CHAPTER # 1

1.1 Introduction

The exotic properties of non-equilibrium low-temperature plasmas are the basis of numerous innovative technological applications, such as TV-displays, semi-conductor device manufacturing, mobile phones, solar-cells, high efficiency lighting, fine cleaning and coating of optical components, aerospace applications, nano-technology, bio-medicine, cancer treatments etc. Many products could not exist without plasmas.

Most plasma treatments are based on surface processes. They rely on a synergy of physical bombardment of the surface and chemically reactive species, such as radicals. Electrons determine process such as excitation, ionization, and dissociation governing the chemically reactive species. Physical bombardment of substrates is primarily through energetic ion impact.

Low temperature plasmas have relatively low degrees of ionisation compared to high temperature magnetic fusion plasmas and laser produced plasmas. The plasma consists mainly of background neutral particles and a few charged species.

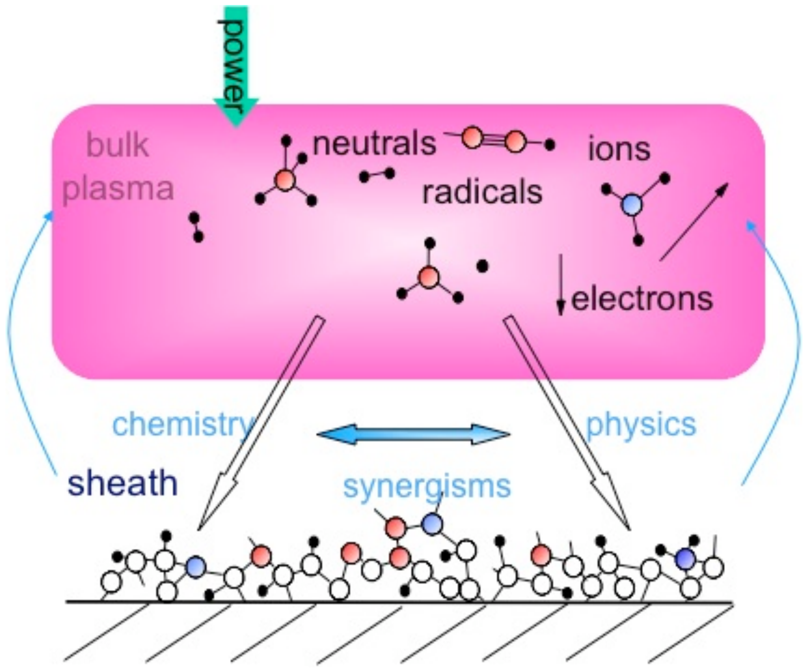

Figure 1.1: *Plasmas are a complex state, involving many different types of particles and processes.*

This course discusses the important electron and ion parameters in technologically relevant plasmas and also the dominating processes. Various methods for production of these non-thermal plasmas and a few of the most relevant applications will be presented.

1.2 Non-equilibrium non-thermal plasmas

The unique properties of industrial plasmas lie in the fact that the plasma species are not all in thermodynamic equilibrium; the plasma species, electron, ions and neutrals have different temperatures. While the neutral and ion species have a relatively low temperature the electrons are rather hot. This higher mean kinetic energy of electrons in a 'cold' background gas is the basis of many technological applications. This key property of plasmas has the facility to produce a unique chemically active environment, characterized by a high electron temperature, without inducing corresponding physical damage, due to high gas temperatures, to an object immersed in the plasma.

Temperature is a measure of the average thermal kinetic energy per particle. Due to the large mass difference between the electrons and other particles in the plasma (heavier ions and neutrals) the energy transfer is rather inefficient, since the transfer of energy depends on the mass ratio of the colliding species. For this reason the ion and neutral temperature may be very different (usually lower - close to ambient temperature ~ 0.05 eV) from the electron temperature (~ 1 – 5 eV). The ions and neutrals are not in thermal equilibrium with electrons.

Based on the relative temperatures of the electrons, ions and neutrals, plasmas are classified as "thermal" or "non-thermal". Thermal plasmas have electrons and the heavy particles at the same temperature i.e. they are in thermal equilibrium with each other. Non-thermal plasmas on the other hand have the ions and neutrals at a much lower temperature (normally room temperature) whereas electrons are much "hotter".

1.3 Quasi-neutrality

A plasma can be defined as a collection of charged particles exhibiting collective effects. This goes beyond charges exerting forces on each-other, but that these forces are as important, and can even dominate, the externally applied forces on the system. In other words, the 'self-generated' electric fields play an essential role in the particle motion. One of the most fascinating aspects of a plasma is its ability to screen externally applied electric and magnetic fields from the plasma bulk.

