 \ll 1/\tau_m k_{mi}
\end{aligned}
$$

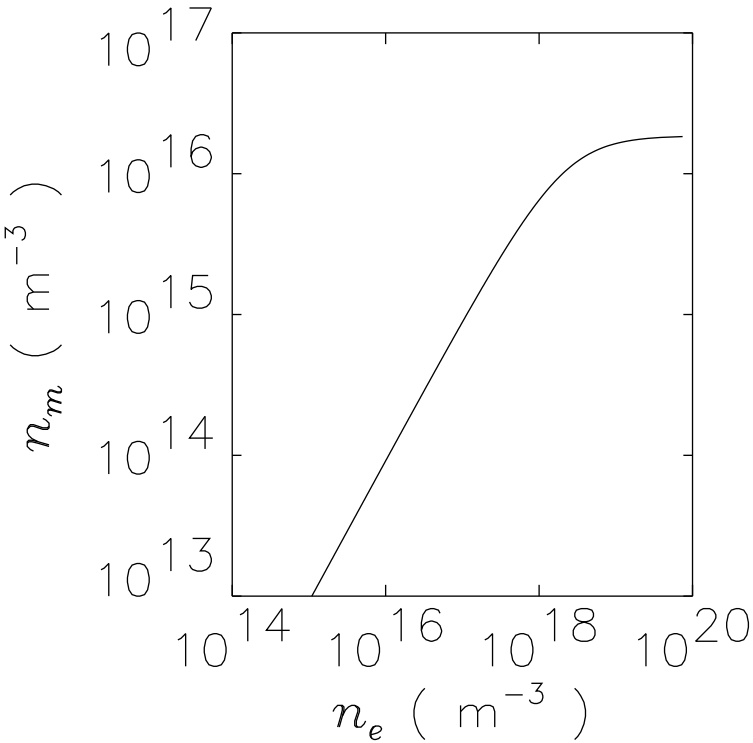
but in real life k_{0m} is a function of T_e which depends on n_m.

Examples: Discharge in Argon with Chemistry



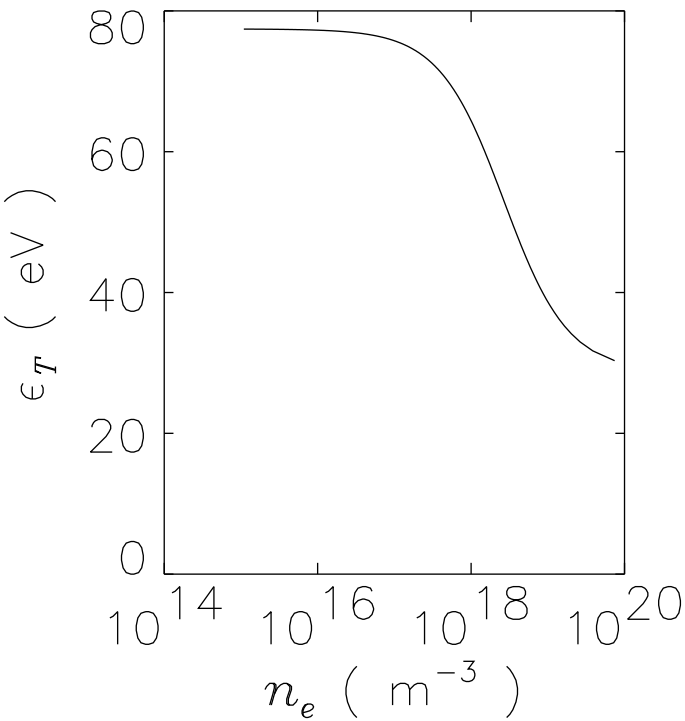
At large n_e, T_e is affected by excited states.

Examples: Discharge in Argon with Chemistry



n_m has limiting behaviour as previously discussed

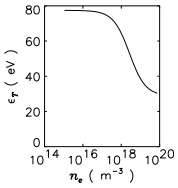
Examples: Discharge in Argon with Chemistry



ϵ_T falls because an increasing fraction of the power is used for ionization (and not radiation)

Global Models

Examples: Discharge in Argon with Chemistry

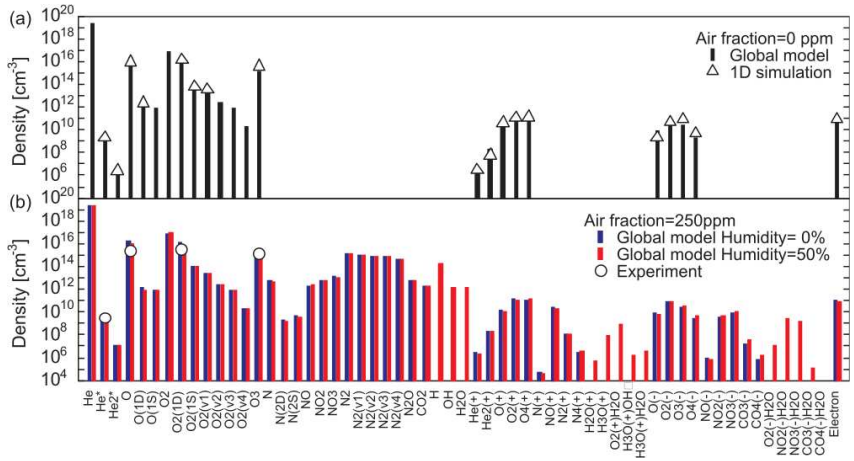


ϵ_T falls because an increasing fraction of the power is used for ionization (and not radiation)

An additional example appended at the end of this lecture discusses the important but not insuperable difficulties that are presented by electronegative discharges.

