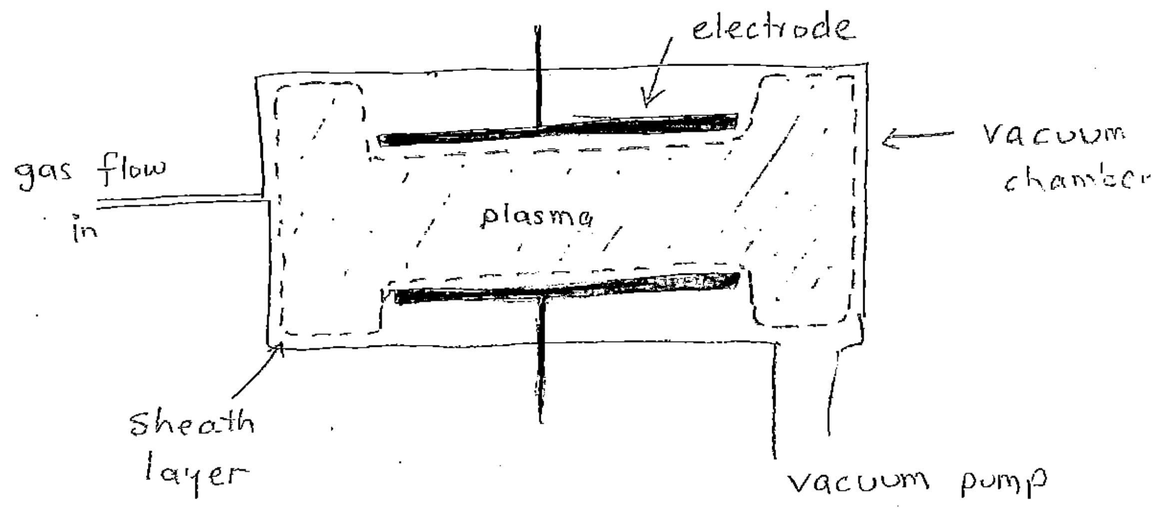
1. General Image of a Plasma.

There are many types of plasmas, and each separate type of plasma has various characteristic features. Most plasmas have a vacuum chamber, a vacuum pump, a gas flow system and electrodes. Not all plasmas have all of these features. However, in this course, we will use the general image of a plasma which is shown in the figure below.



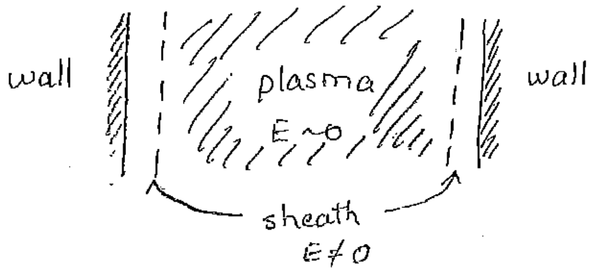
This plasma has various important general features. These are listed below, and then described briefly.

- sheath layer
- different types of particles
- reactions in the plasma
- reactions at the walls
- power input to the plasma
- power loss from the plasma.
- gas flow into and out of the chamber.

Sheath layer

In the figure, the plasma fills the entire chamber, and there is a sheath layer between the main plasma and the walls and electrodes. This sheath layer always exists. It is the interface between the main plasma, and the solid surfaces of the chamber walls.

In the main plasma, the electric field is very small, while in the sheath, there might be a very large electric field. This is a very important aspect of the plasma.



Particles in the plasma

In a plasma, there are

- neutral particles
- ions
- electrons.

In some plasmas, there might be many types of neutral particles, and there might be many different types of ions.

Always, in the main plasma, the number of positively charged particle is the same as the number of negatively charged particles

$$n^+ \simeq n^-$$

In a simple plasma, we can write this as

$$n_i \simeq n_e$$

Reactions in the plasma

There will always be some reactions in the plasma. The most important reaction is the ionization reaction, which we usually write as

$$e + \text{atom} \rightarrow e + (\text{ion} + e^-) .$$

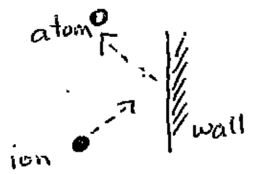
This reaction creates new ions and electrons which are necessary to sustain the plasma.

There are many, many, other types of reactions. We will study these reactions, in detail, later.

Reactions at the walls

There are always reactions at the walls, because electrons, ions and neutral particles are always hitting the walls. One example of a reaction is

$$\text{ion} \xrightarrow{\text{wall}} \text{neutral atom}.$$



This reaction causes charged particles to be lost from the plasma.

Power input to the plasma

In a plasma, there must be some mechanism which causes the plasma to be generated and sustained, so there must be some power which is input to the plasma. The two most common forms of input power mechanism are

- applying a dc or rf voltage to an electrode
- applying rf or microwave electric fields.

Usually, this power is absorbed by the electrons in the plasma.

Power loss from the plasma

The power (and energy) which is input to the plasma must exit the plasma by some means. This power loss might be

- light leaving the plasma
- chamber walls becoming hot
- material inside the plasma being altered

This aspect of plasmas is often forgotten. There is always input power for a plasma. This is obvious, and much attention is paid to this. However, there must be power loss too. The loss mechanism is just as important as the input power mechanism.

Usually, we want to use the plasma in an application, and the power loss is very important for the application. We need to use the power efficiently. For example, in a plasma-display-panel (PDP) plasma, we want to create a bright light source. Hence, it is important for the energy, which is used to make the PDP plasma, to be converted into light. If most of the energy is lost by some other mechanism, such as heating the PDP cell, then this is very inefficient. If we don't understand the power loss mechanism, then we can't make the PDP cell work efficiently.

Gas flow

For most plasma systems, gas flows into the chamber and then leaves the chamber through a vacuum pump. If the plasma is stable, then the inflow and outflow must be same.

The input flow speed can be written in the units of $m^3 s^{-1}$, but this means that the number of particles entering the chamber is not known. Usually, the flow is given in units of standard cubic centimeters per minute (sccm) or standard litres per minute (slm).

Note that

$$1 \text{ sccm} \sim 2.7 \times 10^{19} \text{ particles per minute}.$$

Also, notice that this flow rate is very small, because a cubic centimeter is small.

volume ~ 1 cc

2. General Properties of plasmas

Before you can begin to discuss about plasma mechanisms and reactions, it is important that you first have some idea about the meaning of the basic properties of plasmas. If you don't understand these basic plasma properties, it is difficult to understand complicated discussion about reactions and other things. The most basic plasma properties are

(i) Gas Density, Pressure.

(ii) Neutral particle density

(iii) electron density

(iv) electron energy and electron temperature

(v) ion density

(vi) plasma potential.

(vii) ionization ratio

(i) Gas density n_g and pressure p:

- This is one of the easiest properties to understand. The gas density is just the number of atoms or molecules of the gas which are in a unit volume. The gas density n_g is related to the pressure by

$$p = n_g k T_g \qquad (\mathrm{Pa}).$$

where k is Boltzmann's constant and T_g is the gas temperature in K. (Because of the temperature dependence, a hot gas at 1 Pa contains fewer particles — n_g is lower — than a cool gas at 1 Pa).

- Plasmas are operated over a wide range of pressure, from about 10^{-6} atm to about 5 atm or so.

• By using the above equation, you can calculate that at a gas pressure of 1 mTorr (~ 0.15 Pa), and for $T_g \sim 300K$, the gas density is $n_g \sim 3.3 \times 10^{19} m^{-3}$. This is a very large number, and is difficult to imagine. However if you consider a $10\mu m \times 10\mu m \times 10\mu m$ box (this size is, maybe, just visible by eye), then, at 1 mTorr, there are ~ 30,000 particles inside the box.

(ii) Neutral density n_0

• This property is often the same as the gas density n_g. In a simple discharge, using a gas such as argon or helium, there is only one type of neutral particle (the gas atom) and so $n_0 = n_g$.

• In complex gas mixtures, there can be many types of neutral particles. For example.

- O_2 plasma $\longrightarrow$ O_2, O
- CH_4 plasma $\longrightarrow$ CH_4, CH_3, CH_2, CH, H, H_2, C, C_2 C_2H_6 .....

For the cases where there are many types of ~~plasmas~~ neutral particles we don't use the symbol n_0, but usually write n_{CH_4}, n_{CH_3} .... etc.

(iii) Electron density n_e

• This is one of the most important plasma quantities because most of the reactions in the plasma occur because of a collision between an electron and another particle.

• Most plasmas have n_e between $10^{14} m^{-3}$ and $10^{20} m^{3}$. These numbers are very large, but if you imagine the same $10\mu m \times 10\mu m \times 10\mu m$ box, then the number of electrons in the box is between ~ 0.1 and ~ 100,00 (Note that this is much less than the n_0 which was mentioned above).

(iv) Electron energy and electron temperature, T_e

- the energy of the electrons is extremely important because many important collisions in the plasma are collisions between electrons and other particles. Most collisions, such as ionization (e + atom $\rightarrow$ e + (ion + e)) have a threshold energy. So the energy of the electron determines whether this reaction will occur, or not occur.

- the electron temperature, T_e, is an indication of the average electron energy. There are many many electrons, and some have very high energy and some have very low energy. The electron temperature is an indication of the average energy.

- Because electron properties are very important, we will consider electron temperature and energy, in much more detail, later in this course.

(v) ion density n_i

- Ion density is the density of ions in the plasma. If there is only one kind of ion, then usually we write n_i

- In many plasmas, such as in argon, there are only positive ions. In these plasmas, always (except in the sheaths).

$$n_i = n_e$$

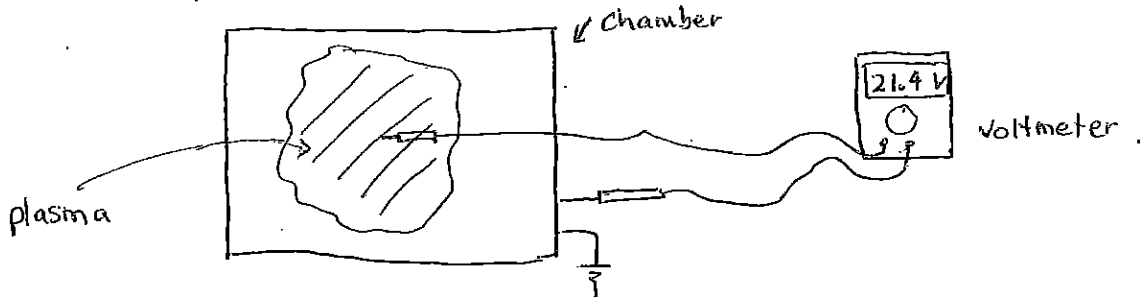
- In some plasmas, there can be negative ions as well as positive ions. In this case

$$n_{i+} = n_{i-} + n_e.$$

(vi) Plasma potential ϕ

- this is the voltage that the plasma has. This voltage exists because the number of negatively charged particles is very very slightly less than the number of positive particles. This creates a small positive voltage

- The plasma potential is sometimes very hard to understand at first, but it is simply a voltage. If you used voltmeter with one pin arm in the plasma, and one pin arm attached to ground, the voltmeter would show a voltage — this is the plasma potential.



- the plasma potential, for virtually all plasmas, must be positive when compared to the chamber walls. (If the chamber walls were ~~mo~~ at higher voltage than the plasma, all the electrons would quickly leave the plasma and the plasma would be extinguished).

(vii) ionization ratio

- this is the ratio of ion density to neutral gas density n_i/n_g. In most discharges, $n_i \ll n_g$.

- for example, in a high pressure plasma $n_g \sim 10^{25}\ m^{-3}$ and n_i might be $10^{20}\ m^{-3}$. n_i seems to be large, but there are 10^5 times more neutral particles than charged particles. So nearly all the particles in the plasma are neutral

- in a high density plasma processing reactor, the ionization ratio can become "high". For example, if $n_g \sim 10^{19}\ m^{-3}$, sometimes, $n_e \sim 10^{18}\ m^{-3}$. So nearly 10% of the gas atoms are ionization.

- In <u>most</u> plasmas, the ionization ratio is small ($\sim 10^{-3}$ or smaller). Only in fusion plasmas does the ratio become close to one.

3. General Behaviour of different particles

In a plasma, there are various different kinds of particles. Each kind of particle has its own characteristic behaviour. The main purpose of this section is to describe the general behaviour of the three main types of particles

(i) Stable neutral particles

(ii) Positive ions

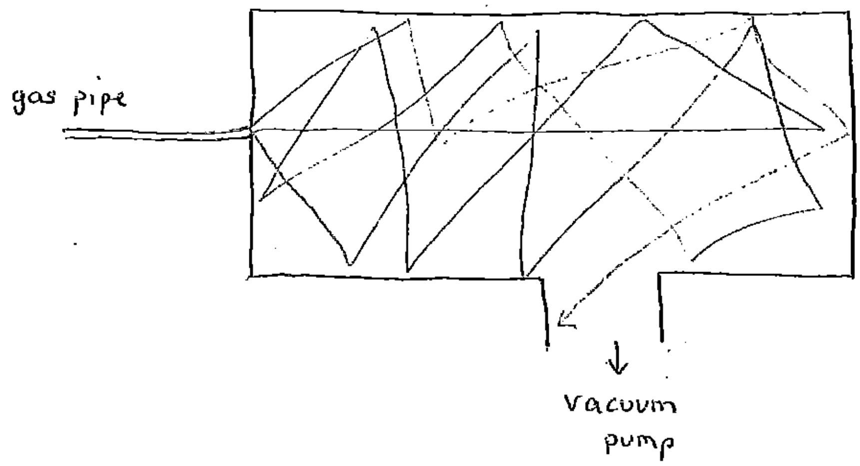
(iii) electrons.

In later sections, we will consider more detailed behaviour, but in this section, we will only consider general behaviour.

(i) Stable neutral particles.

- These particles have two types
  - particles in the gas which enters the chamber
  - stable particles which are formed by reactions in the plasma.

- The basic "life" of a gas molecule or atom is that
  - it enters the chamber through the gas system
  - it moves through the chamber, colliding with other particles and colliding with walls
  - it exits the chamber through the pumping port.



energy and velocity

- Mostly the neutral particles have a fairly low energy, because there is no method to directly heat them. The gas temperature is about 300 ⟺ 700 K and so the average energy is approximately

$$E_{ave} = \frac{kT}{e} \sim 0.025 \rightarrow 0.05 \text{ eV}$$

- For an argon atom (mass = 40 Amu) this means that

$$v \sim 300 \rightarrow 500 \text{ m s}^{-1} \qquad (\approx 500 \text{ m s}^{-1} = 1800 \text{ km/h}$$

time taken to move across plasma

- this depends on the size of the plasma, of course. For the example above, and a chamber with diameter 20 cm, this time is

$$t = \frac{0.20 \text{ m}}{v} \approx 0.5 \text{ ms}$$

particle lifetime

- In a vacuum system, the time that a gas particle is inside the chamber (i.e. the time between entering the chamber and exiting through the pump) is given by

$$\tau = \frac{V}{S}$$ where V = chamber volume, S = pumping speed.

- for example above, with $V \sim 1\ m^3$ and a pumping speed of $30\ ls^{-1}$

then
$$\tau = \frac{V}{S} = \frac{1\ m^3}{0.03\ m^3 s^{-1}} \sim 30\ sec.$$

Notice that this is a <u>very</u> long time compared with the time taken for the neutral atom to move across the chamber ($\sim 0.5\ ms$).

- Hence, the neutral particles move through the chamber <u>many</u> times. They pass through the chamber and have <u>many</u> collisions with other particles and with the walls

(ii) <u>Positive Ions</u>

- Ions usually have a low energy, although a little higher than the neutral particles. This is because they receive some energy from small electric fields in the plasma, and some from electron collisions. Typically, they might have temperature of $\sim 1000 \rightarrow 2000\ K$, which is an energy of $0.1 \rightarrow 0.3\ eV$.

- in the sheaths, there is a strong electric field, and the ions can gain energy from this field before they strike the walls of the chamber. When the ions hit the walls, they can have a large energy.

- the basic life of the ions is

  (i) created by ionization collision

  (ii) move slowly towards the walls

  (iii) gain energy in the sheaths and strike the walls.

  ((iv) Becomes a neutral atom and returns to the plasma)

Energy and Velocity

- Typical energy 0.2 eV → for an argon atom this is

$$v \sim 1000 \text{ m s}^{-1}$$ ie, slightly faster than the atoms.

Lifetime

- Again, for a chamber with diameter ~~radius~~ 20 cm, (radius 10 cm), the time taken for the ion to move from the center to the walls is

$$\tau = \frac{0.1 \text{ m}}{10^3 \text{ m s}^{-1}} = 0.1 \text{ ms}.$$

- If there are collisions, this time is lengthened, of course.

- Notice, this is a much, much shorter time than the neutral atoms.

