

# Using Monte Carlo Simulations to Derive Electron Energy Distribution Function (EEDF)

Ivan Sepulveda

Faculty Advisor: Milka Nikolic

Summer 2017- Summer 2019

---

A three-dimensional Monte-Carlo simulation is used to obtain Electron Energy Distribution Function demonstrated by electrons inside low temperature plasma generated in pure argon.

---

## 1 Introduction

Over the past handful of decades the semiconductor industry has consistently miniaturized computer chips but in recent times seems to have hit their limit. The process of using high-speed plasma discharges to create these integrated circuits is known as plasma etching. By studying the properties of plasma, one can hope to be able to improve plasma etching process.

The electron energy distribution function is one of the key properties in understanding low-temperature plasma. One could attempt to experimentally measure the properties of a plasma by inserting a certain tool known as the Langmuir probe. Unfortunately, as soon as the probe is inserted, the properties of the plasma would change.

Theoretically, plasma properties could instead be measured using numerical simulations. Many would initially attempt to solve the Boltzmann equation. Doing so would require variables including number of electron density within the plasma, the element which composes the plasma as well as density of atoms within the plasma, and what types of collisions are possible (i.e. purely elastic, ionization, excitation, etc.).

Another effective approach would be to create a Monte-Carlo simulation. A Monte-Carlo simulation is a method of approximately solving mathematical and physics problems by the simulation of random qualities. In our study we simulate the propagation of electrons through argon plasma. The electrons follow the electric field lines but their collisions with Argon atoms are somewhat random: collision angles as well as the types of collisions it experiences are based off probabilities from previously measured cross sections.

First, this report will cover our theoretical calculations and approach. Afterwards, we will go over the logical and analytical assumptions and calculations and how they are calculated and implemented in the script. Subsequently leading us to explain results obtain from running the script under different conditions by altering variables including propagations allowed and magnitude of the electric field applied. Finally, we will analyze our results and draw upon conclusions and whether or not they agree with both our theory and results measured from outside sources.

## 2 Theory

### 2.1 Plasma description

The word "plasma" comes from a Greek word " $\pi\lambda\alpha\sigma\mu\alpha$ " which means "mold" and it describes the property of ionized gas to follow the shape of vessel where it was generated. To

understand the concept of plasma we first start with the description of the gas consisting of mostly neutral particles (atoms and molecules). Such gas can be made mostly of atoms (inert gases like neon or argon) or of molecules ( $O_2$ ,  $H_2$ ) or even mixtures like air. One of the main characteristics of the neutral gas is that all particles have the same macroscopic properties (energy, temperature, velocity, density...).

When the gas is heated, electrons in atoms and molecules can gain enough energy to break the atomic/molecular bonds and free themselves. This process commonly known as ionization. When only one electron is stripped from the atom/molecule, the atom/molecule is singly ionized, when two electrons are stripped the particle is doubly ionized and so forth. If the electron doesn't gain enough energy to break the atomic/molecular bond it may jump to an empty orbital at higher energy level of the atom/molecule. This process is called excitation. Electrons cannot stay long in excited energy levels (about  $10^{-9}$  s) and will radiate down to lower energy levels while emitting photons of energy equal to the energy initially gained. Electron transitions from some energy levels are not allowed by laws of quantum mechanics and these energy levels are called metastable levels. Electrons in these metastable states can go back to ground state only during the collision between two atoms/molecules through a process a known as quenching. In addition, the free electrons can also collide with atoms/molecules and either elastically scatter off of the particles or ionize or excite the given particle. This heated gas consisting of neutral particles, excited particles, positive ions, negative ions, and free electrons that is overall still neutral is called plasma.

Plasmas heated to the temperatures higher than 10,000 K have most of their particles ionized and are called high temperature plasmas (stars, tokamak,...). These plasmas are in thermal equilibrium which means that all plasma species (electrons, ions, and neutral particles) have the same temperature (ref. H. Griem, Plasma Spectroscopy (McGraw-Hill, New York, 1964)). On the other hand, each species in the low temperature, nonequilibrium plasmas (heated below 10,000 K) has different properties. The electron temperatures may reach several thousand Kelvins while heavy particles have temperatures similar to room temperature. There are "hot" electrons that collide with plasma species and are capable of exciting and ionizing atoms and molecules, generating in that way new electrons necessary to sustain plasma system and producing a chemically-rich environment. As a consequence, nonequilibrium plasmas have a particular use in the plasma processing industry for applications to plasma cleaning and etching, or to the deposition of thin film layers. Hence, characterizing these discharges (i.e. describing the conditions for their generation, estimating parameters for optimal use, etc.) is of vital importance.

## 2.2 Collision theory

In our study we simulated electron motion inside low temperature argon plasma generated by heating argon gas with radio-frequency (RF) electromagnetic (EM) waves in order to calculate the distribution of electron energies inside the plasma. We applied a DC biased voltage to our plasma in order to create an electric field in the positive x direction. Due to the applied electric field, electrons accelerated within the plasma in the direction opposite to the electric field. Based on the laws of classical mechanics (Newton's 2nd law), we derived the 3D equations of motion of the electron:

$$\sum \vec{F} = e\vec{E} = m_e\vec{a}, \quad (2.1)$$

where  $e = 1.6 \times 10^{-19}$  C is the charge of an electron,  $m_e = 9.1 \times 10^{-31}$  kg is the mass of an electron, and  $\vec{a}$  is the vector acceleration of the electron.

In x direction:

$$a_x = \frac{eE}{m_e} \quad (2.2)$$

$$v_x = v_{0x} + a_x t \quad (2.3)$$

$$x = x_0 + v_{0x}t + \frac{1}{2}a_x t^2 \quad (2.4)$$

In y direction:

$$a_y = 0 \rightarrow v_y = v_{0y} = const \rightarrow y = y_0 + v_{0y}t \quad (2.5)$$

In z direction:

$$a_z = 0 \rightarrow v_z = v_{0z} = const \rightarrow z = z_0 + v_{0z}t \quad (2.6)$$

While moving inside the plasma, electrons could collide with argon atoms or with other electrons. In this study we only included electron collisions with argon atoms while the electron-electron collisions were neglected. There are two types of collisions that the electron could undergo:

- Elastic collision - where the total kinetic energy of the system electron-argon atom is conserved.
- Inelastic collision - where the fraction of the electron's initial kinetic energy is lost in the collision. The lost energy could be used to heat the system, deform argon atoms, ionize or excite the argon atoms etc.

Our simulation includes probabilities for these types of electron collisions: elastic scattering off of the argon atom, ionization or excitation of the argon atom, or no collision at all. The probability for a certain collision is calculated based on an experimentally measured cross-section for given collision. A detailed description on how we obtained the probabilities for various collisions is given in subsections below.

During the collision with the argon atom, electron will change its energy and velocity (magnitude and direction). We applied the conservation of momentum and total energy to find electron energy and velocity after the collision:

$$\vec{p}_e + \vec{p}_a = \vec{p}'_e + \vec{p}'_a \quad (2.7)$$

$$E_i = E_f + E_a + \Delta E_{loss} \quad (2.8)$$

where  $\vec{p}_e$  and  $\vec{p}_a = 0$  are electron and atom momenta before the collision,  $\vec{p}'_e$ , and  $\vec{p}'_a$  are electron and atom momenta after the collision,  $E_i$  is electron initial kinetic energy,  $E_f$  is electron's kinetic energy after the collision,  $E_a$  is the kinetic energy of the argon atom after the collision, and  $\Delta E_{loss}$  is the energy lost during the inelastic collision (to ionize or excite the argon atom).

