GASEOUS IONIZATION AND ION TRANSPORT: An Introduction to Gas Discharges

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CHAPTER 1

PREFACE

Gas-phase ions are ubiquitous in the universe, and are often cited as making up more than 99% of known matter [REF-Burnett] in the universe - all stars, for example are in a plasma state consisting of gaseous ions and electrons. However, in every day life on Earth, gaseous ions are not as common and certainly not understood by the general public. If you were to take a poll of the general population about engineering and science topics, nearly everyone would understand what robotics is and most would likely be able to surmise, on some level, what an aerospace engineer does. In fact, most people can probably identify that a car is more aerodynamically sound than a truck. However, if you ask the general population what the ‘plasma’ in plasma television stands for, they would not be able to tell you. Further, most scientists and engineers do not really understand either as plasma science and technology is not a common subject covered by undergraduate students most core disciplines such as mechanical engineering, biochemistry, or materials science. But plasma science is an incredibly important field. Besides entertainment (the aforementioned plasma television), plasmas and their closely related cousin, gas discharges, have been instrumental in modern life, affecting everything from the computer revolution to everyday lighting and transportation. Plasma processing, such as reactive ion etching and sputter metal deposition, has been essential to the development of the modern day computer chip. Automobiles are started by spark plugs, which are, at their heart, gas discharges. Fluorescent lighting and the more recent, energy-efficient compact fluorescent light bulbs found in most homes are gas-discharge lamps. The list could really go on and on, from printers to air filters, from analytical chemistry to manufacturing, plasmas and gas discharges have a profound impact on modern life. Even today, there are promising developments in plasma science such as atmospheric plasma jets for killing tumors and healing wound, microplasma arrays for high efficiency lighting, and plasma thrusters for more efficient space travel. Regardless of how well appreciated plasma science is, it continues to be relevant in a wide-variety of technologies as well as a field of active research and fundamental discovery.

The purpose of this text is to introduce graduate-level engineering and science students to the fundamentals of gaseous ionization and ion transport in order to (a) expand their understanding of the physics behind many key technologies today and (b) prepare them to conduct research both in their graduate career and beyond. At the conclusion of this book, the reader should understand what an ion is, common methods of generating ions, methods of manipulating their motion, and the basic properties of some of the more common discharges used today. Additionally, this book will introduce some choice applications that are of high interest to author as well as emerging topics that will be shaping research in the near and long-term future. That, in sum, is essentially what this book is. It would be prudent, however, to also address what this book isn’t. This book is not a plasma
physics book, and it is not meant to cover all aspects of plasma physics. In fact, if such a book existed that covered all aspects of plasma physics, it would be both extremely dense and extremely large. Rather, this book is focused on specific concepts that are important to non-equilibrium, low temperature discharges. These discharges find wide applicability today and are of significant interest in the scientific community.

I know of no single book that covered all the topics I am interested in, in the depth I am interested in. Therefore, I pulled information from many sources - both textbooks and journal articles. However, because this is essentially a formal collection of class notes, I do not cite these references especially well. Therefore, I’d like to acknowledge these five books that I found especially useful in putting together this manuscript:


This book is a living document, meaning that it will be updated, modified, and corrected as long as I continue to study and teach in this field. Those readers who stumble across this document and find errors, please do send them to me as they are unavoidable. Those who wish to use this text to support their research, appropriate citation would be appreciated. Suggestions on ways to improve it are most welcome.

Best regards,
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Chapter 2

Introduction

Lectures 1-2

The main focus of this manuscript to gain an understanding of gaseous ionization and ion transport in relation to gas discharges. However, for the uninitiated, even these terms may be unfamiliar. Therefore, it is best to begin with a short discussion of the basic concepts.

What is a gas discharge or plasma? A gas discharge is essentially an electrical flow (current) across an interstitial gap of gas — turning the insulating gas into a conductor. (For this reason, it was originally associated with the discharge of a capacitor.) It is characterized by the generation of ions in the gas by an applied electric field (or magnetic field, though that is not of interest here). However, discharges occur in nature as well — the most obvious being lightning. Plasma and gas discharges are closely related and both consist of gaseous ions. There more specific differences will be discussed in Section 2.1.

What is an ion? A gas discharge requires the generation of ions, which is called ionization. But what is an ‘ion’? An ion is an atom or molecule where the total number of electrons is not equal to the number of protons. Therefore, the atom or molecule carries either excess positive charge (# protons ≠ # electrons) or excess negative charge (# electrons ≠ # protons) — thus it is either a positive or negative ion. Electrons themselves are often called negative ions, but for the purposes of this manuscript we will delineate negative ions as an atom or molecule with net negative charge and electrons simply as electrons. (Similarly, we will call positive ions an atom or molecule with net positive charge and protons just protons.)

Why are these ions important? Consider basic electronics. When a voltage drop is applied across a conductor (metal), a flow of electrons (negative charge) is generated. What is voltage? Voltage is merely electrical potential energy so the electrons want to go from ‘high’ potential energy to ‘low’ potential energy - in the same way that a ball wants to roll down a hill due to a gravitational potential energy difference. In the gravitational analog, the potential energy is

\[ U = mg \cdot dy. \]  

The force on mass \( m \) is determined by the spatial derivative of the potential energy, and the familiar form is obtained.

\[ F = -\frac{dU}{dy} = -mg. \]  

Similarly, the electrical potential energy is the voltage (\( \Phi \)) multiplied by charge (\( q \)),

\[ U = q\Phi. \]
The force on charge \( q \) is therefore

\[
F = -\frac{dU}{dx} = -q\frac{d\Phi}{dx} = -qE_x. \tag{2.4}
\]

Here, \( E_x \) is the electric field and \( F \) is the Coulombic force. From this, it is easy to see that the electric field (force) is related to the electric potential by a derivative. More generally, this relationship is a gradient

\[
\vec{E} = -\nabla \cdot \Phi. \tag{2.5}
\]

The potential energy distribution is governed by Poisson’s equation or

\[
\nabla^2 \Phi = -\frac{(n_+ - n_-)}{\epsilon_0}, \tag{2.6}
\]

where \( \epsilon_0 \) is the permittivity of free space \( (\epsilon_0 = 8.85 \times 10^{12} F/m) \). \( n_+ \) and \( n_- \) are the charge concentrations of positive ions and negative ions/electrons, respectively with units of \( [C/m^3] \). (That is, \( n = qN \), where \( N \) is the number density).

So in electronics, the motion of electrons is due to the force from the applied potential energy voltage difference. This induces an electrostatic field \( E \) that drives the charges creating current \( i \), which is nothing more than the time derivative of charge

\[
i = \frac{dq}{dt}. \tag{2.7}
\]

The units of current is charge per unit time or ampere \([A]\), where \([A] = [C/s]\). Typically, we refer to a current density with the symbol \( j \) to indicate current through an area or \([A/m^2]\). \(^1\)

Ions in the gas phase have charge \( q \) and therefore also respond to an applied voltage, which is merely an applied electric field, to form what is called a discharge current. Therefore, one can conclude that the two most important facets of understanding gas discharges are:

1. The creation of charges (ionization).
2. The motion of charges (ion transport).

This manuscript is organized to consider these two concepts separately, though they are intimately connected. After first discussing the basic properties of ions and how they are formed, the motion of ions in a gas will be discussed as this eventually leads to the formation of a gas discharge.

### 2.1 Classification of Gas Discharges

Gas discharges can be broadly classified into two groups \(^2\) based on how they are operated:

**DC Discharges** Direct current (DC) discharges are under the influence of a static electric field

- glow discharge
- corona discharge
- hollow cathode discharge

---

\(^1\)Current density can also be thought of as a current flux - the flux of current through and area - but it is convention to call it current density.

\(^2\)We neglect here magnetically driven discharges as they are not of significant interest in this context.
AC Discharges Alternating current (AC) discharges are under the influence of an unsteady, periodic electric field:

- dielectric barrier discharges
- radio frequency (RF) $10^2 - 10^8 \text{Hz}$ (e.g. capacitively coupled plasma)
- microwave $10^9 - 10^{11} \text{Hz}$
- optical $10^{11} \text{Hz}$

Other types of discharges are also used (e.g., pulsed DC) as well, but are not covered in detail here.

Discharges consist of different types of particles - the background gas (neutral), excited gas particles (neutral), ionized gas molecules (positive and negative ions), and electrons. Each of these species will have some average kinetic energy. Generally, energy $\epsilon$ (Joules, J or electron volts, eV) can also be described by a temperature $T$ (Kelvin, K) using the Boltzmann constant $k_B$,

$$\epsilon = k_B T,$$

where $k_B = 1.3807 \times 10^{-23} J/K = 8.617343 \times 10^{-5} eV/K$. Therefore, discharges can also be classified by their thermodynamic properties:

**Non-Equilibrium, Low Temperature** - also called non-thermal plasmas such as glow discharges, corona discharges, dielectric barrier discharges, and RF discharges

- the temperature (energy) of the electrons is much higher than the temperature (energy) of the gas and ions
- $T_{gas} \sim T_{ion} \sim 10^2 K$; $T_{elec} \sim 10^4 K$

**Equilibrium, Moderate Temperature** - also called thermal plasmas such as arc discharges

- the temperature (energy) of the electrons and the temperature (energy) of the gas and ions are in equilibrium and well above room temperature
- $T_{gas} \sim T_{ion} \sim T_{elec} \sim 10^4 K$ (thermalized arcs, also called thermal plasmas)

**Equilibrium, High Temperature** - thermonuclear fusion

- the temperature (energy) of the electrons and the temperature (energy) of the gas and ions are in equilibrium and well above practical temperatures
- $T_{gas} \sim T_{ion} \sim T_{elec} \sim 10^6 K$

**What is a plasma?** Plasma is often called the 4th state of matter (99% of the universe) and closely tied to gas discharges. A plasma is essentially a gas that consists of free ions and electrons and therefore is electrically conductive, but the overall state of the plasma is charge neutral. Full decomposition typically occurs at very high temperature, whereas at moderate and low (room) temperatures the plasma is partially ionized. A discharge is, in contrast, simply the conduction of current across an insulating gas, but, in practice, a self-sustained discharge typically has a plasma (net neutral) region. The term gas discharge is often used when describing phenomena in the first two categories above (non-equilibrium, low temperature and equilibrium, moderate temperature) but is often used interchangeably with plasma. The term plasma is used exclusively when describing the category at extreme temperatures. In this book, the term discharge will be used preferentially.

---

3This is often semantics though, as a plasma is nothing but a charged gas. Conceptually, as temperature increases a solid turns into a liquid, a liquid into a gas, and a gas into a plasma.

4For example, a glow discharge, dielectric barrier discharge, and corona discharges are all examples of non-thermal plasmas whereas an arc discharge is an example of a thermal plasma.
Part I

Ionization
CHAPTER 3

OVERVIEW

The term ionization broadly refers to the generation of charges (or charge carriers) such that the interstitial gas between two electrodes transforms from a insulator into a conductor. There are essentially two types of processes that are important in the creation of charges. The first are gaseous processes — that is, the charges are created from the gas molecules itself. The second are cathode processes — that is, the charges are created from the solid structure of the electrodes (or, more specifically, the negatively charged cathode) and then the charges are injected into the gas. Generally, the charges of interest are electrons, but because electrons are created during the same process as positive ions, this part is called Ionization.

Both of these two processes will be covered here, including some mechanisms that are generally trivial and not important. In the summary, the important ionization mechanisms for low temperature, non-equilibrium discharges will be highlighted.
Chapter 4

Gaseous Processes

Lectures 2-5

4.1 Gaseous Reactions

Consider a gas that also has some naturally occurring, free electrons. When a potential difference is applied across the gas, the free electrons will be accelerated by the resulting electric field. Along the way, they collide with the interstitial gas atoms or molecules ($M$). These collisions represent chemical reactions and they can be broadly classified into three groups (illustrated in Figure 4.1):

- **Elastic**: $e^- + M \rightarrow e^- + M$
- **Excitation**: $e^- + M \rightarrow e^- + M^* \text{ iff } \epsilon_e \geq E_{M^*}$
- **Ionization**: $e^- + M \rightarrow 2e^- + M^+ \text{ iff } \epsilon_e \geq E_{ion}$

Note that for the excitation and ionization reactions, the kinetic energy of the incident electron $\epsilon_e$ must be greater than or equal to the minimum energy required for excitation $E_{M^*}$ or ionization $E_{ion}$, respectively. Because some of the kinetic energy of the incident electron goes to exciting/ionizing the target atom, these are *inelastic* collisions as compared to the first reaction which is an elastic collision.

One often concludes that the reaction that is most interesting in the context of a discharge is the ionization reaction because it creates a second electron (plus a positive ion) and therefore is the charge producing reaction. However, all of these reactions are essential to the formation of a discharge and in most applications the excitation reaction is the essential reaction as it produces the effect desired of the discharge (such as light). Each of these is considered in a bit more detail below.

4.1.1 Elastic Collisions

The elastic collision is the one that is easiest to conceptualize. The electron and molecule collide like two billiard balls, and all the energy of the collision is maintained (for the most part) as kinetic ...
4.1. Gaseous Reactions

energy — that is, kinetic energy is conserved. In these binary (two-body) collisions, the electron is moving much faster than the molecule, and therefore the gas molecule is typically considered at rest. The electron collides with the molecule and caroms off at a new trajectory. These are the dominant type of collisions and can occur for any kinetic energy of the incident electron $\epsilon_e$.