Example: Complex Chemistry

- Global models are useful for *complex chemistry*
- Possibly hundreds of species, thousands of reactions
- Even today, this can be computationally challenging for multi-dimensional models



From Murakami *et al*, Plasma Sources Sci. Technol. 22, 015003 (2013). Simulated mass spectrum using a humid air chemistry model with 59 species and 1048 reactions. The model has limited treatment of vibrational and rotational kinetics.

Example: Special Challenges for Complex Chemistry

1. Derivation of balance equations by hand is impractical
2. Rate constants are not known exactly
3. Literature contains many corrupt (wrong) values

```
N2(A3) + O => NO + N(2D) ! 7.0d-12
N2(A3) + O => N2 + O(1S) ! 2.1d-11
N2(A3) + N => N2 + N ! 2.0d-12
N2(A3) + N => N2 + N(2P) ! 4.0d-11*(300.0d0/Tgas)**0.667
N2(A3) + O2 => N2 + O + O(1D) ! 2.1d-12*(Tgas/300.0d0)**0.55
N2(A3) + O2 => N2 + O2(a1) !  2.0d-13*(Tgas/300.0d0)**0.55
```

Partial reaction scheme for ZDPlasKin `http://www.zdplaskin.laplace.univ-tlse.fr/`, a free global model solver

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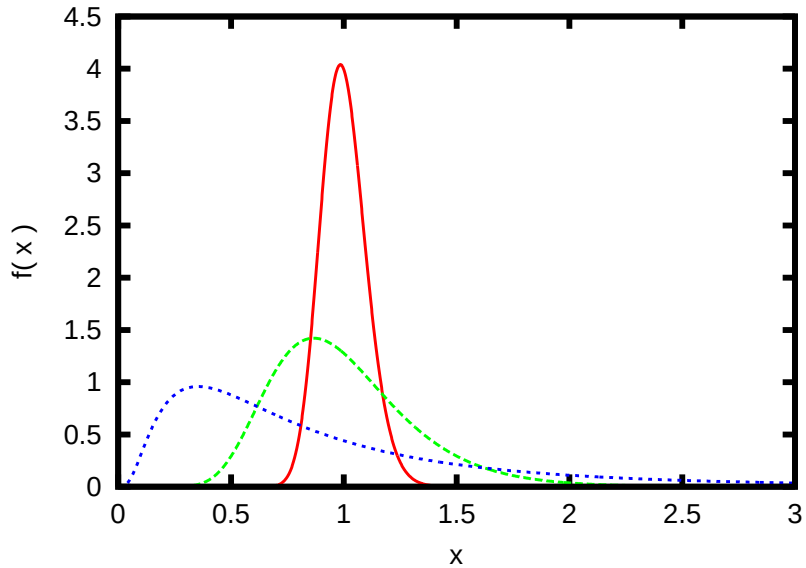
Except as a learning exercise, no one should attempt to code up a significantly complex chemistry model by hand. There are freely available tools (such as ZDPlasKin), which also offer good solutions to the problem of integrating the resulting ordinary differential equations, which may be so stiff as to present difficulties to many solution algorithms.

Example: Uncertain Rate Constants

- Uncertainty in rates $\Rightarrow$ Uncertainty in prediction
- A Monte Carlo approach:
  1. Define uncertainty for each rate (*e.g.* experimental error)
  2. Hence define a probability distribution for each rate
  3. Draw a set of rate constants from the probability distributions
  4. Solve the model in the usual way
  5. Repeat to build probability distributions for plasma species, *etc*

Probability Distributions

- For each rate we choose a mean k and a width parameter Δk
- Δk depends on the source of data
  $\Rightarrow$ Must identify the source!
- We assume a lognormal probability distribution
- Each rate is supposed to be an independent random variable

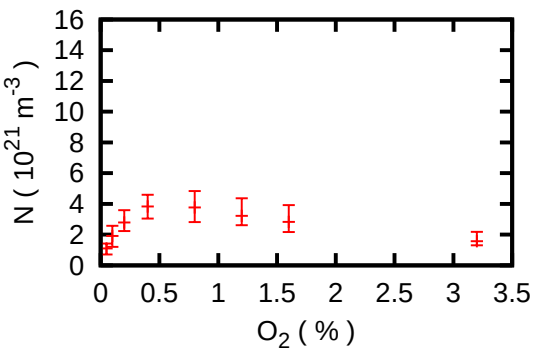


Example: A Chemistry Model

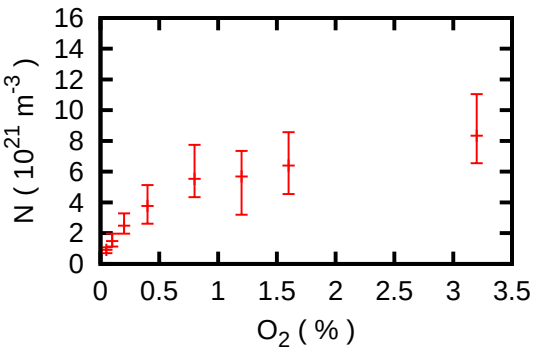
- He/O_2 chemistry in atmospheric pressure plasmas
- Moderately complex chemistry, $\sim$ 20 species, $\sim$ 370 reactions
- Sources of rate data:

Directly determined	162	44 %
Derived semi-empirically/theoretically	143	38 %
Analogy with a related process (Guess?)	67	18 %

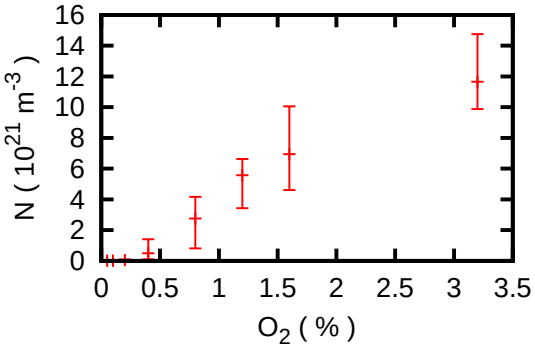
Results: Radicals



O



$O_2(^1\Delta)$



O_3

Quality of Transmission of Data

- The reaction

$$\begin{aligned} \mathrm{O}(^1D) + \mathrm{O_3} &\rightarrow 2\mathrm{O} + \mathrm{O_2} \\ &\rightarrow 2\mathrm{O_2} \end{aligned}$$

  is the subject of ∼10 experimental studies and three critical reviews (1987,2004,2011)
- The critical recommendation is

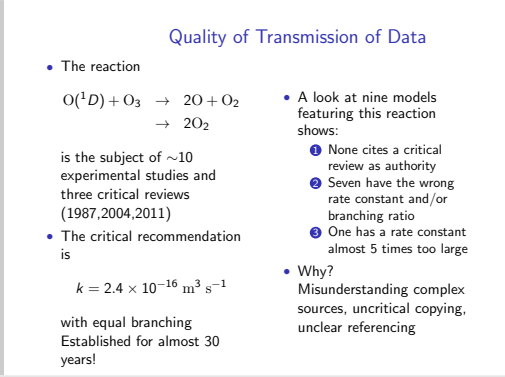
$$k = 2.4 \times 10^{-16}\ \mathrm{m^3\ s^{-1}}$$

  with equal branching
  Established for almost 30 years!

- A look at nine models featuring this reaction shows:
  1. None cites a critical review as authority
  2. Seven have the wrong rate constant and/or branching ratio
  3. One has a rate constant almost 5 times too large
- Why?
  Misunderstanding complex sources, uncritical copying, unclear referencing

Global Models

Quality of Transmission of Data



The problem here is partly historical. A full review of the sources for a significantly complex chemistry model involves inspecting hundreds to thousands of documents. When these documents were at best scattered among print journals in some library, and at worst archived in some inaccessible place, the task of accessing all of them becomes insupportable. This situation encouraged much recycling from previously published models, which led in practice to a complete loss of contact with primary sources, and extensive corruption in transmission. *Caveat lector!* Electronic archives have greatly improved this state of affairs. There is now much less excuse than there used to be for not consulting original sources.

Surface Chemistry

- Surface chemistry is important
- Example: Atomic radicals, *e.g.* O, F, are often critical. Dominant processes are gas phase dissociation:

$$F_2 + e \rightarrow 2F + e,$$

and surface recombination

$$2F + S \rightarrow F_2$$

$\Rightarrow$ Chemistry on the surface can be crucial

Surface Chemistry

- A key concept is a "surface site": A place where an atom or molecule can attach to the surface.
- The "surface site density" is a key quantity—this limits the amount of material that can attach to a surface.
- Site density $n_0' \sim 10^{19}$ m^{-2} $\sim \frac{1}{r_A^2}$, dependent on surface material, morphology, *etc, etc*.