Let's assume that the electron traveling in positive z-direction ( $\vec{v}_i = (0, 0, v_i)$ ) collides with the stationary argon atom and scatters at angles  $\theta$  and  $\phi$  in 3D, see Fig. 2.1. The electron velocity after the collision in spherical coordinates is given as

$$\vec{v}_f = v_f \cos\phi \sin\theta \hat{\mathbf{i}} + v_f \sin\phi \sin\theta \hat{\mathbf{j}} + v_f \cos\theta \hat{\mathbf{k}} \quad (2.9)$$

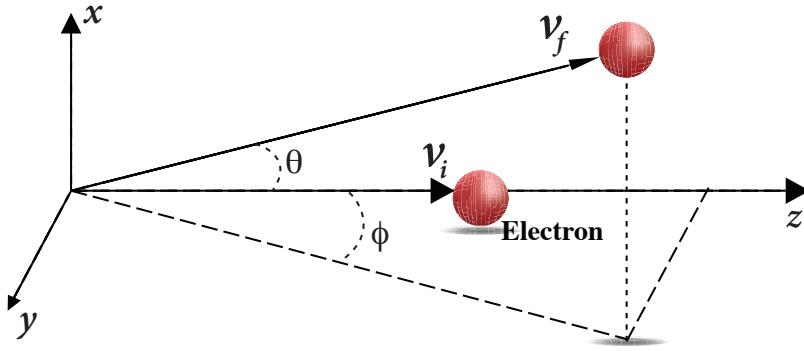


Figure 2.1: Rotated coordinate system with  $v_i$  parallel to z-axis.  $\theta$  and  $\phi$  correspond the angles in standard spherical coordinates.

The conservation of momentum will give us

$$0 = m_e v_f \cos\phi \sin\theta + m_a v_{ax} \rightarrow m_a^2 v_{ax}^2 = m_e^2 v_f^2 \cos^2\phi \sin^2\theta \quad (2.10)$$

$$0 = m_e v_f \sin\phi \sin\theta + m_a v_{ay} \rightarrow m_a^2 v_{ay}^2 = m_e^2 v_f^2 \sin^2\phi \sin^2\theta \quad (2.11)$$

$$m_e v_i = m_e v_f \cos\theta + m_a v_{az} \rightarrow m_a^2 v_{az}^2 = m_e^2 (v_i - v_f \cos\theta)^2 \quad (2.12)$$

Adding the three equations leads to

$$m_a^2 v_a^2 = m_e^2 v_i^2 + m_e^2 v_f^2 - 2m_e^2 v_i v_f \cos\theta \quad (2.13)$$

We can substitute  $v_a$  in the equation for the conservation of energy

$$\frac{1}{2} m_e v_i^2 = \frac{1}{2} m_e v_f^2 + \frac{1}{2} m_a v_a^2 + \Delta E_{loss} \quad (2.14)$$

and solve for the magnitude of the electron velocity after the collision

$$v_i^2 - \frac{m_e}{m_a} v_i^2 - \frac{2\Delta E_{loss}}{m_e} = \frac{m_e}{m_a} v_f^2 + v_f^2 - \frac{2m_e}{m_a} v_i v_f \cos\theta \quad (2.15)$$

The general solution has a pretty complex form:

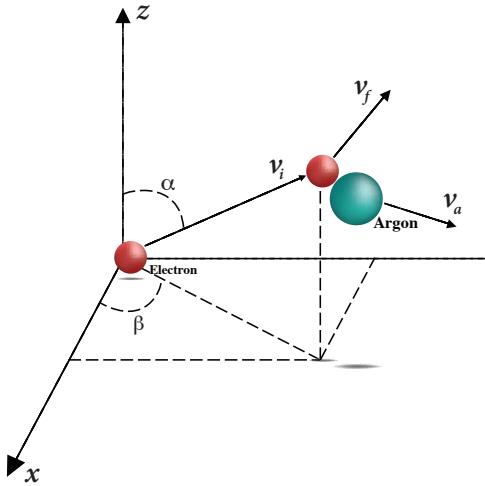
$$v_f \sqrt{1 + \frac{m_e}{m_a}} = \frac{m_e}{m_a} \frac{v_i}{\sqrt{1 + \frac{m_e}{m_a}}} \cos\theta + \sqrt{v_i^2 - \frac{m_e}{m_a} v_i^2 - \frac{2\Delta E_{loss}}{m_e}}, \quad (2.16)$$

but since  $m_e \ll m_a$ , the equation can be simplified to

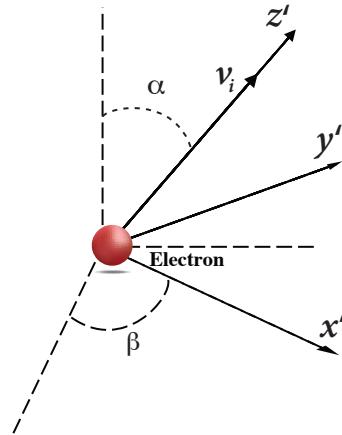
$$v_f = \sqrt{v_i^2 \left(1 - \frac{2m_e}{m_a} (1 - \cos\theta)\right) - \frac{2\Delta E_{loss}}{m_e}}. \quad (2.17)$$

In general, the initial velocity of the electron can be in any direction ( $\vec{v}_i = (v_i, \alpha, \beta)$ ) so in order to obtain the direction of the final velocity of the electron we will first rotate the coordinate system about  $\alpha$  and  $\beta$  to align  $\vec{v}_i$  with z-axis, as shown in (reference figures) By applying rotation matrices we get

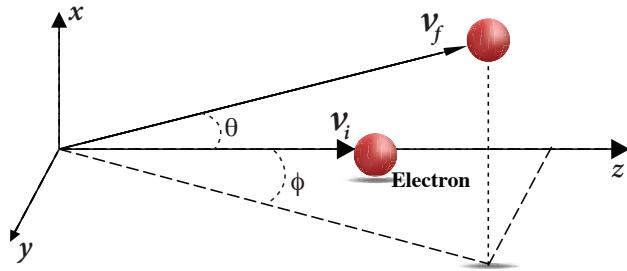
$$\vec{v}'_i = R_y(\alpha) R_z(\beta) \vec{v}_i = v_i \begin{pmatrix} \cos\alpha & 0 & -\sin\alpha \\ 0 & 1 & 0 \\ \sin\alpha & 0 & \cos\alpha \end{pmatrix} \begin{pmatrix} \cos\beta & \sin\beta & 0 \\ -\sin\beta & \cos\beta & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \sin\alpha \cos\beta \\ \sin\alpha \sin\beta \\ \cos\alpha \end{pmatrix} \quad (2.18)$$



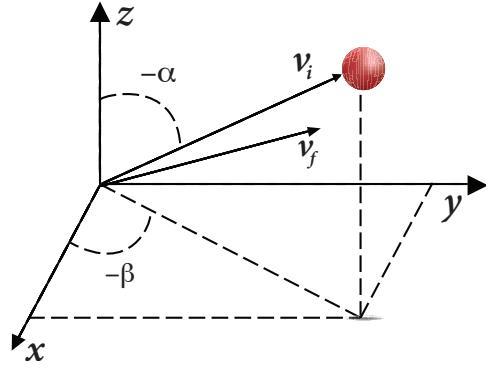
(a) SubFigure One of Four



(b) SubFigure Two of Four



(c)  $\phi$  is defined as the angle made by the projection of  $V_f$  on the ZY-Plane while  $\theta$  is the angle between  $V_i$  and  $V_f$ .



