Optical Diagnostics of Electron Energy Distributions in Low Temperature Plasmas

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Acknowledgments

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Overview

• introduction

• emission model - relationship between optical spectrum and electron energy

• metastable concentrations from emission spectra

• non-Maxwellian eedfs from inductively coupled plasma emission spectra (and physical mechanism)

• electron temperature from intensity ratio using 2 transitions
LTPs are non-equilibrium systems

\[ e^- (1-10 \text{ eV}) \]
\[ \text{ions (cool)} \]
\[ \text{neutrals (cool)} \]
LTPs are non-equilibrium systems

**Plasma**

EM power input

- $e^-$ (1-10 eV)
- ions (cool)
- neutrals (cool)
LTPs are non-equilibrium systems

EM power input

Plasma

\[ e^- \text{ (1-10 eV)} \]

\[ \text{ions (cool)} \]

\[ \text{neutrals (cool)} \]
LTPs are non-equilibrium systems

Plasma

EM power input

- $e^-$ (1-10 eV)
- ions (cool)
- neutrals (cool)
LTPs are non-equilibrium systems

$e^{-} + A \rightleftharpoons$

Plasma

$e^{-}$ (1-10 eV)

ions (cool)

neutrals (cool)
LTPs are non-equilibrium systems

Plasma

EM power input

\[ e^- (1-10 \text{ eV}) \]

\[ \text{ions (cool)} \]

\[ \text{neutrals (cool)} \]

collisions with high energy e\textsuperscript{-} drive:

* excitation (glow)
* ionization (sustains plasma)
* high-T chemistry in low-T gas

\[ e^- + A \rightarrow \]
LTPs are non-equilibrium systems

EM power input

Plasma

\[ e^- (1-10 \text{ eV}) \]

| ions (cool) | neutrons (cool) |

\[ e^- + A \rightarrow \]

*collisions with high energy $e^-$ drive:*

*excitation (glow)*

*ionization (sustains plasma)*

*high-T chemistry in low-T gas*
LTPs are non-equilibrium systems

EM power input

Plasma

$e^- (1-10 \text{ eV})$

------------------

ions (cool)

neutrals (cool)

collisions with high energy $e^-$ drive:

• excitation (glow)
• ionization (sustains plasma)
• high-T chemistry in low-T gas

e^- + A \rightarrow
LTPs are non-equilibrium systems

EM power input

Plasma

$e^{-}$ (1-10 eV)

- ions (cool)
- neutrals (cool)

$e^{-} + A \rightarrow$

* collisions with high energy $e^{-}$ drive:
  - excitation (glow)
  - ionization (sustains plasma)
  - high-T chemistry in low-T gas
LTPs are non-equilibrium systems

EM power input

Plasma

$e^- (1-10 \text{ eV})$

-------------

ions (cool)

neutrals (cool)

collisions with high energy $e^-$ drive:

- excitation (glow)
- ionization (sustains plasma)
- high-T chemistry in low-T gas

$e^- + A \Rightarrow$

• electrons are key link in process outcomes
Electron energy distribution functions

- Maxwellian EEPF appears as straight line - equilibrium
- ICP: EEDFS with ‘depleted’ high energy ‘tails’ seen by many
  - Attributed to:
    - Inelastic collisions
    - Escape to walls
- Energetic electrons important!
  - Ionization
  - Gas phase chemistry

From Godyak et al., PSST 11, 523 (2002)
Argon emission spectrum

- Ultimate Goal: use emission spectra to extract encoded EEDF details
Ar energy level diagram

- Allowed transitions resulting in photon emission
Inductively coupled plasma

- Operates in Ar or Ar/Ne at 13.56 MHz
- Electron energy distribution functions (EEDF)
  - Langmuir probes
  - optical diagnostics
Emission model

- **Goal:**
  - photon emission rate for $i \rightarrow j$

- **Approach:**
  - account for mechanisms that populate emitting state - level $i$
Emission model

- Goal:
  - photon emission rate for \( i \rightarrow j \)