Global Models

Surface Chemistry

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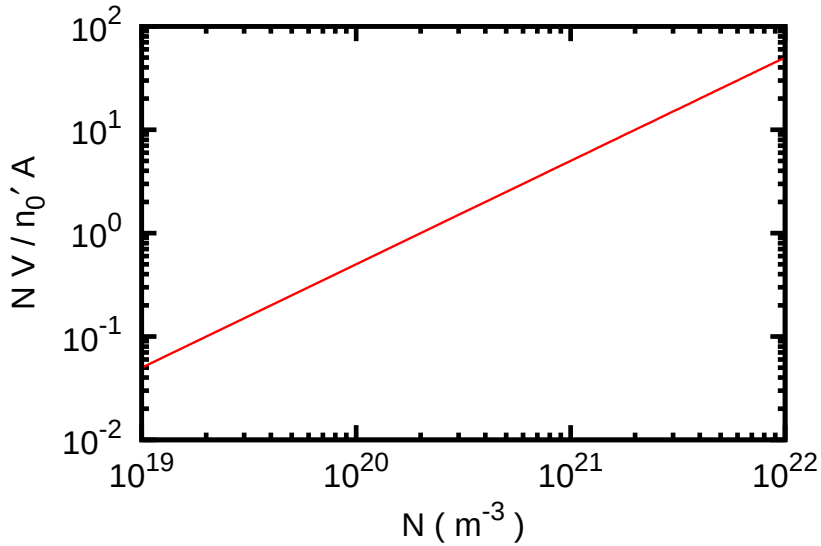
This discussion ignores much important detail. When one tries to capture the proper physics, one immediately has a complex model containing many parameters that are difficult to determine with any confidence, see Cartry et al. [2000] for example. However, that discussion is suggestive of the difficulties that occur in trying to give a clear interpretation to experiments, *e.g.* Kota et al. [1999].

Surface Chemistry

- Think of chamber with $R = 0.1$ m, $L = 0.1$ m
- Assume $n_0' = 10^{19}$ m^{-2}
- For any pressure $\lesssim$ 10 mTorr or 1 Pa

$$n_0' A \gtrsim NV$$

$\Rightarrow$ There is (potentially) more material absorbed on the surface than in the gas phase!



Surface Chemistry

- The most important cases are atomic radicals produced in the gas phase

$$O_2 + e \rightarrow 2O + e$$

  and recombining on the surface.
- Surface recombination is complex and not always well understood.
- A simple model, an atom striking the surface recombines with a second atom in chemically bound (chemisorbed) surface state:

$$O(g) + O(s) \rightarrow O_2(g)$$

Global Models

Surface Chemistry

In many plasma processing chemistries, atomic radicals such as O and F are crucial. For instance, in etching with both SF_6 and fluorocarbons, the ratio of these species critically affects the feature profile, see Lieberman and Lichtenberg [2005]

Surface Chemistry

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$$O(g) + O(s) \rightarrow O_2(g)$$

Surface Chemistry

- Surface recombination is experimentally characterized by a coefficient:

$$\gamma_{rec} = 1 - \frac{\Gamma_{away}}{\Gamma_{towards}}$$

- Experimentally, $\gamma_{rec} \sim 0.1 - 0.5$
- One can express

$$\tau_{rec} = \frac{\Lambda^2}{D} + \frac{2V(2 - \gamma_{rec})}{Av\gamma_{rec}}$$

where D is a diffusion coefficient, Λ a diffusion length, and v the thermal speed

Global Models

Surface Chemistry

Surface Chemistry

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where D is a diffusion coefficient, Λ a diffusion length, and v the thermal speed

These expressions quoted here were first derived by Chantry [1987], and have been widely used. For instance by Booth and Sadeghi [1991], Thorsteinsson and Gudmundsson [2010].

As noted above, much complex and poorly understood physics is incorporated in the coefficient γrec. Experimentally, this coefficient varies with the surface material, the temperature, and often depends on the history of the relevant surface. This is a major cause of modelling uncertainty.

Summary

- Global models are useful for simple models of low and intermediate pressure discharges.
- Can have complex chemistry, surface interactions and time dependence.
- *Must* have approximate spatial uniformity
- *Must* make gross assumption on electron energy distribution function
- Limited by availability of rate data
- Common practices lead to poor data integrity

$\Rightarrow$ Accuracy limited (in principle) by spatial uniformity and shape of electron energy distribution function
$\Rightarrow$ Accuracy limited (in practice) by availability of rate data, and poor practice in handling the data that we have

Acknowledgement: MMT has been supported by Science Foundation Ireland, under grant numbers 07/IN.1/I907 and 08/SRC/I1411, and by Association EURATOM-DCU

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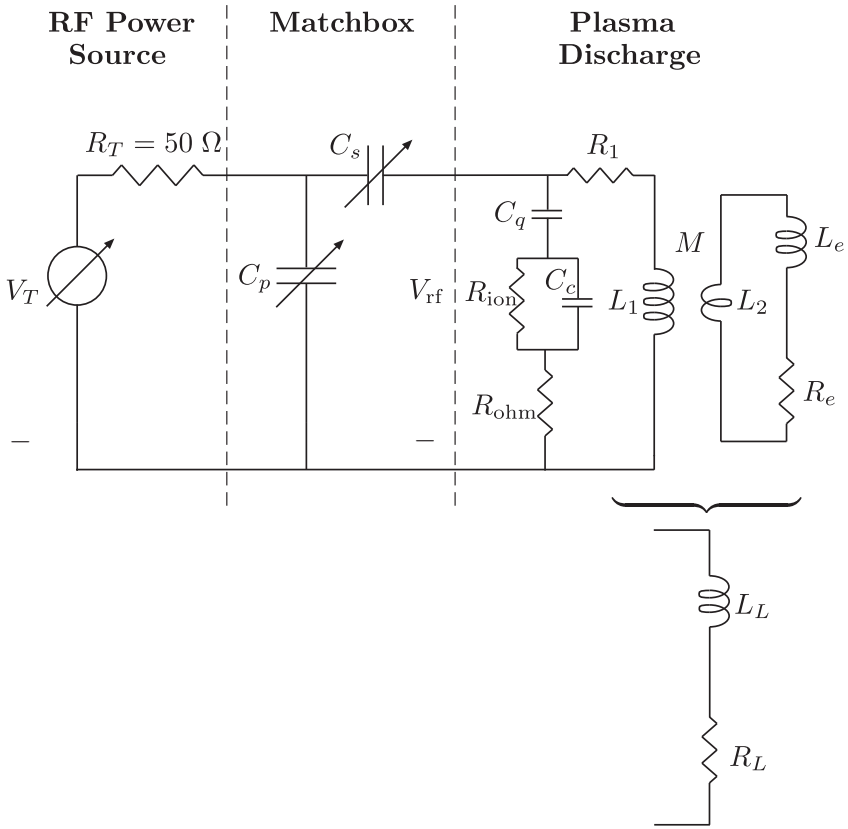
Further Examples: Discharge in Oxygen with Chemistry and Time Dependence