(d) We now revert back to our original coordinate system by rotating by  $-\alpha$  and  $-\beta$

Figure 2.2: Collision Illustrations

$$\vec{v}_i' = v_i \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \quad (2.19)$$

Then we will rotate  $\vec{v}_i'$  about  $\theta$  and  $\phi$  to find the direction of  $\vec{v}_f$ ,

$$\vec{v}_f = R_z(-\phi)R_y(\theta)\vec{v}_i' = v_i \begin{pmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos\theta & 0 & \sin\theta \\ 0 & 1 & 0 \\ -\sin\theta & 0 & \cos\theta \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \quad (2.20)$$

$$\vec{v}_f = v_i \begin{pmatrix} \sin\theta \cos\phi \\ \sin\theta \sin\phi \\ \cos\theta \end{pmatrix} \quad (2.21)$$

We take into account the change in speed calculated in Eq. 2.17 and rotate the coordinate system back about  $-\alpha$  and  $-\beta$  to original orientation

$$\vec{v}_f = R_z(-\beta)R_y(\alpha)\vec{v}_f = v_f \begin{pmatrix} \cos\beta & -\sin\beta & 0 \\ \sin\beta & \cos\beta & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos\alpha & 0 & \sin\alpha \\ 0 & 1 & 0 \\ -\sin\alpha & 0 & \cos\alpha \end{pmatrix} \begin{pmatrix} \sin\theta \cos\phi \\ \sin\theta \sin\phi \\ \cos\theta \end{pmatrix} \quad (2.22)$$

$$\vec{v}_f = v_f \begin{pmatrix} \sin\alpha \cos\beta \cos\theta - \sin\beta \sin\phi \sin\theta + \sin\theta \cos\alpha \cos\beta \cos\phi \\ \sin\alpha \cos\beta \cos\theta + \sin\beta \sin\theta \cos\alpha \cos\phi - \sin\theta \cos\beta \sin\phi \\ -\sin\alpha \sin\theta \cos\theta + \cos\alpha \cos\theta \end{pmatrix} \quad (2.23)$$

We also ran our simulation in two dimensions using the same approach. Conservation of momentum in 2D

$$m_e v_i = m_e v_f \cos\theta + m_a v_{ax} \rightarrow m_a^2 v_{ax}^2 = m_e^2 (v_i - v_f \cos\theta)^2 \quad (2.24)$$

$$0 = m_e v_f \sin\theta + m_a v_{ay} \rightarrow m_a^2 v_{ay}^2 = m_e^2 v_f^2 \sin^2\theta \quad (2.25)$$

Adding the two equations leads to

$$m_a^2 v_a^2 = m_e^2 v_i^2 + m_e v_f^2 - 2m_e^2 v_i v_f \cos\theta \quad (2.26)$$

It is obvious that Eq. 2.26 is equal to Eq. 2.13, which means that the final velocity of the electron in 2D can be found using the same equation as in 3D, Eq. 2.17.

For the electron traveling at an angle  $\alpha$  relative to x-axis, the direction of the final velocity is

$$\vec{v}'_i = v_i \begin{pmatrix} \cos\alpha & \sin\alpha \\ -\sin\alpha & \cos\alpha \end{pmatrix} \begin{pmatrix} \cos\alpha \\ \sin\alpha \end{pmatrix} = v_i \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad (2.27)$$

$$\vec{v}_f = v_i \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = v_i \begin{pmatrix} \cos\theta \\ \sin\theta \end{pmatrix} \quad (2.28)$$

$$\vec{v}_f = v_f \begin{pmatrix} \cos\alpha & -\sin\alpha \\ \sin\alpha & \cos\alpha \end{pmatrix} \begin{pmatrix} \cos\theta \\ \sin\theta \end{pmatrix} = v_f \begin{pmatrix} \cos(\alpha + \theta) \\ \sin(\alpha + \theta) \end{pmatrix} \quad (2.29)$$

## 2.3 Structure of Argon Atom

To better understand complexity of argon kinetics it is necessary to first establish an understanding of the Ar atom structure. When in ground state, argon has an electron configuration  $1s^2 2s^2 2p^6 3s^2 3p^6$  with shorthand notations  $3p^6 1S_0$  and total angular momentum  $J = 0$ . From the ground state, electrons in Ar atom can be excited to higher energy levels when enough energy is added to the system. An electron transition between two energy levels is most likely to happen when the added energy is equal to the energy difference between two levels [5]. Because of the atomic fine structure, the first excited state,  $3p^5 4s$  consists of 4 energy levels while the second excited state consists of 10 levels. In this work we will use Paschen notation for Ar structure due to its simplicity. Table 1 presents electron configuration of neutral Ar atom (Ar I) for the first 15 energy levels together with the Paschen notation for each corresponding level.

Paschen label	Level	J	Energy (eV)
ground	$3p^6 \ ^1S_0$	0	0.0
$1s_5$	$4s[3/2]_2 \ ^3P_2$	2	11.55
$1s_4$	$4s[3/2]_1 \ ^3P_1$	1	11.62
$1s_3$	$4s'[1/2]_0 \ ^3P_0$	0	11.72
$1s_2$	$4s'[1/2]_1 \ ^1P_1$	1	11.83
$2p_{10}$	$4p[1/2]_1 \ ^3S_1$	1	12.91
$2p_9$	$4p[5/2]_3 \ ^3D_3$	3	13.08
$2p_8$	$4p[5/2]_2 \ ^3D_2$	2	13.09
$2p_7$	$4p[3/2]_1 \ ^3D_1$	1	13.15
$2p_6$	$4p[3/2]_2 \ ^3P_2$	2	13.17
$2p_5$	$4p[1/2]_0 \ ^3P_0$	0	13.27
$2p_4$	$4p'[3/2]_1 \ ^1P_1$	1	13.28
$2p_3$	$4p'[3/2]_2 \ ^1D_2$	2	13.30
$2p_2$	$4p'[1/2]_1 \ ^3P_1$	1	13.33
$2p_1$	$4p'[1/2]_0 \ ^1S_0$	0	13.48

Figure 2.3: Cross Section schematics

The first excited,  $4s$ , levels with  $J = 1$ , ( $1s_2$  and  $1s_4$ ) satisfy the selection rules and decay very fast in the ground state ( $J = 0$ ) with radiative life times of 1.96 ns and 8.4 ns, respectively [5] (Right Source?). These levels are called resonant levels. Optical transitions from the levels with  $J = 2$ , ( $1s_5$ ) and  $J = 0$ , ( $1s_3$ ) are electric dipole forbidden and electrons in these states cannot decay back to ground state by emitting a photon (radiative decay). This leads to very long life times of these states (about  $10^{-4}$  s). These states are called metastable levels. Atoms in these states decay back to ground state mostly through collisions with the other argon atoms in ground states. This process is called collisional quenching. Metastable atoms play an important role in characterization of plasmas. Due to their high energy and long life time they are considered an important energy reservoir, which could be transmitted to the rest of plasma particles by collisional processes.

The most dominant processes in low temperature argon plasmas are the electron excitations to the second excited ( $2p$ ) energy levels during the electron collision with the argon atoms in the ground and the first excited ( $1p$ ) states [6]. Resonant  $1s$  levels depopulate to ground state quickly by emitting a photon, thus the probability of an electron colliding with Ar atom in the resonant state is negligible and is not included in study. On the other hand, due to their long life time, metastable levels contribute significantly to the collision processes in plasma. For that reason, our model included the possibility of an electron colliding with the argon atoms in both ground and metastable states and then exciting that atom to the second excited state ( $2p$  level).

In addition, this work included the possibility of an electron being elastically scattered off of the ground state argon atoms as well as the possibility of electron ionizing the ground state argon atoms. **Only if we add e - e collisions: Lastly, we also included a possibility of an electron colliding with another free electron in plasma.** All other collisional processes are excluded from this study, due to their low probability.

In the next few sections, we will describe the process to obtain the probabilities for the collisional processes included in this study.