4.1.2 Excitation Collisions

Consider a gaseous atom or molecule. The atom consists of a core of neutrons and protons and outer shells of electrons. Electron energies are quantized that is, an electron attached to the atom can only exist in discrete energy levels, and these correspond to the filled orbits (shells) of the atom or atoms in the molecule. Consider an oversimplified example:

The orbits of an molecule yield the following possible electron energies: 1 eV, 3 eV, 5 eV, 10 eV, 12 eV. This means that the electron cannot have an energy of 2 eV, 2.5 eV, 10.9 eV, etc.

There are other types of energies in an atom or molecule that are quantized. For instance, in a diatomic molecule, the two atoms can vibrate against each other, rotate about each other, etc. Together, these are all generally called the energy modes and their degeneracies (number of available states per energy level) for an atom or molecule including translational, rotational, vibrational, and electronic energies. Above the ground (lowest) energy state of the neutral atom/molecule, each one of these energy levels is considered to be an excited state. This can be visualized conceptually using a generic energy level diagram (Figure 4.2).

When a free electron is accelerated to sufficient energy, the kinetic energy of the electron is
transferred to the neutral molecule, raising it to an excited state. Therefore, kinetic energy is not conserved in this collision, and it is called inelastic. Typically, an excitation collision/reaction requires an electron kinetic energy of a few to many eV. Most molecules have a large number of possible excited states, and each has a different threshold energy. Therefore, the kinetic energy of the incoming electron $\epsilon_e$ must exceed the threshold energy of an individual excitation reaction $E_M$ for that excitation to be possible.

The reason a discharge glows is because once a neutral is excited, it will relax back to its ground state. In doing so, it releases that energy difference in the form of a photon, and, if the energy gap coincides with a visible wavelength, the photon is visible. For this reason, the color of a discharge depends on the type of gas used, because the wavelength of emitted light depends on the energy levels available to the atoms or molecules in the gas. (For example, a discharge in neon will be bright orange while a discharge in argon will be deep purple, and a discharge in air is typically a deep blue with white streamers.) Further, some of these states are more stable than others. Therefore, while some states relax quickly back to ground others stay in their excited (energized) state, and these are called metastables.  

4.1.3 Ionization Collisions

At sufficient kinetic energy energy, a free electron may actually cause an electron to detach from the neutral resulting in a second free electron and a positive ion. The energy required for this reaction is typically around 10-20 eV and is called the ionization energy $E_{ion}$. Therefore the incident free electron must have a kinetic energy of $\epsilon_e \geq E_{ion}$ to create an ion. This is called electron-impact ionization and it is the dominant way that electrons are produced in a gas discharge.

4.1.4 Collisions Summary

In general, the nature of these collisions are probabilistic. That is, even if an electron has sufficient energy to create an excited state or ion, there is only a small probability that this may occur. These probabilities are determined by the collision cross-section, denoted by $\sigma(\epsilon_e)$ in units of [$m^2$], which is a function of the incident electron kinetic energy $\epsilon_e$. At low incident electron kinetic energies ($\leq 1$ eV), only elastic collisions are possible, at moderate energies (1-10 eV) elastic and excitation collisions occur, and at high energies ($\geq 10$ eV) elastic, excitation, and ionization reactions are all possible. Of course, the exact energy range is different for each gas and is determined by the minimum kinetic energy required for excitation reactions and ionization to occur. Interestingly, since the collision cross-section depends on the kinetic energy of the incident electron, $\sigma = f(\epsilon_e)$, ionization is most probable when $\epsilon_e \sim 70$ eV even though the threshold energy is only $\sim 10 - 20$ eV. This will be discussed in more detail in Section XX.

Though excited states are not charge carriers, they are, in many ways, the most important species in the discharge. In terms of the physics of the discharge, they play a crucial role because each time a free electron creates an excited neutral it loses its kinetic energy (the energy is spent exciting the neutral to a higher energy state). Therefore, they act as an energy sink, delaying ionization reactions from occurring. Therefore, in order to accurately capture the ionization in a discharge, it is also necessary to understand the impact that excitation reactions play in the charge creation process.

2From an application perspective, these excited and metastable states are very important because they are very chemically reactive. Many discharge applications, such as the emerging field of plasma medicine for wound healing, take advantage of the reactive oxygen and nitrogen species produced in an air discharge by these excited states. Therefore, in any detailed analysis of a discharge, it is important to accurately capture the kinetics of the excited states.
4.2. Electron Impact Ionization - The $\alpha$ Process

It should be noted that the three reactions discussed above are not the complete story. Other reactions, such as 3-body reactions and double ionization, are also possible, though they play significant roles under very specific regimes (such as at elevated pressures). The most important of these other reactions is electron attachment, where a free electron attaches to a neutral molecule creating a negatively charged molecular ion. This is relevant specifically in electronegative gases, including oxygen ($O_2$) and sulfur hexafluoride ($SF_6$), and can act as an electron sink though the negative ions are still charge carriers producing current. The details of electron attachment will not be covered in this book, but is available in many other texts.

4.2 Electron Impact Ionization - The $\alpha$ Process

4.2.1 Ionization Frequency

Consider a gas with free electrons being accelerated by an electric field. Each electron is undergoing some collisions (elastic, excitation, or ionization) and therefore each has a different energy $\epsilon_e$. Therefore, at energy $\epsilon_{e,1}$ there are $x_1$ number of electrons and at energy $\epsilon_{e,2}$ there are $x_2$, and so forth. (e.g., there are 10 electrons with kinetic energy of 5 eV, 100 electrons with 10 eV, 17 electrons with 15 eV, etc.) This collection of energy occupation is described by the electron energy distribution function often abbreviated as $n(\epsilon_e)$, which has units of eV$^{-1}$.

We can now define the collision frequency $\nu$ with units [s$^{-1}$], or the number of collisions undergone by an electron per unit time. It will depend on the probability that the electron hits a neutral molecule, which we already know depends on the collision cross section $\sigma(\epsilon_e)$ in [m$^2$], the number of electrons that have that kinetic energy $n(\epsilon_e)$, the rate at which the electrons are moving or speed $v$ in [m/s], and the total number of available neutral molecules that the electron can collide with described the by the number density $N$ in [#/m$^3$]. The collision frequency of an electron is therefore

$$\nu = \frac{N \int n(\epsilon_e)\sigma(\epsilon_e)v d\epsilon_e}{\int n(\epsilon_e)d\epsilon_e}.$$

(4.1)

This collision frequency considers any kind of collision, be it elastic, excitation, or ionization. If only the ionization collisions are considered, only the ionization cross-section $\sigma_{ion}(\epsilon_e)$ is required, and the ionization frequency due to electron impact is

$$\nu_{ion} = N \frac{\int n(\epsilon_e)\sigma_{ion}(\epsilon_e)v d\epsilon_e}{\int n(\epsilon_e)d\epsilon_e}.$$

(4.2)

In essence, $\nu_{ion}$ [s$^{-1}$] is the number of ionization events performed by a single free electron per second, or the rate of ion production.

The ratio of only the integrals (that is $N$ is not considered) is, by definition, the energy average of the product $\sigma_{ion} v$ or

$$<\sigma_{ion}v> = \frac{\int n(\epsilon_e)\sigma_{ion}(\epsilon_e)v d\epsilon_e}{\int n(\epsilon_e)d\epsilon_e}.$$

(4.3)

Therefore the ionization frequency can also be written as

$$\nu_{ion} = N <\sigma_{ion}v> = Nk_{ion},$$

(4.4)

where $k_{ion} = <\sigma_{ion}v>$ defines the ionization reaction rate constant $k_{ion}$ [m$^3$/s].
4.2. Electron Impact Ionization - The $\alpha$ Process

4.2.2 Temporal Electron Avalanche

With the ionization frequency now defined, the creation of electrons (recall each ionization event also creates an electron) can now be considered. The time-dependant creation of electrons by free electrons is simply the ionization rate for a single free electron $\nu_{ion}$ multiplied by the number of free electrons $N_e$ [#/m$^3$]. However, this implies that the number of free electrons is constantly increasing because every ionization event creates a new electron. Therefore, the time rate-of-change of the number of free electrons can be described by

$$\frac{dN_e}{dt} = \nu_{ion} N_e.$$  \hspace{1cm} (4.5)

If it is assumed that $\nu_{ion}$ is constant, than this 1st-order differential equation is easily solved,

$$N_e(t) = N_{e,0} e^{\nu_{ion} t}, \hspace{1cm} (4.6)$$

where $N_{e,0} = N_e(t = 0)$, or the number of free electrons at time zero ($t = 0$). Eq. 4.6 implies that there is an exponential growth in the number of electrons over time—this is called an electron avalanche. However, it is not necessary to only think of the avalanche in time. In fact, it is often much easier to picture it in space, and this will be considered next.

4.2.3 Spatial Electron Avalanche

If the number of electrons created per second is defined as $\nu_{ion}$ [#/s], a similar concept can be defined in space. That is, the number of electrons created by a single electron as it travels a distance of one centimeter is $\alpha$ [#/cm]$^4$. The ratio of these two $\nu_{ion}/\alpha$ simply has the units of [m/s]—velocity. This is called the drift velocity of an electron $v_d$, and it will be more formally defined later in Ch. XX. For now, it is sufficient to recognize that

$$\nu_{ion} = \alpha v_d.$$ \hspace{1cm} (4.7)

Note that $\nu_{ion}$ is the ‘true’ description of the ionization rate—it is defined by the drift velocity and energy distribution. In contrast, $\alpha$ is a derived quantity literally defined by Eq. 4.7. However, $\alpha$ is fairly easy to measure (not directly, of course), and it is in many ways a more convenient way to think about electron impact ionization. Generally, $\alpha$ is more appropriate for DC discharges than AC discharges (especially when at high frequency). $\alpha$ is called Townsend’s first ionization coefficient, and electron-impact ionization is often referred to as the $\alpha$-process. Much like with the temporal electron avalanche $\nu_{ion}$, a spatial electron avalanche can be described using $\alpha$.

Consider the one-dimensional control volume shown in Figure 4.3. Consider some number of electrons $N_{e,x}$ entering the control volume at $x$, and some new number $N_{e,x+dx}$ leaving at $x + dx$. Because of conservation, the difference between these two must be equal to the number created (or destroyed) within the control volume $N_{e,gen}$. That is

$$N_{e,x+dx} - N_{e,x} = N_{e,gen}. \hspace{1cm} (4.8)$$

Now consider this generation source term. Over a the distance $dx$ a single electron creates $\alpha$ new electrons. Therefore the total number generated by $N_{e,x}$ entering the control volume is

$$N_{e,gen} = N_{e,x} \alpha dx \hspace{1cm} (4.9)$$

$^4$The use of cm here is arbitrary and simply the standard convention. $\alpha$ could just as easily be defined over a meter, mile, or light year.
The term $N_{e,x+dx}$ can be expanded through a Taylor series to be

$$N_{e,x+dx} \approx N_{e,x} + \frac{\partial N_{e,x}}{\partial x} dx$$  \hspace{1cm} (4.10)

Substituting Eqs. 4.9 and 4.10 into Eq. 4.8, gives

$$N_{e,x} + \frac{\partial N_{e,x}}{\partial x} dx - N_{e,x} = N_{e,x} \alpha dx$$  \hspace{1cm} (4.11)

By canceling $dx$ and converting the partial derivative into a full derivative, the following 1st-order differential equation is obtained.

$$\frac{dN_e}{dx} = \alpha N_e.$$  \hspace{1cm} (4.12)

It should be readily apparent that Eq. 4.12 is the spatial analogy to Eq. 4.5. If some number of electrons $N_{e,0}$ are initiated at the cathode ($x = 0$), the solution to this equation is

$$N_e(x) = N_{e,0} e^{\alpha x}.$$  \hspace{1cm} (4.13)

This is also called an electron avalanche—but now it is in space. That is, a single electron produces exponentially more electrons as it traverses a gap from the cathode to the anode. If the cathode and anode are separated by a distance $d$, the electron current passing through the anode $i_{\text{anode}}$ is simply

$$i_{\text{anode}} = (-q)N_{e,0} e^{\alpha d}.$$  \hspace{1cm} (4.14)

where $q$ is a unit charge ($q = 1.602 \times 10^{-19}$). At steady state, the positive ions reach the cathode in the same numbers as the electrons at the anode (save for the small initial number of electrons at the cathode $N_{e,0}$) and the current everywhere is approximately $i \approx i_{\text{anode}} \approx i_{\text{cath}}$. Now is this true generally? No—the massive ions move much slower than the small electrons, so the ion current is actually lower. Further, ion removal from the domain is slower than electron removal, resulting in ion accumulation in the domain.\(^5\) This in turn would affect the electric field through

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\(^5\)Note that here we are talking about general ion generation in a gap. As we will see in Ch. XX, this is only true when the avalanche is forming but before a self-sustained discharge is initiated. Once this “breakdown” occurs, the relationship between the ion and electron densities becomes more complex, and it is no longer true that there is a net ion accumulation over the entire domain.
4.2. Electron Impact Ionization - The $\alpha$ Process

Poisson's equation, Eq. 2.6. However, generally, it can be assumed that the field is 1-D and uniform (i.e., not a function of space) and given by $|E| = \Phi/d$. Now note that the current equation Eq. 4.14 can be rewritten as

$$\ln(i_{anode}) = \alpha d + C,$$

where $C$ is some constant. In practice, $\alpha$ is determined experimentally by varying $d$ but maintaining a constant $E$ (that is, the applied potential $\Phi$ is also varied). The measured current at the anode can then be plotted as $\ln(i_{anode})$ versus $d$, and extracting the slope gives a value for $\alpha$.