(iii) Electrons

- In most plasmas, the electrons are the plasma species which is directly heated. Thus, the electrons have much higher average energy than the heavier plasma particles (such as ions and neutral particles). The electrons gain energy through the electric fields in the plasma, and move quickly through the plasma. Usually, though, the electrons can't leave the plasma because of the sheaths (which act as a barrier to the electrons) and so the electrons get reflected back into the plasma.

energy and velocity

- the average electron energy is about 3~4 eV
- this corresponds to

$$v \sim 10^6 \text{ m s}^{-1}$$

- at this speed it only takes ~ 200 ns to move across the plasma chamber that we used as an example previously.

lifetime

- It is hard to calculate the lifetime directly but the electron lifetime <u>must</u> be the same as the ion lifetime. Therefore for the example used so far,

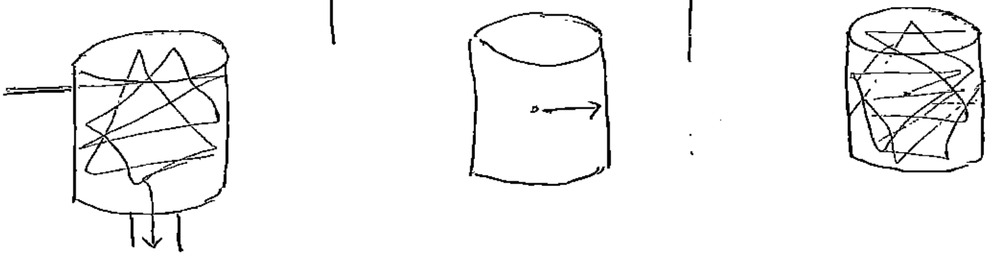
$$\tau \sim 0.1 \text{ ms.}$$

- notice that, with a 0.1 ms lifetime, and a speed of $10^6 ms^{-1}$ the electrons can move 500 times across a 20 cm chamber.

Summary of the example.

- low pressure Argon plasma
- chamber ~ 20 cm diameter, 20 cm length.

	neutrals	ions	electrons
E	0.03 eV	0.2 eV	3 eV
v	400 ms^{-1}	1000 ms^{-1}	10^6 ms^{-1}
$\tau_{transit}$	30 sec	0.1 ms	200 ns
$\tau_{lifetime}$	30 sec	0.1 ms	0.1 ms



Summary

- This discussion was about the general behaviour of plasma particles. This is only a "general" description.

- Note that there was no mention of collisions. In nearly all plasmas, there are enough particles for collisions to become important. These affect the lifetimes very much.

- Also, there might be electric or magnetic fields. These affect the ions and electrons greatly.

- Hence, the situation in a real plasma might be quite differen to this general discussion. However, this discussion is useful because it provides a rough guide to the very different behaviour of the different particles in the plasma. The general summary might be

neutrals → slow, low energy, long-lived

ions → slow, (low energy in plasma / high energy in sheath) short-lived

electrons → very fast, high energy, short-lived.

4. Particle and Energy Balance

In Section 1, a general image of a plasma was discussed. ~~[illegible]~~ Two of the important things mentioned there were that we have to consider

- gas flow in and gas flow out of the chamber
- power in and power loss from the plasma.

In this section, we will discuss these things in more detail.

4.1 Particle Balance

Particle Creation

As mentioned earlier, there are two main ways in which particles are created. These are

- by gas flowing into the chamber
- by particles being created in collisions.

One example of the second kind of particle creation is the creation of O atoms in an O_2 plasma,

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

The O atom is not originally in the gas, but it is formed in the plasma.

Particle Loss

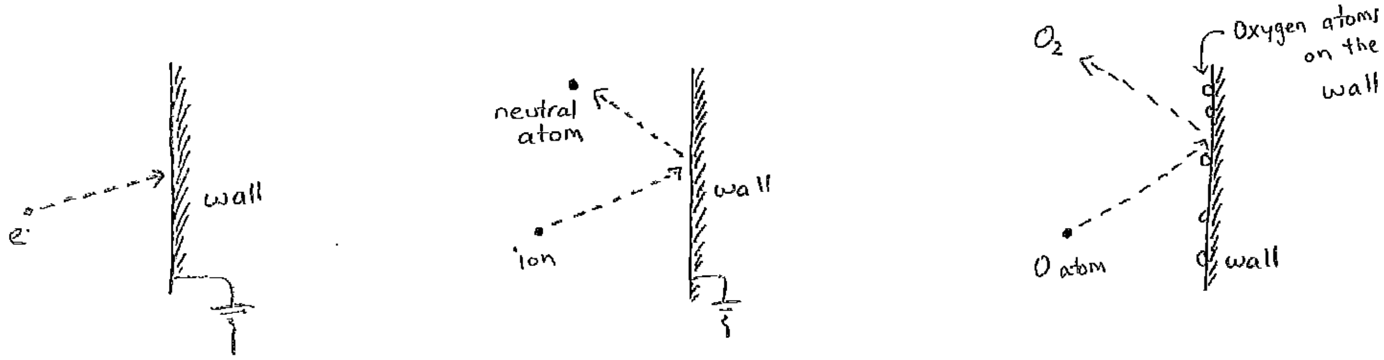
There are several different kinds of particle loss. These are

- particles being removed from the chamber by the vacuum pump
- particles hitting the walls and being transformed into other particles.
- particles being converted into other particles by collisions.

The first type of loss is easy to understand

The second type of loss includes examples such as

- electrons hitting the walls, and being lost to ground
- ions hitting the walls, and being converted into neutral atoms
- neutral particles hitting the walls, and being converted into different particles



The third type of loss includes examples such as

- recombination reactions $e + \text{ion} \rightarrow \text{atom}$

  $O + O \rightarrow O_2$

- atoms being lost by ionization $e + O \rightarrow O^+ + 2e^-$

- in more complicated discharges, particles are created and lost in collisions such as

  $CH_3 + e \rightarrow CH_2 + H + e$ (loss of CH_3, creation of CH_2, H)

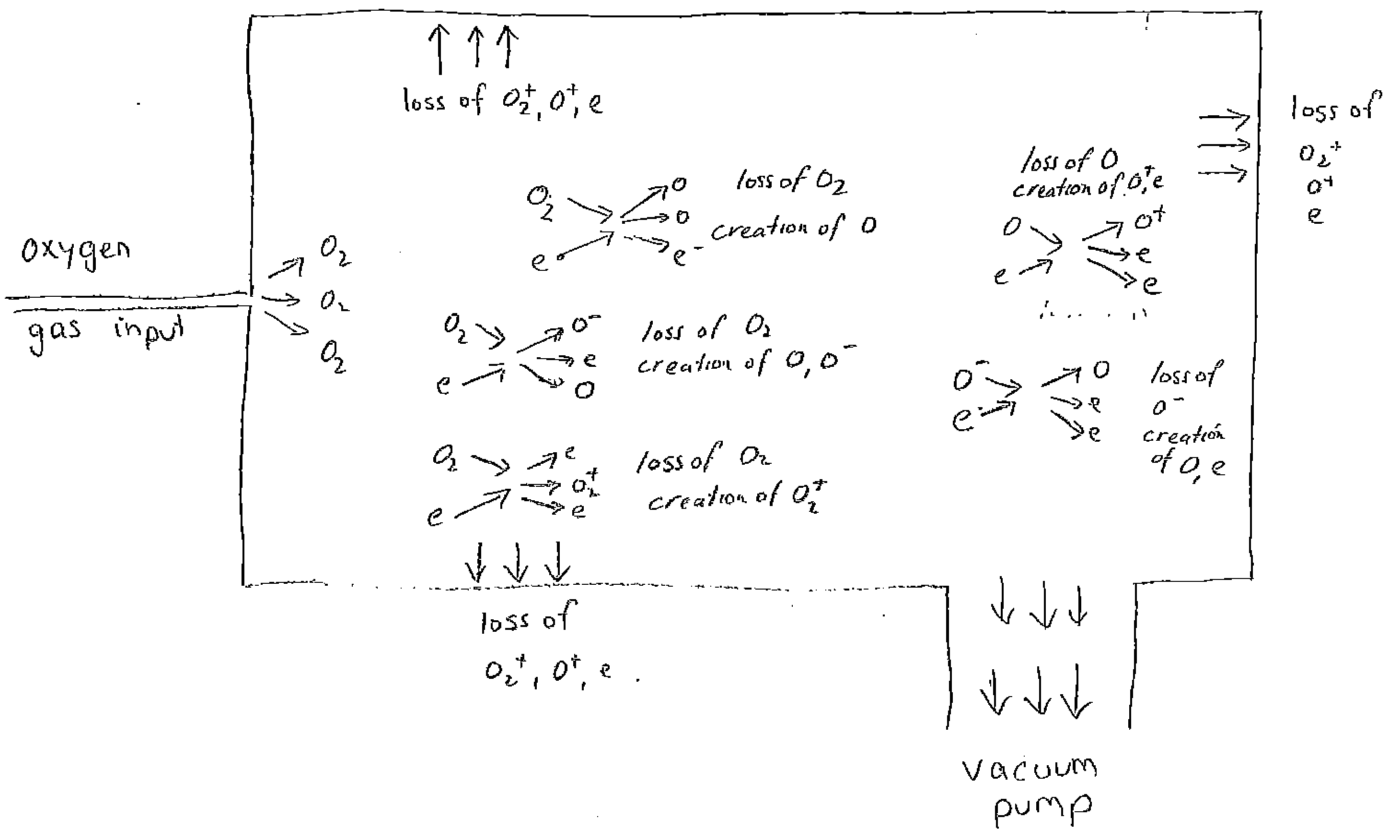
Particle Balance.

In the previous two subsections, particle creation and particle loss were discussed. In a stable plasma, these processes must balance,

ie, rate of particle creation = rate of particle loss

This must be true for all particles - electrons, ions, neutral particl

Example O_2 plasma



There are many different creation and loss mechanisms in an O_2 plasma. When the plasma is stable, all of these processes must be balanced.

4.2 Energy Balance / Power Balance

In a stable plasma, the amount of power which is input to the plasma must be equal to the power loss from the plasma.

power in = power out (loss).

This can also be written as

energy in = energy out (loss).

Power Input

There are various methods of putting power and energy into a plasma, but nearly all involve the application of an electric field. And nearly always, the power is absorbed by electrons. There are various kinds of electric field

- dc
- ac – low frequency
  high frequency (RF)
  ultra-high frequency
- microwave

Later, we will discuss these different forms of power input. In this section, however, the most important thing is that a specific amount of power goes into the plasma.

Power loss

This is one of the most important things which must be understood for you to understand plasmas properly. There are various types of power loss. The main types are listed below, and then discussed in more detail

- creation of new particles
- generation of light
- energy carried by particles which hit the walls.

(i) creation of new particles

One of the main processes in plasmas is the creation of new particles. Neutral, stable gas particles are fed into the chamber, and then new particles are formed by collisions. It is important to notice that this process consumes energy.

For example, in a plasma containing CF_4 gas, some of the collisions are

$$e + CF_4 \rightarrow CF_3 + F^-$$
$$e + CF_3 \rightarrow CF_2 + F + e$$
$$e + CF_3^- \rightarrow CF_3 + 2e$$

All of these reactions require energy, and nearly always the kinetic energy of the electron provides that energy.

Another example is the simple ionization collision in an argon plasma. In this collision, an argon ion is created, and, like the reactions above, this reaction requires energy.

$$e + Ar \rightarrow Ar^+ + 2e$$

This reaction requires 15 eV of energy. Therefore, we can consider that it "costs" 15 eV to create an ion.

(ii) Generation of light

One of the most obvious characteristics of plasmas is that they emit light. It requires energy to create this light.

The light is produced by atoms in the plasma which have gained energy in a collision, and then lose this energy by emitting light. For example

$$e + Ar \Rightarrow Ar^{*} + e$$

$$Ar^{*} \rightarrow Ar + h\nu \leftarrow \text{photon.}$$

The atom gains energy from the electron and becomes "excited". The excited atom Ar^{*} is unstable, and it quickly loses energy, by emitting light, and returns to its usual, stable state.

Notice that, like the ionization collisions, this process requires energy. Hence, some of the energy/power which is consumed by the plasma is used to generate light.

(iii) Energy carried by particles which strike the wall.

This is one of the most important loss mechanisms. In a stable plasma, particles (neutral particles, ions, electrons) are continually leaving the plasma. These particles have kinetic energy, and when they hit the chamber walls, this energy is transferred to the walls. The result is that the walls become hot.

This energy loss can be very high. For example, ions which strike the chamber walls have been accelerated by the electric field in the sheath region, and so they have large energy when they hit the walls.

Sometimes, as in plasma processing, this particle energy is useful, and it is used to modify materials such as Silicon. In other plasmas, such as lamps and gas lasers, the particle energy can be a problem, because the chamber walls become so hot that the plasma becomes inefficient.

Energy Balance

In the simplest way, we can write the power balance equation as [power in = power out] but it is more useful to consider the three types of power loss considered above.

$$\left[\text{Power in}\right] = \left[\begin{array}{c}\text{power used to}\\ \text{create particles}\end{array}\right] + \left[\begin{array}{c}\text{power used}\\ \text{to create}\\ \text{light}\end{array}\right] + \left[\begin{array}{c}\text{power loss to}\\ \text{the chamber}\\ \text{walls}\end{array}\right]$$

Energy Flow in a Plasma

The ideas discussed above can be used to give a general idea of the power and energy flow in a plasma. This can be represented by

Power in $\longrightarrow$ Power absorbed by electrons $\longrightarrow$ new particles created by electron collisions $\longrightarrow$ all particle species carry energy to the walls.

The last step is usually the important step for plasma applications (generation of light, plasma processing etc). Hence we can also write the flow as

Power in $\longrightarrow$ power absorbed by electrons $\longrightarrow$ new particles created by electron collisions $\longrightarrow$ new particles perform useful actions

4.3 Summary

For understanding plasmas, it is necessary to have some idea of the important mechanisms in the plasma. A useful way of considering the plasma is to view it in terms of the particle and energy balances which are discussed above.

creation of particles = loss of particles

power input to the plasma = power lost from the plasma.

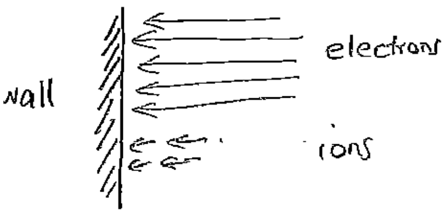
Later in this course, we will consider these balance equations much more carefully.

5. Sheaths, Electric Fields and the Plasma Potential

It was mentioned in Section 1 that the sheaths, which surround the main plasma, are one of the most important regions of the plasma. The sheaths act as a kind of boundary between the plasma and the chamber boundary. Also, they keep the plasma stable, by preventing electrons from leaving the plasma, and forcing the ions to leave the plasma. In this section, these sheath mechanisms will be discussed.

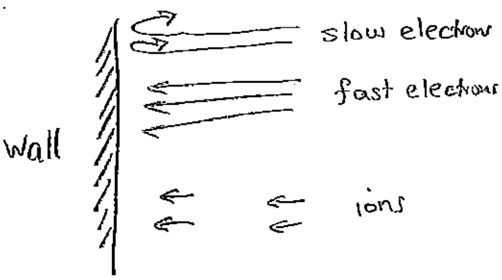
5.1 Generation of the sheaths and the plasma potential

Stage 1.

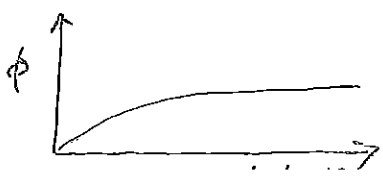


When the plasma is first started, there are roughly equal numbers of electrons and ions throughout the "plasma". However, because the electrons move so much faster than the ions, they leave the plasma much more rapidly.

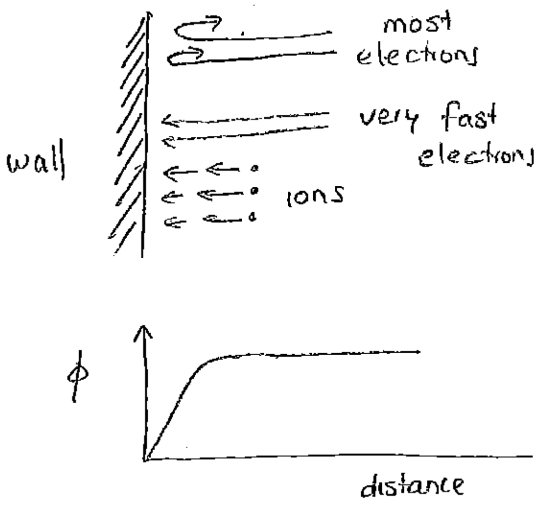
Stage 2



Because the electrons leave the plasma more rapidly than the ions, the density of ions is greater than the electron density. This charge imbalance makes the plasma slightly positively charged. (ie, the plasma potential becomes positive). Th creates a small electric field, which helps to stop the electrons leaving, and forces the ions towards the walls.



Stage 3



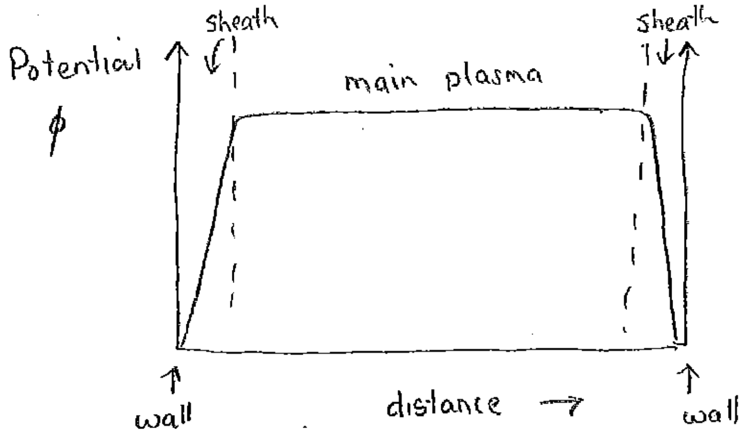
This process continues (electrons leaving, plasma potential increasing) until the electric field is strong enough to stop most of the electrons leaving the plasma. When the plasma potential is large enough,

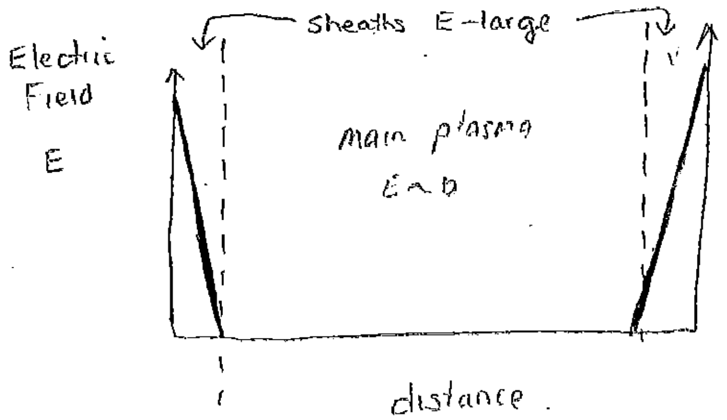
$$\left[\begin{array}{c}\text{number of}\\ \text{electrons}\\ \text{leaving}\end{array}\right] = \left[\begin{array}{c}\text{number of}\\ \text{ions leaving}\end{array}\right]$$

and the plasma becomes stable.