Instability of inductive discharges in electronegative gases.
New things:

- Explicit model for inductive and capacitive power coupling to electrons
- Negative ions
- Time dependent density and electron temperature

Further Examples: Discharge in Oxygen with Chemistry and Time Dependence



$$P_{ind} = \frac{I_{rf}^2 R_{ind} n_e n_{ind}}{n_e^2 + n_{ind}^2}$$

$$P_{cap} = \frac{I_{rf}^2 R_{cap} n_{cap}}{n_e}$$

(Heuristic expressions giving reasonable behaviour, and assuming circuit response allows I_{rf} to be constant)

Further Examples: Discharge in Oxygen with Chemistry and Time Dependence

$$
\begin{array}{ccccc}
O_2 + e & \rightarrow & O_2^+ + 2e & & k_i = k_{i,0} \exp(-\epsilon_i / k_B T_e) \\
O_2 + e & \rightarrow & O^- + O & & k_a = k_{a,0} \exp(-\epsilon_a / k_B T_e) \\
O^- + O_2 & \rightarrow & O + e + O2 & & k_d \\
O^- + O_2^+ & \rightarrow & 3O & & k_r
\end{array}
$$

$$
\begin{array}{rcl}
k_{i,0} & = & 2.13 \times 10^{-14}\ \mathrm{m}^{-3}\ \mathrm{s}^{-1} \\
\epsilon_i & = & 14.5\ \mathrm{eV} \\
k_{a,0} & = & 7.89 \times 10^{-17}\ \mathrm{m}^{-3}\ \mathrm{s}^{-1} \\
\epsilon_a & = & 3.07\ \mathrm{eV} \\
k_r & = & 1.0 \times 10^{-13}\ \mathrm{m}^{-3}\ \mathrm{s}^{-1} \\
k_d & = & 5.0 \times 10^{-18}\ \mathrm{m}^{-3}\ \mathrm{s}^{-1}
\end{array}
$$

N.B. Model values, no necessary connection with any real rate constants, living or dead!

Examples: Discharge in Oxygen with Chemistry and Time Dependence

$$
\begin{aligned}
\Gamma_+ &= u_B n_+ = u_B \left(n_e + n_-\right) \\
\Gamma_e &= \frac{1}{4} n_e \left(\frac{8 k_B T_e}{\pi m_e}\right) \exp\left(-\frac{e\Phi}{k_B T_e}\right) \\
\Gamma_- &= \frac{1}{4} n_- \left(\frac{8 k_B T_-}{\pi m_-}\right) \exp\left(-\frac{e\Phi}{k_B T_-}\right)
\end{aligned}
$$

where

$$\Gamma_e + \Gamma_- = \Gamma_+$$

determines Φ

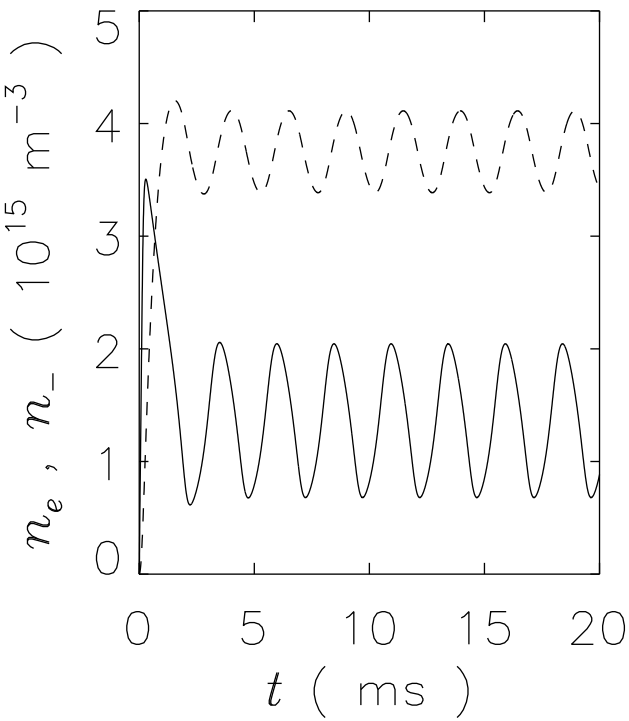
Further Examples: Discharge in Oxygen with Chemistry and Time Dependence