4.2.4 Townsend's First Ionization Coefficient $\alpha$

As stated previously, $\alpha$ is called **Townsend's first ionization coefficient** and electron-impact ionization is often referred to as the $\alpha$-**process**. Physically, $\alpha$ is the *number of ions created by a single electron over a distance of 1 cm*. Therefore, it is clear that the units of $\alpha$ are [$#/cm$]. Further, it should be clear that the number of ionization collisions will be related to how fast the electrons are accelerated because the collision cross section is energy dependent (as previously touched upon in Sec. 4.1 and will be discussed further in Ch. XX). Additionally, it makes conceptual sense that the number of ions generated should depend on how many gas atoms available for ionization (i.e., the gas density). Therefore, we can see that $\alpha$ should be a function of the electric field $E$, which provides the force that accelerates the electrons to suitable kinetic energies, and the gas pressure $p$, which defines the number of gas atoms. In fact, what is critical is the ratio of the electric field to the pressure, $E/p$, which is often called the reduced electric field. Ultimately, a *similarity law*\(^6\) describes $\alpha$ as a function of $p$ and $E/p$,

$$\alpha = pf(E/p).$$

Therefore, an alternative approach to experimentally determining $\alpha$ is to vary $p$ and maintain $E/p$ as a constant, and then analyze the resulting current data using the relation

$$\ln(i_{anode}) = \frac{\alpha}{p}(pd) + C.$$  \hspace{1cm} (4.17)

It should be noted that the product $pd$ and the reduced pressure $E/p$ are both crucial properties in electrical discharges, as will be discussed in Ch. XX, and form the basis for important scaling relationships.

The most common form of *alpha* was originally derived by Townsend (albeit under some faulty assumptions), but has been verified experimentally as well,

$$\alpha = Ap \exp \left[ \frac{-Bp}{E} \right],$$  \hspace{1cm} (4.18)

where $A$ and $B$ are constants that depend on the gas composition with units of $[1/cm - Torr]$ and $[V/cm - Torr]$, respectively (for a list of typical values, see Table 4.1 of Raizer [REF]).\(^7\) Other empirical forms include

$$\alpha = Cp \exp \left[ -D \sqrt{\frac{p}{E}} \right],$$  \hspace{1cm} (4.19)

\(^6\)In truth, this relationship can be derived phenomenologically by considering the mean free path and accelerating electric field, as Nasser showed in Ch. 7 of his book [REF].

\(^7\)Note that in Townsend’s analytical form, the constant $A$ is approximated by $A = 1/(pd)$ and the constant $B$ is approximated by $B = A/E_{ion}$, where $l$ is the mean free path and $E_{ion}$ is the ionization energy.
4.3 Ion Impact Ionization - The $\beta$ Process

for noble gases and

$$\alpha = 1.17 \times 10^{-4} p \left( \frac{E}{p} - 32.2 \right)^2 \quad (4.20)$$

for air in the reduced electric field range of $E/p = 44 - 176$ V/cm – Torr.$^8$

4.3 Ion Impact Ionization - The $\beta$ Process

Electron impact ionization ($\alpha$-process), where an electron collides with a neutral particle to create a second free electron and positive ion, is the dominant gaseous ionization mechanism. However, it is reasonable to anticipate that ions accelerated by the electric field would also collide with neutral molecules to form a second ion and a free electron. This is called the $\beta$-process where $\beta$ is Townsend’s second ionization coefficient and is defined in the same manner as $\alpha$ (the number of ions a single ion creates over 1 cm). Using a similar approach as shown in Eqs. 4.8-4.12, a new differential equation can be obtained that describes both the $\alpha$- and $\beta$-processes to generate positive ions $N_i$,

$$\frac{dN_i}{dx} = \alpha (N_{e,0} + N_i) + \beta N_{i,0}. \quad (4.21)$$

Here, $N_{e,0}$ is the initial number of electrons and $N_{i,0}$ is some initial number positive ions (presumably created by earlier electron-impact collisions before entering the control volume). By considering that the total number of electrons $N_e$ created across the electrode gap as simply the sum of the initial number $N_{e,0}$ and the total number of ions $N_{i,0} + N_i$,

$$N_e = N_{e,0} + N_{i,0} + N_i, \quad (4.22)$$

and plugging this in Eq. 4.21, an equation similar to Eq. 4.13 can be derived,

$$N_e(x) = N_{e,0} \frac{(\alpha - \beta) e^{(\alpha - \beta) x}}{\alpha - \beta e^{(\alpha - \beta) x}}. \quad (4.23)$$

This equation also shows an exponential avalanche production of electrons but considers both electron- and ion-impact events. Originally derived by Townsend [REF], it was assumed that the $\beta$ process was equally as relevant as the $\alpha$ process in discharges. However, this ultimately turned out to not be true [REF]. For electron impact, the kinetic energy of the electron must exceed the ionization energy $E_{ion}$ of the neutral. However, for ions to ionize a neutral it must have a kinetic energy at least $> 2E_{ion}$. This is because the electric field of the ion itself is sufficiently strong to polarize the neutral causing a much softer collision. In most gases where $E_{ion} \sim 10$ eV and ionization is most probable at $\epsilon_e \sim 70$ eV, a positive ion requires approximately 400 eV in order to ionize a neutral. Further, ions move much slower than electrons (consider that the mass of proton alone is 3 orders of magnitude greater than that of an electron). Therefore, for ions to readily contribute to a discharge, they must be accelerated to much higher energies and this takes a much more time than accelerating their electron counterparts. Therefore, the time scale of discharge formation is much too fast for ions to contribute. Therefore, while ion-impact ionization is not non-existent, it plays a minor role in discharge formation especially in low-temperature, non-equilibrium discharges - and it is considered a negligible effect.

$^8$It is convention to present reduced electric field $E/p$ in units of [V/cm-Torr], a typical values is between 10-1000 V/cm-Torr. However, an alternative representation is to use the gas number density $N$ rather than the pressure. In this case, the reduced electric field is $E/N$ and an alternative unit called the Townsend [Td] is used, named after pioneering scientist Sir. John Sealy Townsend, whose name appears throughout this book. The Townsend takes a value of $1Td = 10^{-17}$Vcm²
4.4 Photon Impact Ionization - Photoionization

Similar to electron and ion impact, photons (from either external sources or from the plasma glow itself) of sufficient energy can ionize a neutral atom as well as excite it to a higher state (absorption) or even dissociate a polyatomic molecule. The energy of a photon is

\[ \epsilon_{\text{photon}} = h\nu = \frac{hc}{\lambda} \]  \hspace{1cm} (4.24)

where \( h \) is Planck's constant \((h = 4.135667 \times 10^{-15} \text{ eV/s})\), \( \nu \) is the frequency of the light in Hz, \( \lambda \) is the wavelength of the light, and \( c \) is the speed of light \((299792458 \text{ m/s})\). If angular frequency \( \omega \) \( [\text{rad/s}] \) is considered instead, then the reduced Planck's constant \( \hbar = h/2\pi \) is used to obtain \( \epsilon_{\text{photon}} = \hbar\omega \).

The photo-reactions therefore are

**Excitation:** \( h\nu + M \leftrightarrow M^* \) iff \( h\nu \geq E_M^* \).

**Ionization:** \( h\nu + M \rightarrow M^+ + e^- \) iff \( h\nu \geq E_{\text{ion}} \).

The questions remains, much like the \( \beta \)-process, whether photoionization is relevant. Consider cesium vapor, which is the easiest element to ionize with an ionization threshold of only \( E_{\text{ion}} = 3.87 \text{ eV} \). Substituting into Eq. 4.24, the wavelength of light necessary to ionize cesium is \( \lambda \approx 320 \text{ nm} \), which is in the ultraviolet part of the electromagnetic spectrum. For any other atom or molecule, more energy is required (smaller wavelengths), so photoionization is, for the most part, an ultraviolet process.

One might conclude from this simple calculation that for all gases, ionization only occurs for \( \lambda < 320 \text{ nm} \). This is not quite right. It is possible to ionize gas at \( \lambda < 320 \text{ nm} \). Ionization can occur in *steps* where the neutral is first excited to a metastable state, and then another collision induces the ionization. Therefore, the second collision does not require the threshold energy \( E_{\text{ion}} \) because the neutral is already in an energetic (excited) state (recall Fig. 4.2). This is called *step ionization*. Recall two guiding principles:

1. The excited and ionized states of a neutral are quantized.
2. Conservation of energy applies.

In an *electron-impact* reaction, the electron simply loses kinetic energy during the reaction such that, simplistically, either \( \epsilon_{e,\text{out}} = \epsilon_{e,\text{in}} - E_{M^*} \) or \( \epsilon_{e,\text{out}} = \epsilon_{e,\text{in}} - E_{\text{ion}} \) for excitation and ionization reactions, respectively. However, in a *photon-impact* reaction, there are three possible energy conservation mechanisms

- The photon energy is absorbed and greater than the excitation/ionization energy thereby emitting a new photon: \((h\nu)_{\text{out}} = (h\nu)_{\text{in}} - E_{M^*} \) or \((h\nu)_{\text{out}} = (h\nu)_{\text{in}} - E_{\text{ion}} \).
- The photon is absorbed and greater than the excitation/ionization energy, and the excess energy is imparted onto the excited neutral/ion as kinetic energy: \( \Delta \epsilon_{M^*} = (h\nu)_{\text{in}} - E_{M^*} \) or \( \Delta \epsilon_i = (h\nu)_{\text{in}} - E_{\text{ion}} \) (Here, \( \epsilon_{M^*} \) is the kinetic energy of the excited neutral and \( \epsilon_i \) is the kinetic energy of the resultant ion formed by photoionization).\(^9\)

\(^9\)An electron will also lose a minute amount of energy in an elastic collision, though it is typically assumed that none is lost because the neutral is massive compared to the electron.

\(^{10}\)Note that prior to impact from an electron or a photon, a neutral molecule will have some kinetic energy due to its thermal state, and this value can be estimated from a Maxwellian distribution, as will be discussed in Ch. XX.
• The photon is absorbed and greater than the ionization energy and the excess energy is imparted on the newly free electron as kinetic energy, \( \epsilon_{e,ej} = (h\nu)_{\text{in}} - E_{\text{ion}} \).

Therefore, it clear that while direct photoionization is unlikely, photoionization process can play an important role under the right circumstances.

So where do the photons come from? They can come from an external source (e.g., a laser) or from the gas itself. Recall, when an excited neutral relaxes back to its ground state, it emits a photon with \( (h\nu)_{\text{emit}} = \epsilon_{M^*} \). This is called resonance radiation. In weakly ionized plasmas, photoionization is typically a secondary effect and less significant than electron-impact ionization, though not negligible.

4.5 Neutral Impact Ionization - Thermal Ionization

This is also similar to electron-impact ionization but is simply neutral-impact ionization. The kinetic energy of a gas molecule can be approximated by \( \epsilon_M \sim \frac{3}{2}k_BT \) where \( k_B \) is the Boltzmann constant \( (k_B = 8.617343 \times 10^{-5} \text{eV}/\text{K}) \) and \( T \) is the gas temperature. From an order-of-magnitude analysis, \( T \sim 10^5 \text{K} \) for a neutral to have kinetic energy approach that of the ionization energy \( E_{\text{ion}} \sim 10 \text{eV} \), so it is clear that for this phenomena to be important the gas must be at extreme temperatures (thermal plasmas), and it is not relevant for non-equilibrium, low-temperature plasmas.

4.6 Step (Penning) Ionization

Step ionization, also called the Penning effect\(^{11}\) is a common gaseous ionization process that occurs in mixtures of two different gasses called Penning mixtures. In this case, the ionization is not by ion or electron impact, but by an excited neutral. An excited neutral of one species \( (X^*) \) collides with a second neutral of a different species \( (M) \), and during the energy exchange, an electron is ejected from the target neutral: \( X^* + M \rightarrow X + M^* + e^- \). Penning ionization occurs when the gas \( X \) has a higher ionization energy than the gas \( M \), or \( E_{\text{ion},X} > E_{\text{ion},M} \), but gas \( X \) also has a metastable (long lasting) excited state \( X^* \) that has a greater energy than the ionization energy of the gas, or \( E_{X^*} \geq E_{\text{ion},M} \). For example, consider a mixture of argon (Ar) and neon (Ne). The ionization energy of Ar is \( E_{\text{ion},Ar} = 15.7 \text{eV} \) whereas the ionization energy of Ne is \( E_{\text{ion},Ne} = 21.6 \text{eV} \).\(^{12}\) However, Ne has a metastable state that has an excitation energy of \( E_{Ne^*} = 16.6 \text{eV} \). Therefore when a metastable Ne\(^*\) and neutral Ar collide, there will be an energy exchange as the Ne\(^*\) relaxes to its ground state, and that energy is sufficient to ionize Ar. However, because of the complex thermodynamics of discharges where all the reaction processes affect the energy distribution, this type of Penning reactions is best only when the gas admixture is Ne + 0.1% Ar, as opposed to 10% Ar for example. In this case, the excited state of Ar has an energy of \( E_{Ar^*} = 11.5 \text{eV} \), such that increasing the Ar concentration increases the number of Ar\(^*\), but quenches Ne\(^*\) thereby quenching Penning ionization. Typical Penning gas admixtures include Ar in Ne, krypton (Kr) in Ar or Ne, xenon (Xe) in Ar or helium (He). The most prominent impact of using a Penning gas rather than a pure gas is that the overall current will be increased due to the increased ionization. Typically, it is most effective to be at low reduced electric fields \( (E/p \sim 0.5 - 30 \text{V/cm} - \text{Torr}) \) to get the greatest benefit from the Penning effect.