The result of this process is a plasma potential like the one shown below. The potential changes very rapidly near the walls, and becomes fairly constant in the main part of the plasma.

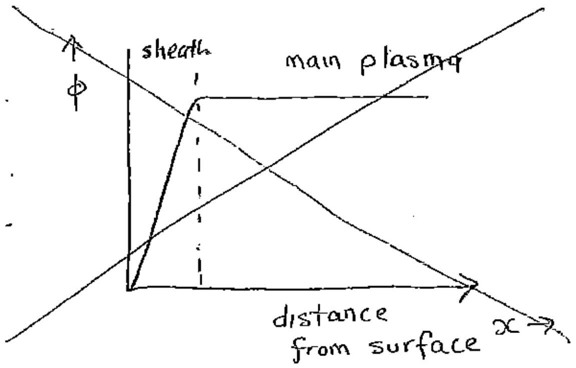
The <u>sheath region</u> is the region near the walls, where the plasma potential is not constant, and, consequently, the electric field is large.

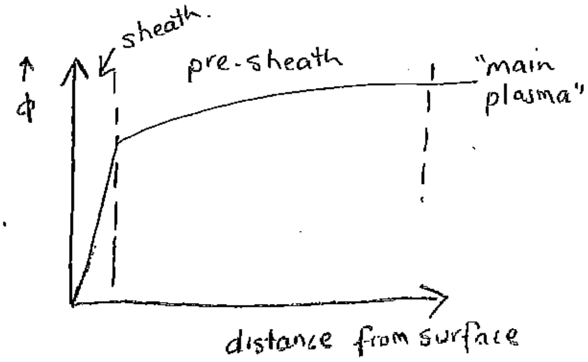




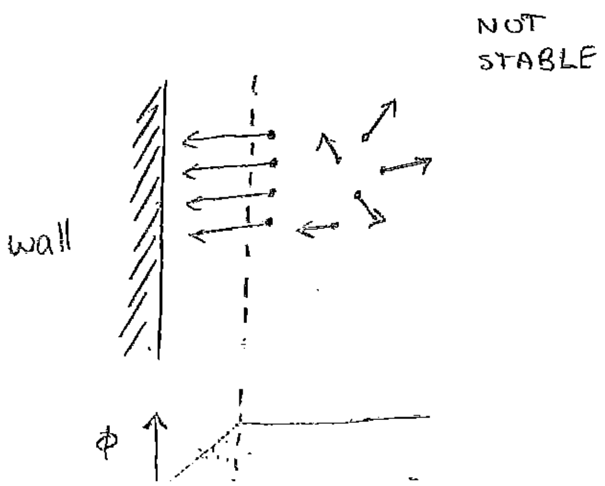
5.2 Pre-sheath region

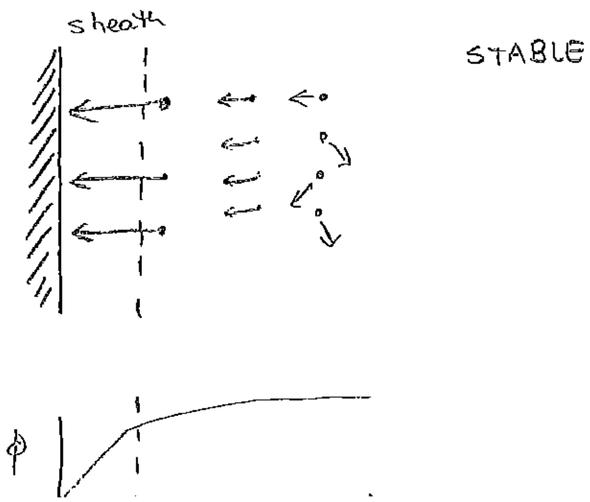
In the picture shown in the previous section, the plasma potential is shown as being constant in the main plasma (and so $E=0$) and changing very rapidly in the sheath (and so E is large). Actually, however, there is a transition region between these two extreme cases. This transition region is called the pre-sheath.





The pre-sheath region exists because of the balance between electrons and ions leaving the plasma. The reason for this is that the ions are slow moving, and only the ions which are very close to the sheath edge will enter the sheath and leave the plasma. It is necessary for ions from the central region of the plasma to be able to move towards the sheaths. If the plasma potential is constant away from the sheath, however, then this will not happen. There needs to be a small slope in the plasma potential for the ions to move efficiently towards the sheath





Another way of considering the formation of the pre-sheath is as follows

- the electrons which enter the sheath can come from far away
- the ions which enter the sheath must come from close to the sheath edge
- Hence, close to the sheath edge, more ions than electrons are being "lost". So the positive plasma potential close to the sheath edge is reduced
- This reduction of the plasma potential near the sheath edge results in a potential difference between the central plasma and the plasma near the sheath. This forces ions to move towards the sheath.
- The actual distribution of plasma potential is the distributio[n] which exists when these electron and ion flows become balanced.

5.3 Some important properties of the sheath.

Each of the following things are useful to remember. The actual size of each property is determined by the need to balance the electron and ion loss rates from the plasma.

(i) Bohm velocity u_B

This is the velocity of the ions at the sheath edge. It is given by

$$u_B = \left(\frac{k T_e}{m_i} \right)^{1/2}$$

We will not discuss the derivation of this velocity, but it is an important property to remember. When the ions have this velocity the loss of

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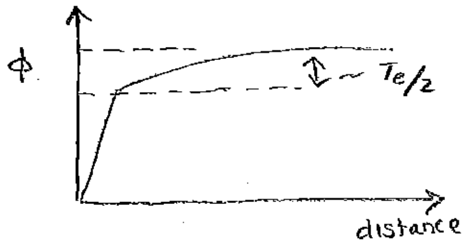
We will not discuss the derivation of this velocity, but it is an important property to remember. When the ions have this velocity, the loss of ions and electrons at the sheath edge is balanced.

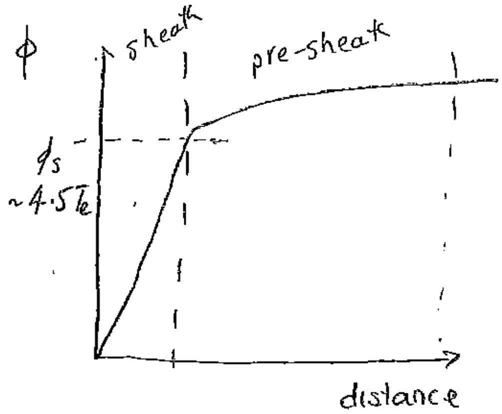
(ii) Pre-sheath potential.

This is the potential difference between the main plasma and the sheath edge. It is also the potential needed to accelerate the ions to the Bohm velocity. It's value is roughly equal to $T_e/2$.



(iii) Sheath Potential

This is the potential between the wall surface and the sheath edge. Usually, it has a value of $4\sim5\ T_e$. The exact factor ($4\sim5$) depends on the type of ions in the plasma, but for most cases, a value of about 4 or 5 is reasonably accurate.

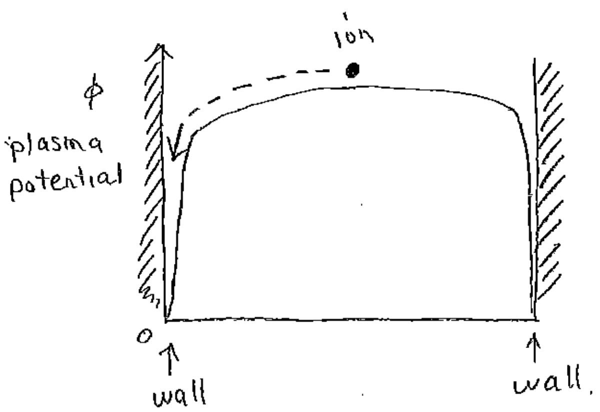


Notice that this ~~is~~ value is for the case where no separate potential is applied to the wall surface. In those cases, such as near a dc or rf electrode, the sheath will be determined mostly by the applied voltage.

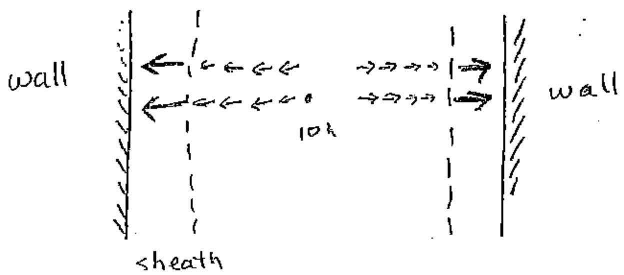
5.4 Particle Flow

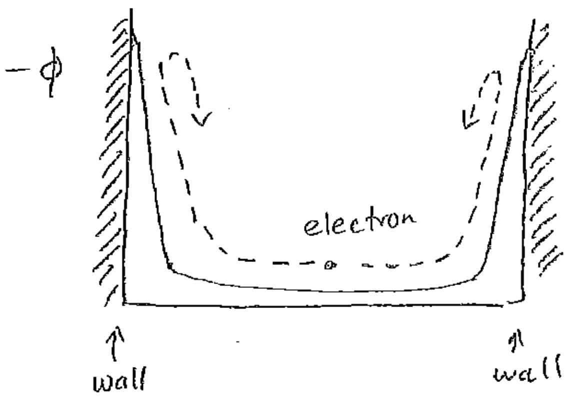
At the end of Section 4, the idea of "energy flow" in a plasma was presented. By using some of the discussion above, we can also consider the idea of "particle flow".

- somewhere in the plasma, ions and electrons are created by ionization collisions
- the electrons move throughout the plasma and are prevented from leaving the plasma by the sheaths and the electric fields there
- the ions move (slowly) from the place they were created towards the sheaths. Eventually they "fall out of" the plasma at the sheaths.

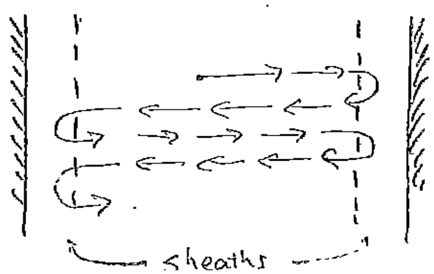


plasma potential helps the positively charged ions to move towards the edge.





plasma potential helps to stop electrons from leaving the plasma. Only the high energy electrons can reach the walls.



5.5 Summary

- sheaths and the plasma potential are very important in determining plasma properties
- the properties of the sheath, and the distribution of plasma potential are determined by the balance between electron and ion loss from the plasma.
- remember that this is only a general description. The sheath properties of different plasmas depend on many specific details of each plasma. Also, other things, such as collisions of the electron energy distribution function are also important.
- we will have to consider sheath properties again later in the course, after we have studied collisions.

6. Electron Energy and Temperature

In Section 4, particle balance was discussed, and it was shown how this balance is determined, to a large extent, by reactions which involve electrons. Also, energy balance was discuss , and it was shown how this depends on energy transfer from electrons to other particles (by collisions)

In Section 5, the sheath properties and the plasma potential were discussed, and most of the properties have some dependence on the electron energy and temperature.

Hence, it can be seen that the electron properties are very important. They are one of the most important properties because reactions and collisions in the plasma are initiated by high energy electrons.

In this section, we will discuss the distribution of electron energy, and the electron temperature.

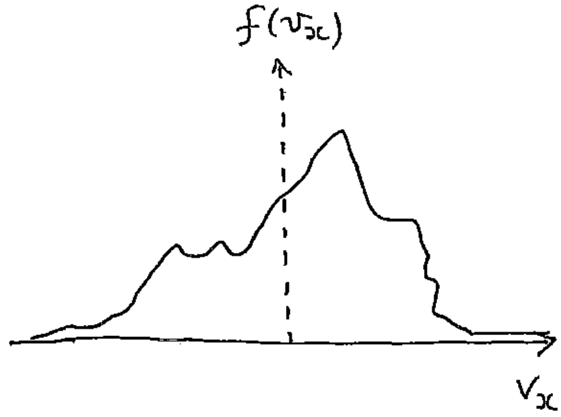
6.1 Velocity & Energy Distribution Functions

In a plasma, all of the electrons do not have exactly the same energy. There is a range of electron energy — some electrons have very low energy, and a few electrons have very high energy. The distributio of energy is called the Electron Energy Distribution Function (EEDF). Another important function, called the Electron Velocity Distribution function (EVDF) is closely related to the EEDF.

Firstly, we will discuss velocity and energy distribution functions in general terms.

General Distribution $f(v)$

- One example of a possible velocity distribution is shown in the figure. Some particles have positive velocity and some particles have negative velocity



- This is only a 1-D distribution. It shows one component, v_x, of the velocity $\underset{\sim}{v} = (v_x, v_y, v_z)$.

- It is very important to note that the distribution gives the number of particles which have velocity between v_x and $(v_x + \Delta v_x)$. This interval, Δv_x, is very important. It does not make sense to talk about how many particles have velocity $V_x = 300\ ms^{-1}$, for example, because there are <u>no</u> particles with $v_x = 300.0000\ldots\ ms^{-1}$. We can, however discuss how many particles have V_x between $299.5\ ms^{-1}$ and $300.5\ ms^{-1}$.

*
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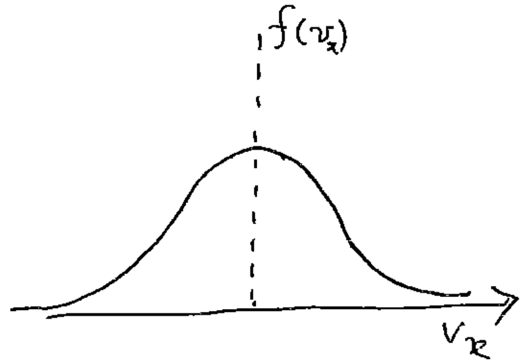
It is important to remember that, when we use an EVDF (or EEDF), we are always talking about particles within a certain velocity (or energy) interval

Maxwellian Distribution

For the case when particles have many collisions, the most common form of velocity distribution is



$$f(v_x) = A\, e^{-\frac{V_x^2}{V_{th}^2}} \qquad \text{(Eq. 6.1)}$$

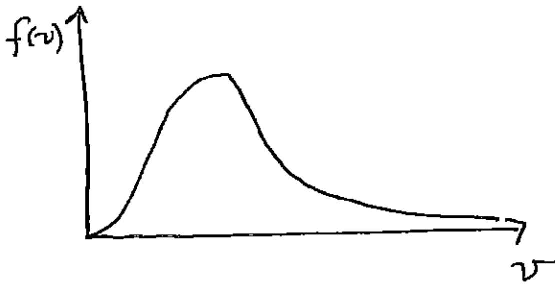
- V_{th} is called the thermal velocity and A is a constant

$$v_{th} = \left(\frac{2kT}{m}\right)^{1/2}.$$

- This distribution has a Gaussian shape $\left(f \propto e^{-a^2}\right)$ and is called Maxwellian distribution.

- note this is only a 1-D distribution.

3-dimension "speed" distribution



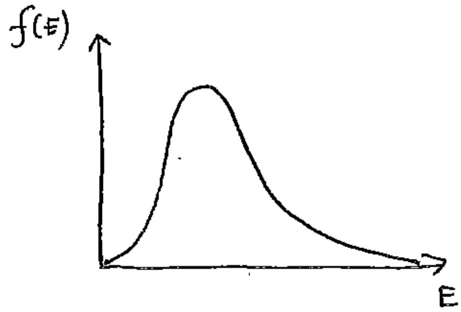
This is given by

$$f(v) = A^* v^2 e^{-\frac{v^2}{v_{th}^2}} \qquad \text{(Eq 6.2)}$$

where A^* is a constant and

$$v = (v_x^2 + v_y^2 + v_z^2)^{1/2}$$

Energy distribution



This is given by

$$f(E) = A^{**} E^{1/2} e^{-E/kT} \qquad \text{(Eq 6-3)}$$

where $E = \frac{1}{2}mv^2$ and A^{**} is a constant.

The size of the constants A^* and A^{**} can be found by the conditions that

$$n = \int_0^\infty f(v)\,dv \qquad \text{and} \qquad n = \int_0^\infty f(E)\,dE$$

where n is the particle density

By solving this we get.

$$A^* = n \left(\frac{m}{2\pi kT}\right)^{3/2} \qquad A^{**} = \frac{n}{\pi^{1/2}(kT)^{3/2}}$$

Sometimes we use these factors, but the most important thing to remember is the form of the distributions, as shown in the 3 figures, and as shown in Equations 6.1, 6.2 and 6.3.

<u>Comments on these distributions</u>

- The above distributions can be used for any particles, not just electrons
- T in the equations is the absolute particle temperature, in K
- the thermal velocity $v_{th} = \left(\frac{2kT}{m}\right)^{1/2}$ is the velocity of the peak in the distribution
- the average velocity is given by

$$v_{ave} = \left(\frac{8kT}{\pi m}\right)^{1/2} \qquad \text{(and is larger than } v_{th}\text{)}.$$

- the average energy is given by $\frac{3}{2}kT$. (for a 3-D distribution)

6-2 The EEDF and the plasma

- The form of the EEDF is important in understanding plasmas because many important collisions and reactions involve high energy electrons.