- Include:
  - electron excitation from level \( l \)
    - excitation probability function of electron energy
Emission model

• **Goal:**
  - photon emission rate for \( i \rightarrow j \)

• **Include mechanisms for populating level \( i \):**
  - electron excitation from level \( l \)
  - radiation trapping: excitation of metastables by photon absorption
Emission model

- **Goal:**
  - photon emission rate for $i \rightarrow j$

- Include mechanisms for populating level $i$:
  - indirect electron excitation from level $l$
  - cascades from higher lying states
Emission model

- Goal:
  - photon emission rate for \( i \rightarrow j \)

- Include mechanisms for populating level \( i \):
  - electron excitation:
    - from ground state
    - from metastable level
Emission model

- cross section vs. electron energy
  - measure of electron impact excitation probability
  - key link between emission intensity and EEDF
  - measured by Chun Lin’s group:
    - excitation from ground state
      - *Ar. Data Nucl. Data Tables* 93, 831 (2007)
    - excitation from ground state
Emission model

- **Goal:**
  - photon emission rate for \( i \rightarrow j \)

- **Include:**
  - electron excitation from level \( l \)
    - cascades
    - metastable contribution
  - radiation trapping of \( 2p_x \leftrightarrow 1s_y \)

- **Inputs**
  - atomic data (\( A_{ij} \), cross sections,...)
  - electron energy distribution function
  - number densities (ground state, \( 1s_y \))
Radiation trapping

- emissions absorbed by Ar \(1s_y\) atoms
- resulting excited atoms re-emit photons
  - re-emission spectra includes multiple levels according to “branching ratios”
  - rate of reabsorption greater for stronger lines
    - *emissions redistributed among lines*

- Account for redistribution with correction factor \(R_{ij}\)

\[
R_{ij} = \frac{g[k\lambda_{ij}\rho] \sum_l A_{il}}{\sum_l g[k\lambda_{ij}\rho] A_{il}}
\]

- \(R_{ij} = 1\) for no reabsorption
- \(R_{ij} < 1\) for strongly reabsorbed lines
- \(R_{ij} > 1\) for weaker lines enhanced by reabsorption of strong lines

\[
g(k\rho) = \frac{2 - e^{-k\rho/1000}}{1 + k\rho}
\]
Excitation from resonance levels $1s_2$ & $1s_4$

- $1s_2$ and $1s_4$ populations significant due to radiation trapping
  - metastables:
    - no radiative losses
    - high concentrations
  - resonance levels:
    - have radiative decay channel to ground state
    - leads to lower concentrations
    - exception: reabsorption when ground state density is high
  - *Electron impact excitation from resonance levels significant*
    - cross sections not measured
    - estimates used
Emission model

\[ \Phi_{ij} = K n_e R_{ij} \left[ \sum_l n_l k^l_{ij} \right] \]

- sum over initial level \( l \) (ground state, 1s_2, 1s_3, 1s_4, 1s_5)
- reabsorption correction factor \( R_{ij} \) is function of 1s_y concentrations
- \( k^l_{ij} \) is the electron impact excitation rate
  - depends on cross sections, EEDF

\[ k^l_{ij} = \sqrt{\frac{2}{m_e}} \int_0^\infty Q^l_{ij}(E) f_e(E) \sqrt{E} dE \]

- use ratios to standard line to eliminate \( K, n_e \)

\[ \frac{\Phi_{ij}}{\Phi_{i'j'}} = \frac{R_{ij} \sum_l n_l k^l_{ij}}{R_{i'j'} \sum_l n_l k^l_{i'j'}} \]

- calculate line ratios for multiple trial EEDFs
- seek EEDF giving best match to observed line ratios
Trials for Maxwellian EEDF

- minimum $\chi^2$ gives best fit electron temperature

![Graph showing reduced $\chi^2$ vs. $T_e^{OES}$ (eV)]