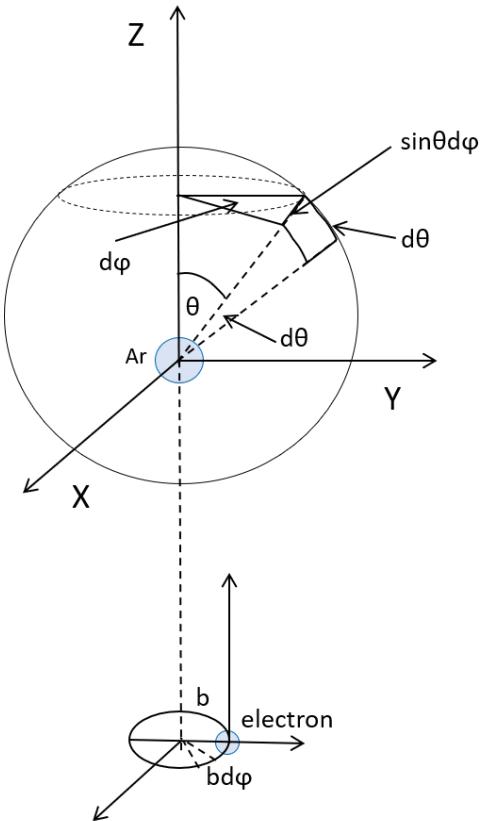


Figure 2.4: Cross Section schematics

## 2.4 Cross Sections

Collisional cross-section is the fundamental quantity to describe a collision. It is the probability for a given process to happen and is defined as the area around colliding particles within which they must meet in order to collide with each other. Therefore the cross-section is given in the units of area [ $\text{m}^2$ ].

To fully understand the meaning of the cross-section let's imagine an electron with energy  $\varepsilon$ , traveling in the positive z-direction. The electron scatters off of an argon atom positioned at the coordinate beginning, as shown in Fig. 2.4. We can define impact parameter,  $b$ , as the perpendicular distance to the closest approach if the electron were undeflected. Then the differential size of the cross section is the area element in the plane of the impact parameter

$$d\sigma = b db d\phi \quad (2.30)$$

After the collision, the electron will scatter at an angle  $\theta$ . The differential angular range of the scattered electron is the solid angle element

$$d\Omega = \sin\theta d\theta d\phi \quad (2.31)$$

The ratio of  $d\sigma$  by  $d\Omega$  is called a differential cross-section. The differential cross-section determines the area within which electron's path would need to pass in order for it to scatter into a range of angles  $d\theta$ . We can calculate the integrated (total) cross-section by integrating differential cross-section over all possible angles [1]:

$$\sigma(\varepsilon) = \int \frac{d\sigma}{d\Omega} d\Omega = \int \frac{d\sigma}{d\Omega} \sin\theta d\theta d\phi = 2\pi \int_0^\pi \frac{d\sigma}{d\Omega} \sin\theta d\theta \quad (2.32)$$

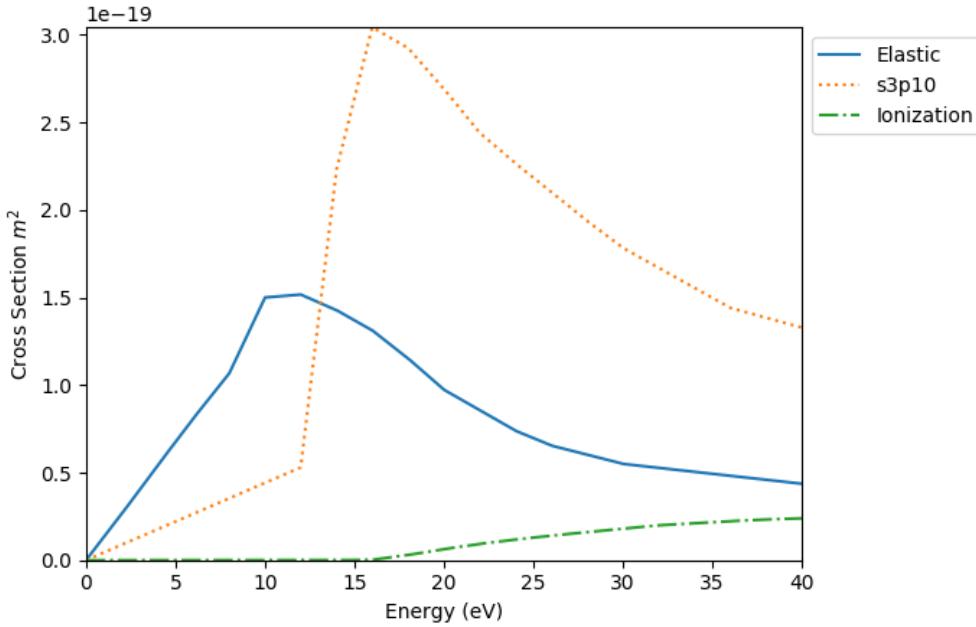


Figure 2.5: Cross Section as a function of electron energy for various collisions  
 -Dotted orange line: sum of all cross sections for inelastic excitation collisions [2, 3]  
 -Solid blue line: cross sections for elastic scattering off Ar Atom [4]  
 -Dash-dot green line: cross section for ionization inelastic excitation collisions [4]

Depending on the type of the collision, we distinguish between cross-sections for elastic and inelastic collisions. In this study, we considered cross-sections for elastic scattering of an electron off of a neutral argon atom, cross-sections for electron impact inelastic collisions in which argon atom was singly ionized, and electron impact excitation cross-sections from ground and first excited argon energy levels (4s states) to second excited energy levels (4p states).

Available experimental and theoretical cross-sections from the argon metastable (4s) levels are very sparse. Further more, even among available cross-sections there is a disagreement by a factor 2-4 between the results. In this study we used experimental cross-sections from [2, 3, 4]. Figure 2.5 shows an example of cross-sections for elastic scattering, ionization, and electron impact excitation. **Here you will explain what is in the figure 2.5. State that excitation cross-section has the highest value (highest probability for collision at energy equal to excitation energy while ionization cross-section has pretty much constant value once we were above the threshold for ionization.**

## 2.5 Collision Frequencies

Once we know the cross-sections for the collisions, we need to find how often collisions happen. The number of collisions the electron undergoes in 1 s is proportional to the number of argon atoms (more atoms means more collisions), cross – sections (higher probability for collision means more collisions), and the speed or energy of the electron (more energy means more collisions). For that purpose, we defined a collision frequency:

$$f(\varepsilon) = N_A \sigma(\varepsilon) v = N_A \sigma(\varepsilon) \sqrt{\frac{2\varepsilon}{m_e}} \quad (2.33)$$

where  $N_A$  is the number of argon atoms per unit volume (population density),  $\sigma(\varepsilon)$  is the cross – section, and  $v$  is the electron's speed. The speed of the electron can be found from electron's

kinetic energy,  $\varepsilon = \frac{1}{2}mv^2$ , where  $m_e$  is the mass of the electron. The units of the collision frequency are Hz ( $s^{-1}$ ).

We can also find the total (cumulative) collision frequency as a sum of all collision frequencies:

$$f_{total} = \sum_{j=1}^n f_j \quad (2.34)$$

where  $n$  is the number of collision possibilities included in the model (i.e.  $f_1$  – elastic scattering,  $f_2$  – ionization,  $f_3$  – excitation from level 1 to 2, and so forth).

## 2.6 Null Collision Frequency

Depending on the probability for the collision it may happen that no collision occurred during one step. This is best seen if we add all collision frequencies and plot them as functions of electron energy. For simplicity, let's just discuss three possible collisions (elastic scattering, ionization and excitation). To express the collision frequency for the excitation in the example below, we summed up all collision frequencies for all possible excitation processes. In our simulation we, of course, dealt with collision frequency for each excitation process individually.

Each collision frequency is calculated from the provided cross – sections and the density of plasma. We presented these values in Table 1.