For example

(excitation and emission) $e + Ar \rightarrow Ar^* + e \rightarrow Ar + \underline{\underline{h\nu}} + e.$

(ionization) $e + Ar \rightarrow Ar^+ + 2e.$

(dissociation) $e + CF_4 \rightarrow CF_3 + F + e$

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

- All of these reactions require a certain amount of energy, (called the threshold energy). Usually this is energy is provided by the kinetic energy of the electron. So the amount of a particular reaction (such as ionization) which occurs depends on how many electrons have energy higher than the threshold energy.

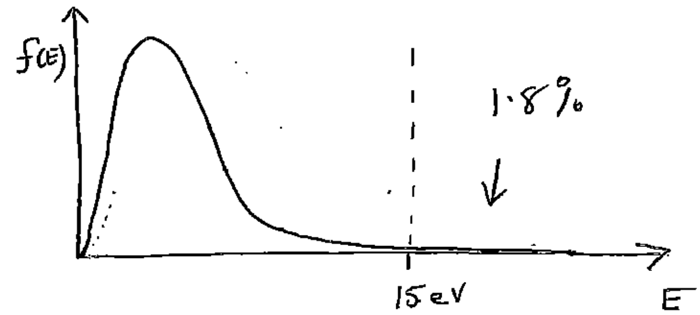
- In glow discharges, the average electron energy (which is nearly the same thing as the electron temperature T_e), is usually in the range of 1–5 eV. The threshold for most reactions is usually 10 eV or higher, so the number of electrons which can cause reactions is usually <u>much</u> less than the total electron number.

  – For example, in an argon plasma with $T_e = 3\,eV$, the number of electrons which can cause ionization (15 eV) is very few

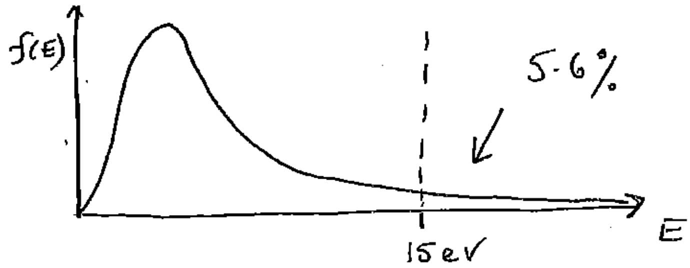
- However, a small change in temperature can lead to a huge increase in the number of high energy electrons

For example T = 3 eV

1.8% of electrons have E > 15eV



T = 4eV
5.6% of electrons have E > 15eV



- So it is important to remember that small changes in the electron temperature can have enormous effects on the types of reactions which take place in a plasma

6.3 Other types of distributions

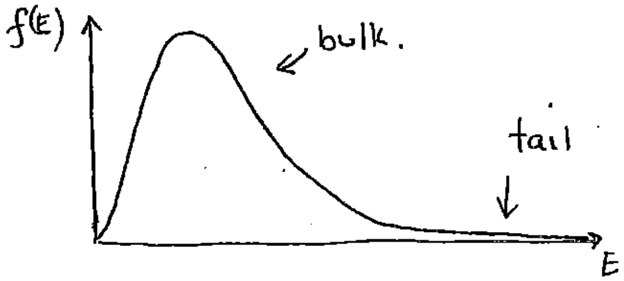
In this section, so far, we have only discussed Maxwellian distributions. There are various other types of distributions, too. These include the Druvestyn distribution, bi-Maxwellian distribution, and various others. Right now, we will not discuss these, but it is important for you to remember that other distributions exist.

The Maxwellian distribution is the most common distribution found in plasmas, but others also are possible.

6.4 High energy tail of a distribution

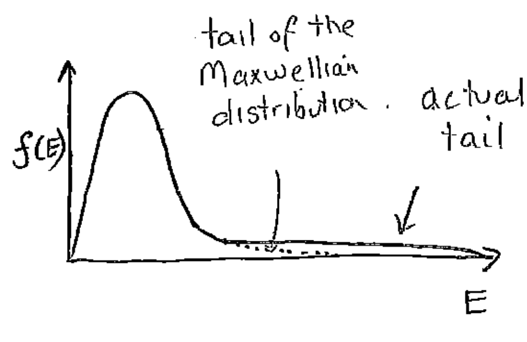
- Because most reactions in plasmas are caused by the high energy electrons, the high energy part of the EEDF is often discussed separately from the rest of the distribution

- In this case, the EEDF is divided up into
    - the "bulk" part, which contains most of the electrons
    - the "tail", which may only contain a few percent of the electrons



- the electron temperature T_e is representative of the "bulk" part of the distribution.

- another common form of distribution is the "Maxwellian distribution with a high energy tail". In this distribution, most of the distribution can be described by $f(E) = A e^{-E/kT}$ but there are more high energy electrons than are given by a Maxwellian distribution



6.5 Summary

- the distribution of electron energy is a very important plasma property because reactions in the plasma are determined by the electron energy.

- the most common distribution is called the Maxwellian distribution

$$f(E) \propto E^{1/2} e^{-E/kT}$$

- $v_{ave} = \sqrt{\frac{8kT}{\pi m}}$ $\qquad E_{ave} = \frac{3}{2} kT$

- In most glow discharges, the high energy part of the EEDF is most important. This is often called the "tail" of the distribution

7. Other basic information

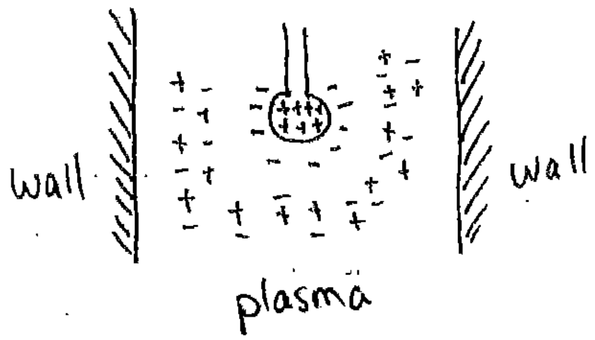
Until now, we have discussed most of the basic aspects of plasma physics. This section contains a brief description of some phenomena which we haven't discussed so far. Some of these phenomena have been described in other lecture courses, and so only a brief description is given here. Other phenomena will be discussed later in this course, and so only a few introductory remarks are given here. The topics covered in this section are:

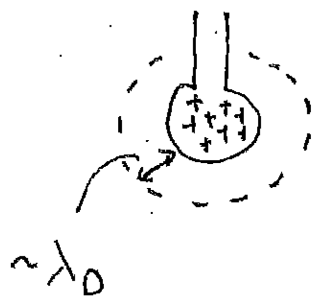
- basic plasma quantities
  - debye length, plasma frequency
- Single particle motions
- Diffusion.

One important thing to realize is that although these topics are only briefly mentioned here, they are as important as the topics discussed in Sections 1–6.

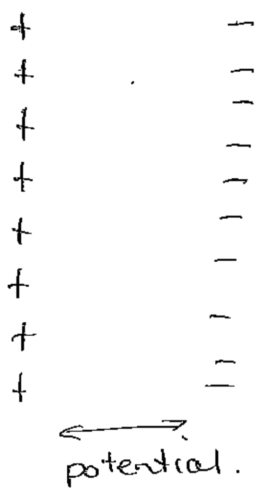
7.1 Debye length λ_D

This length is an indication of the distance in a plasma over which an electric field can exist. The electrons and ions are both charged particles, and when there is an electric field, they will move to cancel the electric field. Hence, large electric fields cannot exist over long distances. The distance for which the field does have an effect is called the Debye length.





Another way of thinking about the Debye length is to consider how far apart the charged particles can separate due to their kinetic energy. When the particles become separated by a long distance, an electric field (and hence potential) is created between the particles. As the distance ~~particles~~ between

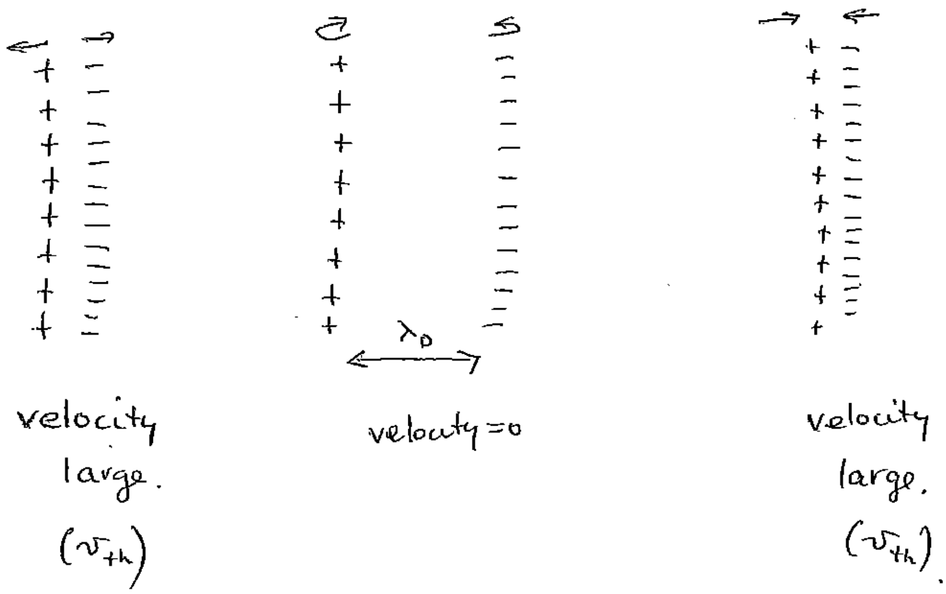


the particles become larger, the potential becomes so large that the particles have to stop. (The maximum distance between the particles is determined by their kinetic energy.)

Once the particles have stopped, they will begin to move back <u>towards</u> each other, and the potential and electric field will decrease, and then become zero. ~~The~~

The maximum distance is

$$\lambda_D = \left(\frac{\epsilon_0 T_e}{e\, n_e} \right)^{1/2} \qquad [T_e] \text{ in eV} \quad [n_e] \text{ in } m^{-3}$$



Notice that

- λ_D is large when T_e is large (ie electrons have high energy)
- λ_D is small when n_e is large.

In glow discharges, λ_D is mostly determined by n_e. This is because T_e is usually between 1 and 5 eV, which is only a small range. The density, however, can vary between 10^{14} and 10^{21} m^{-3}. This is a huge range.

Examples:

(i) excimer laser $n_e \sim 10^{20}$ $T_e \sim 1\,eV$

$\lambda_D = 0.7\,\mu m$

(ii) ECR plasma $n_e \sim 10^{18}$ $T_e \sim 3\,eV$

$\lambda_D = 12\,\mu m$

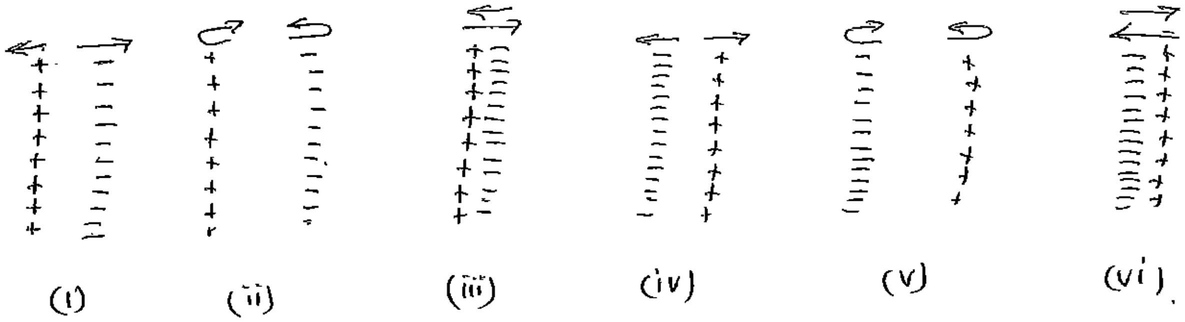
(iii) RF plasma $n_e \sim 10^{15}$ $T_e \sim 3\,eV$

$\lambda_D = 0.4\,mm$

7.2 Plasma Frequency ω_p

This is the frequency at which the plasma responds to any effects.

One way to consider this frequency is to consider the situation described above for the Debye length. When the electrons and ions move back together, they will begin to move apart again, because of their kinetic energy.



The plasma frequency is the frequency of this oscillation motion. It is different for electrons and ions and is given by

$$\omega_{pe} = \left(\frac{e^2 n_e}{\epsilon_0 m_e} \right)^{1/2}$$

$$\omega_{pi} = \left(\frac{e^2 n_i}{\epsilon_0 m_i} \right)^{1/2}$$

The difference between these two frequencies is the particle masses.

Response to electric fields

One important thing to remember is that this frequency $\omega_{pe,i}$, is the maximum frequency at which these particles can respond to changes in the plasma, such as applied electric and magnetic fields. This is important for many plasma heating mechanisms, because ac electric fields are often used. If the applied field frequency is too high, then the particles cannot respond. There are 3 cases

$\omega_{AC} < \omega_{pi}, \omega_{pe} \rightarrow$ both electrons and ions are affected by the field.

$\omega_{pi} < \omega_{AC} < \omega_{pe} \rightarrow$ only electrons are affected

$\omega_{pi}, \omega_{pe} < \omega_{AC} \rightarrow$ neither particles ~~can~~ are affected

Usually $\omega_{pe} \sim 1 - 50$ GHz

$$\omega_{pi} \sim \frac{1}{100}\,\omega_{pe}$$

Example RF plasmas

Most RF plasmas are operated at ~ 13 MHz.

- For an argon plasma

$$n_e \sim 5 \times 10^{15}\ m^{-3} \Rightarrow \omega_{pe} \approx 4\ GHz$$

$$\omega_{pi} \approx 15\ MHz$$

Hence, the ions are not really affected by the changing electric field. Only the electrons can respond to the 13 MHz electric field.

- For a hydrogen plasma

$$n_e \sim 10^{15}\ m^{-3} \Rightarrow \omega_{pe} \approx 2\ GHz$$

$$\omega_{pi} \approx 40\ MHz$$

Hence, for a hydrogen RF plasma, both the ions and the electrons are affected by the 13 MHz electric field.

7.3 Effect of E and B fields on single particles.

For single particles moving in a plasma, there are various situations to consider

(i) no E, no B

(ii) $E \neq 0$, $B = 0$

(iii) $E = 0$, $B \neq 0$

(iv) $E \neq 0$, $B \neq 0$

(i) $E = 0$, $B = 0$

In the main regions of most plasmas, there are no large electric and magnetic fields. In this situations, a particle moves in a straight line until it hits something

(ii) $E \neq 0$, $B = 0$

This is also straight forward. The ions and electrons will move in the direction of the field (they will move in opposite directions, of course).

(iii) $E = 0 \quad B \neq 0$

The charged particles are affected greatly by a magnetic field. They will move in circles around the field lines, (because of the force $\underline{F} = q\, \underline{v} \times \underline{B}$). This is called cyclotron motion. The radius and frequency of the circular motion are

$$r_c = \frac{m v_\perp}{q B} \qquad \text{cyclotron radius}$$

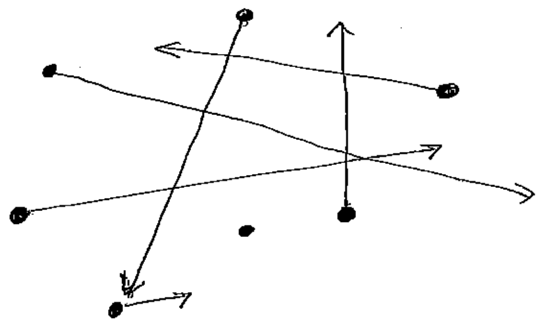
$$\omega_c = \frac{q B}{m} \qquad \text{cyclotron frequency.}$$

Note that

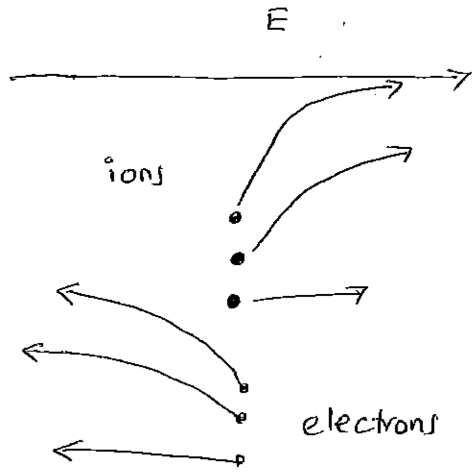
- these are different for ions and electrons
- for even small B, the electron cyclotron radius is relatively small.
- the cyclotron radius is sometimes called the Larmor radius

$\therefore$ electrons are affected <u>much</u> more than ions

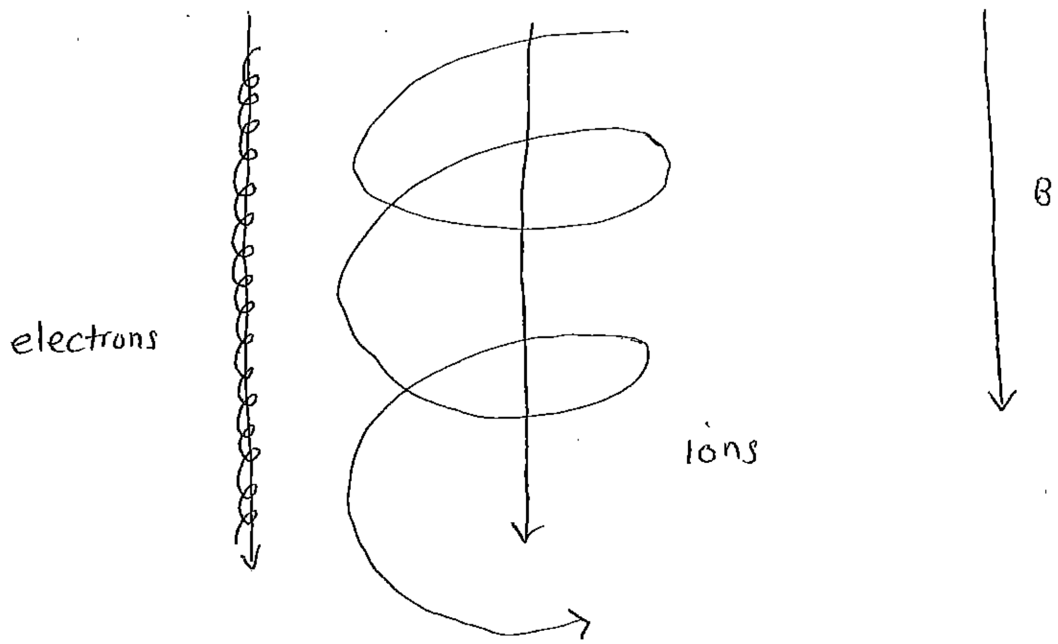
$E = 0$, $B = 0$



$E \neq 0$ $B = 0$



$E = 0$ $B \neq 0$



(iv) $E \neq 0 \quad B \neq 0$

There are various cases to consider when both electric fields and magnetic fields exist. The exact motion of ions and electrons depends on

- relative directions of E, B
- time dependence of E, B
- any spatial variations of E, B.