\(^{11}\)Named after Dutch physicist Frans Michel Penning, who first reported it in 1927.

\(^{12}\)Note that ionization energy is often presented as either eV/atom or kJ/mol where the unit conversion is 1 kJ/mol = 0.010364 eV/atom.
4.7 Other Gaseous Ionization Mechanisms

There are additional gaseous reactions that can result in ionization, those these are not typical and only occur under special circumstances or by design.

Electron attachment: As discussed in Sec. 4.1, some gasses are electronegative and therefore prefer to have an additional electron (negative ion) rather than losing as electron, with the most common being oxygen ($O_2$) and sulfur hexafluoride ($SF_6$) as well as halogens such as chlorine (Cl) and fluorine (F) and halogen-containing chemicals. The general reaction is: $M + e^- \rightarrow M^-$, but a dissociative reaction is also possible: $XM + e^- \rightarrow X + M^-$. Sometimes an electron attachment coefficient is defined denoted either as $\eta$ (or $\delta$) that is the analog to $\alpha$. It is fairly straightforward to derive the electron avalanche including an electron attachment coefficient, but that is not included here. Sometimes, such as in electrospray mass spectrometry, a gas such as $SF_6$ is introduced to act as an electron scavenger to reduce the chance for discharge initiation.

Associative ionization: In this reaction, an excited neutral ($M^*$) collides with a second neutral of the same species ($M$), to form a positively charged diatomic molecule: $M^* + M \rightarrow M^+_2 + e^-$. Note that this can also occur in gas mixtures and is called associative Penning ionization where the reaction is: $X^* + M \rightarrow MX^+ + e^-$. 

Ionization by X-Rays: This is essentially a special case of photoionization, where the electromagnetic radiation (photons) are in the x-ray regime: $h\nu + M \rightarrow M^+ + e^-$ where $10^{16}Hz \leq \nu \leq 10^{19}Hz$ (or $0.1nm \leq \lambda \leq 10nm$).

4.8 Summary

The purpose of this chapter was to overview the creation of electrons in the gas phase that help turn an insulating gas into a conductive gas—that is, a discharge. The following processes were discussed:

- the $\alpha$ process (electron impact) is dominant
- the $\beta$ process (ion impact) is largely negligible
- photoionization (photon impact) can be important
- thermal ionization (neutral impact) is typically not important
- step or Penning ionization is important in appropriate gas admixtures called Penning gasses
- electron attachment is important in electronegative gasses
- associative ionization (excited neutral reaction) can be important in special cases
- x-ray ionization (photon impact) is not important in special cases

It is important to remember, that all of these ionization reactions are probabilistic. For instance, though an electron with kinetic energy greater that the ionization energy may create an ion through the $\alpha$ process, it is not guaranteed that this type of collision will occur—an elastic or excitation reaction could occur instead. These probabilities will be discussed in Part 2 when the concept of the collision cross-section $\sigma$ is introduced.
5.1 General Electron Emission

We consider cathode charge production processes, we are generally considering the production of electrons at the cathode. Under appropriate conditions, electrons can be ejected from the surface of a metal (or semi-conductor) into the gas phase, and this is called electron emission. In the formation of a discharge, these electrons now participate in α and excitation and contribute to the overall electron current across the electrode gap. Cathode emission processes are very important in the formation of discharges—especially DC discharges. However, in order to understand electron emission we should make sure we understand the basics of solid state physics that allows electrons to be ejected from a surface.

5.1.1 The Solid State

Generally, solid state physics is the study of solid matter, typically from an atomic perspective. At the most fundamental level, energy can be transported via four types of energy carriers. The easiest to conceptualize are electrons and atoms/molecules. As electrons move through a solid, liquid, or gas, they both have kinetic energy that represents the motion of energy through the medium. Photons, or electromagnetic waves, also have kinetic energy and can move through solid, liquid, or gas. Unlike electrons and atoms/molecules, photons have no mass, though they do exhibit characteristics of both waves and particles. Finally, in the solid phase, because the atoms/molecules are rigid, the energy carriers are phonons. Phonons are wave packets that move along the bonds between atoms in a solid structure. Conceptually, one can envision a solid where the atoms are arranged in a crystal lattice as a complex spring-mass system with the springs representing the bonds between neighboring atoms and the masses the atoms themselves. As one atom vibrates, the energy is translated to neighboring atoms via the bonds. This wave motion of vibration can be characterized as a phonon. From the perspective of gas discharges, the most important of these energy carriers are electrons because they also carry charge and can be accelerated by an electric field. In this book, we will focus on the solid state nature of electrons and the implications for electron emission into the gas discharge.

\footnote{As opposed to solid mechanics, which studies solid matter from a continuum perspective.}
5.1. General Electron Emission

Generally, the crystal lattice is the structure or organization of atoms in the solid material. It can take a simple cubic form (such as in sodium chloride) or more complex hexagonal and diamond-like structures. From the view of a single atom, each electron associated with the atom has a potential energy due to local attraction to the protons in the nucleus. The electrons also inhabit discrete, quantized energy states called orbitals. In the atomic structure, the valence electrons are in the outermost shells such that they are loosely bounded to the nucleus and therefore free to move. Most metals only have partially filled outer shells such that there is “space” for these valence electrons to move. In a crystal structure where atoms are bonded together, these outer orbits are hybridized, and the atoms now effectively “share” these electrons. Thus when a force is applied to the electrons, such as an electric or magnetic field, the electrons are free to move, which is how electricity is generated. In insulators, these orbitals are completely filled such that the electrons cannot move.

In metals, we treat all the electrons in the outer shell as free, independent particles often called the free electron model, electron gas, or Fermi gas. However, these electrons are still governed by quantum mechanics and have discrete available energy levels. Here an extremely simplified view of these concepts will be described in order to set the stage for understanding electron emission. The energy and momentum of the free electrons are described by Schrödinger’s equation,

\[ -\frac{\hbar^2}{2m_e} \nabla^2 \Psi(\vec{r}) = E \Psi(\vec{r}), \]  

where \( \hbar \) is the reduced Planck’s constant, \( m_e \) is the electron mass, \( E \) is the energy, and \( \Psi \) is the electron wavefunction. The wavefunction \( |\Psi^2| \) can be thought of as an electron probability or likelihood of an electron being at the distance \( \vec{r} \). A general solution to Schrödinger’s equation is

\[ \Psi(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}}, \]  

where \( V \) is a volume and \( \vec{k} \) is a wave vector. From this solution, the energy of the electron comes from the eigenfunctions of Schrödinger’s equation,

\[ \epsilon(k) = \frac{\hbar^2 k^2}{2m_e}, \]  

and the electron momentum is

\[ \vec{p} = \hbar \vec{k}. \]

There are two important aspects of this solution. First, like any partial differential equation, there are an infinite number of solutions associated with its eigenvalues. The eigenvalues, however, take discrete values. Accordingly, the eigenvalues of Schrödinger’s equation lead to discrete values for the wave vector such as (in 1-D),

\[ k_x = \frac{2\pi n}{L_x}, n = 1, 2, 3..., \]

where \( L_x \) is the length of the crystal in the \( x \) direction. Because of the Pauli exclusion principle, only two electrons (one spin up and the other spin down) may occupy any wave vector. Similarly, discrete electron wave vectors can be described in (2-D) and (3-D).  

---

3When we use the term quantum or quantized, we mean a discrete set of values rather than a continuous set of values. At the macro scale, we think in terms of a continuum (energy can go from \( 0\to\infty \)), but at the atomic scale only discrete levels are possible.
With the wave vectors known, it is now possible to define the density of states. The density of states is the number of states \( N \) at each energy level available to be occupied. Conceptually, it is easiest to think of an theater. The first energy level is ground floor level, and there are a certain number of seats or energy states \( N \). The mezzanine is the second energy level with its own number of seats (states), followed by the first balcony, second balcony, and so forth. Mathematically, the density of states is the

\[
D(\epsilon) = \frac{1}{V} \frac{dN}{d\epsilon},
\]

and it can be shown that in 3-D, the density of states for electrons is

\[
D(\epsilon) = \frac{1}{2\pi^2} \left( \frac{2m_e}{\hbar} \right)^{3/2} \sqrt{\epsilon}.
\]

Now conceptually, Eq. 5.7 only represent the available energy states. However, what is still unknown is how many electrons are in those states, or continuing the analogy, how many tickets have been sold for the seats in the theater. This is described by the statistics of the electrons.

5.1.2 Fermi-Dirac Distribution and the Work Function

The electron occupation for free electrons is described by the Fermi-Dirac distribution:

\[
f(\epsilon) = \frac{1}{\exp\left(\frac{\epsilon - \mu}{k_B T}\right) + 1}.
\]

where \( \epsilon \) is the energy of the electrons, \( \mu \) is the chemical potential of the metal, and \( T \) is the temperature of the metal. This distribution \( f(\epsilon) \) takes a value between 0 and 1, where 1 indicates that the all the states at energy \( \epsilon \) are occupied and 0 indicates that all states at energy \( \epsilon \) are no occupied. Any value between 0 and 1 is the probability of occupation. At 0 K, the distribution is shown in Fig. 5.1a, and it is clear that every level up to some energy \( \epsilon_F \) is fully occupied. \( \epsilon_F \) is called the Fermi energy and represents the maximum energy an electron occupies at 0 K. As the temperature increases, the energy of the electrons increases and a few of the electrons near the Fermi energy are energized to a higher energy state. All the low energy states are still occupied, but the occupation probability of the higher energy states is now greater than 1 as shown in Fig. 5.1b.

At some point, the highenergy electrons will have sufficient energy to actually break away from the surface. The minimum energy (above the Fermi energy) required to remove an electron from the solid to the vacuum outside the surface is called the work function, \( \phi \) [eV]. Therefore, generally, an electron emits when it has an energy greater than the work function. This is shown in Fig. 5.2, which is an electron motive diagram. The vertical axis is energy, and the left of this axis represents the solid while the right represents the vacuum. The work function is the barrier potential energy and appears as a “step” into the vacuum level. Also to the left of the axis is the Fermi-Dirac distribution of the electrons in the metal at some \( T > 0 \) K. It is clear that only a small number occupy the high energy states that are above the work function, and thus only a small number will be emitted. Electrons can be energized to occupy these states in different ways - by adding heat (thermionic emission), by absorbing the energy of a photon (photoemission or the photoelectric effect), from an electric field (field emission), or from an ion or excited metastable impacting the surface (secondary emission).
5.1. General Electron Emission

Figure 5.1: Plots of the Fermi-Dirac distribution function at (a) \( T = 0K \) and (b) \( T = 300K \) and \( T = 1000K \) at a Fermi energy of \( \epsilon_F = 5eV \).

emission). This last one, secondary emission, is the critical one for gas discharges and it is called the \( \gamma \)-process. However, a rudimentary understanding of the other three (and why they may or may not be important) is essential as well.

5.1.3 Thermionic, Photo, and Field Emission

Though these emission processes are less essential to a discharge than secondary emission except in special cases, it is important to understand their underlying physics, and thus they will be considered first.

5.1.4 Thermionic Emission

In thermionic emission, the metal is heated to such an extent that the electrons pass over the work function potential barrier as shown in Fig. 5.2. Generally, the emission current density \( j \) [A/m\(^2\)] can be determined using

\[
j = q \int_0^\infty N(\epsilon)T(\epsilon)\,d\epsilon,
\]

where \( N(\epsilon) \) is the supply function and depends on the density of states and Fermi-Dirac statistics and \( T(\epsilon) \) is the transmission coefficient and is determined by solving Schrodinger’s equation for the wave function of the electron in the solid and in the vacuum. Conceptually, this can be thought of as the following: the current density depends on the number of available electrons at an energy level \( (N(\epsilon)) \) that make it out of the solid \( (T(\epsilon)) \), and by integrating over all energies, the total current is determined. Using a simplistic approach, it is clear that \( T(\epsilon) = 0 \) if \( \epsilon < \phi \) (the energy is below the work function) and \( T(\epsilon) = 1 \) if \( \epsilon > \phi \). However, a more detailed analysis of the transmission coefficient can be used, and in the case of thermionic emission this leads to the Richardson-Dushman equation\(^6\)

\[
j = AT^2 \exp \left( -\frac{\phi}{k_BT} \right),
\]

\(^6\)Named after Englishman Owen Willans Richardson who won a Nobel Prize in 1928 for his work on thermionic emission and Russian Saul Dushman who derived the general form and the form of the constant, respectively.
only these electrons have sufficient energy to overcome the work function and be emitted

\[ \epsilon_F \]

\[ \phi \]

\[ \text{Solid} \]

\[ \text{Vacuum} \]

Figure 5.2: An electro motive diagram illustrating how only a small electron population have sufficient energy to overcome the potential barrier (work function) to be emitted into the vacuum.

where \( T \) is temperature of the cathode in [K] and \( A \) is the Richardson constant given by

\[ A = \frac{4\pi m_e k_B q}{h^3}. \]  \hspace{1cm} (5.11)

By this definition, \( A \) is a universal constant equal to \( 1.20173 \times 10^4 \) \([A/m^2 - K^2]\). Note that the exponential relationship is an inverse function of \(-T\), which implies that in order to obtain any appreciable current, the cathode must be heated to very high temperatures. Consider an order of magnitude approximation where \( \phi \sim 10^0 \text{ eV}, k_B \sim 10^{-4} \text{ eV/K} \) (actually \( 8 \times 10^{-5} \text{ eV/K} \)), and \( T \sim 10^8 \text{ K} \). Plugging these into Eq. 5.10, one obtains

\[ j \sim (10^0)(10^4) \exp \left( -\frac{10^9}{(10^{-4})(10^3)} \right) \sim (10^{10}) \exp (-10^2) \sim (10^{10})(10^{-44}) \sim 10^{-34} A/m^2, \]  \hspace{1cm} (5.12)

For a reasonably sized 25 cm\(^2\) (0.0025 m\(^2\)) electrode, this corresponds to a current \( \sim 10^{-37} \text{ A} \). Consider instead, a temperature closer to \( 10^3 \text{ K} \), then

\[ j \sim (10^6)(10^6) \exp \left( -\frac{10^9}{(10^{-4})(10^3)} \right) \sim (10^{12}) \exp (-10^1) \sim (10^{12})(10^{-5}) \sim 10^7 A/m^2. \]  \hspace{1cm} (5.13)

For the same electrode size, the current is something \( \sim 10^4 \text{ A} \), which is much higher than is realistic, but illustrates the impact of the exponential temperature dependance on the resulting current. Therefore, thermionic emission is only significant in high-temperature (thermal) plasmas or
when there is appreciable cathode heating such as in arcs\(^7\). But in low-temperature plasmas where the gas and ion temperature \(\sim 300\) K, it is not significant at all.