- $T_e^{OES} = 2.4$ eV at 15 mTorr
- $T_e^{OES} = 5.5$ eV at 2.5 mTorr
Emission model predictions

- contributions from ground state vs. $1s_y$ levels

**2.5 mTorr**
\[ T_{\text{eff}} = 5.4 \text{ eV} \]
\[ n_m/n_0 = 1.4 \times 10^{-3} \]

**15 mTorr**
\[ T_{\text{eff}} = 2.7 \text{ eV} \]
\[ n_m/n_0 = 3.2 \times 10^{-4} \]
Inductively coupled plasma source

- 2.5 turn flat coil antenna
- 13.56 MHz
- 50 cm diameter chamber

<table>
<thead>
<tr>
<th>gas</th>
<th>variable</th>
<th>pressure (mTorr)</th>
<th>Power (W)</th>
<th>$n_e$ (cm$^{-3}$)</th>
<th>$T_e$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>pressure</td>
<td>1-25</td>
<td>600</td>
<td>$10^{10}$-$10^{12}$</td>
<td>2-6</td>
</tr>
<tr>
<td>Ar</td>
<td>power</td>
<td>2.5, 15</td>
<td>20-1000</td>
<td>$10^9$-$10^{12}$</td>
<td>5, 3</td>
</tr>
<tr>
<td>Ar/N$_2$</td>
<td>0-86% N$_2$</td>
<td>2.5, 15</td>
<td>600</td>
<td>$10^{10}$-$10^{11}$</td>
<td>5, 3</td>
</tr>
<tr>
<td>Ar/Ne</td>
<td>1-40% Ar</td>
<td>10</td>
<td>600</td>
<td>$10^{10}$-$10^{11}$</td>
<td>3-6</td>
</tr>
<tr>
<td>Ne</td>
<td>pressure</td>
<td>5-25</td>
<td>600</td>
<td>1-3 $\times$10$^{10}$</td>
<td>5-7</td>
</tr>
</tbody>
</table>
Ground state density

- $n_0 = \frac{kT_{\text{gas}}}{p}$
- gas temperature determined with laser absorption spectroscopy
- Doppler width of $3p^54s - 3p^54p$ transition line

![Diagram of experimental setup]

- External-cavity Diode laser
- Wave meter
- Photodiode
- Plasma
- Inductively-coupled 13.56 MHz plasma, 2.5-turn antenna

![Graphs showing wavelength and gas temperature vs. pressure]
Optical emission spectroscopy (OES)

- 300-1600 nm wavelength range
- 0.13 nm resolution
- Detectors:
  - PMT 300-870 nm
  - Ge detector: 300-1600 nm
OES also produces $x = 1.2$

- emission model agrees well with measurement*

Measurement of $1s_y$ concentrations

- **Method #1: optical absorption spectroscopy (OAS)**
  - white light absorption
  - column density measurement
- **Method #2: OES (next slide)**

![Graph showing transmission vs. wavelength for 25 mTorr and 1.0 mTorr]
Metastable/resonant densities from OES

- compare OES vs. OAS measurement methods
- OES preferable due to simplified instrumentation
- OES technique:
  - takes advantage of reabsorption by $1s_y$ metastable and resonance levels
  - reabsorption changes branching fraction
  - use ratio of lines from same upper state
    \[ \frac{\Phi_{ij}}{\Phi_{ij'}} = \frac{A_{ij}^0}{A_{ij'}^0} \frac{g[ij(n_j)]}{g[ij'(n_{j'})]} \]
  - extract set of $n_j$ densities from fit of model to observed ratios of different line pairs
Metastable/resonant densities from OES

- OES method works over wide parameter range
EEDF from Langmuir probe

\[ f_e(V) = \frac{2m_e}{e^2 A} \sqrt{\frac{2eV}{m_e}} \frac{d^2 I}{dV^2} \]

- compare to emission model output

\[ f_e(V) = \frac{2m_e}{e^2 A} \sqrt{\frac{2eV}{m_e}} \frac{d^2 I}{dV^2} \]