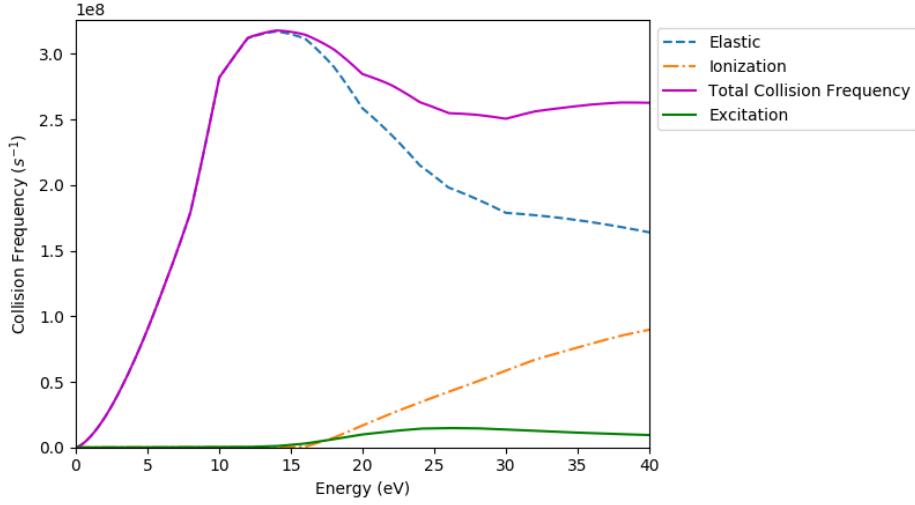
Energy (eV)	elastic ( $\times 10^8 s^{-1}$ )	excitation ( $\times 10^8 s^{-1}$ )	ionization ( $\times 10^8 s^{-1}$ )	total ( $\times 10^8 s^{-1}$ )	null ( $\times 10^8 s^{-1}$ )	tot+null ( $\times 10^8 s^{-1}$ )
0	0	0	0	0	3.180	3.180
5	0.896	0.001	0	0.897	2.284	3.180
10	2.815	0.002	0	2.817	0.363	3.180
14	3.171	0.010	0	3.180	0	3.180
15	3.149	0.019	0.002	3.171	0.009	3.180
20	2.585	0.099	0.167	2.850	0.330	3.180
25	2.068	0.145	0.383	2.596	0.584	3.180

Table 1: Collision frequencies for elastic scattering, ionization and excitation including the null collision frequency.

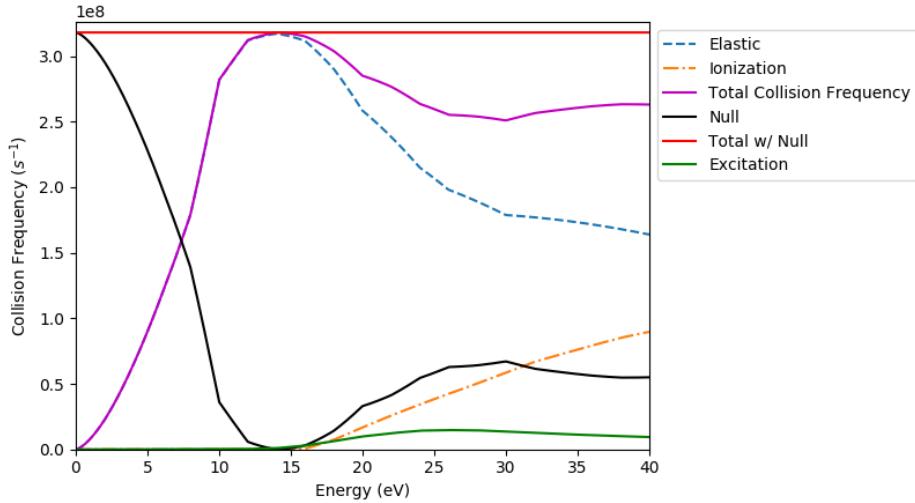
It can be seen that total collision frequency changes for each electron energy. We can assume that at maximum total collision frequency (in this table  $3.180 \times 10^8 s^{-1}$  at 14 eV) one of the three possible collisions had to happen. But at all other energies there was a probability that none of the collisions happened since total frequency is less than  $3.180 \times 10^8 s^{-1}$ . We can assign frequency to this no collision case and call it NULL collision frequency. Null collision frequency can be found as a difference between maximum total frequency at all energies and total frequency for collisions at a given energy (column 6 in the table):

$$f_{null}(E) = [f_{total}]_{max} - f_{total}(E) \quad (2.35)$$

This way, for each energy there is an equal total probability that one of the collisions or no collisions will happen (last column in the table). This will normalize sum of all cumulative probabilities to 1 (there is a 100 percent chance that something will happen). The difference between including the null collisions frequency and not in the calculations can be seen in the Fig. 2.6.



(a) Collision frequency as a function of energy



(b) Collision frequency as a function of energy with null collision

Figure 2.6: Collision Frequency as a function of electron energy for various collisions

- Solid Purple: Total Collision Frequency
- Dashed Blue: Elastic Collision Frequency
- Dash-dot orange line: Ionization Collision Frequency
- Solid green line: Total Collision Frequency for all Excitation Collisions
- Solid black line: Null Collision Frequency
- Solid red line: Null Collision Frequency + Total Collision Frequency

## 2.7 Cumulative Probabilities

There are different ways to calculate probabilities for the certain processes to happen during the collision. We will use a cumulative probabilities approach. We can state that the probability for process 1 (i.e. elastic scattering) to happen be:

$$P_1 = \frac{f_1}{[f_{total}]_{max}} \quad (2.36)$$

where we included the null collision frequency. A cumulative probability for either process 1 (i.e. elastic scattering) or process 2 (i.e. ionization) to happen is then

$$P_2 = \frac{f_1 + f_2}{[f_{total}]_{max}} \quad (2.37)$$

And so forth. A cumulative probability for any of the collisions 1, 2 or 3 to happen is

$$P_3 = \frac{f_1 + f_2 + f_3}{[f_{total}]_{max}} \quad (2.38)$$

In general, a cumulative probability for  $j$  number of processes to occur is

$$P_j(E) = \frac{\sum_{l=1}^j f_l}{[f_{total}]_{max}} \quad (2.39)$$

This means that the cumulative probability for any of all possible processes to occur should be 1. Which makes sense, something has to happen (elastic scattering, ionization, excitation, or no collision).

The order of summation is not important. Note that for each energy of the electron we need to recalculate these probabilities. For example, the figure below, Fig. 2.7 shows an example of different probabilities for collisions. Here again, for the explanation purposes, we summed up probabilities for all excitation processes and represented them as one probability for excitation.

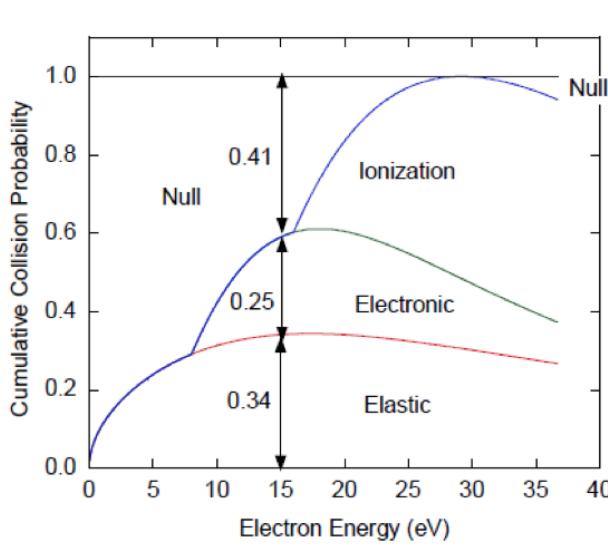


Figure 2.7: Temporary Placeholder

It can be seen from the figure that at 25 eV there is 65% chance that elastic scattering will happen. The cumulative probability is calculated from

$$P_1 = \frac{f_1}{[f_{total}]_{max}} = \frac{2.068}{3.180} = 0.65 \quad (2.40)$$

Cumulative probability for excitation or elastic scattering to happen will be:

$$P_2 = \frac{f_1 + f_2}{[f_{total}]_{max}} = \frac{2.068 + 0.145}{3.180} = 0.70 \quad (2.41)$$

If we want to find just the probability for process 2(excitation), then probability =  $0.70 - 0.65 = 0.05$ . There is only a 5% chance that the excitation would happen when the electron has 25 eV.