If a plasma contains positively as well as negatively charged particles, it has a tendency towards electric neutrality. Consider a collection of charges and try to remove just one. Example, remove one electron, and this leaves behind a net positive charge, which tries to pull it back. Removing a second and so on establishes a larger and larger positive charge, making it more difficult to remove more electrons. A great deal of energy is required to separate the charges, and they consequently tend to stay together.

Plasmas do not contain exactly the same number of positive and negative charges, but the difference is very small in comparison to the overall density and can be neglected.

Density of Electrons (n_e) + Negative ions (n_{i-}) = Density of Positive ions (n_{i+})

Macroscopically, the plasma is electrically neutral. However, as referred to earlier on microscopic scale strong electric fields can exist between the particles. Electrons are light and more mobile than the heavier ions, which we can assume to be immobile.

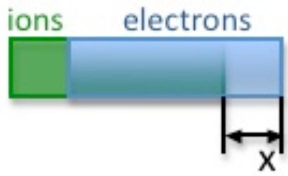

Figure 1.2: *Illustration of charge separation in a plasma*

An electric field is exerted across the distance *x* and holds the charges together. This becomes particularly important in the vicinity of the walls, this will be dealt with later in the module.

1.4 Degree of ionisation

The degree of ionization indicates the percentage of atoms in a plasma that are in the ionized state. Technological plasmas are normally weakly ionised plasmas, in contrast to high temperature magnetic fusion plasmas and laser produced plasmas.

Degree of ionization:

$$I = \frac{n_e}{n_e + n_0} \qquad [1.1]$$

Where n_e is the electron density and n_0 the number density of neutral atoms and molecules. If $I \approx 1$ the plasma is fully ionised e.g. sun, nuclear fusion. Technological processing plasmas are normally weakly ionized where $I << 1$.

Task 1: Consider a plasma at 0.1 Pa, with gas temperature of 400 K, and an electron density of 2 10^{17} Pa, determine the degree of ionization. Discuss whether this is deemed a relatively low or high degree of ionization for a typical technological plasma (e.g. etching plasma in semi-conductor industry) and explain why [6 and references therein]. Discuss any important characteristics of plasmas operated in this regime and the role of the gas temperature.

1.5 Electron temperature

In non-thermal plasmas, electrons play a crucial role. They are the active ‘hot electron gas’. The distribution of electron energies in the plasma governs dissociation, excitation and ionization processes in the plasma resulting in the production of excited, dissociated species, and ionized species in the plasma. The production of these chemically active species is the basis of many technological processes.

Electron energy distribution function:

Momentum transfer between the light electrons and the heavier gas molecules and plasma ions is not very efficient and often the energy deposition into the plasma favours the electrons. As a result ionised gases are described as non-thermal or non-equilibrium, i.e. the constituent e.g. electrons, ions, and gas molecules are each in thermal equilibrium with similar mass species, but not with different mass species.

The velocity distribution of each species can often be represented by a Maxwell-Boltzmann distribution and the energy distribution quantified by a temperature. The electron temperature is typically considerably higher than both the ion and gas temperatures.

$$kT_e >> kT_i \approx kT_{gas}$$

where T_e is the electron temperature, T_i the ion temperature and T_{gas} the gas temperature. Typically electron temperatures are expressed in electron volts (eV) where

kT = 1 eV ≅ 11,600 K

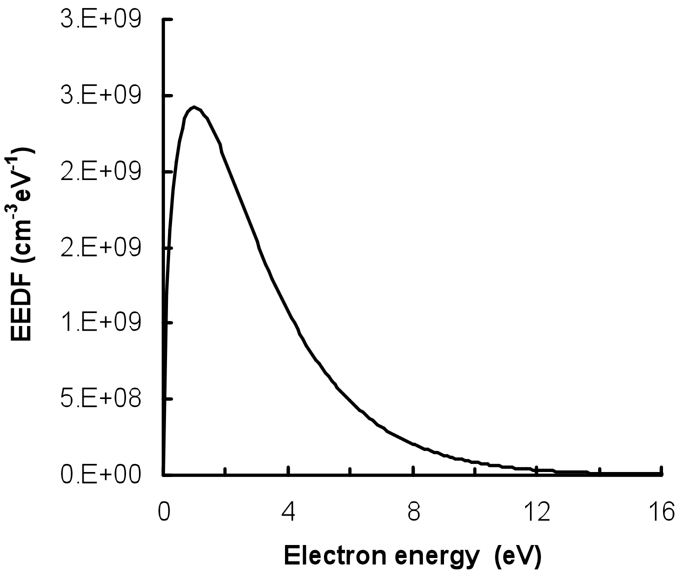

Figure 1.3. *The calculated Maxwell-Boltzmann energy distribution function for an electron density of 10^{10} cm^{-3} at a temperature of 2 eV.*