Each of these cases can be understood by considering the force on the particles $\underset{\sim}{F} = q(\underset{\sim}{E} + \underset{\sim}{v} \times \underset{\sim}{B})$. These separate cases will not be described here, but can be found in any plasma textbook.

7.4 Diffusion

Until now, we have really only considered the effects of electric and magnetic fields on the particle motion. (ie, in section 7.3, in Section 5, sheaths, pre-sheaths etc) There are other factors, however, which also affect particle motion. The most important of the other important factors is diffusion.

This is difficult to explain properly, because we have not yet considered collisions in detail. Hence, only a brief explanation will be given here.

Low pressure and high pressure

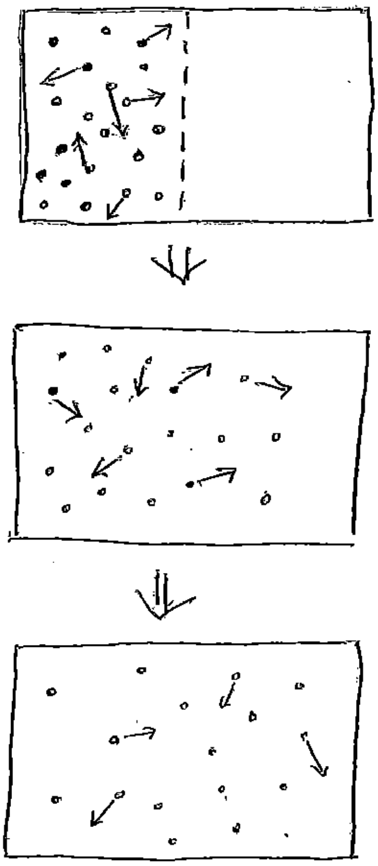
In low pressure plasmas, the particles can move relatively long distances before having collisions. In this ~~ss~~ situation, the particle motion is decided by the electric and magnetic fields.

In high pressure plasmas, however, the process called diffusion becomes important. This is because collisions become important at higher pressure, and these collisions affect the particle motions very much.

Basic meaning of diffusion

Diffusion is the process by which particles which are in an area of high density area tend to move towards an area of low density. The process is caused by the difference in density.

The most commonly used example of diffusion is shown in the figure. At first, all the gas particles are in the left hand side of the box, but due to diffusion, they move into the right handside too. The process is in equilibrium when the density is uniform.



The speed at which diffusion occurs is indicated by the flux due to diffusion. This is the number of particles moving towards the low density region × the particle speed.

The diffusion flux is given by

$$\Gamma_D = D \nabla n$$

where ∇n is the density gradient

D is diffusion co-efficient

$$D = \frac{KT}{m\nu_c}$$

ν_c = collision freq.

$\tau_c = \frac{1}{\nu_c}$

Note that diffusion becomes fast when

(i) ∇n is large

(ii) particle energy is large (kT).

(iii) mass is small

(iv) collisions are few.

Effect of Magnetic Field

If there is a magnetic field in the plasma, the charged particles moved in circles around the field lines. This leads to $D_\perp$ and $D_\parallel$ to B being very very different.

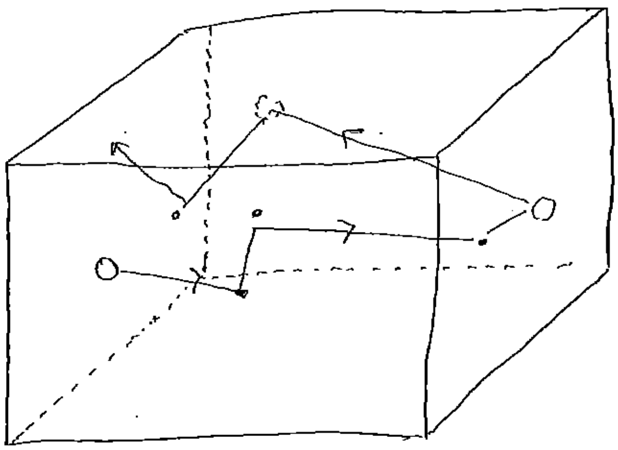
Effect of Diffusion on Particle Flow

In a plasma, there are regions of high plasma potential ϕ and regions of low potential. This affects the charged particle motion.

There are also regions of high density and low density, and regions of high temperature and low temperature. These "imbalances" also affect the particle flow.

The actual distribution of each type of particle is decided by a balance of all these effects.

8. Basic Collision Theory

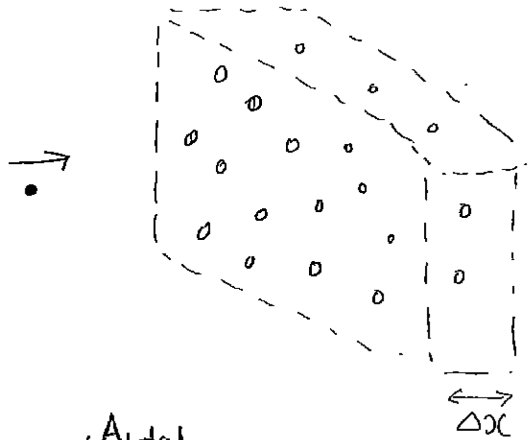


In any gas or plasma, the particles move around inside the gas, having collisions with other particles and with the chamber walls. In most cases, the types of collision which occur determine the basic properties of the system. In a complex mixture of particles, such as a plasma, there are many different kinds of collisions, and understanding which collisions occur is an essential step in understanding the properties of the plasma.

In following sections, we will consider various types of collision process and various types of reactions. In this section, we will consider some basic ~~aspects~~ of collisions and reactions

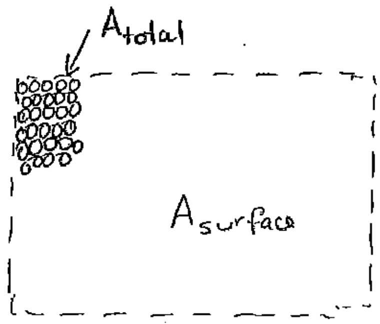
8.1 Basic Properties

Consider a particle approaching a volume of gas, as shown. The probability of the particle having a collision with other particles in the gas can be understood using the idea of collision cross-section, as explained below.



If we look at the volume of atoms from the front, we can see that the area covered by gas atoms is simply given by

$$A_{total} = N A_{atom}$$



where N is the number of atoms in the volume, and A_{atom} is the cross-sectional area of one atom.

The probability of the approaching particle hitting something is then simply given by

$$\text{prob of coll} = \frac{A_{total}}{A_{surface}}$$

$$= \frac{N A_{atom}}{A_{surface}}$$

$$n_g = \frac{N}{A_{surf} \Delta x}$$

$$= n_g A_{atom} \Delta x$$

The area of the atom, A_{atom}, is usually written as σ_c, where σ_c is called the collision-cross-section. (In a very simple way, σ_c can be understood as being just this, the cross-sectional area of the atom, but in reality, it is much more complicated than this).

Now, in the above situation, if a large number of particles N_o approach the volume, then the number of particles which have collisions ΔN, is given by the expression

$$\Delta N = n_g \sigma_c \Delta x$$

Hence, the number of particles which pass through a distance Δx without colliding, ~~is~~ can be found by integrating the above

$$N(\Delta x) = N_0 - \Delta N = N_0 - n_g \sigma_c \Delta x$$

$$\Downarrow$$

$$N(x) = N_0 e^{-n_g \sigma_c x}$$

This is also written as

$$N(x) = N_0 e^{-\frac{x}{\lambda}}$$

where $\lambda = \frac{1}{n \sigma_c}$ is called the mean free path.

mean free path λ.

The quantity, λ, called the mean free path, indicates the average distance a particle travels between collisions. It is an important property of gases and plasmas

collision frequency ν_c

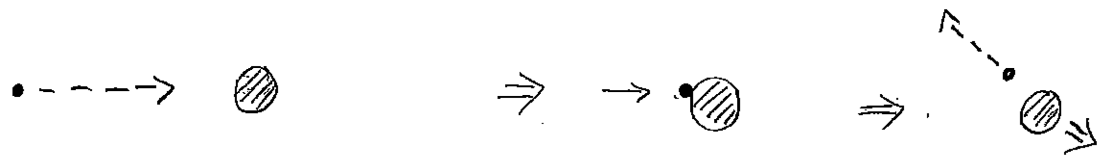
This is the average frequency of collisions, and is given by

$$\nu_c = \frac{\bar{v}}{\lambda}$$

where $\bar{v}$ is the average velocity of the particle.

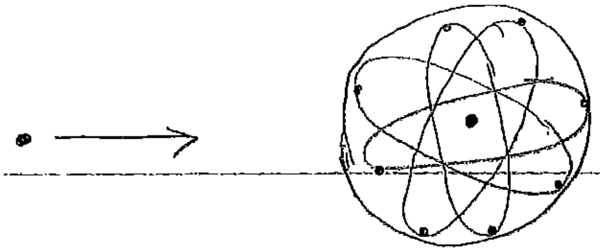
8.2 Models for collision processes

In the above discussion, we have considered the two particles involved in collisions to be hard spheres, similar to billiard balls.



This is a useful image for some types of collisions, and it is useful for understanding ideas such as the mean free path... However, it is NOT a correct image, and it is very difficult to properly understand complicated collision types using this image.

Another type of image shows the electron structure of the atoms (as shown below). This is more correct, but is also not adequate for understanding some complicated collisions.

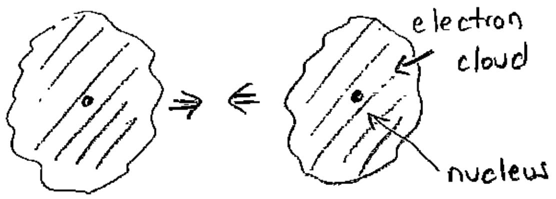


The most correct model for collisions involves the interaction of the electrons surrounding the nucleus of the colliding atom. This is hard to explain directly, but can understood by considering the following examples.

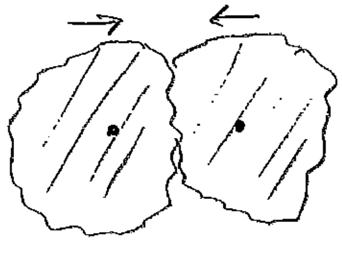
Example 1. Collision of two low energy atoms.

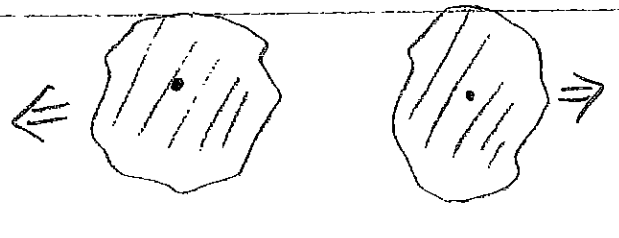
Using the "hard sphere model", the colliding atoms behave just like billiard balls, and so the whole collision process is just an exchange of momentum between the two hard spherical atoms.

Actually, the two atoms both consist of a positively charged nucleus and a negatively charged "cloud" of electrons.



When the first atom approaches the second atom, the two electron clouds come close together, and there is an electric force. The shape of the atoms become deformed, and the repulsive force between the two electron clouds forces the atoms apart.





The result is the same as that given by the hard sphere model, but the collision process is quite different.

and this particle quickly breaks up. One possibility is that it ejects two electrons, and so the result is an ion and two electron

This is probably the best image of an ionization collision

Comments about this model

(1) There are three stages in the collision process

(i) before the collision, when there are two separate particle

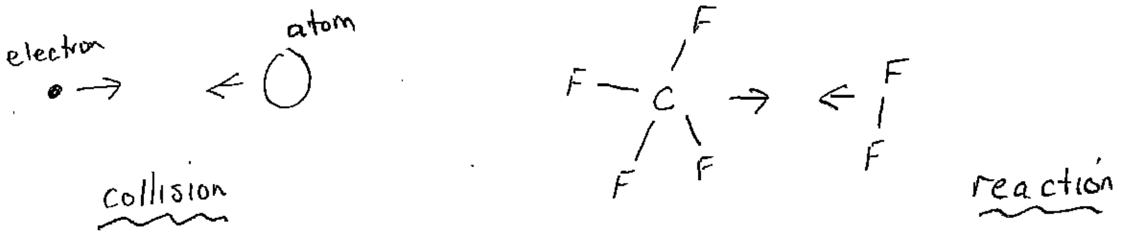
(ii) during the collision; when a very unstable complex particle is formed

(iii) after the collision, when separate particles exist.

(2) It is important to remember that this is just one way of viewing the collision process. It is not exactly correct, because in collision processes, there are quantum mechanical processes, and we haven't consider this at all. This description, or model, however, is certainly useful for gaining an understanding of many collision types

③ Collisions and Reactions

Another thing to note is that, in this description, the difference between "collisions" and "reactions" becomes blurred. The most common image is that 'collisions' are a physical process, and 'reactions' are a chemical process.



However, in this "intermediate particle" model, both processes are the same.

④ Collision Probability

Another useful thing about this model for collisions/reactions is that it introduces the idea of the probability associated with collisions and reactions. This is particularly important because, for many types of collisions and reactions, there is more than one possible result.

For example, consider the collision between a high energy electron and a CF_4 molecule. There are many possible results.

$$e^- + CF_4 \Rightarrow e^- + CF_4 \quad \text{(elastic collision)}$$

$$\Rightarrow CF_3^+ + F \quad \text{(ionization)}$$

$$\Rightarrow CF_3 + F + e^-$$

$$\Rightarrow CF_3^- + F$$

$$\Rightarrow CF_3 + F^-$$

$$\Rightarrow CF_2 + 2F + e^-$$

There is a certain probability of each result occuring. This kind of reaction is difficult to understand with the "hard sphere" model, but it is easier to understand if we consider that an unstable CF_4^- molecule is formed. This molecules then breaks up, and there are various possible ways that this can happen.

8.3 Collision Cross-section

In section 8.1, the collision cross-section was described as being the cross-sectional area of the atom. It is more accurate to ~~to~~ consider σ to be something which is related to the probability of the collision occuring.

For example, in the $e - CF_4$ collision, there are various possible collisions/reactions which can occur. Each of these collisions/reactions has its own cross-section σ, and this σ has very little connection to the physical area of the atom.