Cumulative probability for ionization to happen will be:

$$P_3 = \frac{f_1 + f_2 + f_3}{[f_{total}]_{max}} = \frac{2.068 + 0.145 + 0.383}{3.180} = 0.82 \quad (2.42)$$

Just the probability for ionization is then: probability =  $0.82 - 0.70 = 0.12$ . There is a 12% chance that the electron would ionize argon atom at 25 eV. All that is left is a probability for no collision to happen. In this example it is  $1 - 0.82 = 0.18$ .

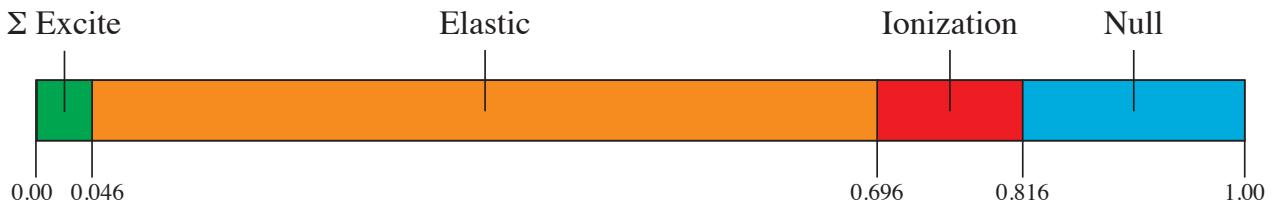


Figure 2.8: Probabilities for an electron with 25 eV.

## 3 Code

### 3.1 Code Structure

The code was written as follows.

As can be seen in Figure 3.1 script was split into two main processes: running the simulation and plotting subsequent results. The former requires many more requisites: in order to create, propagate, and collide the electron, we first need to determine which collision the electron will experience any at all. Probabilities for each collision type will depend on the electrons energy just before impact. Our simulation is accurate up to two decimal points for electron energy in units of electron volts. Unfortunately we run into an obstacle since the cross sections provided are given in multiples of two. By running a quick script to linearly interpolate these cross sections given in the DAT files we overcome this obstacle. Plotting the results is a bit more straightforward. Specific python libraries allow us to quickly create a scatterplot for Energy Distribution as well as the locations of the collisions experienced. One could even sacrifice computational runtime and plot the path experienced by every single electron.

How does it work in a code?

Treat the null frequency as a regular collision frequency (for no collision to happen) and calculate the new total collision frequency that would be equal for all energies. Then calculate cumulative probabilities for each process (collisions and no collision and continue as we already discussed).

Code: Choose a random number  $r_2$  between 0 and 1.

- If  $r_2 \leq P_1$  then process 1 (elastic scattering) will happen.

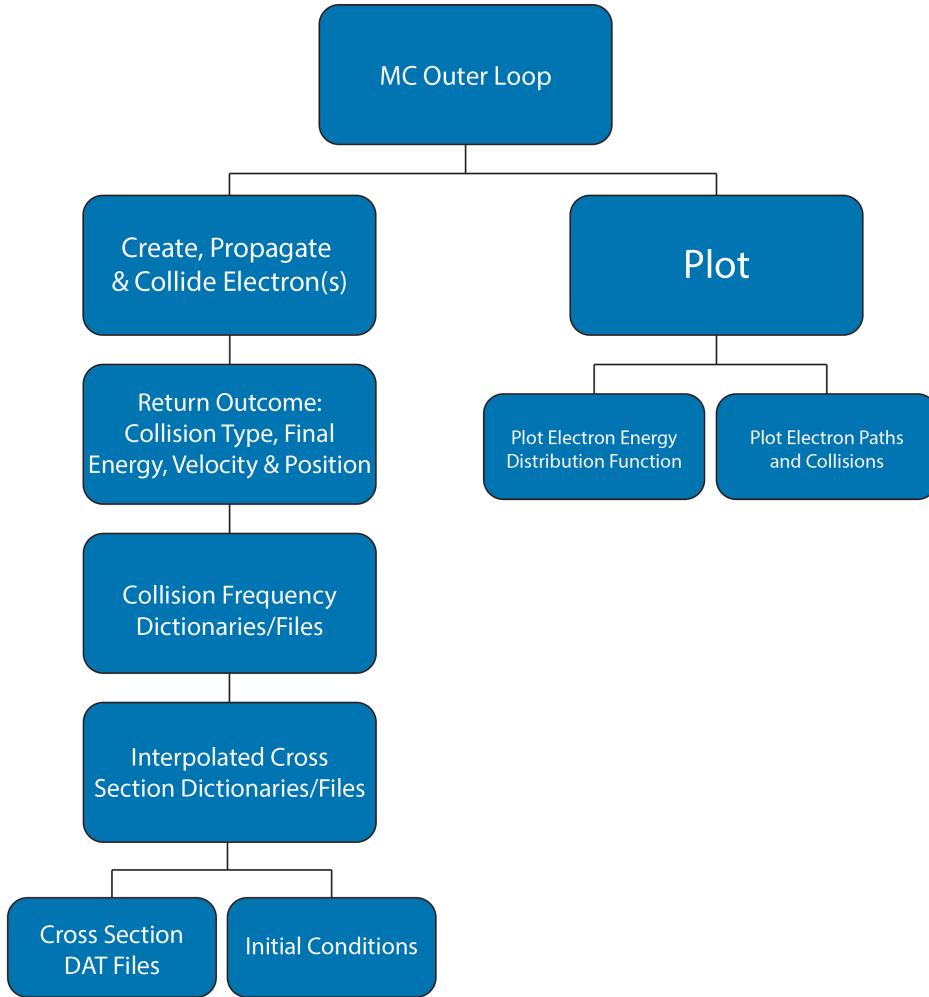


Figure 3.1: Code Structure

- If  $P_1 \leq r_2 \leq P_2$  then process 2 (excitation) will happen.
- If  $P_2 \leq r_2 \leq P_3$  then process 3 (ionization) will happen.
- If  $r_2 < P_3$  then no collision will happen

From the figure we can see that the probability for process 1 (elastic scattering in this picture) to happen is:  $P_1 = 0.29$ . Remember, we are calculating cumulative probabilities so the probability for process 1 or process 2 (excitation in this picture) to happen is:  $P_2 = 0.29 + 0.13 = 0.42$ . And finally, the probability for any of the three processes to happen is:  $P_3 = 0.29 + 0.13 + 0.58 = 1$ .

Code: Choose a random number  $r_2$  between 0 and 1.

- If  $r_2 \leq P_1$  then process 1 (elastic scattering) will happen.
- If  $P_1 \leq r_2 \leq P_2$  then process 2 (excitation) will happen.
- If  $P_2 \leq r_2 \leq P_3$  then process 3 (ionization) will happen.

## 3.2 Calculating Time of Flight

Given the plasma's particle density and the electrons energy, it's time of flight (TOF) can be calculated. Here we define our TOF to be the time interval between collisions. We calculate

our TOF as  $\Delta t$  in equations 3.1 - 3.2 as a function of Total Collision Frequency (TCF) and  $r$ , a randomly generated float between 0 and 1. Unfortunately we run into an issue at first propagation. Because initial energy is set at 0 eV,  $TCF = 0$ . This is corrected by applying a condition such that if the electron has less than 0.01eV, it's  $\Delta t$  will be exactly 100 nanoseconds.

$$E > 0.01\text{eV} : dt = \frac{-\log(1-r)}{TCF} \quad (3.1)$$

$$E \leq 0.01\text{eV} : dt = 10^{-7}\text{s} \quad (3.2)$$

In this simulated experiment, controlled the following parameters of our three dimensional Argon plasma; atom density, electron density, electric field magnitude, and allowed collisions.

We start off by generating some initial conditions. First electron is created its initial position, velocity, and acceleration are set to zero. For simplicity, we round electron mass and charge down to their first decimal:  $m_e = 9.1 \cdot 10^{-31}\text{kg}$ ,  $q_e = 1.6 \cdot 10^{-19}\text{C}$ . We assume that number of argon atoms per unit area is  $N = 10^{21}\text{m}^{-3}$ .