It should be noted, however, that often in many non-thermal plasmas the electrons are actually not in complete thermal equilibrium and cannot be represented by a Maxwell-Boltzmann distribution with a defined temperature. Often they can exhibit bi-Maxwell energy distributions with more than one temperature association.

1.6 Collisions

Moving particles in a plasma collide and interact with eachother. A huge number of interactions can take in a plasma. In each collisions, momentum and energy must be conserved. Collisions can be divided into three classes:

Elastic collisions, the total kinetic energy is conserved in elastic collisions. The momentum is redistributed between the particles, and the incident particles change direction.

Inelastic collisions involve some energy transfer into internal degrees of freedom, for example, into excited states of atoms or molecules. The kinetic energy is not conserved, although the total energy is conserved. Inelastic collisions can also change the number of particles.

Superelastic collisions where the momentum is redistributed between the colliding particles, where the internal energy from one or both of the participants is transferred to the final kinetic energy of the participants.

Elastic collisions

Elastic collisions are governed by conservation of momentum and kinetic energy

$$m_1 v_1 + m_2 v_2 = m_1 v_1^{\prime} + m_2 v_2^{\prime} \qquad [1.2]$$

$$\frac{1}{2} m_1 v_1^{2} + \frac{1}{2} m_2 v_2^{2} = \frac{1}{2} m_1 \left(v_1^{\prime}\right)^2 + \frac{1}{2} m_2 \left(v_2^{\prime}\right)^2 \qquad [1.3]$$

where the primes denote values after the collision.

For analysis it is often simpler to transform to centre-of-mass coordinates. The collision is also treated in the plane so that only the *x* and *y* components of the vectors are needed. Collisions between electrons and neutrals are often dealt with by setting the neutral velocity to zero.

The velocities of both particles change during the collision. An important consideration is the energy exchange in collisions. The average energy lost by a particle of mass m_1 colliding with a stationary target of mass m_2 is proportional to $2m_1 m_2/(m_1 + m_2)^2$. If $m_1 = m_2$ as is often the case of ions in their parent gas (e.g. He^+ ions in helium), the energy loss is 1/2. This implies very efficient energy exchange and has the consequence of keeping ion and neutral energies quite close, compared to electron energies.

Task 2: Show that the average energy lost by a particle of mass m_1 colliding with a stationary target of mass m_2 is proportional to $2m_1 m_2/(m_1 + m_2)^2$.

However, electrons are much lighter than any atom, molecule or ion and this implies poor energy transfer from electrons to the heavier particles. Hot electrons are thermally well insulated from the ions and the background gas.

The collision frequency depends on the relative velocity of the particles. For electrons colliding with (stationary) neutral atoms, the collision frequency is just the number of collisions that an electron with velocity *v* will suffer in unit time. We often wish to compute the actual number of collisions of a particular type, which occur in a given time per unit volume in a plasma. Since both collision partners have a distribution of velocities, averaging over the distributions is needed.

The reaction rate, the number of collisions between particles type *a* and *b*, is given by

$$R_{ab} = n_a n_b K_{ab} \qquad [1.4]$$

where K_{ab} is the rate constant. Units of *R* are $m^{-3}s^{-1}$. For electrons colliding with neutrals we can assume that the neutrals are stationary and no energy loss occurs in the collisions.

Inelastic collisions

When looked at closely, atoms and molecules have an intricate and complex structure. The electrons are bound to the positive nuclei of atoms by electrostatic attraction and energy is needed to remove an electron from an atom. The electrons in atoms and molecules can also be raised to higher energy states. These are called electronic excited states. Molecules also have rotational and vibrational excited states, in which the atoms in the molecule rotate or vibrate with respect to the centre of mass. Only inelastic collisions can form excited states or remove electrons.

<u>Excitation and light emission:</u>

Inelastic collisions can happen when there is enough energy available among the collision partners. The simplest way to form excited states is to bombard atoms with energetic electrons. Some of the energetic electrons give up energy to the electrons in the atoms, raising them to higher energy levels. Usually the excited states have short lifetimes (of the order of a tens of nanoseconds) and the excited electrons drop down to lower energies, eventually stopping in the lowest energy level, the ground state. Energy has to be given up in this process and this is normally through the emission of a photon.