Therefore, it is better to consider the cross-section as related to the probability of the collision occurring, as in Sec. 8-1,

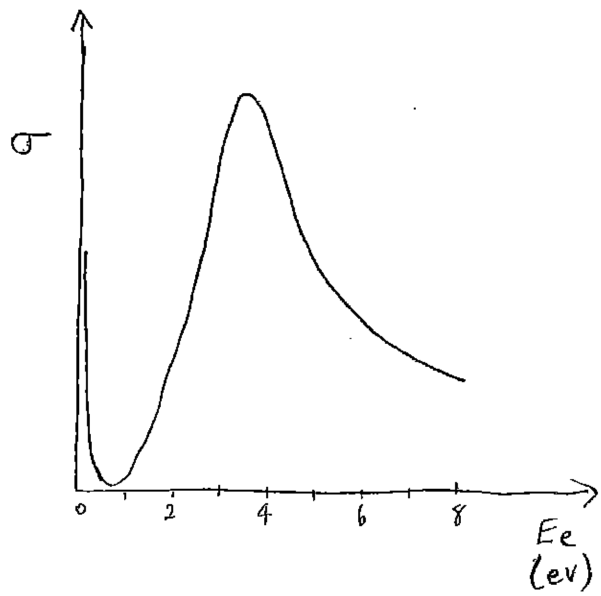
$$\text{prob. collision} = n\,\sigma_c\,\Delta x$$

Energy dependence of σ

Another thing to note is that most collision cross-sections have an energy dependence. This can't be easily understood by the hard shell model, but is easy to understand by considering the collision in terms of the interaction of electrons (and the nucleus)

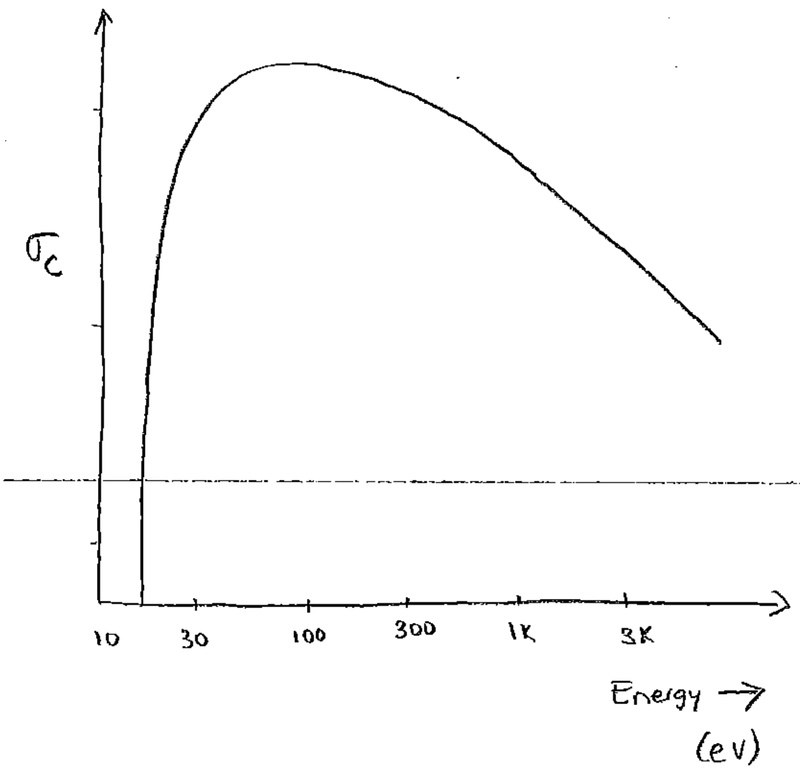
Example 1 $e + Ar \rightarrow e + Ar$ (elastic collision).

This collision has a very strong energy dependence, caused by quantum mechanical effects.



Example 2 $e + Ar \rightarrow e + Ar^{+} + e$ (ionization).

This collision has a threshold energy. If the electron has less than ~15eV, then this collision/reaction cannot occur.



8.5 Summary

- The most useful way of thinking about collisions is to consider the formation of an unstable, intermediate state. This intermediate particle exists for an extremely short time, and then breaks up into different particles

- Actually, there is very little difference between "collisions" and "reactions". From now on, these words will be used interchangedly.

- Important collision related properties are

  $\sigma(\varepsilon)$ the collision cross-section

  λ_{mfp} the mean free path.

  ν the collision frequency.

9. Electron Collisions

We will first consider collisions involving electrons. There are many different types of collisions. These are listed below, and then explained separately

9.1 Elastic Collisions with Neutral Particles

9.2 Inelastic collisions with Neutral Particles

- Ionization
- dissociation
- excitation
- re combination
- negative ion formation

9.3 Coulomb collisions

9.1 Elastic Collisions with Neutral Particles

In these collisions, the electron collides with an atom or molecule. The important thing is that the internal energy of the atom does not change. Only the kinetic energy and velocity of each particle changes.

It is important to note that almost no energy is transferred to the atom in this collision. This is because the atom (or molecule) is so much heavier than the electron.

It can be shown (see Chapman, Chapter 2) that the maximum amount of energy which can be transfered from the electron to the neutral particle is

$$\frac{\Delta E}{E_e} = \frac{4\, m_a m_e}{(m_a + m_e)^2}$$

m_a = atom mass
m_e = electron mass
E_e = electron energy

For the case of atoms such as argon $m_{atom} \sim 10^5\, m_e$, and so the above expression becomes

$$\frac{\Delta E}{E_e} \sim \frac{4\, m_e}{m_a} < 10^{-4}$$

Hence, the energy of both the electron and the atom hardly changes due to this collision. Only the direction of the electron

表 2.3 原子衝突の半径

原 子	半径・r [m]	$\pi r^2 [\pi a_0^2]$
He	1.09×10^{-10}	4.3
Ne	1.30	6.1
Ar	1.82	11.9
Kr	2.08	15.5
Xe	2.42	21.0
H	0.53	1.0
Hg	1.08	4.2

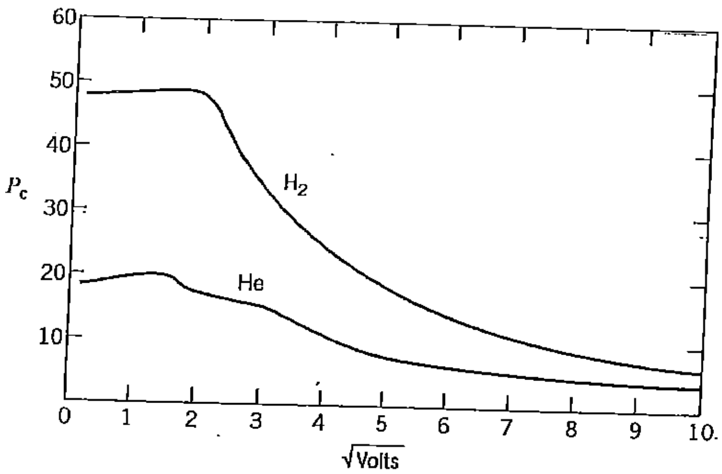


FIGURE 3.9. Probability of collision P_c for electrons in H_2 and He; the cross section is $\sigma \approx 2.87 \times 10^{-17} P_c$ cm^2 (after Brown, 1959).

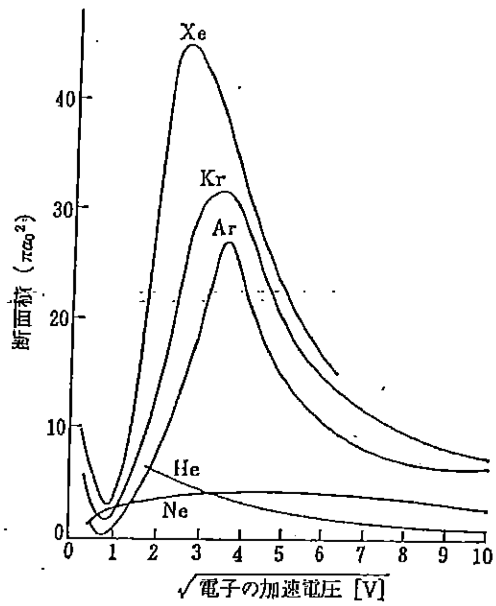


図 2.7 電子衝突に対する断面積

motion changes

It is important to note that, even though the energy transfer is very small, (and hence these collisions doe not seem important) there are actually very many elastic collisions in a plasma. Usually, these collisions are by far the most common type of electron collision.

Because there are so many of these collisions, it is possible (in some plasmas) for some energy to be transferred from the electrons to the neutral particles by ~~these~~ elastic collisions.

Examples of cross-sections

- A simple approximation for the collision cross-section is the cross-sectional area of the atom. This is usually close to the real size.

  ie, $\sigma_c = \pi a^2$ where a = atomic radius.

- Some real cross-sections are shown on the next page. By looking at these real cross-section data, you can understand that $\sigma_c = \pi a^2$ is only a simple approximation.

9.2 Inelastic collisions with neutral particles

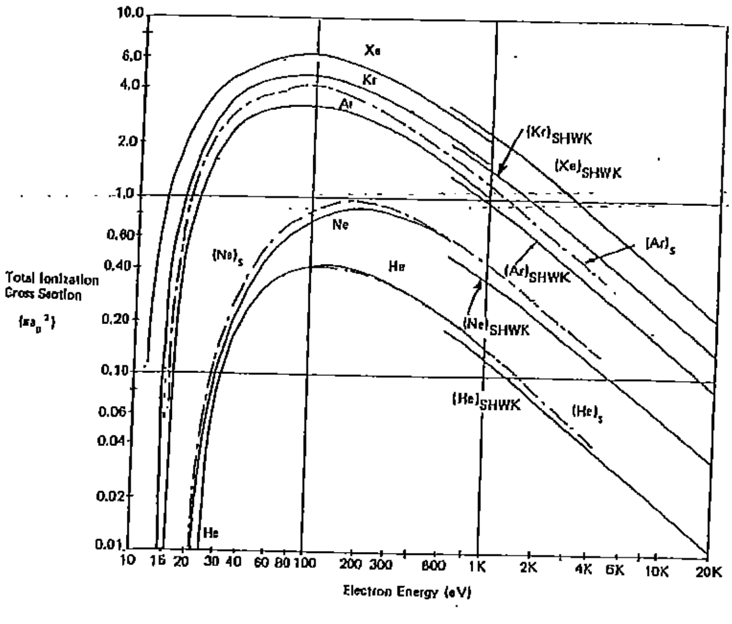
There are many different types of inelastic elastic collisions. The important difference between elastic and inelastic collisions is that the internal energy of the neutral particle is altered by the collisions. The total energy (kinetic + potential) must be conserved in the collision, but the kinetic energy itself is not conserved,

Ionization Collision's $\qquad e + A \rightarrow A^+ + 2e$.

This type of collision is the most important collision in plasmas because it creates new electrons and ions.

This collision has a threshold energy, because it requires energy for the electron to be separated from the atom,

Examples of cross-sections are shown.



Dissociation $\quad e + AB \rightarrow e + A + B.$

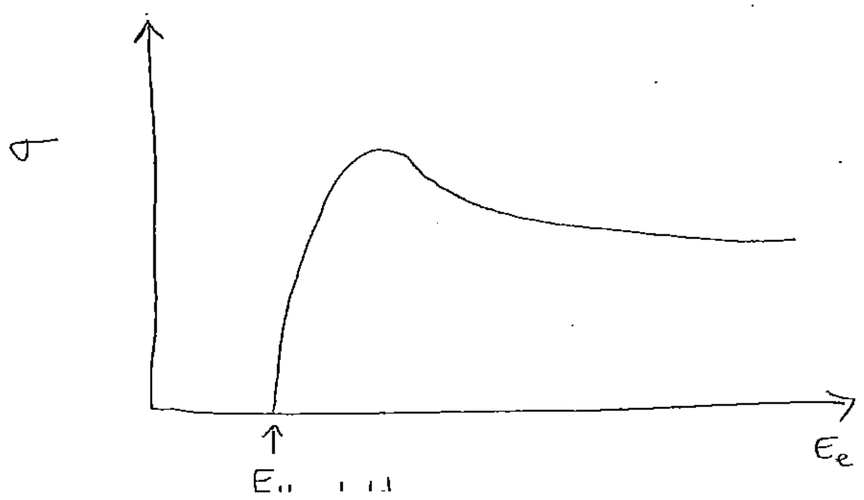
In this collision type, an electron hits a molecule, which then breaks up into different pieces. This collision type always has a threshhold energy, but the size of the threshold energy depends greatly on the molecule.

~~There~~ If the molecule has more than two atoms, then there might be several different possible dissociation reactions.

For example,

$$
\begin{aligned}
e + ABCD &\rightarrow AB + CD + e \\
&\rightarrow ABC + D + e \\
&\rightarrow A + BCD + e. \\
&\vdots
\end{aligned}
$$

The general form of the cross-section is

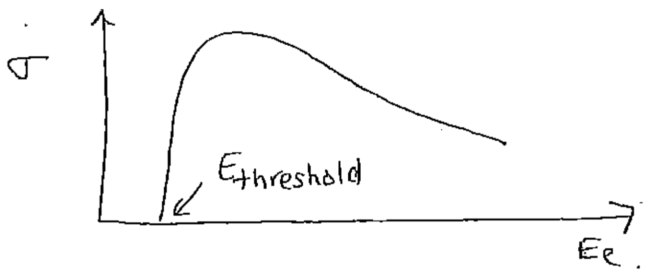


Excitation (and Emission) $e + A \rightarrow A^* + e$

$(A^* \rightarrow A + h\nu.)$

In this collision, the atom absorbs some energy from the electron and its a internal energy changes. This excitation collision is usually followed very quickly by a "relaxation" process, in which the excited atom loses the energy by emitting a photon.

This collision has a threshold energy that depends on the type of atom or molecule. It is always less than the threshhold energy for ionization.



Excitation of Metastable atoms $e + Ar \rightarrow Ar^*$

This collision is essentially exactly the same as the previous one, except that the excited atom does not emit light. It keeps the extra energy it has gained from the electron. The new particle is called a metastable particle, It is not completely stable, but may have a relatively long lifetime.

Recombination $e + Ar^+ \rightarrow Ar$

This collision is the reverse process to ionization. One problem, however, is that it can be shown that it is impossible to conserve energy and momentum for a two particle collision like the one shown. (see Chapman, chapter 2)

Hence, actual recombination collisions have to involve 3 particles, not two.

One possibility is gas-phase recombination

$$e^- + Ar^+ + M \rightarrow Ar + M.$$

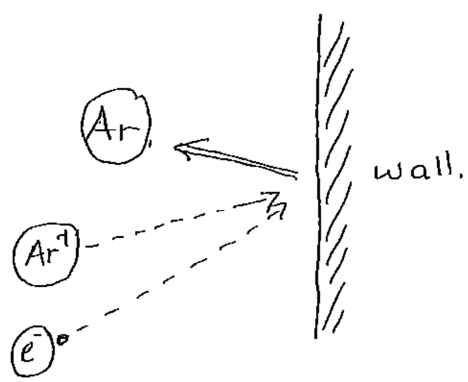
where M is any other particle. The probability of 3 particles colliding at the same time is very low at low gas pressures, and so this collision almost never occurs in many types of plasmas. However, when the gas pressure is high, there are many particles, and this reaction can become important.

Another possibility is wall recombination.

$$e^- + Ar^+ \xrightarrow{wall} Ar$$

In this process, the wall takes the place of the third particle.

This is an important process in all plasmas



Negative ion formation $\quad e + O \rightarrow O^-$

In this reaction, the electron combines with a neutral atom to form a negative ion. The two particle collision shown above is actually impossible because energy and momentum can not be conserved. but

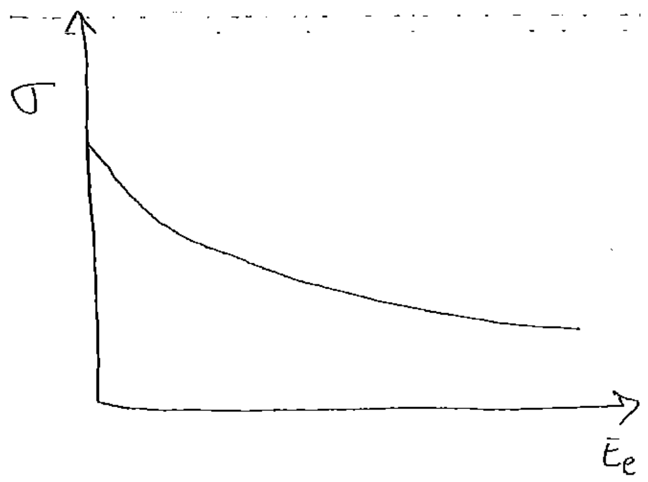
Actually, negative ions are usually formed in dissociation reactions such as

$$e + O_2 \rightarrow O^- + O$$

$$e + CF_4 \rightarrow CF_3^- + F$$

One important thing to remember is that only some atoms and molecules can form negative ions. These species usually contain atoms such as O, Cl, F .... etc. Atoms such as Ar and He do not form negative ions

The cross section has the general form shown. It is large for low energy



Combinations of collision types.

As well as the separate collision types described here, there are many other collisions which involve electrons, but can't be classified into a single category. These are collisions such as

dissociative attachment $e + O_2 \rightarrow O^- + O$.

(the electron attaches to the molecule, which then dissociates).

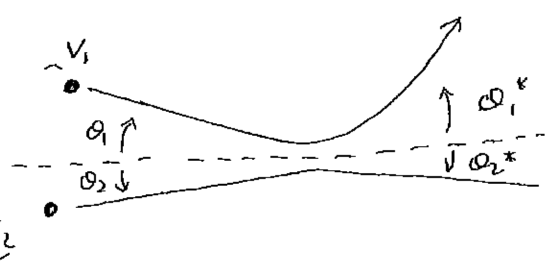
dissociative ionization $e + CF_4 \rightarrow CF_3^+ + F + 2e$.

~~the~~ the molecules dissociates and forms an ion),

9.3. Coulomb collisions

Coulomb collisions are elastic collisions between charged particles. Here, we will consider electron-electron collisions. The result of the collision (i.e., the velocities of the electrons after the collision) is determined by the electric force between the particles.

In this type of collision, the collision cross-section has no relation ~~with~~ to the area of the particle. It is determined by the much much longer range electric force. Examples of collisions are shown below.



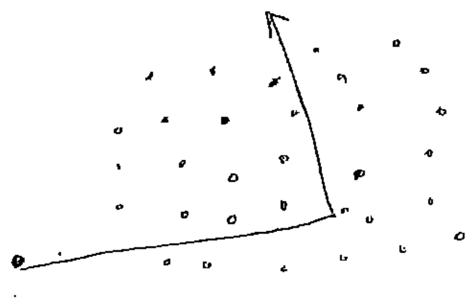
The left diagram is a general picture, when both the electrons have velocity. The right hand figure shows the situation when one electron is at rest. It is possible to transfer from the left diagram co-ordinates to the right diagram co-ordinates by choosing

$$\underline{v}_R = \underline{v}_2 - \underline{v}_1 \qquad m_R = \frac{m_1 m_2}{m_1 + m_2} = \frac{1}{2} m_e$$

(This is useful for calculations).