### 5.1.5 Photoelectric Emission

In photoelectric emission (also called the photoelectric effect\(^8\) or simply photoemission), the solid absorbs incident photons (from a laser, for example) and these excite electrons to higher energy levels. If the electron is excited to an energy greater than the work function, then it can be emitted from the solid. The “classic” relation is that the kinetic energy of the ejected electron will be

\[ \epsilon_e = h\nu - \phi \]  

From this concept, one can derive the energy distribution and therefore current of electrons. (For example, see duBridge, Phys. Rev., 1933, 43, 727-741). Within the context of a discharge, it is important to consider the following two questions:

- The emission currents relation to the intensity of the bombarding light.
- The emission currents relation to the energy (frequency) of the bombarding light.

Light intensity can be loosely defined as the ‘rate of photons’ bombarding a surface. If the light is monochromatic (a single frequency), all photons have the same energy and therefore the same probability of emitting an electron. Therefore, photoemission current is (linearly) proportional to the light intensity. The emission current increases with the frequency (or inversely with wavelength) because the greater the energy of the incoming light the greater the probability that an electron is emitted. Figure 5.3 shows this relationship qualitatively.

![Figure 5.3: Qualitative relationship between current and light intensity for two different frequencies \((\nu_1 < \nu_2 \text{ or } \lambda_1 > \lambda_2)\).](image)

The threshold frequency for photoemission to occur is roughly (though Fowler showed it varies slightly from this)

\[ \nu_0 = \frac{\phi}{h} \]  

\(^7\)This is exactly the case in arcs, which often form localized ion channels called cathode spots that become extremely hot. In fact in arcs, as used in arc welding, thermionic emission is an essential charge producing mechanism.

\(^8\)Note that Albert Einstein won the Nobel Prize in 1905 for his work on the photoelectric effect.
Consider an order of magnitude approximation where $\phi \sim 10^3$ eV, $h \sim 10^{-15}$ eV-s, and $c \sim 10^8$ m/s, then

$$\nu_0 \sim \frac{10^3}{10^{-15}} \sim 10^{15} \text{Hz}, \quad (5.16)$$

which corresponds to a wavelength of

$$\lambda_0 = \frac{c}{\nu_0} \sim 100 \text{nm} \quad (5.17)$$

This wavelength corresponds to the ultra-violet and near visible portion of the spectrum. Because of the relaxation of excited neutrals to their ground state, photons within these wavelengths are frequently emitted in a discharge (recall that this is why they glow). Therefore, depending on the exact cathode material (or $\phi$) and the intensity of the emission in the discharge, photoemission can be an important source of electrons in a discharge.

### 5.1.6 Field Emission

Field emission is different than thermionic and photoemission in that the electron in the cathode does not have to overcome the work function to escape from the cathode. In the presence of a very strong electric field, the potential barrier is both lowered and thinned, that is rather than the “step” potential barrier, the barrier is more triangular as shown in Fig. 5.4.\(^9\) In this case, the electrons can quantum mechanically tunnel through the barrier rather than passing over the barrier.

To determine the field emission current density, Eq. 5.9 is again used, but the transmission coefficient is much different. Using an approximate solution Schrodinger’s equation, Fowler-Nordheim equation, which takes a form similar to the Richardson-Dushman equation, is used to describe field emission\(^10\)

$$j = \frac{A_F N E^2}{\phi t^2(y)} \exp \left( -\frac{B_F N \phi^{3/2} v(y)}{E} \right), \quad (5.18)$$

where $A_F N$ and $B_F N$ are constants ($A_F N = 1.54 \times 10^{-6}$, $B_F N = 6.837$). The variable $y$ can be approximated as

$$y = 3.79 \times 10^{-4} \frac{\sqrt{E}}{\phi}, \quad (5.19)$$

and the functions $t^2(y)$ and $v(y)$ can be approximated as

$$t^2(y) \approx 1, \quad (5.20a)$$

$$v(y) \approx 0.95 - y^2. \quad (5.20b)$$

If Eq. 5.18 was considered by itself, an electric field $\sim 1000$ V/$\mu$m would be required to generate any appreciable field emission current. (Think about that, for an electrode gap of 1 cm, the applied potential would need to be 10000000 V! In order to generate $\sim 40$ $\mu$A of current in a 1 $\mu$m electrode gap using 25 cm$^2$ electrodes, the voltage would need to be nearly 2000 V!) However, the necessary electric field has been observed to be closer to 100 V/$\mu$m in practice and, in special cases, as low as

\(^9\)Any charge, positive or negative, generates an electric potential and field. In this instance, because electric potential can be summed using superposition, we must consider both the potential due to the electron and the potential due to the applied voltage.

\(^10\)The Fowler-Nordheim equation is named after the Englishman Ralph Howard Fowler and the German Lothar Wolfgang Nordheim who published their seminal work in 1928. The approximate solution they used for Schrodinger’s equation was based on the WKB approximation, named after Gregor Wentzel, Hendrik Kramers, and Leon Brillouin, though Harold Jeffreys should also be acknowledged.
10 V/μm. This is because of geometric field enhancement. At the surface of most electrodes, there will be microprotrusions and surface roughness where electric potential lines coalesce thus increasing the local electric field at the cathode surface. This effect is typically included through a factor called $\beta$, and the current density equation can be rewritten as

$$j = \frac{A_{FN}(\beta E)^2}{\phi^2(y)} \exp \left( -\frac{B_{FN} \phi^{3/2}v(y)}{\beta E} \right),$$

where

$$y = 3.79 \times 10^{-4} \frac{\sqrt{\beta E}}{\phi}. $$

For a typical metal, $\beta \sim 50 - 100$, whereas for specialized materials, such as carbon nanotubes or diamond electrodes, it has been reported as high as $\beta \sim 1000$. For the same problem above, $\sim 40 \mu$A of current in a 1 μm electrode gap with 5 cm² electrodes but now with $\beta = 100$, only 20 V is required.

In general it can be concluded that field emission is largely negligible for discharges at any appreciable pressure (1 torr), because the required voltage is simply much too high and other processes dominate well before that voltage is reached. However, the exceptions being when the electrodes are spaced very close together ($\sim 5 \mu$m) and at very low pressure where field emission is the primary mechanism responsible for breakdown.
5.2 Secondary Emission

Secondary emission can be broadly defined as electron emission due to a bombarding particle (ion, neutral, metastable neutral, electron). In some texts photoemission is called a secondary process because it is a particle, but in this book the two processes will be conceptually separated. In general, secondary emission is characterized by the coefficient $\gamma$, which is simply the ratio of emitted electrons to the ratio of incident particles, or

$$\gamma = \frac{N_{e,emit}}{N_{p,incident}}.$$  \hfill (5.23)

$\gamma$ can also be thought of as an ‘emission probability’. The dominant secondary emission process in discharges is ion-induced emission, when the particles bombarding the cathode are positive ions that were formed in the discharge and are accelerated by the electric field toward the cathode. A second, generally less important (though not always negligible) secondary emission process is metastable-induced emission, when the bombarding particles are metastable (long-lived excited neutrals) that were formed in the discharge and slowly diffuse toward the cathode (being neutrals, they are not accelerated by the electric field). Other types of secondary emission (electron, etc.) may occur, but only under special circumstances and will not be considered here.

5.2.1 Ion-Induced Secondary Emission

When considering a positive ion accelerated toward the cathode, it is intuitive to believe that secondary emission occurs because the kinetic energy of the ion ‘knocks’ an electron out of the cathode. While this may occur under special cases, in general the secondary emission process is much more subtle. There are, in fact, two ways the electron is ejected. One is the aforementioned kinetic energy process, but as will be shown this requires much greater energy than is typical for an ion in a discharge. The second is the more subtle, but more prominent, potential energy process (also called the Auger process), which occurs quantum mechanically.

Kinetic Energy Process

In the kinetic energy process, the bombarding ion approaches the cathode and through a ‘binary’ collision with an electron, imparts sufficient kinetic energy for it to overcome the work function $\phi$ of the metal and emit. The threshold velocity necessary to eject an electron can be estimated from this conceptual image.

Consider an electron of mass $m_e$ with energy at the Fermi level $\epsilon_F$, which can easily be converted into a Fermi velocity $v_F$ ($v_F = \sqrt{2\epsilon_F/m_e}$). Recall that the Fermi energy is a property of the cathode metal. The maximum energy exchange from a heavy ion ($m_i >> m_e$) impacting with velocity $v_i$ is

$$\Delta \epsilon = 2m_ev_i(v_i + v_F).  \hfill (5.24)$$

If $\Delta \epsilon = \phi$, the minimum energy required to be emitted for an electron at the Fermi level, then Eq. 5.24 can be rearranged to determine the threshold incident ion velocity,

$$v_{i,th} = \frac{1}{2} \left[ -v_F + \sqrt{v_F^2 + \frac{2\phi}{m_e}} \right].  \hfill (5.25)$$

Now consider an order of magnitude approximation where $\phi \sim 10^9 \text{ eV} \sim 10^{-19} \text{ J}$, $v_f \sim 10^6 \text{ m/s}$,
and \( m_e \sim 10^{-30} \text{ kg} \). Plugging these into Eq. 5.25, one obtains

\[
v_{i,\text{th}} \sim -10^6 + \sqrt{\left(10^{12} + \frac{10^{-19}}{10^{-30}}\right)} \sim -10^6 + \sqrt{\left(10^{12} + 10^{11}\right)} \sim 10^{55} \text{ m/s}. \tag{5.26}
\]

For an air molecule, where \( m_i \sim 10^{-26} \text{ kg} \), \( \epsilon_{i,\text{th}} = (1/2) m_i v_{i,\text{th}}^2 \sim 10^4 \text{ eV} \), which corresponds to a temperature of \( \sim 10^8 \text{ K} \)! Compare this to the typical energy needed for an electron to ionize a neutral molecule \( \sim 10^{-100} \text{ eV} \), and it is clear that most ions will never approach an energy of a 1000-10000 eV in a typical discharge. In fact, in a low-temperature discharge, the ion temperature is on the same order of magnitude as the gas temperature or six orders of magnitude than that necessary for kinetic secondary emission. Therefore, while there may be a small population of high-energy electrons, non typically approach these types of energies. Therefore, generally the kinetic process only contributes very little to ion-induced secondary emission.

**Potential Energy (Auger) Process**

The potential energy process is the dominant ion-induced secondary emission mechanism. As the ‘slow’ ion approaches the surface, it creates a electrical potential energy well as it comes within a few atomic radii of the surface (5-10 Å). The potential barrier is therefore only a few atomic radii as well. An electron with some energy \( \epsilon_{e,\text{cath}} \) defined relative to the work function (and typically near the Fermi energy) tunnels out of the solid (similar to field emission), gets trapped in the potential well, and interacts with the ion. There are two possibilities: neutralization and Auger emission (which is ion-induced secondary emission). These will be discussed separately.

**Neutralization** In neutralization, the electron is captured in one of the excited states by the positive ion to form a neutral gas molecule.

\[
e_{\text{cath}}^- + M^+ \rightarrow M^*
\]

Both metastable and short lived excited states are possible. The resultant energy state of this excited neutral (the former ion) is simply the difference between the ion’s energy and the energy gained from the electron that tunneled from the cathode,

\[
E_{M^*} = E_i - \epsilon_{e,\text{cath}}.
\]

As with all excited states and metastables, the electron will relax down to a ground state, releasing a photon. This is called recombination radiation, or

\[
M^* \rightarrow M + h\nu
\]

where the photon has an energy equal to the difference in the excited and ground states in the neutral

\[
h\nu = E_{M^*} - E_M.
\]

This process is illustrated qualitatively in Fig. 5.5. Neutralization is far more probable than secondary emission, whether it be kinetic energy secondary emission or Auger secondary emission.