### 3.3 Interpolating Cross Sections

After interpolating all given cross sections and plugging them into eq. 3.3 we find that  $TCF_{Max} = 5,553.813 \cdot 10^6$  at 19.44 eV. At this exact energy, we make it so that the electron has to collide, or in other words at this energy  $f_{null} = 0$  Hz. As displayed in the table below, we see that null frequency quickly starts to increase the within just a few electron volts of the our peak.

$$f = N_A \sigma(\epsilon) \sqrt{\frac{2\epsilon}{m_e}} \quad (3.3)$$

```
def collision_frequency(energy_eV, process_cross_section_dictionary):
    if isnan(energy_eV) or energy_eV > 99.99:
        energy_eV = 99.99
    cf = (2*energy_eV*eV_J/me)**0.5
    cf = cf*process_cross_section_dictionary[iround(ener_eV)]
    cf = cf *argon_volume_density
    return cf

def total_CF(energy, dictionary_of_cs_dictionaries):
    sum = 0
    for processD in dictionary_of_cs_dictionaries:
        sum += collision_frequency(energy, dictionary_of_cs_dictionaries[processD])
    return sum
```

Note: The function "isnan()" is used frequently to filter out values that are neither integers nor floats; this function returns a boolean depending on whether or not "energy\_eV" is a real comprehendable value. At times calculations in Python can become so large or small that a value is no longer considered an integer nor a float so "NaN" values are built-in into Python to prevent system overwhelming. ("NaN" being short for "Not a Number").

After moving the electron in this time according to the equations of motion, you should calculate the new position (x and y) and the new velocity  $v$ . We calculate the magnitude of the velocity as  $v = \sqrt{v_x^2 + v_y^2}$ . Since the only force acting upon the electron is the Coulomb force  $F =$

$qE$ , all the work done by this force will be converted into electron's kinetic energy and is calculated using the standard  $E = \frac{1}{2}m_e v^2$ . where  $v$  is the magnitude of the electron's velocity. Up until the first collision the electron will only have a  $v_x$  component. To determine if the electron collided or not, first we determine its Maximum Total collision frequency and make the assumption that at that energy, the electron has to collide whether it be elastically or inelastic. For every other energy, there will be a null collision frequency (NCF) greater than zero.

### 3.4 Integration

### 3.5 Random Number Generation

## 4 Results

In this study, we simulated the conditions observed in the experiment obtained in the plasma laboratory at Department of Physics and Astronomy, USF. The experiment was conducted in radio-frequency cavity discharge, shown in Fig. 4.1. A commercial RF generator operating at frequency of 13.56 MHz, was used to sustain a cylindrical cavity discharge at powers between 15 – 100 W. The working pressure in the evacuated quartz chamber was kept between 15 and 50 mTorr. The measurements were performed in pure argon that was fed into the chamber through a gas manifold. Gas flow was established by a Agilent technologies rotary vane pump.

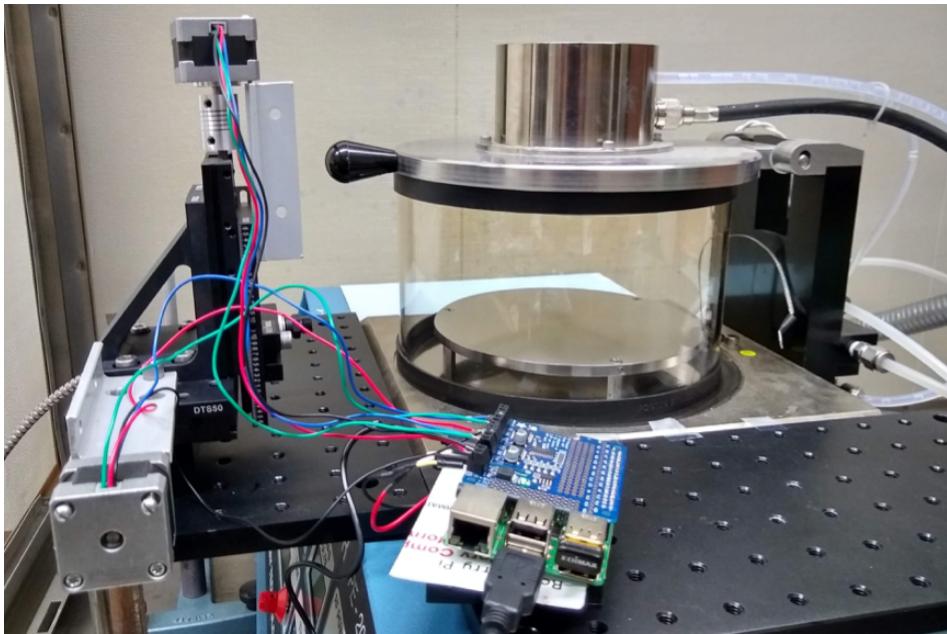


Figure 4.1: Experimental setup

We estimated the gas temperature in plasma to be  $T_g = 500$  K [ref]. The population densities of ground state argon atoms,  $N_g$  were then calculated by employing the ideal gas equation:

$$P = N_g k_B T_g \quad (4.1)$$

$$N_g = \frac{P}{k_B T_g} \quad (4.2)$$

where  $P$  is gas pressure and  $k_B = 1.38 \times 10^{-23}$  J/K is Boltzmann constant. For the values of pressure used in this experiment, population densities varied between  $N_g = 10^{20} - 10^{21}$  m $^{-3}$ . The calculations performed by applying a different numerical method based on the experimental data showed that the population densities of argon metastable,  $4s$  levels, were four orders of magnitude smaller than the ground state populations. Thus, we assumed that they varied between  $N_s = 10^{16} - 10^{17}$  m $^{-3}$ . Finally, we propagated electrons inside the constant electric field oriented in the x – direction. The values of the electric field for which we ran the simulation varied between  $E_x = 10 - 50$  V/m.

We obtained the distribution of electrons relative to their energies,  $f(\varepsilon)$ . In order to be able to compare our results with published work, we normalized the distribution function such that

$$\int_0^\infty F(\varepsilon) d\varepsilon = 1 \quad (4.3)$$

Since in our simulation, we had discrete values of binned energy the integral became the sum

$$\sum_0^n F(\varepsilon) \Delta\varepsilon = 1 \quad (4.4)$$

To normalize the function, we divided by its norm,

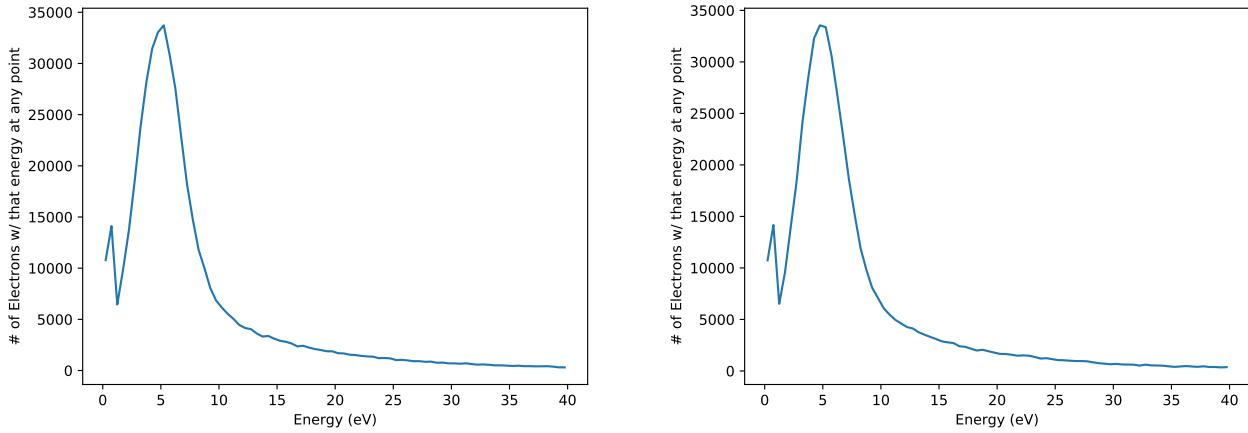
$$F(\varepsilon) = \frac{f(\varepsilon)}{\sum_0^n f(\varepsilon) \Delta\varepsilon} \quad (4.5)$$