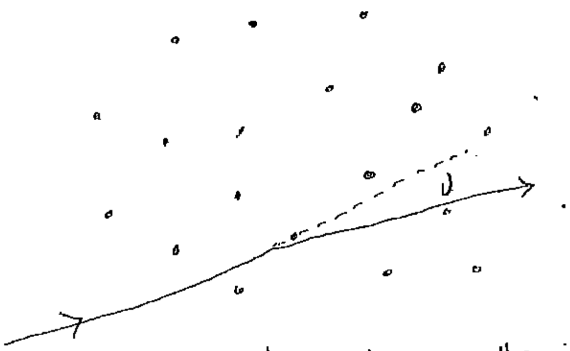
Large angle and small angle collisions.

There are some Coulomb collisions in which the velocity of the particles is changed by a large amount. In this case, the electrons must collide nearly "head on", and the scattering angle is large.

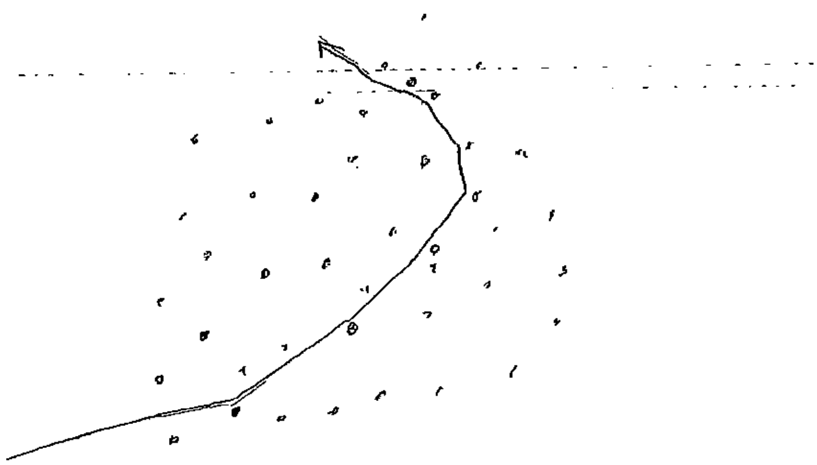


Large angle scattering

However, the range of the Coulomb force is quite large, and there are many collisions in which the velocities of the ~~pa~~ electrons only change by a small amount. These are called ~~la~~ small angle collisions. In this case, even though the effect of one collision is small, the effect of many successive collisions can be quite large. This effect (many small angle collisions) is extremely important.



small angle scattering



Effect of many small angle collisions

Cross-sections for Coulomb collisions

It is possible to calculate the cross-section for both a single large angle scattering collision, and for many small angle collisions. In each case, we calculate the cross-section for a total angle of $> 90°$.

For a single collision $\quad \sigma_{90} = \frac{1}{4} \pi b_0^2$

where $\quad b_0 = \dfrac{e^2}{4\pi\varepsilon_0 W_R}$

$$W_R = \frac{1}{2} m_R V_R^2$$

For many small collisions $\quad \sigma_{90} = \dfrac{8}{\pi} b_0^2 \ln \Lambda$

where $\quad \Lambda = \dfrac{\lambda_{Debye}}{b_0}$.

The second σ_{90} is much larger than the first, and this shows that the small angle scattering effect is dominant.

Hence, for electron Coulomb collisions

$$\sigma_{90} = \frac{8}{\pi} b_0^2 \ln \Lambda.$$

Energy dependence of σ

From the expression for σ_{90}, and b_0, we can see that the cross section energy dependence is

$$\sigma_{90} \propto \frac{1}{\varepsilon^2} = \frac{1}{v^4} \qquad (\varepsilon = \omega_R).$$

This is a very very strong dependence. The cross-section is largest for low energy electrons, and very small for high energy electrons.

This can be understood partially by considering that the electron-electron interaction is very short (in time) for ~~per~~ electrons which travel very fast. Hence, the effect of the interaction will be small for high energy electrons.

10. Heavy Particle Collisions

In this section, we will consider the types of collisions which involve the heavy particles in the plasma — the ions and neutral particles

10.1 Ion Collisions

The main collision types for ions are

(i) Elastic collisions

- ion - electron Coulomb collisions
- ion - ion " "
- ion - neutral elastic collisions

(ii) Charge exchange collisions

(iii) ion - ion recombination

(iv) ion - impact ionization

The first two types of collisions are the most important. In some plasmas, the other collisions may also be important

Coulomb Collisions (ion-ion, ion-electron).

These collisions can be considered in exactly the same way as electron-electron Coulomb collisions, which were discussed in Section X. The same ideas, such as "small-angle scattering" and "large-angle scattering", can be used to understand Coulomb collisions involving ions.

The cross-section, which is the same as that given before, is

$$\sigma_{Coulomb} = \frac{8}{\pi} b_0^2 \ln \Lambda \qquad \left.\begin{array}{l} b_0 = \frac{e^2}{4\pi\varepsilon_0 w_R} \\ w_R = \vdots \\ \Lambda = \end{array}\right\} \text{Same as Sec. 9.}$$

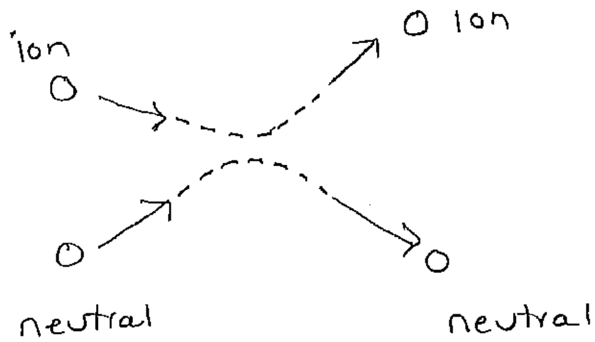
There are some important differences between ion-ion, and electron-ion collisions. This is mainly due to the difference in mass between electrons and ions.

In ion-ion coulomb collisions, the two particles have about the same mass, and so a large amount of energy can be transferred between the particles.

In ion-electron Coulomb collisions, the two particles have very different mass, and so almost no energy can be transferred (This is the same as for electron-neutral elastic collisions)

Hence, even though the two collision types are theoretically

Ion-Neutral Elastic Collisions



In nearly all respects, this type of collision can be considered in the same way as neutral-neutral collisions.

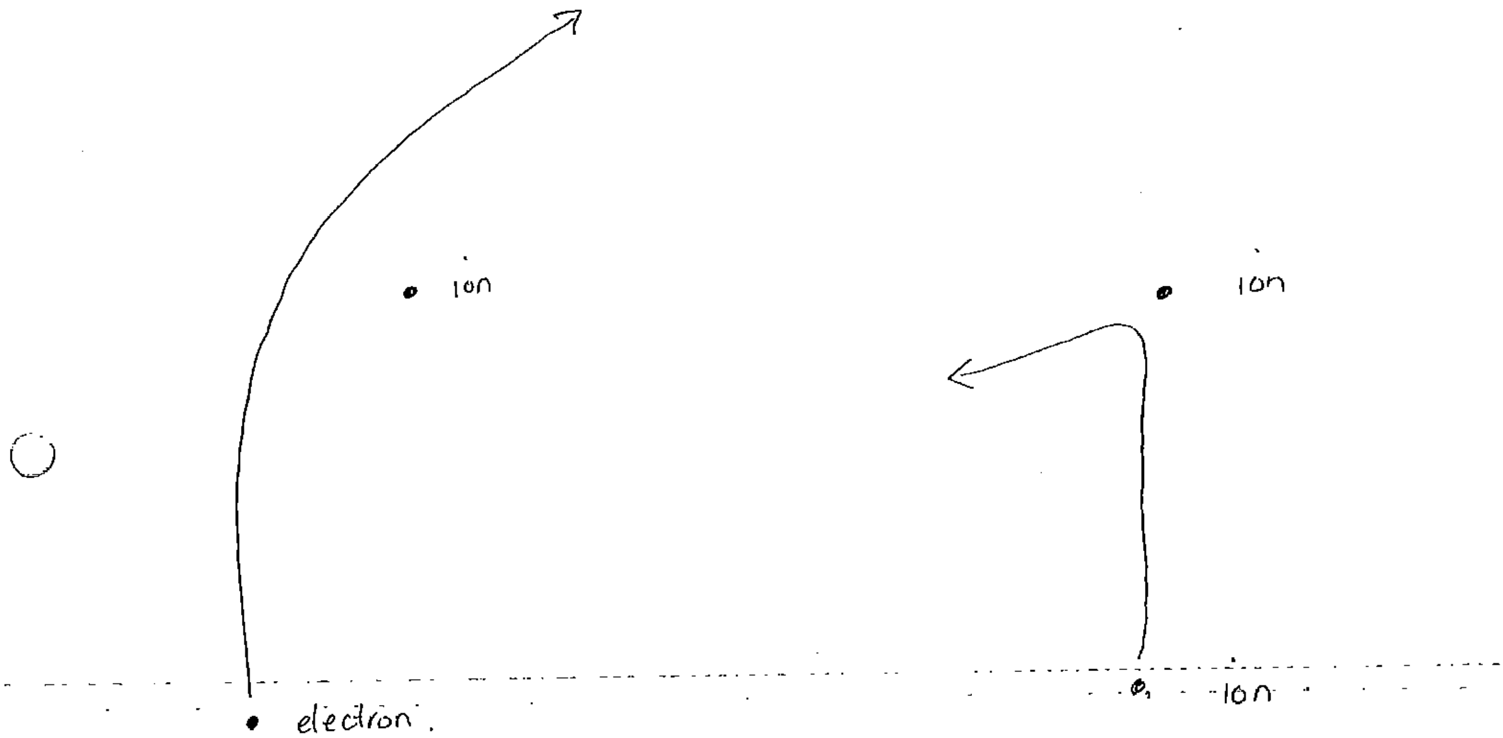
The cross-section for these collisions is usually close to the physical size of the neutral particle. For example, in an $Ar^+ + N_2 \rightarrow Ar^+ + N_2$ collision, the cross-section is roughly equal to the cross-sectional area of the N_2 molecule.

One important point about ion-neutral collisions is that (like neutral-neutral collisions) the two particles have roughly the same mass, and so a large amount of kinetic energy can be transferred between the particles.

Another important point is that ion-neutral elastic collisions have to be considered together with ion-neutral charge-exchange collisions. These are discussed next.

very similar (ie, both are charged particle collisions), their effect on the plasma properties is quite different.

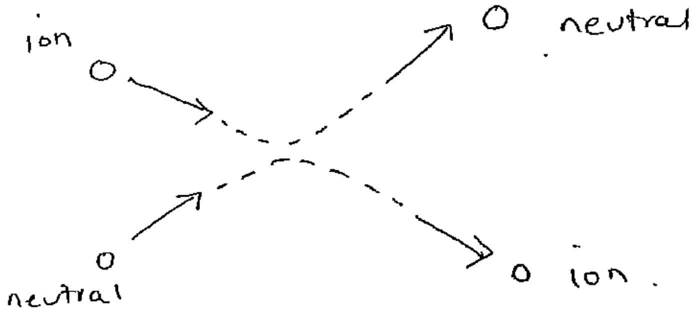
Another thing to remember about these collisions is that (like electron-electron collisions) these are not physical collisions where the particles actually touch each other. The collision is actually determined by the way the electric fields of the particles interact.



electron-ion collision

ion-ion collision

Ion-Neutral Charge Exchange Collisions



This collision is similar in some ways to the ion-neutral elastic collision discussed previously, but the important difference is that the two particles change as a result of the collision.

In the collision, an electron from the neutral particle moves to the ion. Hence, the ion becomes a neutral particle, and the neutral becomes a positively charged ion.

At first, this collision seems nearly the same as the ion-neutral elastic collision, and so it may not seem important. However, the big difference is that the energy of each particle changes. In a plasma, usually the ions have higher average energy than the neutral particles. So in this collision the ~~fas~~ ion, which is fast, turns into a neutral particle. The original neutral particle, which is slow, turns into an ion. So the ions in the plasma lose energy by charge-exchange collisions. The neutrals gain energy

Resonant and non-Resonant charge exchange,

When the ion and the neutral particle are both the same species, the collision process is called resonant charge-exchange

e.g. $Ar + Ar^+ \rightarrow Ar^+ + Ar$.

It is relatively easy for the electron to move from the atom to the ion.

When the ion and neutral particle are different particles, the collision process is called non-resonant charge exchange,

e.g. $Ar + N_2^+ \rightarrow Ar^+ + N_2$

In this case, it is more difficult for the electron to move to the ion. The cross-section for this collision (i.e. the probability of the collision) is less than for resonant processes.

cross-sections. Some cross-sections are shown on the next page. For resonant charge-exchange, the cross-section is similar in size to that for the elastic collision process.

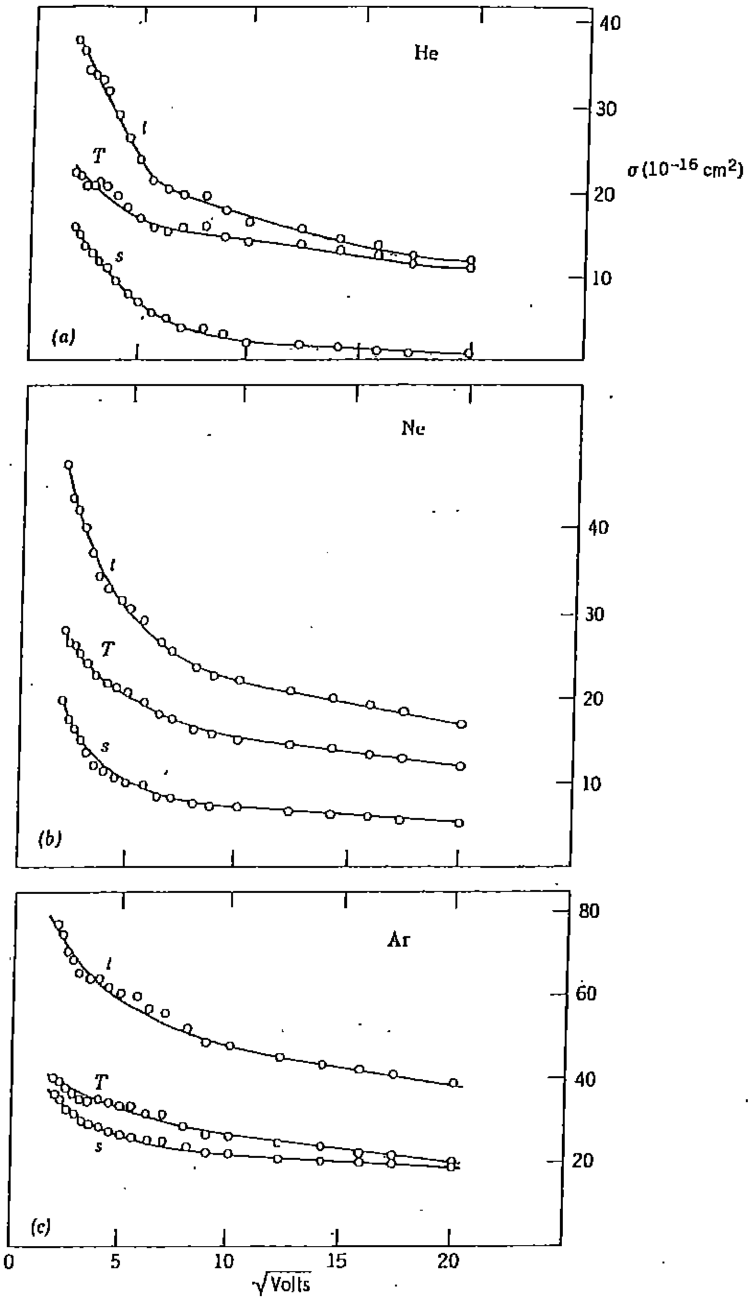


FIGURE 3.15. Experimental values for elastic scattering (*s*), charge transfer (*T*), and the sum of the two mechanisms (*t*) for helium, neon, and argon ions in their parent gases (McDaniel et al., 1993).

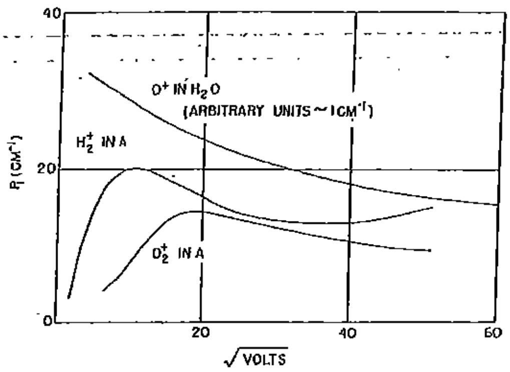
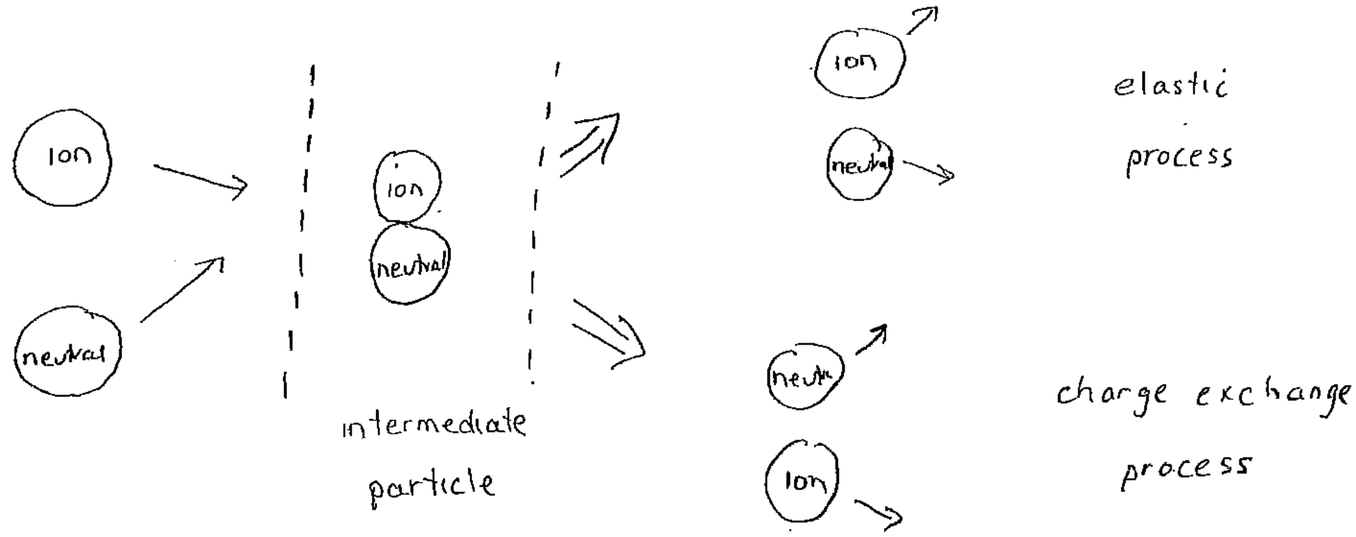


Fig. 2.17. Charge-transfer cross sections of 0^+ in water and $0^+{}_2$ and H_2^+ in argon.