**Auger Emission** In Auger emission, the electron is captured in the ground state by the positive ion to form a neutral gas molecule. However, there will be an energy mismatch between the captured electron \( \epsilon_{e1,\text{cath}} \) and the ground state of the neutral gas molecule \( E_M \), or

\[
\Delta \epsilon = \epsilon_{e1,\text{cath}} - E_M.
\]
A second electron in the cathode at a energy of $\epsilon_{e,\text{cath}}$ absorbs this excess energy of neutralization and is ejected from the cathode if it now is at an energy level above the work function. That is, the second electron in the cathode absorbs the excess energy and is promoted to a high energy state. Quantitatively, there will be emission if

$$\Delta \epsilon > \epsilon_{e,\text{cath}},$$

recalling that $\epsilon_{e,\text{cath}}$ is defined relative to the work function. We can write this reaction as

$$e^-_{1,\text{cath}} + e^-_{2,\text{cath}} + M^+ \rightarrow e^- + M$$

The energy of the ejected electron will clearly be

$$\epsilon_e = \Delta \epsilon - \epsilon_{e,\text{cath}} = (\epsilon_{e1,\text{cath}} - E_M) - \epsilon_{e,\text{cath}}.$$  

Typically, we set both the work function and the ionization energy $E_i$ as the reference point as shown in Figs. 5.5 and 5.6. In this case, we can rewrite the excess energy as

$$\Delta \epsilon = E_i - \epsilon_{e1,\text{cath}},$$

and we can consider the energy required to cause Auger emission as

$$E_i - \epsilon_{e1,\text{cath}} > \epsilon_{e,\text{cath}},$$

and the ejected electron has an energy of

$$\epsilon_e = \Delta \epsilon - \epsilon_{e,\text{cath}} = E_i - \epsilon_{e1,\text{cath}} - \epsilon_{e,\text{cath}}.$$  

So, in summary, we can consider what could happen when an ion approaches the cathode surface:

1. The ion is neutralized to an excited state and relaxes back (potential process) neutralization. (highly probable)

2. The ion is neutralized to its ground state and imparts energy on a second electron in the cathode where $\Delta \epsilon = E_i - \epsilon_{e1,\text{cath}} < \epsilon_{e,\text{cath}}$ (potential process) neutralization. (moderately probable)

3. The ion is neutralized to its ground state and imparts energy on a second electron in the cathode where $\Delta \epsilon = E_i - \epsilon_{e1,\text{cath}} > \epsilon_{e,\text{cath}}$ resulting in an emitted electron (potential process) secondary emission. (less probable)

4. The ion impacts the surface with sufficient kinetic energy to promote an electron above the work function resulting in an emitted electron (kinetic process) secondary emission. (high non-probable)

Now let’s consider approximations for ion-induced secondary emission and the secondary emission coefficient $\gamma_i$.\footnote{The subscript $i$ in $\gamma_i$ indicates the secondary emission coefficient for ion bombardment.} The condition for Auger emission $\Delta \epsilon > \epsilon_{e,\text{cath}}$ is most easily met when both $\epsilon_{e1,\text{cath}} = \epsilon_{e2,\text{cath}} = \phi$ as shown in Fig. 5.7. In this case, the condition for secondary emission is that the ionization energy must be greater than twice the work function

$$E_i \geq \phi$$  

(5.27)
If this is the *easiest case*, then it is clear that the *maximum* kinetic energy of an emitted electron must be

\[ \epsilon_{e,\text{max}} = E_i - 2\phi. \]  

(5.28)

For potential processes, unlike kinetic processes, there is no “threshold velocity”; neutralization will occur even if there are low speed ions. The driving requirement as to whether an auger neutralization/ionization process occurs is whether the ionization energy of the gas neutral is more than twice that of the work function; thus the gas molecule and cathode material chemistry must match.\(^\text{12}\)

What is a good match? For a gas, it is best to have a high ionization energy and for the cathode it is best to have a low work function. Or simply

**Gas:** high ionization energy → noble gases (He > 25 eV, Ne > 20 eV, Ar, Kr, Xe, Rn)

**Cathode:** low work function → alkali (Li ~ 2.93 eV, Na ~ 2.36 eV, K ~ 2.29 eV, Rb, Cs) or alkaline earth metals (Be, Mg, Ca, Sr, Ba, Ra).

Based on this limiting criterion, empirical relations for \( \gamma_i \) can be proposed\(^\text{13}\)

\[ \gamma_i \approx 0.016(E_i - 2\phi), \]  

(5.29)

where the energy difference is in eV. Now, it essential to note that this is only an *approximation*, and is accurate to only within 50% for clean metals. The reality is that surface conditions, morphology,

---

\(^\text{12}\)This is not entirely true, there is some dependence not only on the speed of the ion but also its angle of impact, but from a very basic level these can be neglected.

impurities, and contamination play a very important role. In practice, $\gamma_i$ typically ranges from $10^{-4}$ to $10^{-1}$, which shows that typically less than 10% and often less than 1% of the ions in the discharge produce secondary emitted electrons. However, this small supply of electrons is essential to discharge formation, as will be discussed in Sec. XX.

### 5.2.2 Metastable-Induced Secondary Emission

Like an ion, a metastable can also induce an energy exchange process at the cathode that results in electron emission (Fig. 5.8). Like Auger emission, it is a potential energy process because the metastable has excess energy—recall it wants to eventually relax back to its ground state. For this reason, it is fairly efficient at secondary emission. This is often called Auger de-excitation-emission (or Auger relaxation-emission). The energy of the ejected electron will now be

$$\epsilon_e = E_{M^*} - \epsilon_{e_{2,\text{cath}}}.$$  

Again, like with Auger neutralization-emission, the “best case scenario” is when the electron in the cathode solid is at the Fermi level or $\epsilon_{e_{2,\text{cath}}} = \phi$. In this case, the condition for secondary emission is that the excited energy of the gas molecule must be:

$$E_{M^*} \geq \phi.$$  

In general, $\gamma_{M^*}$ for metastable action can range from $10^{-2}$ to $10^{-1}$. Note that is at least on equal if not greater than secondary emission due to ions. However, the primary difference between a
metastable gas molecule and a gas ion is the that the metastable is neutral, which means that it is not accelerated toward the cathode. It only gets there by random processes which means thermal diffusion.\textsuperscript{14} In this sense, metastable-induced secondary is a fairly inefficient process, though the actual ejection of an electron by a metastable is relatively efficient. A large number of metastables will be lost by returning to the ground state, diffusing to the anode, or to other walls/boundaries, thus in many cases, metastable secondary emission is negligible compared to ion secondary emission since virtually all ions will reach the cathode, provided the electrode geometry is reasonable. In practice, it is difficult to distinguish between the ion ($\gamma_i$), metastable ($\gamma_{M*}$), and photoemission ($\gamma_{hv}$) cathode processes that occur during a discharge therefore, we generally collect them all into a single, effective coefficient that we call $\gamma \sim 10^{-2} - 10^{-1}$.

5.3 Summary

The purpose of this chapter was to overview the creation of electrons from the cathode that are critical charge carriers in a discharge. The following processes were discussed:

- the ion-induced $\gamma_i$ process is dominant and it is an Auger potential energy process rather than a kinetic process
- the ion-induced $\gamma_{M*}$ process is less important and it is an Auger potential energy process

\textsuperscript{14}The random motion of the neutral due to its thermal kinetic energy and collisions with other molecules.
Figure 5.8: Illustration of the easiest Auger emission process where the two cathode electrons are at the Fermi energy.

- photoemission (the photo electric effect) can be important depending on the gas (producer of photons) and cathode material (work function)
- thermionic emission is typically not important unless the cathode is at high temperature (such as in equilibrium discharges like arcs)
- field emission is typically not important except in some special cases (extremely small gaps or very high vacuum)

It is important to remember, that more than one of these emission phenomena can be active in a given discharge scenario and it is virtually impossible to identify exactly how the electron was produced. However, as will be seen in Ch. XX, these \( \gamma \) processes are essential to the formation of gas discharges.
Part II

Ion Transport
Chapter 6

Overview

Before discussing the properties of gas discharges, such as their initiation, current-voltage response, and structure, we have to establish a clearer picture of how ions and electrons (and neutrals for that matter) move, in a very general way. This is in fact very closely tied to ionization since the primary ionization process, the $\alpha$-process is a collision process thus relying on how the particles move and interact. This Part of the book is separated into a few different sections. First, we will discuss general transport concepts; that is, general equations for continuum and kinetic transport and other topics often found in a statistical mechanics class. Second, we will outline the concepts behind collisions and mean free path, including collision cross-sections. Finally, we will wrap up with a derivation of the important equations that govern transport in a discharge.
Chapter 7

General Transport Concepts

Lectures 12-15

There are two critical forces when describing the motion of a single charged particle. The first is the influence of an electrical field or the Coulombic force,

\[ \vec{F} = q\vec{E}. \]  

(7.1)

and the second is the influence of a magnetic field or the Lorentz force

\[ \vec{F} = q(\vec{v} \times \vec{B}). \]  

(7.2)

However, while these equations are simple and easy to understand, to understand discharges as a whole, it is insufficient to think of individual particles alone. We must think “bigger” that is how do many charged particles move and, how do collections of charge and uncharged particles move? This can be considered in two ways we can treat the charged particles like a continuum most often thought analogously to a fluid or we can treat the charged particles like collections of individual particles. These are often called the fluid-treatment and kinetic-treatment. The focus of this chapter, however, is on the general concepts of fluid and kinetic transport, treating these generally before we discuss specific concepts particular to discharges in the ensuing chapters.

7.1 Continuum Perspective

In many disciplines, we are taught various transport equations - the Navier-Stokes equations in fluid mechanics, the heat equation in heat transfer, and so forth. However, rather than jumping directly into the transport equations for gas discharges, it is prudent to discuss a general transport equation. If this equation is clear, than the specific transport equations for gas discharges follow naturally.

The general transport equation or, more accurately, the scalar transport equation is a general conservation equation for the motion of a scalar quantity of some medium (gas, liquid, solid, plasma) through a domain. This equation is a continuum equation because it does not treat individual particles but rather the bulk - that is, the scalar quantity is the average across the entire “medium”. Consider, for example a gas. When we describe the scalar quantity of speed, we do not imply that every atom in the gas is moving at the same speed. Some may be (and, in fact, are) moving at different speeds than their neighbors. However, on average, the gas is moving at speed \( u \). When we
discuss the kinetic perspective (Section ??), we will in fact account for the varying speeds of each individual atom.

So let's begin to think about transport generally from a control volume approach. Here we will only consider a 1-D cartesian domain, but it is fairly straightforward to extend this to 3-D and/or cylindrical or spherical coordinates. The net “transport” of any scalar, specific quantity \( \phi \) is the balance of the influx of \( \phi \) across the boundaries into the domain, outflux of \( \phi \) across the boundaries from the domain, the accumulation of \( \phi \) in the domain, the generation of \( \phi \) within the boundaries of the domain, and the loss of \( \phi \) within the boundaries of the domain. These are illustrated in Fig. 7.1. So the general conservation equation is the

\[
\phi_{\text{accum}} = \phi_{\text{in}} - \phi_{\text{out}} + \phi_{\text{gen}} - \phi_{\text{loss}}.
\]  

Figure 7.1: Basic control volume for the transport of a scalar quantity.

Let's consider each of these terms individually:

**Accumulation**: The accumulation term occurs in the volume over time or

\[
\phi_{\text{accum}} = (\rho \phi V)_{t+\Delta t} - (\rho \phi V)_t = (\rho \phi dx)_{t+\Delta t} - (\rho \phi dx)_t
\]

A Taylor expansion can be applied to these terms

\[
(\rho \phi dx)_{t+\Delta t} \approx (\rho \phi dx)_t + \frac{\partial (\rho \phi dx)}{\partial t} dt
\]

such that the accumulation term now becomes

\[
\phi_{\text{accum}} \approx (\rho \phi dx)_t + \frac{\partial (\rho \phi dx)}{\partial t} dt - (\rho \phi dx)_t = \frac{\partial (\rho \phi)}{\partial t} dx dt
\]

since the volume \( dx \) is invariant with time.

**Influx and Outflux**: The influx and outflux terms can be considered together as

\[
\phi_{\text{in}} - \phi_{\text{out}} = (J_x dt)_x - (J_x dt)_{x+\Delta x}
\]

where \( J_x \) is the flux of \( \phi \) in the \( x \) direction. Again, a Taylor expansion can be applied to these terms

\[
(J_x dt)_{x+\Delta x} \approx (J_x dt)_x + \frac{\partial (J_x dt)}{\partial x} dx
\]

---

1What is meant by “specific”? A specific quantity is a scalar per unit mass. For example, we can have internal energy per unit mass, entropy per unit mass, etc. Though we often think about physical properties, this concept can be in fact be non-intuitively applied to other common engineering quantities. For example, the specific form of momentum is velocity (momentum per unit mass).
such that the flux balance terms now become
\[
\phi_{\text{in}} - \phi_{\text{out}} = (J_x dt)_x - \left[(J_x dt)_x + \frac{\partial (J_x dt)}{\partial x} dx \right] = -\frac{\partial (J_x)}{\partial x} dx dt
\]
since the volume \( dx \) is invariant with time.