$$
\begin{aligned}
\frac{dn_e}{dt} &= (k_i - k_a) N n_e + k_d N n_- - \Gamma_e A_{eff}/V \\
\frac{dn_-}{dt} &= k_a N n_e - k_r n_- n_+ - k_d N n_- - \Gamma_- A_{eff}/V \\
\frac{dT_e}{dt} &= \frac{2}{3}\frac{P_{abs} - P_{loss}}{n_e} - T_e \frac{1}{n_e}\frac{dn_e}{dt}
\end{aligned}
$$

A_{eff} as in previous examples (questionably)

$P_{abs} = P_{ind} + P_{cap}$

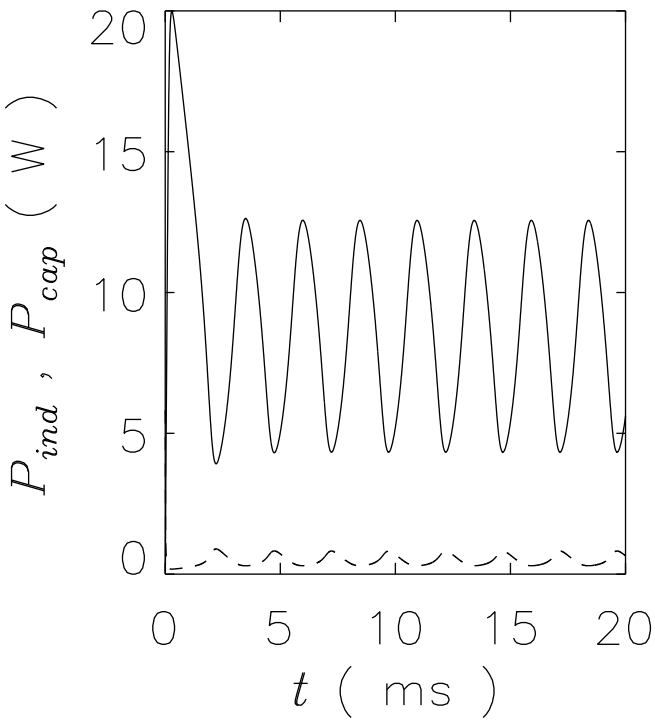
Further Examples: Discharge in Oxygen with Chemistry and Time Dependence



n_e — solid line

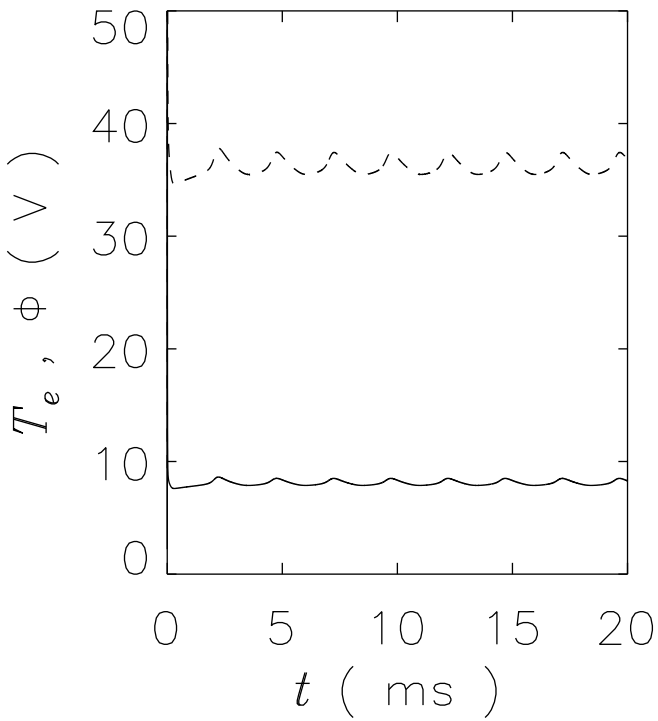
n_- — dashed line

Further Examples: Discharge in Oxygen with Chemistry and Time Dependence



P_{ind} — solid line
P_{cap} — dashed line

Further Examples: Discharge in Oxygen with Chemistry and Time Dependence



T_e — solid line
Φ — dashed line

Further Examples: Discharge in Oxygen with Chemistry and Time Dependence

Linearized equations:

$$\begin{aligned}
\frac{d\tilde{n}_e}{dt} &= \ldots + k_d N \tilde{n}_- + \ldots \\
\frac{d\tilde{n}_-}{dt} &= \left(k_a N - k_r n_-\right) \tilde{n}_e + \ldots \\
\frac{d\tilde{T}_e}{dt} &\approx 0
\end{aligned}$$

Potential oscillation if $k_a N < k_r n_-$

Simple Harmonic Motion equations:

$$\begin{aligned}
\frac{dx}{dt} &= v \\
\frac{dv}{dt} &= -\omega^2 x
\end{aligned}$$