We can write the process as

$$A + e^- \rightarrow A^* + e^- \rightarrow A + e^- + h\upsilon$$

where A is the atom, $h\nu$ is a photon of frequency ν and e^- is the electron. ν depends on which energy level in the atom was excited. The lowest level in argon lies at 11.5 eV above the ground state. This gives a photon deep in the ultraviolet region of the electromagnetic spectrum. The above reaction does not affect the atom, it simply converts a part of the electron's kinetic energy to light.

There is an important exception to the general rule that excited states decay quickly to the ground state. Radiative transitions are governed by selection rules (which express conservation laws) and not all are allowed. For example, the $1s_3 \rightarrow 1p_0$ and $1s_5 \rightarrow 1p_0$ transitions in argon are forbidden. An electron can certainly excite the valence electron to the upper level, but the excited atom cannot decay to the ground state by emitting a photon. It remains excited for a relatively long time (milliseconds, or even seconds in some cases). These are metastable states and they are very important in low temperature plasmas.

<u>Light emission</u>

Plasmas exhibit various emission characteristics and thus are often used as light sources in various applications. The emission from the plasma is based on the following principle:

- Energetic electrons excite atoms/molecules
- Spontaneous decay leads to emission of a photon

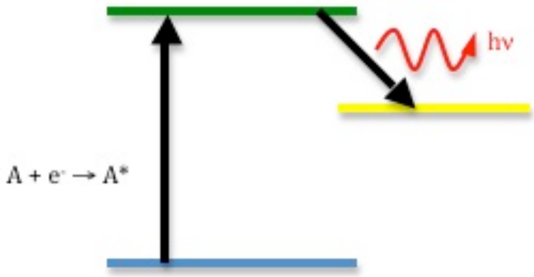

Figure 1.4: *Electron impact excitation and spontaneous decay results in light emission*

Ionization:

To make a plasma we need to produce free electrons and ions and again this can be achieved by bombarding atoms or molecules with energetic electrons

$$A + e^- \rightarrow A^+ + 2e^-$$

In this ionisation process the electron loses energy corresponding to the ionization energy E_i and we may consider that this energy is carried as potential energy by the positive ion. It is released when the ion eventually recombines with another electron to form a neutral atom again.

Species	He	Ne	Ar	Kr	Xe
Ionization energy (eV)	24.6	21.5	15.8	14.0	12.1

Table 1.1: *Ionization energies of different noble gases*

The ionization energies of noble gases are given in Table 1.1. These are the lowest energies needed to produce an electron ion pair and one of the outermost electrons (valence electrons) is removed. The cross section for the collision of course depends on the particular species, but in all cases the ionisation energy is a threshold below this the cross section is zero. If enough energy is available, a whole range of processes become accessible. It is possible to remove any electron, not just valence electrons, and it is even possible to remove more than one electron in a single collision.

Task 3: Consider how the ionization energies depend on the mass of the noble gas.

Dissociation:

In a plasma chemistry context it is very important that electrons can efficiently dissociate molecules into atoms or radicals (chemically reactive fragments). The simplest process is electron impact dissociation

$$AB + e^- \rightarrow A + B + e^-$$

Again the cross section for this process has a threshold energy which is the bond energy. The minimum energy necessary to separate an atom from a molecule. Fragmentation usually occurs.

Summary of energy thresholds:
Ionization energy of atoms and molecules – usually 10 – 20 eV
Excitation energy of atoms and molecules – usually 8 – 12 eV
Binding energy of molecules – usually 1 – 6 eV

Task 4: Is the rate of ionization or dissociation higher and why?

There is an enormous range of possible inelastic collisions. Here are a few examples:

Photoionisation: $A + h\nu \rightarrow A^{+} + e^{-}\left(+h\nu^{\prime}\right)$

De-excitation: $A^{*} + e^{-} \rightarrow A + e^{-}$
This is a superelastic collision. The electron gains kinetic energy.

Stimulated emission: $A^{*} + h\nu \rightarrow A + 2h\nu$
This is the basis of gas discharge lasers.

Penning ionisation: $A^{*} + B \rightarrow A + B^{+} + e^{-}$
This is particularly important in dealing with long-lived A^{*} states, e.g. metastables. The ionisation energy of species B must be lower than the energy of the metastable.