**Generation and Loss:** The generation and loss terms are conceptually similar and thus can be considered together as

\[
\phi_{\text{gen}} = S_{\text{gen}} dx dt
\]
\[
\phi_{\text{loss}} = S_{\text{loss}} dx dt
\]

where \( S_i \) is the generation/loss rate of \( \phi \) per unit volume. In this case, there is no need for a Taylor expansion to simplify the terms.

With these approximations for each term, Eq. 7.3 can be rewritten as

\[
\frac{\partial (\rho \phi)}{\partial t} dx dt = -\frac{\partial (J_x)}{\partial x} dx dt + S_{\text{gen}} dx dt - S_{\text{loss}} dx dt.
\] (7.4)

Canceling the \( dx \) and \( dt \) terms, Eq. 7.4 reduces to the general scalar transport equation:

\[
\frac{\partial (\rho \phi)}{\partial t} + \frac{\partial (J_x)}{\partial x} = S_{\text{gen}} - S_{\text{loss}}.
\] (7.5)

It should be clear that this can be easily expanded into 3-dimensions as

\[
\frac{\partial (\rho \phi)}{\partial t} + \vec{\nabla} \cdot \vec{J} = S_{\phi},
\] (7.6)

where we have combined the sources and sinks of \( \phi \) into a single term \( S_{\phi} \) for simplicity. The only term that is not well defined in Eq. 7.6 is the flux vector \( \vec{J} \). This term actually can represent a variety of physics, depending on what is driving the flux of the scalar. Here, we will layout two terms that comprise the flux vector in fluid dynamics - advection and diffusion. **Advection** is the transport of the scalar quantity due to the bulk motion of a fluid the fluid carries the scalar quantity. **Diffusion** is the transport of the scalar quantity due to spreading the random motion of particles due to a concentration gradient. These terms can be written as:

**Advection** \( \vec{J}_{\text{adv}} = \rho \phi \vec{v} \) where \( \vec{v} \) is the bulk velocity of the fluid

**Diffusion** \( \vec{J}_{\text{diff}} = -D \vec{\nabla} \rho \phi \) where \( D \) is the diffusivity of the scalar \( \phi \) in the bulk medium

Plugging these into Eq. 7.6 and with some rearranging produces a general advection-diffusion equation:

\[
\frac{\partial (\rho \phi)}{\partial t} + \vec{\nabla} \cdot (\rho \phi \vec{v}) = \vec{\nabla} \cdot (D \vec{\nabla} \rho \phi) + S_{\phi}.
\] (7.7)

As written here, this is called **conservative form** since all quantities are explicitly conserved. There are mathematical manipulations that can be used to change this form of the equation and put it into **non-conservative** form as well. Now, let’s begin with this general form and consider some of the classic transport equations and dissect them.

The **continuity** equation is based on the principle of conservation of mass. Therefore, the scalar of interest is mass. Since \( \phi \) is defined as a specific quantity (per unit mass), we can define it as \( \phi = \text{mass per mass} \). That is, \( \phi = 1 \). In general, we can neglect sources or sinks of mass so that \( S_{\phi} = 0 \). In terms of mass diffusion, we typically consider the diffusion of mass of one type through
7.2. Statistical and Kinetic Perspective

a medium of another type. If we have a homogeneous medium that we are considered, such as in most of fluid dynamics, this can also be neglected $\vec{J}_{\text{diff}} = 0$. Since we are not considering charged particles $\vec{J}_{\text{drift}} = 0$. Therefore Eq. 7.6 reduces to the familiar continuity equation,

$$\frac{\partial (\rho)}{\partial t} + \nabla \cdot (\rho \vec{v}) = 0.$$  (7.8)

The Navier-Stokes equations are based on the principle of of conservation of momentum. Therefore, the scalar of interest is momentum. Typically, we consider momentum as $mv$. But as a specific quantity, this must be per unit mass so that $\phi = mv/m$ or $\phi = v$. The diffusion of momentum is due to viscous forces and thus $D = \nu$ where $\nu$ is the kinematic viscosity of the fluid. A source of momentum is a force on the fluid such as a body force (the gravity-driven buoyancy force) or pressure forces. Ignoring body forces, this becomes $S_\phi = -\frac{dp}{dx}$. Therefore Eq. 7.6 reduces to the following,

$$\frac{\partial (\rho u)}{\partial t} + \nabla \cdot (\rho \vec{v} u) = \nabla \cdot (\nu \nabla u) - \frac{dp}{dx}.$$  (7.9)

Note, this does not appear like the typical Navier-Stokes equation that is familiar to most. First, we if we assume uniform density, we can rewrite the diffusion term in terms of the dynamic viscosity $\mu = \nu \rho$. Further, with mathematical manipulation\(^2\), it is possible to rearrange it the left hand side as well. This produces

$$\rho \frac{\partial (u)}{\partial t} + \rho v \nabla \cdot (u) = \nabla \cdot (\mu \nabla u) - \frac{dp}{dx}.$$  (7.10)

7.2 Statistical and Kinetic Perspective

Suppose we wanted to understand a system of $N$ gas particles in a volume $V$.\(^3\) To understand the system, we need to evaluate the position and velocity of each particle. If each particle is interacting with each other through some force\(^4\), then we would need to solve

$$m_i \frac{d\vec{v}_i}{dt} = \sum_{j=1}^{N-1} F_{ij}(r_i, r_j, t) \text{ for } i = 1, 2, 3, ..., N.$$ 

This is just not possible even given the computing power of modern technology. Statistical mechanics helps us to understand the microscopic properties of the gas and relate them to the macroscopic properties of the gas by obtaining the equilibrium distribution of particles in the gas. Kinetic theory considers the transport of individual particles under non-equilibrium conditions in order to relate microscopic properties to macroscopic transport properties. In many cases, gas discharges are not at equilibrium, as we will see, and we will need to take a kinetic perspective when analyzing the transport and transport properties. Much like the scalar transport equation described in the previous section, there is a kinetic transport equation called the Boltzmann transport equation that we will derive in this section. However, before doing so, we will establish a basic foundation in statistical and kinetic concepts.

7.2.1 Statistical Mechanics

If we have a gas of $N$ particles, each with their own kinetic energy $\epsilon$, we can organize them into "energy levels" each with some subset $N_i$ of the total number of particles, as shown in Fig. 7.2. We call each energy level $\epsilon_i$ with $N_i$ particles a macrostate, and each macrostate consists of

\(^2\)That is, applying the chain rule, expanding the dot products, and applying the continuity equation.

\(^3\)For calibration, there are $\sim 10^{26}$ gas particles in 1 mm\(^3\) volume at standard temperature and pressure.

\(^4\)For example, gravitational or Coulombic.
individual energy states called microstates. These microstates are based on the quantized energy that is a result of the quantum mechanics and Schrödinger's equation. The macrostates or energy levels therefore have subsets consisting of the quantum microstates. We call these microstates the degeneracy $g_i$ of the macrostate $\epsilon_i$. The number of microstates corresponds to the thermodynamic probability $W$ of being in that macrostate - that is, we define **thermodynamic equilibrium** as the most probable macrostate.

![Figure 7.2: A gas with $N$ particles split into different energy levels $\epsilon_i$.](image)

If a certain number of assumptions are made\(^5\), then Maxwell-Boltzmann statistics\(^6\) gives us the number of microstates per macrostate or thermodynamic probability

$$W = N! \prod_{i=0}^{\infty} \frac{g_i^{N_i}}{N_i}.$$  \hspace{1cm} (7.11)

This thermodynamic probability leads to a number of important gas properties. Indeed, from this probability a molecular **partition function** $Z$ can be derived, which describes how the particles are distributed among the various energy levels. From Maxwell-Boltzmann statistics, this partition function takes the form of\(^7\)

$$Z = \sum_{i=0}^{\infty} g_i \exp \left( -\frac{\epsilon_i}{k_B T} \right).$$  \hspace{1cm} (7.12)

We can then use this partition function to determine the probability that some particles are at a specific energy level $i$ via

$$\frac{N_i}{N} = \frac{\exp \left( -\frac{\epsilon_i}{k_B T} \right)}{Z}. \hspace{1cm} (7.13)$$

**Thermodynamic Properties**

Consider some of the classical thermodynamic properties. For example, internal energy $U$. Conceptually, the internal energy is merely the total energy in the gas, or if some of the particles $N_i$ occupy energy level $\epsilon_i$, we can simply sum over all energy levels

$$U = \sum_{i=0}^{\infty} \epsilon_i N_i.$$ 

Using the chain rule, in differential form (that is, the change in internal energy) this becomes

\(^5\)(1) The time-average for a thermodynamic variable is equivalent to the average over all possible microstates. (2) All microstates are equally probable. (3) The particles are independent.

\(^6\)Named after James Clerk Maxwell and Ludwig Eduard Boltzmann, whose tombstone bears his equation for entropy $S = k_B \log(W)$. Interestingly, they derived these formulae independently.

\(^7\)The exponential term arises due to the application of Lagrange multipliers to the mathematical form of the thermodynamic probability.
\[ dU = \sum_{i=0}^{\infty} \epsilon_i dN_i + \sum_{i=0}^{\infty} N_i d\epsilon_i. \]

Now, consider how internal energy is changed from the first law of thermodynamics - either through adding heat or doing work to the system. It should be clear that adding heat to the system changes the number of particles or occupancy at each level; that is, some particles will be elevated from level \( i \) to level \( i + 1 \), for example. Therefore, heat addition \( \delta Q \) is related to

\[ \delta Q = \sum_{i=0}^{\infty} \epsilon_i dN_i. \]

On the other hand, if work is done to or by the system, the energy levels change (new energy levels can become available, for example) such that work \( \delta W \) is simply

\[ \delta W = \sum_{i=0}^{\infty} N_i d\epsilon_i. \]

So even on a molecular level, the fundamental concept of conservation of energy holds true. Now with some mathematical manipulation\(^8\), it can be shown that the internal energy is

\[ U = \sum_{i=0}^{\infty} \epsilon_i N_i = \frac{N}{Z} \sum_{i=0}^{\infty} \epsilon_i g_i \exp \left( \frac{-\epsilon_i}{k_B T} \right) = N k_B T \left[ \frac{\partial (\ln Z)}{\partial T} \right]_{V,N}. \quad (7.14) \]

So now, if the partition function of a gas is known and the number density \( N \), volume \( V \), and temperature \( T \) are known, then we can determine the internal energy.

Now consider the following thought experiment. A chamber \( A \) is separated by a vacuum chamber \( B \) by a valve. When the valve is opened, particles expand from \( A \) into \( B \). This process is irreversible and thus the entropy rises and we can show that

\[ S_{AB} = S_A + S_B. \]

The thermodynamic probability also increases because the final state is more probable than the initial state, but probabilities combine multiplicatively so that

\[ W_{AB} = W_A W_B. \]

So the question is, how is the additive entropy related to the multiplicative probability? Only one mathematical function converts a multiplicative operation to an additive operation - a logarithm. What Boltzmann showed is that, based on this concept, the entropy of a system can be defined as

\[ S = k_B \ln(W). \quad (7.15) \]

Again using mathematical manipulation, this can be defined in terms of the partition function,

\[ S = k_B \ln(W) = N k_b \left( 1 + \ln \left( \frac{Z}{N} \right) + T \left[ \frac{\partial (\ln Z)}{\partial T} \right]_{V,N} \right). \quad (7.16) \]

\(^8\)Taking partial derivatives, for example.
So now, if the partition function of a gas is known and the number density $N$, volume $V$, and temperature $T$ are known, then we can determine the entropy of the gas.

The beauty of statistical mechanics is that, based on the partition function, formulae for the chemical potential, Helmholtz free energy, pressure, Gibbs free energy, and enthalpy can all be derived explicitly as well as the ideal gas law $(pV = Nk_BT)$.

7.2.2 Kinetic Theory

Kinetic theory comes from the statistics of the gas particles and from it we can determine transport properties much like statistical mechanics was used to determine internal properties. First, however, we should consider some basic kinetic concepts that are critical to gas discharges. As implied by its name, kinetic theory focuses on the translational states of the particles in the gas, as opposed to the rotational, vibrational, or electronic.

Maxwell-Boltzmann Distributions

In the continuum perspective, we treat a gas (or fluid or solid) as a uniform body that moves as a single continuous body. A gas flow at 1 m/s implies the entire gas medium is moving at 1 m/s. However, at the particle level, each particle is moving at its own speed, undergoing collisions with its neighbors, and therefore have different energy. If we consider the entire ensemble of particles, we anticipate that there will be variation in the velocity, speed, and energies of all the particles, but distributed about some mean value. From the partition functions described in the previous section, it is possible to determine the equilibrium distributions for these properties and these are called the infamous Maxwell-Boltzmann distributions, which are the gaseous analogy to the Fermi-Dirac distribution for electrons discussed in Section 5.1.