![Graph of Electron Density vs. Pressure](image1.png)

![Graph of Electron Temperature (T_{eff}) vs. Pressure](image2.png)

10 cm

inductively-coupled 13.56 MHz plasma
2.5-turn antenna
Comparison assuming Maxwellian EEDF

- \( T_e \) computed from
  - emission model
  - Langmuir probe fit
  - *agreement not great*

- reason for poor fit
  - EEDF is *not* Maxwellian
  - emission model: lower \( T_e \) needed to suppress ground state contribution
  - *actually, EEDF “tail” is depleted compared to Maxwellian*

- other (less likely) possibilities:
  - incorrect \( n_i \) values
  - incorrect cross sections
Non-Maxwellian EEDF

- Langmuir probe measurement in ICP shows tail depletion

![Graph showing electron energy distribution function (EEDF) with probe measurement and Maxwellian fit. The graph depicts the electron energy in electron volts (eV) on the x-axis and the electron energy density (EEPF) in cm$^{-3}$ eV$^{-3/2}$ on the y-axis. The graph includes data for 20 mTorr and 600 W.]
EEDF tail depletion

- impact of ‘missing’ energetic electrons greater for excitation from ground state

![Graph showing electron energy distribution function (EEPF) and Maxwellian fit.]

- EEPF (cm$^{-3}$ eV$^{-3/2}$) vs. Electron Energy (eV)
- Probe measurement
- Maxwellian fit
- Ground state threshold
- 'missing' electrons
Representing EEDF in emission model

- Goal: account for non-Maxwellian energy dependence
- use “generalized x-form”

\[ f_x(E) = c_1 T_x^{-3/2} \sqrt{E} e^{-c_2 (E/T_x)^x} \]

- \( T_x \) is an effective electron temperature (\( T_x = 2/3 <E> \))
- \( c_1 \) and \( c_2 \) are functions of \( x \)
- \( x=1 \) corresponds to a Maxwellian
- \( x=2 \) corresponds to a Druyvesteyn
- \( x \)-form good fit for most ICP conditions
EEDF with $x=1.2$

- $x=1.2$ fits Ar probe data well up to $\sim 25$ mTorr
- $x$ increases above 25 mTorr to about $x=1.6$ at 50 mTorr
OES results for non-Maxwellian EEDF

- using $x=1.2$ improves agreement between OES and probes

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Ar pressure dependence

- Comparison of a) Maxwellian and b) $x=1.2$ form for
  - Probes (solid)
  - OES (open)
  - ‘global’ model (line)
- Global model
  - Volume averaged
  - Particle balance – ionization rate must match wall losses
Electron energy distribution function

- For the ICP EEDF, we seek
  - quantitative representation
  - physical justification

- Generalized \((x, T_x)\) form
  - \(x=1\) for Maxwellian
  - \(x=2\) for Druyvesteyn
  - \(T_x = 2/3 <E>\)

\[
f_x(E) = c'_1 T_x^{-3/2} \sqrt{E} e^{-c'_2 (E/T_x)^x}
\]

- Our probe, optical data yield \(x \sim 1.2\) over wide range of operating parameters
Electron confinement: 1D

- $V_p = \text{sheath voltage}$
- $E_e > V_p$: unconfined
- Produces ‘truncated’ Maxwellian in 3D?
- Not observed experimentally
Electron confinement: 1D

- $V_p =$ sheath voltage
- $E_e > V_p$: unconfined
- Produces ‘truncated’ Maxwellian in 3D?
- Not observed experimentally
Electron confinement in 3D

Depends on both:
- Electron energy
- Direction of motion

$E_e > eV_p$:
- Necessary condition for escape
- Not sufficient - some electrons with $E_e > eV_p$ are confined

- To escape, need $E_e > eV_p$ in direction normal to wall
Electrostatic confinement: electron velocity space picture

- Plasma bounded by rectangular ‘box’
- $V_p$ is plasma potential relative to walls
- For isotropic distribution, shaded area defines fraction of confined electrons