Global Models

Further Examples: Discharge in Oxygen with Chemistry and Time Dependence

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Linearized equations:

$$\frac{d\tilde{n}_e}{dt} = \ldots + k_d N \tilde{n}_- + \ldots$$
$$\frac{d\tilde{n}_-}{dt} = (k_a N - k_r n_-)\,\tilde{n}_e + \ldots$$
$$\frac{d\tilde{T}_e}{dt} \approx 0$$

Potential oscillation if $k_a N < k_r n_-$

Simple Harmonic Motion equations:

$$\frac{dx}{dt} = v$$
$$\frac{dv}{dt} = -\omega^2 x$$

Oscillatory instabilities of this kind occur experimentally and have been widely discussed, see Tuszewski [1996], Chabert et al. [2001]. The model discussed here is too simple to be convincing. Discussion on the details is still in progress in 2012.

Further Examples: Electronegative discharges

Difficulties:

- Negative ions affect Bohm speed
- Discharge may be stratified
- Two regimes:
  1. Detachment dominated: $O^- + O_2(\Delta) \rightarrow O + e + O_2$
  2. Recombination dominated: $O^- + O_2^+ \rightarrow O + O_2$

  each with distinct theoretical character

Global Models

Further Examples: Electronegative discharges

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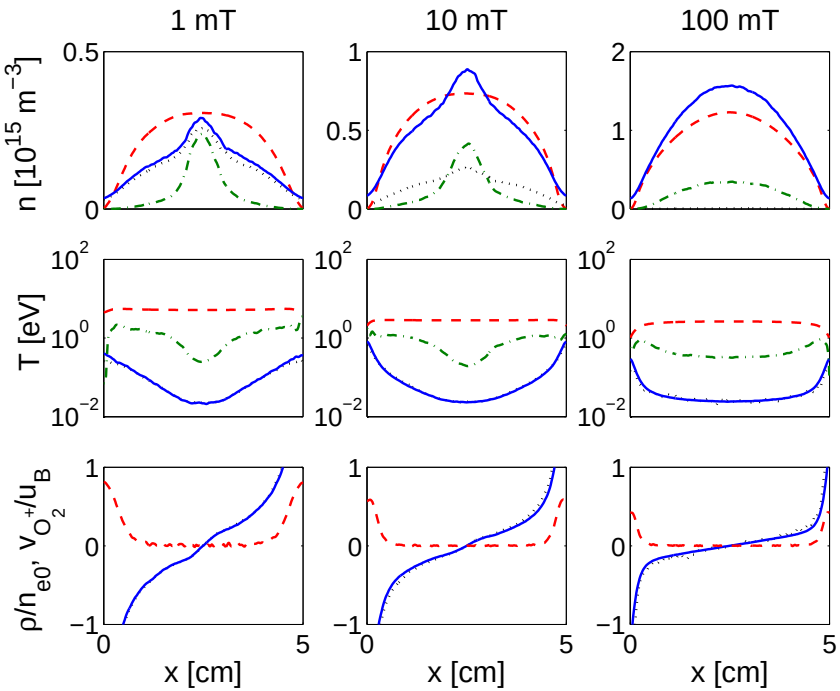
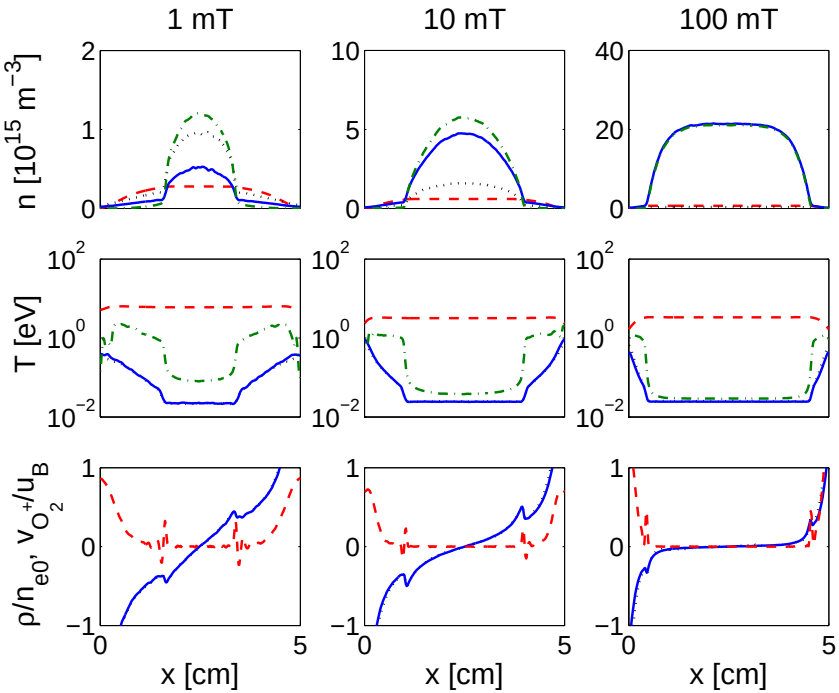
  each with distinct theoretical character