If we consider a volume of particles undergoing no external forces but at some temperature $T$, we can define a probability density function\(^9\) for the relevant kinetic properties. The Maxwell-Boltzmann distribution for the particles' momentum $\vec{p}$ is

$$f(\vec{p}) = \left(\frac{1}{2\pi mk_BT}\right)^{3/2} \exp\left(-\frac{p_x^2 + p_y^2 + p_z^2}{2mk_BT}\right), \quad (7.17)$$

where $m$ is the mass of particles. However, since momentum is related to velocity by $\vec{p} = m\vec{v}$, a Maxwell-Boltzmann velocity PDF can be defined

$$f(\vec{v})dv_xdv_ydv_z = f(\vec{p})dp_xdp_ydp_z,$$

to arrive at

$$f(\vec{v}) = \left(\frac{m}{2\pi k_BT}\right)^{3/2} \exp\left(-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2k_BT}\right), \quad (7.18)$$

However, perhaps more interesting, is the corresponding distribution for a single direction, such as $v_x$, which is nothing but

$$f(v_x) = \left(\frac{m}{2\pi k_BT}\right)^{1/2} \exp\left(-\frac{mv_x^2}{2k_BT}\right), \quad (7.19)$$

\(^9\)What is a probability density function (PDF)? It is the function that describes the likelihood that some variable $x$ will take a value. It is typically a continuous distribution written as $f(x)$ or $p(x)$ and has the units of $[x^{-1}]$. The probability distribution function is the integral of the PDF - that is the probability that $x$ is less than or equal to some chosen value $x^*$ is $Pr[x \leq x^*] = \int_{-\infty}^{x^*} f(x)dx$. One essential property of PDFs is that $\int_{-\infty}^{\infty} f(x)dx = 1$. In other words, the probability that $x$ exits between $-\infty$ and $+\infty$ must be 1 - that is, $x$ must exist.
This PDF is plotted in Fig 7.4a. Note that this *equilibrium* distribution is equally distributed in both the positive and negative directions. This is a *normal* or Gaussian\(^\text{10}\) distribution, and the average \(x\)-velocity comes by taking the first central moment of the PDF or

\[
\bar{v}_x = \int_{-\infty}^{\infty} v_x f(v_x) dv_x = \left( \frac{m}{2\pi k_BT} \right)^{1/2} \int_{-\infty}^{\infty} \exp \left( -\frac{mv_x^2}{2mk_BT} \right) d\left( -\frac{mv_x^2}{2mk_BT} \right) = 0. \tag{7.20}
\]

Note the physical significance of this PDF. This implies that in a group of particles, they have as much likelihood of moving the positive direction as the negative direction, such that their mean directional motion is zero. This matches conceptually with our vision of a room of gas particles that is nominally at “rest” even though the particles are moving.

Figure 7.4: (a) The Gaussian distribution for the \(x\)-component of velocity for molecular hydrogen at 300 K. (b) The equivalent Maxwell-Boltzmann distribution for speed.

The corresponding Maxwell-Boltzmann speed PDF can be derived by taking \(v = \sqrt{v_x^2 + v_y^2 + v_z^2}\) and is

\[
f(v) = \frac{4v^2}{\sqrt{\pi}} \left( \frac{m}{2\pi k_BT} \right)^{3/2} \exp \left( -\frac{mv^2}{2mk_BT} \right). \tag{7.21}
\]

This distribution is shown in Fig. 7.4b. Note, unlike the PDF for \(v_x\), the PDF for \(v\) is not centered around zero since this would imply no motion. The mean speed can be determined similarly to the mean \(x\)-velocity and is

\[
\bar{v} = \left( \frac{8k_BT}{\pi m} \right)^{1/2}. \tag{7.22}
\]

Additionally, a root mean square (RMS) velocity can be extracted from the PDF as

\[
v_{RMS} = \sqrt{\bar{v}^2} = \left( \frac{3k_BT}{m} \right)^{1/2}. \tag{7.23}
\]

Notice that \(v_{RMS} > \bar{v}\).

The Maxwell-Boltzmann distribution can be derived by relating the kinetic energy \(\epsilon\) to the speed \(v\) or

\(^{10}\text{Named after Johann Carl Friedrich Gauss, a German mathematician and physicist}\)
 statistical and kinetic perspective

\( \epsilon = \frac{1}{2}mv^2 \).

arriving at
\[
f(\epsilon) = \frac{2}{\sqrt{\pi}} \left( \frac{\epsilon}{(k_B T)^3} \right)^{1/2} \exp \left( -\frac{\epsilon}{k_B T} \right).
\] (7.24)

Like the speed distribution, this PDF is not centered around zero since \( \epsilon = 0 \) implies no motion. Note
that there is a long tail to the distribution that implies that there is a low probability that some of
the particles in the ensemble will have excessively high energies. As we will learn, these can be
important to the ionization process. The mean energy of the ensemble can be derived two ways. The
more rigorous way is via
\[
\bar{\epsilon} = \int_0^\infty \epsilon f(\epsilon) d\epsilon = \frac{3}{2} k_B T.
\] (7.25)

However, thinking about it more simply, the mean energy will be simply the energy associated with
the mean of the speed squared or
\[
\bar{\epsilon} = \frac{1}{2} m \bar{v}^2 = \frac{1}{2} m v_{RMS}^2 = \frac{1}{2} m \left( \frac{3k_B T}{m} \right) = \frac{3}{2} k_B T.
\] (7.26)

Not surprisingly, we arrive at the same value. This is important, because we can now relate the
temperature of the particles to their average energy.

7.2.3 Boltzmann Transport Equation

The backbone of understanding transport from a kinetic perspective is the Boltzmann transport
equation or BTE - the kinetic analog to the scalar transport equation discussed in Sec. 7.1. Like
the scalar transport equation, the BTE represent the general transport of a quantity. However,
whereas the the scalar transport equation considered the transport of the average quantity \( \phi \), the
BTE considers the transport of the distribution of the quantity \( f(\phi) \). That is, the BTE models
non-equilibrium transport. Consider Fig. 7.5 which shows a packet of particles moving through
time. The packet initially has some distribution \( f(\vec{r}, \vec{v}, t) \). That is at one instant in time some
PDF describes how the particles are distributed in space \( \vec{r} \), velocity (or momentum) \( \vec{v} \), and time \( t \).
However, as this packet of particles moves through time, the distribution will change as particles
undergo interactions with each other and their surroundings to obtain \( f(\vec{r} + d\vec{r}, \vec{v} + d\vec{v}, t + dt) \). This
distribution function \( f \) should obey a conservation equation in time and space \( \vec{v} \) velocity space. We

Consider not physical space, but phase space \((x, v_x)\) as shown by the control volume in Fig. 7.6
that has dimensions \( dxdv_x \). Consider first the particles that flow in/out of the control volume in
the $x$ direction. The particle distribution $f(x, v_x, t)$ flows into control volume the with some speed $v_x$ and exit with a new distribution in space, but the same speed $f(x + dx, v_x, t)$. Now consider the distribution of particles $f(x, v_x, t)$ moving in/out of the control volume in $v_x$ direction. As they leave the control volume, they will have different speeds $f(x, v_x + dv_x, t)$. The rate at which they enter this speed dimension is their acceleration $a_x$, or the rate of change of speed. If we also consider the time rate of change of $f(x, v_x, t + dt)$ we can apply Taylor expansions to arrive at

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial x}(fv_x) - \frac{\partial}{\partial v_x}(fa_x)$$  \hspace{1cm} (7.27)

Figure 7.6: Basic control volume for the transport of of the distribution function in phase space. Collisions cause the sudden appearance/disappearance in the $v_x$ direction of phase space.

The first term on the right hand side, $\frac{\partial}{\partial x}(fv_x)$ should look familiar as it is directly analogous to the advective term in Eq. 7.7. We can see how this equation describes non-equilibrium transport. We know that the Maxwell-Boltzmann equations define the equilibrium distribution $f$, but if this distribution is changing in time and/or (physical/velocity) space, then it changing from its equilibrium state. At the continuum scale, we ignore these small perturbations from equilibrium, but at the microscopic scale these perturbations become relevant and thus the BTE is required. We can generalize this to three-dimensions as

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \nabla_{\vec{r}} f + \vec{a} \cdot \nabla_{\vec{v}} f = 0$$  \hspace{1cm} (7.28)

Here, $\nabla_{\vec{r}}$ is the gradient in physical space whereas $\nabla_{\vec{v}}$ is the gradient in velocity space. A few notes on Eq. 7.28. This is called the collisionless Boltzmann Transport Equation or Vlasov equation, because it only accounts for the transport of the distribution. Collisions can also affect the distribution and will add more terms. Another thing to note is that $f$ is a scalar, so this is directly analogous to the scalar transport equation except now there are 7 dimensions - time, three in physical space, and three in velocity space. Finally, the acceleration term $\vec{a}$ can be correlated to an applied force such as an electric or magnetic field or gravity - that will affect the distribution.

---

11 Or the flow rate of velocity, as opposed to the flow rate of position.
12 That is, $\nabla_{\vec{v}} = \frac{\partial}{\partial v_x} \hat{i} + \frac{\partial}{\partial v_y} \hat{j} + \frac{\partial}{\partial v_z} \hat{k}$ and $\nabla_{\vec{r}} = \frac{\partial}{\partial x} \hat{i} + \frac{\partial}{\partial y} \hat{j} + \frac{\partial}{\partial z} \hat{k}$, respectively.
13 Named after Anatoly Alexandrovich Vlasov, prominent Russian physicist. Technically, Vlasov adapted this equation specifically for plasmas by converting the generic acceleration term into its force equivalents, using the Coulomb and Lorentz forces - sometimes the Vlasov-Maxwell equation. He formulated this equation to study the effects of long-range interactions due to Coulombic forces between charged particles rather than 1-to-1 collisions that we usually consider.
If one considers a collision between two particles, it will change both their physical position \( \vec{r} \) and their velocity \( \vec{v} \) such that it is clear that the distribution of particles \( f(\vec{r}, \vec{v}, t) \) will change. However, on a matter of time scales, the evolution of the particles in space is very slow relative to the evolution of their distribution. However, the change in velocity is essentially instantaneous. That is a particle can change its speed from \( v_x \) to \( v_x + \Delta v_x \) very quickly, and this is like a particle ‘suddenly’ appearing in or disappearing from the phase space control volume in Fig. ??.. That is, the collisions act as a source/sink function to the change in the distribution. We can add this term as a change of the distribution in time to obtain the general Boltzmann transport equation

\[
\frac{\partial f}{\partial t} + \vec{v} \cdot \nabla_{\vec{r}} f + \vec{a} \cdot \nabla_{\vec{v}} f = \left. \frac{\partial f}{\partial t} \right|_c
\]

(7.29)

There are different ways to represent the collision term \( \left. \frac{\partial f}{\partial t} \right|_c \) based on what are called integral formulations. In general, the BTE must be invoked when studying discharges that have non-equilibrium, that is non-Maxwellian, particle distributions.

Once we have solved the BTE, we can extract properties about the particles in the gas. Consider a generic space with some boundary conditions where the BTE has been solved to determine the distribution function \( f(\vec{r}, \vec{v}, t) \). At this point, we only have knowledge of the distribution in physical and velocity space. To convert this to real properties, we multiply the property by the distribution function and integrate over velocity space. That is

**Particle density** \( N(\vec{r}, t) = \int f(\vec{r}, \vec{v}, t)d^3v \) in \([m^{-3}]\).

**Particle flux** \( \vec{J}(\vec{r}, t) = N(\vec{r}, t)\vec{a} = \int \vec{v}f(\vec{r}, \vec{v}, t)d^3v \) in \([m^{-2}s^{-1}]\) where \( \vec{a} \) in the mean particle velocity.

**Particle energy** \( w = \frac{1}{2}m \int v^2 f(\vec{r}, \vec{v}, t)d^3v \) where \( w \) is the energy density in \([J/m^3]\). This can be multiplied by the mean particle velocity to determine the energy flux in \([W/m^2]\).

Beginning with the BTE, one can actually derive the general transport equations. We do this by taking moments of the BTE, which means we multiply the BTE by a scalar of interest \( \phi \) and integrate over all velocity space or

\[
\phi \int \left[ \frac{\partial f}{\partial t} + \vec{v} \cdot \nabla_{\vec{r}} f + \vec{a} \cdot \nabla_{\vec{v}} f = \left. \frac{\partial f}{\partial t} \right|_c \right] d^3v
\]

The nice thing about this is that integrals as operators have linear properties such that every term in the BTE can be considered individually. Consider, for example, the first term in the BTE. This will become

\[
\phi \int \frac{\partial f}{\partial t} d^3v = \phi \frac{\partial}{\partial t} \int f d^3v = \phi \frac{\partial N(\vec{r}, t)}{\partial t} = \frac{\partial N(\vec{r}, t)\phi}{\partial t} - N(\vec{r}, t) \frac{\partial \phi}{\partial t} - \frac{\partial N(\vec{r}, t)\phi}{\partial t}.
\]

Note that the term \( \frac{\partial \phi}{\partial t} = 0 \) because the scalar is not changing in time, but rather the particles carrying the scalar are changing in time. If we conduct a similar exercise on every term, then the BTE will reduce to

\[
\frac{\partial N\phi}{\partial t} + \nabla_{\vec{r}} \cdot (N\vec{v}\phi) - N [\vec{a} \cdot \nabla_{\vec{v}} N] = S_{\phi i}
\]

(7.30)

We will show examples of this in Ch. 8.
7.3 Summary

The purpose of this chapter was to overview general transport concepts that are applicable to any system, and will be invoked here for the study of discharges. There are a few primary points that were discussed:

- if the particle distribution in a medium is in equilibrium, the general scalar transport equation can be used to described the transport of various properties
- if the particle distribution in a medium is in equilibrium, the Boltzmann transport equation can be used to described the transport of the distribution of the particles
- the equilibrium distributions for particles (speed, velocity, and energy) can be described using statistical approaches and are called the Maxwell-Boltzmann distributions