Sphere = constant electron energy, $E_e > eV_p$

Electrons moving normal to walls in “loss cone” escape*

Electron confinement factor: cartesian

- Analytic function multiplies Maxwellian:

\[ c_{f-3D\text{cart}}(E;V_p) = \begin{cases} 
1 & \text{for } E < eV_p \\
3 \sqrt{eV_p/E} - 2 & \text{for } eV_p \leq E \leq \sqrt{2} eV_p 
\end{cases} \]

- Corrected distribution:
  - \( f(E, V_p) = c_f(E, V_p) f_{\text{Max}}(E) \)

- Further correction needed for \( E > \sqrt{2} eV_p \)
Electron confinement factor: cylindrical

- Electron velocity space
- System with cylindrical walls
- Analytic correction for isotropic velocity distribution

\[ u_z^{\text{limit}} = \sqrt{\frac{2eV_p}{m_e}} \]

\[ u_r^{\text{limit}} = \sqrt{\frac{2eV_p}{m_e}} \]

\[ c_f^{\text{3D}}(E; V_p) = \begin{cases} 
1 & \text{for } E < eV_p \\
\sqrt{eV_p/E} - \sqrt{1 - eV_p/E} & \text{for } eV_p \leq E \leq 2eV_p \\
0 & \text{for } E > 2eV_p 
\end{cases} \]
$V_p$ oscillates in time for rf plasma

- Time averaged corrected Maxwellian fits $x=1.2$ form
Increase in $x$ with pressure

- Energetic electron losses due to inelastic collisions increase with pressure leads to enhanced EEDF tail depletion.
$T_e$ comparison at higher pressures

- assuming $x=1.5$ for $25 < p < 50$ (mTorr) improves agreement
Extension to Ar(3p$^5$5p) emissions - limitations

- 3p$^x$ levels have longer radiative lifetimes than 2p$^x$ levels
  - 2p$^x$ levels: 20-35 ns
  - 3p$^x$ levels: 80-160 ns

- Longer radiative lifetime increases chances of electron-atom collision while atom is in excited level
  - electron-quenching: non-radiative decay out of level
  - electron-transfer: excitation from 3p$^x$ to another 3p$^x$’ level
  - emissions redistributed
  - need modified emission model

- Cross sections not measured for excitation from resonance levels - must use theoretical estimates
Emission model including 2p and 3p

- improved agreement with probe (7%), vs. 12% with 2p alone
Can we obtain $T_e$ with single line ratio?

- 419.8 and 420.1 nm - close in wavelength
- make use of difference between ground state and metastable cross sections

$T_{eff} \approx 5.9$ eV exc. from gs

$T_{eff} \approx 2.8$ eV exc. from $3p^54s$

419.83 nm $3p_5$ 420.07 nm $3p_9$
Emission model predictions

• We sought a simple relation between line ratio and $T_e$

• Not so simple in practice:
  - excitation depends on $n_m/n_0$ and $n_r/n_0$
  - electron quenching/transfer depends on $n_e$

• Family of curves rather than single universal curve

![Graph showing line ratio vs. $T_{x=1.2}$ (eV) for different electron densities and excitation ratios.](image)
$T_e$ from 420.1/419.8 nm line ratio

- ±12% accuracy
Conclusions

• Non-Maxwellian EEDFs captured using Ar emissions for wide range of ICP conditions

• “x-form” of EEDF
  ▪ captures EEDF tail depletion
  ▪ good match between methods and global model
  ▪ range of $x$: 1.2-1.5
  ▪ energetic $e^-$ depletion attributed to inelastic collisions and wall losses

• emission model must include contributions from:
  ▪ excitation to higher lying states followed by cascade
  ▪ metastable excitation
  ▪ reabsorption
  ▪ for longer radiative lifetime, also electron quenching/transfer

• OES can be used to determine $1s_y$ concentrations

• 420.1/419.8 nm line ratio can predict $T_e$ if metastable, resonance and electron densities are known