The literature on electronegative discharges is large, controversial, and at times contradictory. See for example works by Edgley and von Engel [1980], Daniels and Franklin [1989], Daniels et al. [1990], Franklin and Snell [1992, 1999], Lichtenberg et al. [2000], Franklin [2001]

Further Examples: Electronegative discharges



Detachment dominated



Recombination dominated

Further Examples: Electronegative discharges

- Is it reasonable at all to capture this complexity in a "global" model?
- There are plausible models applicable to various regimes
- These can be stitched together (not very rigorously) to make a model that usually gives sensible results

Global Models

Further Examples: Electronegative discharges

- Is it reasonable at all to capture this complexity in a "global" model?
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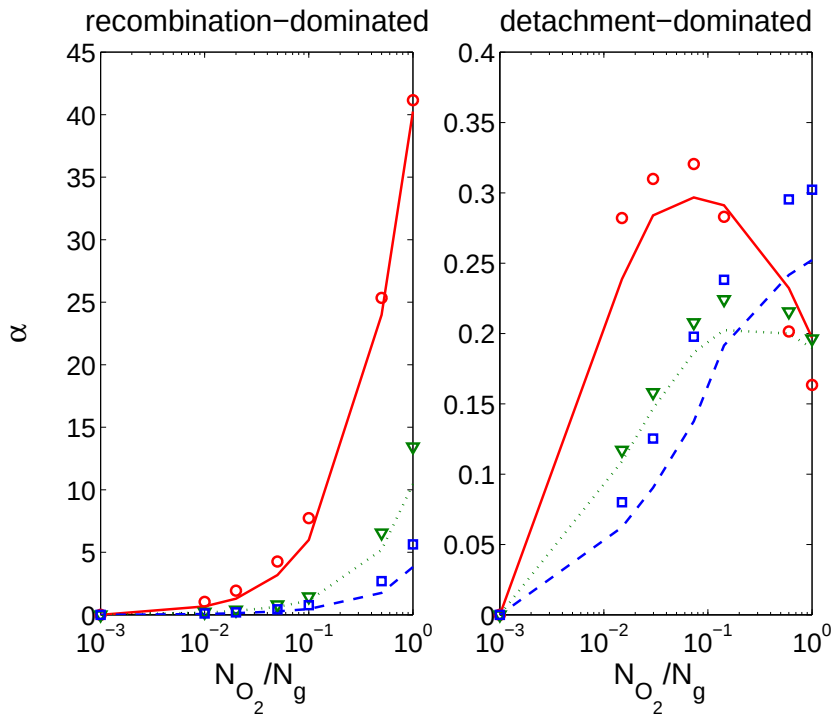
The synthesis suggested here is described by Monahan and Turner [2008].

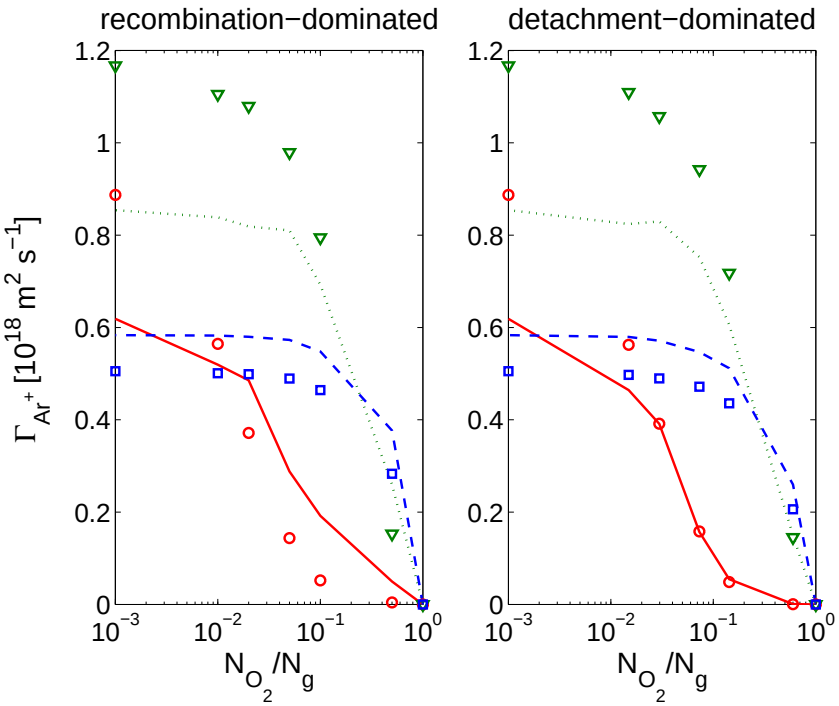
Further Examples: Electronegative Discharges

- How can we test such a model?
- Against a large suite of particle-in-cell simulations
- These simulations are one-dimensional, and nominally for Ar/O_2 mixtures
- The degree of detachment dominance can be manipulated by adjusting the $O_2(\Delta)$ density

Further Examples: Electronegative Discharges



Electronegativity $\alpha = \frac{n_-}{n_e}$



Ar ion flux