Photodissociation: $AB + h\nu \rightarrow A + B$

Dissociative attachment: $AB + e^{-} \rightarrow A^{-} + B$
This is normally the main negative ion formation mechanism and can be particularly important in electro-negative plasmas.

Ion-atom ionisation: $A^{+} + B \rightarrow A^{+} + B^{+} + e^{-}$

Mutual neutralisation: $A^{+} + B^{-} \rightarrow A + B$

1.7 Collision cross-sections

Collision cross sections (σ) quantify the probability of a collision occurring between two or more particles. It is basically a measure of the probability that an encounter will occur between particles. Cross-sections have a dimension of area (e.g. m^2). For two bodies in collision this represents the effective area of a particle as seen by another passing particle. This is unique to any pair of particles, for example the interaction between two charged particles will be stronger than that for two uncharged particles and so the cross section will be larger. The strength of the interaction between the two particles will also depend on the length of time for which they interact i.e. their relative velocity or energy. There may also be threshold energy for a reaction to be possible e.g. the ionization of a molecule (O_2) by an electron, the kinetic energy in the collision must at least be equal to the ionization potential of the molecule (12.5 eV). Information about cross sections for the many diverse reactions in a plasma is essential for an accurate insight into the plasma chemistry. Unfortunately in many cases the data can be sparse.

1.8 Mean free path

Moving particles in a plasma will collide with each other. The mean free path is the average distance a particle moves before it collides. The mean free path λ is given by:

$$\lambda = \frac{1}{n_0 \sigma} \qquad [1.5]$$

where σ is called the collision cross-section.

The mean free path depends on the density of the background neutral gas and the collision cross sections.

In weakly ionized plasmas n_e, n_i << n_0 so the most frequent collisions are among neutrals. See table 1.2 for typically mean free paths of different collision processes at different pressures.

Pressure	Spacing between atoms	Mean free path	
		Ar - Ar	e^- - Ar
1 Pa	0.16 μm	8 mm	40 mm
20 Pa	0.06 μm	0.4 mm	2.3 mm

***Table 1.2**: Typical mean free paths at different pressures*

Task 5: If the average relative velocity of the particles involved in collisions is *v* then determine an expression for

(a) the mean time between collisions

(b) the collision frequency

1.9 Creating low temperature plasmas

Examples of the various discharge types are given below and the distinction between thermal and non-thermal can be recognised. These discharges will be discussed in more detail later in this module.

Low-pressure discharges:
Glow discharge plasmas: ***non-thermal*** plasmas generated by applying an electric field to a gas (dc or kHz) e.g. fluorescent light bulb. An example of a glow discharge is a DC glow discharge where a direct current (dc) applied across two metal plate electrodes sustains the plasma.

Capacitively coupled plasma (CCP): similar to glow discharge plasmas, but generated with high frequency RF electric fields, typically 13.56 MHz. These are widely used in the semi-conductor industry for nano-fabrication and integrated circuit manufacturing for plasma etching and plasma enhanced chemical vapor deposition.

Inductively coupled plasma (ICP): similar to a CCP and with similar applications but instead of electrodes a current carrying coil induces a current in the plasma for sustainment.
Wave heated plasma: similar to CCP and ICP in that it is typically RF (or microwave), but is heated by both electrostatic and electromagnetic means. Examples are helicon discharges, electron cyclotron resonance (ECR), and ion cyclotron resonance (ICR). These typically require a coaxial magnetic field for wave propagation.

Low pressure parameter range:
electron density: 10^8 to 10^{13} cm^{-3}
electron temperature: 0.1 to 10 eV
neutral pressure: 1 to 1000 mTorr
power input: 1 to 10000 Watts
size (volume): 1 to 10^6 cm^3

High pressure:
Corona discharge: this is a ***non-thermal*** discharge generated by the application of high voltage to sharp electrode tips. It is commonly used in ozone generators and particle precipitators.

Dielectric barrier discharge (DBD): is a ***non-thermal*** discharge generated by the application of high voltages across small gaps wherein a non-conducting coating prevents the discharge transition to a thermal plasma mode. It is also widely used in the treatment of textiles. The application of the discharge to synthetic fabrics and plastics functionalizes the surface and allows for paints, glues and similar materials to adhere.

Arc discharge: this is a high power ***thermal*** discharge of very high temperature ~5,000 K. It can be generated using various power supplies. It is commonly used in metallurgical processes. For example it is used to melt rocks containing Al_2O_3 to produce aluminium.

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