Note that the units of the normalized EEDF are [eV $^{-1}$ ]. Besides EEDF, the results can be expressed using another function named electron energy probability function (EEPF) that is related to EEDF as

$$G(\varepsilon) = \varepsilon^{-1/2} F(\varepsilon). \quad (4.6)$$

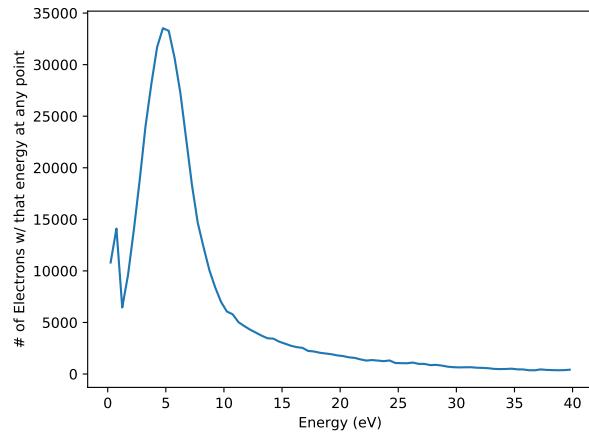
Obviously, the units of EEPF are [eV $^{-3/2}$ ].

Figure 4.2 shows EEDF calculated for  $N_g = 10^{21}$  m $^{-3}$ ,  $N_s = 10^{17}$  m $^{-3}$  and various external electric fields.



(a)  $5 \times 10^5$  Propagations,  $E_{Reduced} = 10\text{V/m}$

(b)  $5 \times 10^5$  Propagations,  $E_{Reduced} = 25\text{V/m}$



(c)  $5 \times 10^5$  Propagations,  $E_{Reduced} = 50\text{V/m}$

Figure 4.2: Electron Energy Distribution Functions of a Variety of Conditions

We compared our work to the work of [5, 6]. Hagelaar *et al* solved the Boltzmann equation by expanding the solution into a series of Legendre polynomials and taking only the first two expansion terms. Their work is published in a free software BOLSIG+ [5]. Boffard *et al* studied the global model of EEDF that would cover the region of electron energy distribution as it varied from Maxwellian to become Druyvesteyn like. Such a distribution is called a two-parameter distribution and its general form is

$$F_x(\varepsilon) = C_1 T_x^{-3/2} \sqrt{(\varepsilon)} e^{-C_2(\varepsilon/T_x)^x} \quad (4.7)$$

where

$$C_1 = x \left( \frac{2}{3} \right)^{3/2} \frac{[\Gamma(5/2x)]^{3/2}}{[\Gamma(3/2x)]^{5/2}} \quad (4.8)$$

$$C_2 = \left( \frac{2}{3} \right)^x \left[ \frac{\Gamma(5/2x)}{\Gamma(3/2x)} \right]^x \quad (4.9)$$

with  $\Gamma(y)$  being a Gamma function of  $y$  and  $T_x = T_e$  representing the effective electron temperature defined as 2/3 of the average electron energy,  $\langle \varepsilon \rangle = \frac{3}{2}T_e$  where electron temperature is expressed in electron volts (eV). The average energy of the electrons can be found from the distribution function as

$$\langle \varepsilon \rangle = \int_0^\infty \varepsilon F(\varepsilon) d\varepsilon \quad (4.10)$$

Thus,

$$T_e = \frac{2}{3} \int_0^\infty \varepsilon F(\varepsilon) d\varepsilon \quad (4.11)$$

We calculated EEDF for various reduced electric fields and then used it to determine the effective electron temperature for the given E/N from Eq. 4.11. Here you will plot the relationship between Te and reduced field like fig.10 on my dissertation)

## 5 Acknowledgements

This work was supported by the University of San Francisco.

## References

- [1] M. A. Lieberman and A. J. Lichtenberg, *Principles of Plasma Discharges and Materials Processing* (Academic Press, New York, 1994).
- [2] A. Dasgupta, M. Blaha, and J. L. Giuliani, Phys. Rev. A, **61**, 012703 (1999).
- [3] D. M. Filipovic, B. P. Marinkovic, V. Pejcev, and L. Vuskovic, J. Phys. B: At. Mol. Opt. Phys. **33**, 677 (2000).
- [4] A. V. Phelps and L. C. Pitchford, Phys. Rev. A, **31**, 2932 (1985).
- [5] G. J. M. Hagelaar and L. C. Pitchford, Plasma Sources Sci. Technol. **14**, 722 (2005).
- [6] J. Boffard, R. O. Jung, C. C. Lin, and A. E. Wendt, Plasma Sources Sci. Technol. **19**, 065001 (2010).

## A Appendix: Conversion of physical units

In this work we expressed pressure in units of Torr rather than Pascals (Pa). Torr is related to Pascal as  $1 \text{ Torr} = 133.3 \text{ Pa}$

$$1 \text{ Torr} = 133.3 \text{ Pa} \quad (\text{A.1})$$

In order to compare our data with other published work, we expressed our results in terms of the reduced electric field too. The reduced electric field is defined as the electric field over the population density of all plasma particles. Since in low temperature plasmas (similar to the

experiment that we are simulating) majority of particles are in the ground state, it is safe to assume that the reduce electric field is

$$\frac{E}{N} = \frac{E}{N_g} \quad (\text{A.2})$$

where  $N_g$  represents the populations density of the ground state particles. The units of the reduced electric filed can be derived as

$$\frac{E}{N} = \frac{\text{V}}{\text{m}^{-3}} = \text{Vm}^2 \quad (\text{A.3})$$

Additionally, we expressed reduced electric field in units of Townsends rather than Volts times meter squared as,

$$1 \text{ Td} = 10^{-21} \text{ V} \cdot \text{m}^2 \quad (\text{A.4})$$

## B Appendix: Comparing Our Results to Similar Studies

Once you obtain EEDF  $f(\epsilon)$  as a function of number of electrons – find its sum and multiply with the binned energy  $\Delta\epsilon$ :

$$\sum_0^n f(\epsilon)\Delta\epsilon \quad (\text{B.1})$$

Then divide your  $f(\epsilon)$  by this norm to obtain normalized EEDF  $F(\epsilon)$

$$F(\epsilon) = \frac{f(\epsilon)}{\sum_0^n f(\epsilon)\Delta\epsilon} \quad (\text{B.2})$$

BOLSIG+

Open bolsig software and load Ar cross-sections. Choose new run and put  $T_g = 500$  K (just like in our simulation) and for reduced electric field you'll need to calculate. If we used only  $N_g = 10^{21} \text{ m}^{-3}$  as in our population densities, then

$$\text{Reduced\_Electric\_Field} = \frac{E}{N_g} \quad (\text{B.3})$$

The same applies for 25 V/m and 50 V/m. Run BOLSIG and export the values for EEDF. They actually calculated the electron energy probability function (EEPF) that is related to EEDF as So, multiply the results for each energy by . Now we can plot both results and compare.

To compare with two parameter approach, use the equation

where  $T_x$  is the electron energy found from the average energy . Here  $T_e$  is given in Kelvins. In plasma physics, we like to express temperature in electron Volts just like energy too. This really means that we multiplied the temperature in Kelvins by the Boltzmann constant given in eV/K and effectively get

where  $k_B$  became part of the temperature.

Average energy of the electrons can be found from the distribution function (recall quantum mechanics class)

Once you calculate EEDF with MC or bolsig, use it to see how much is the electron temperature. Then, use that electron temperature to calculate EEDF from two parameter approach so you can compare.