J. B. Hasted, Proc. Roy. Soc. (London) A212, 235 (1952)

• One thing to note about ion-neutral collisions is that they are easiest to understand by the process shown below



When the two particles come close together, there is a certain probability that the collision will be elastic (ie, the particles won't change) and there is a certain probability that the collision will be a charge-exchange collision (ie, the particles do change).

• Another thing to note about this collision is that the cross-section is highest at low energy, because this means the particles are close together for a longer time. When the particles are moving quickly, however, they are not close together for very long. Hence, the reaction/collision is less likely to happen at high energy

Ion- Ion Recombination

This is a collision/reaction in which two ions recombine to form two neutral particles

e.g. $Cl^- + Cl^+ \rightarrow 2Cl.$

In the last section, we noted that electron-ion recombination cannot occur unless there is a third particle in the collision (ie, $Ar^+ + e + Ar \rightarrow 2Ar$) Ion-ion recombination, however, can occur in the gas phase easily, because two particles are produced, and energy and momentum can be conserved. In some plasmas, when there are many negative ions, this type of collision process can be important.

10.2 Neutral Collisions

There are many types of collisions and reactions that involve neutral particles. In the previous sections, we have discussed most of these already.

ie/ electron - neutral — ionization
dissociation
⋮

ion - neutral - elastic
- charge-exchange
⋮

In this section we will discuss the few collision types that we haven't yet considered.

Neutral - Neutral Elastic Collisions

Amongst all the different collision types, these collisions are probably the easiest to understand. The two particles in the collision behave like billiard balls.

The cross-sections for elastic collisions are usually roughly equal to the physical size of the particles (i.e. equal to the cross-sectional area of the particle

There are several important points to remember about elastic neutral-neutral collisions.

① In a plasma, usually $n_0 \gg n_e, n_i$ and so there are many many more neutral particles than charged particles. Hence neutral-neutral collisions are by far the most common collision type. The collision frequency is usually several orders of magnitudes large than for other collisions.

② Because the neutral particles have about the same mass, lots of energy can be transferred between the particles in this collision. This transfer of energy helps to distribute energy fairly evenly between the neutral particles.

For example, consider a neutral particle with energy 0.5 eV in a gas with average neutral energy of 0.05 eV (~700 eV),

first collision,

After 1st collision, 0.5 eV, 0.05 eV → 0.3 eV, 0.25 eV

After 2nd collision 0.3 eV, 0.05 eV → 0.2 eV, 0.15 eV

After 3rd collision

0.2 eV → 0.15 eV

0.05 eV → 0.1 eV

After 4th collision

0.15 eV → 0.12 eV

0.05 eV → 0.08 eV

⋮

○ After about 6 or 7 collisions, the energy of the fast neutral particle will be transferred to other neutral particles. It does not take very long for the fast particle to lose its energy.

Ionization by Metastable Collisions

There is another ionization process called Penning ionization in which ionization occurs due to collisions of metastable particles.

e.g. $$He^{*} + Ne \rightarrow He + Ne^{+} + e^{-}$$

As we know already, there is a threshold energy needed for ionization to occur. The collision of two ordinary neutral atoms is extremely unlikely to produce ionization because the neutral particles usually have such low energy.

Some metastable atoms, however, already have very high internal energy. (For example, He metastable ions have 20 eV interval energy). So when these metastable atoms collide with a neutral particle with ionization energy lower than the metastable energy, ionization is possible.

This kind of ionization can sometimes be important in plasmas with many metastable atoms.

Other neutral collisions/reactions

There are, of course, many other collision processes involving neutral atoms. These collisions/reactions all have their own particular cross-sections, and it is difficult to summarize them here.

Examples are $CF_3 + F_2 \rightarrow CF_4 + F$

11. Effects of Collisions (1).

In the last two sections, we considered the various different types of collisions which occur in plasmas. There are so many different types of collisions that sometimes it can be difficult to understand which collisions are very important, and which collisions are not so important.

Also, as we discussed much earlier, plasma properties are decided by a balance of many different processes, and not by any single process. For this reason, also, it can be difficult to understand or imagine the effects of just one type of collision.

Despite these difficulties, it is possible to make a few general comments about the effects of some collision types. In this section, we will try to explain the general effects of some types of collisions.

11.1 Effect of electron-neutral elastic collisions

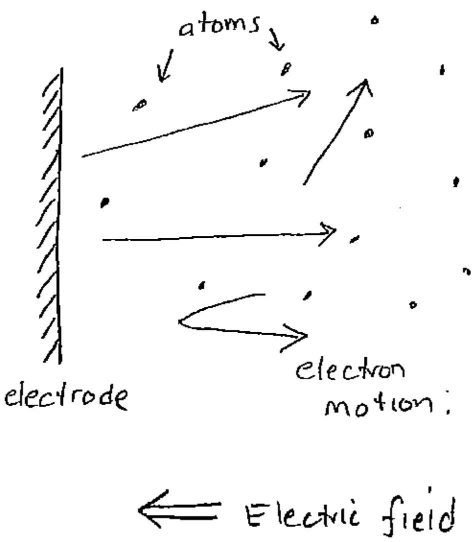
These collisions were discussed in the section about electron collisions. In that section, it was explained how the energy of the electron and the neutral particle do not change much as a result of the collision (because the electron mass is much, much smaller than the neutral mass). In this type of collision, the only thing which changes is the direction of the electron velocity. This may seem to be fairly unimportant, but it means that there is a big difference between plasmas with many electron-neutral collisions and plasmas with few electron-neutral collisions.

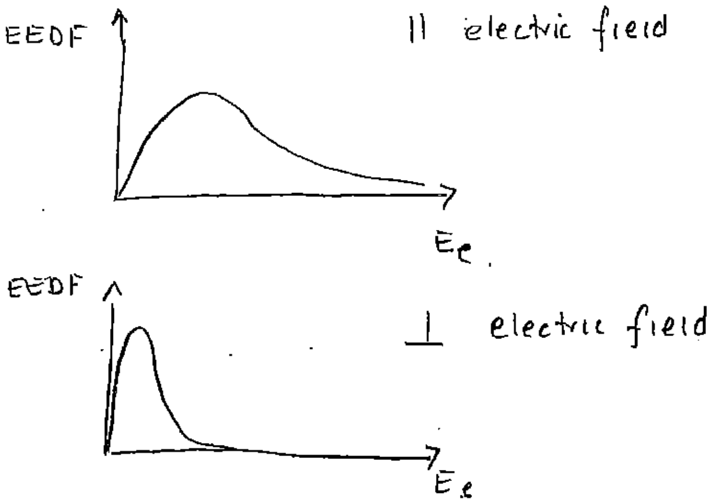
Plasma with few e-n collisions (e-n = electron-neutral

In a plasma with few e-n collisions, the electrons can move long distances before having a collision. So the velocity and energy of the electrons is determined mostly by the electric (and magnetic) fields in the plasma. And usually, electric (and magnetic) fields have some particular direction associated with them.

For example, in a plasma with electrodes, the electric field is in the direction perpendicular to the electrodes. The electrons

... gain energy in this direction. This means that the energy and velocity distributions will be different for different directions in the plasma.





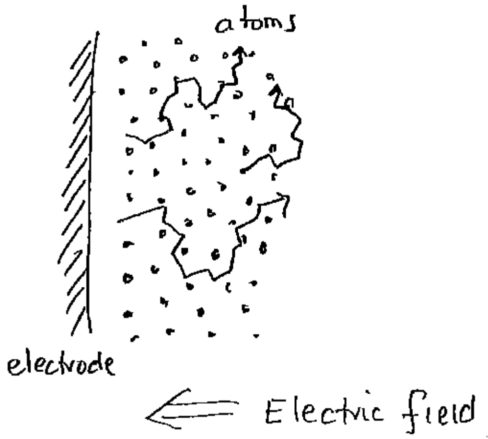
In particular, the electron energy perpendicular to the electric field will be much less than the energy in the direction parallel to the electric field

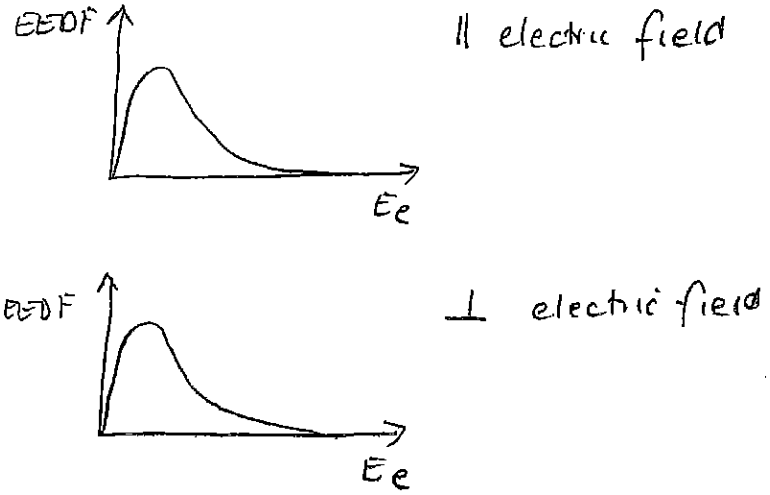
Plasma with many e-n collisions

When there are many e-n collisions, there are several important effects. Firstly, the electrons can not move long distances between collisions, and so the energy gain from the electric field is different. Secondly, the energy that the electrons gain is transferred, by collisions, into ~~many~~ all directions. The e-n.

collisions do not change the electron energy but the direction of the electron motion is changed.

In the example above, for the plasma with electrodes, this means that the energy which is gain in the direction of the electric field is transferred into directions perpendicular to the field. So the EEDFs for ⊥ and ∥ to the field will be approximately the same





∴ Any situation in which there is a preferred direction is called "anisotropic", and any situation in which all directions are the same is called "isotropic".

Hence, in summary.

few e-n collisions ⇒ possibility of anisotropic EEDFs

many e-n collisions ⇒ isotropic EEDFs.

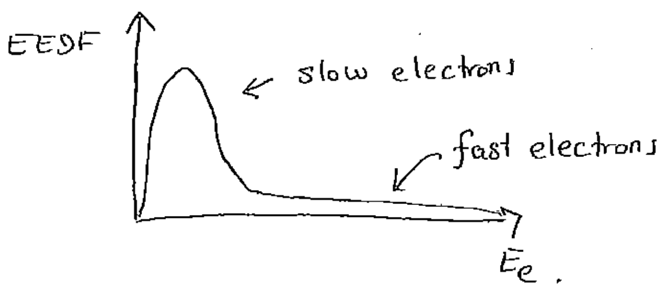
11.2 Effect of electron-electron Coulomb collisions

Electron-electron collisions (e-e collisions) are also elastic collisions involving electrons, and so the general conclusions made above for e-n collisions is also true for e-e collisions (i.e. many e-e collisions produce an isotropic EEDF.) However, there is a big difference between e-n elastic collisions, and e-e Coulomb collisions, and this means that other effects are also important.

In e-e collisions, the electrons can change energy (i.e, energy is transferred from the faster electron to the slower electron).

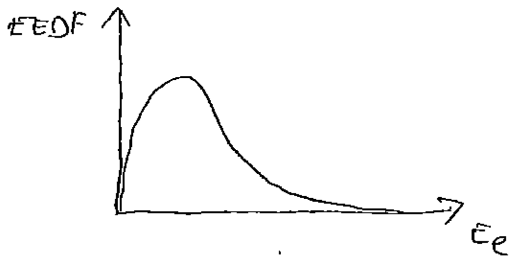
∴ Plasma with few e-e collisions

In this plasma, the electrons can gain energy from the electric field, and keep this energy. This results in a difference between electrons which have gained energy, and electrons which have not gained energy. So the EEDF might be



Plasma with many e-e collisions

In this type of plasma, the electrons will still gain energy from the electric field, but some of this energy will be transferred to slower electrons by e-e collisions. (This is the same process that was described in the section about neutral-neutral collisions.) So in this case, the EEDF will contain fewer fast electrons, but the slow electrons will have a higher average energy (because they gain energy from e-e collisions). So in this case, the EEDF might be



In the section about EEDFs (section 6), it was explained that, when there are many collisions, the energy distribution function tends to become Maxwellian.

Hence the effect of e-e collisions can be summarized as

few e-e collisions $\Longrightarrow$ non-Maxwellian EEDF
- possibility of many high energy electrons

many e-e collisions $\Rightarrow$ Maxwellian EEDF.

IMPORTANT

In the last two subsections (11.1 and 11.2) we have discussed the general effects of e-n and e-e collisions, and made conclusions about the EEDF. Of course, the EEDF is decided by a variety of factors, and not just these effects. These general trends, however, are true for virtually any type of plasma.

11.3 Effect of ion-neutral collisions

There are two main types of ion-neutral collisions (elastic collisions and charge-exchange collisions). In elastic collisions, about half of the energy higher energy particle is transferred to the lower energy particle. In charge-exchange collisions, all of the energy of the higher energy particle is transfered to the lower energy particle. So in both collision types, energy is transferred efficiently. In nearly all plasmas, ions have a higher average energy than the neutral particles, so the effect of ion-neutral collisions is, in general, to transfer energy from ions to neutral particles.

In the two subsections below, the general effect of these collisions is discussed. Note that in a complicated plasma, which contains many types of ions and many types of neutral particles, the discussion below might be too simple. Generally, however, this discussion is reasonable.

Plasma with few ion-neutral collisions

In a plasma with few ion-neutral collisions, the ions and the neutrals form two distinct groups of heavy particles. The ions can gain some energy from the electric fields in the plasma, but the neutral particles are not affected by this.

In a simple way, the situation can be thought of as the neutral particles being unaffected by the ions. The neutral particles behave as if they were in a gas, rather than a plasma. The presence of the charged particles (ions and electrons) does not affect the neutral particles

Plasma with many ion-neutral collisions

In this kind of plasma, the ions transfer some of their energy to the neutral particles, and the average ion energy and average neutral energy should be similar. The result is that the neutral particles have a higher average energy, and so, a higher temperature. In this case, the neutral particles are affected by the presence of ions (and electrons). The neutral properties are not the same as for a gas.

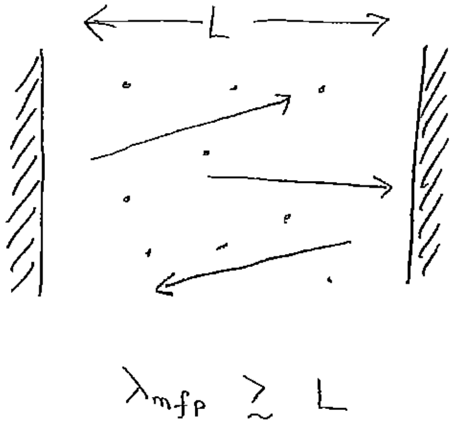
11.4 Comparing Collision Properties

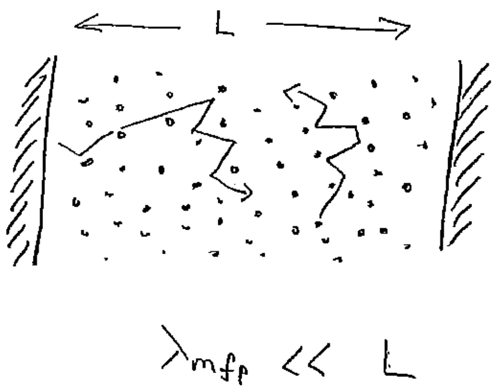
In the previous 3 sub-sections, the general effects of 3 types of collisions were discussed. In these discussions, the terms "few collisions" and "many collisions" were used. To use these comparisons properly, though, you have to be able to compare the collision frequency with something else. (ie. How many collisions is "many collisions" ??). To do this properly, you have to consider other physical characteristics of the plasma.

In a simple way, it is possible to think high pressure = many collisions, and low pressure = few collisions. However, there are some collisions in which pressure is [illegible] unimportant, and anyway, what pressure is "high pressure". We have to consider other physical characteristics of the plasma. In particular, we have to compare the collision frequency with <u>other</u> relevant collision frequencies.

<u>For example: e-n collisions</u>

In this case, to decide the importance of e-n collisions, you have to compare ν_{en} with the frequency of collisions with the <u>walls</u>. Another way to consider this is to compare the collision mean free path λ_{mfp} with the characteristic size of the plasma L (which is usually the distance between the walls or the electrodes)

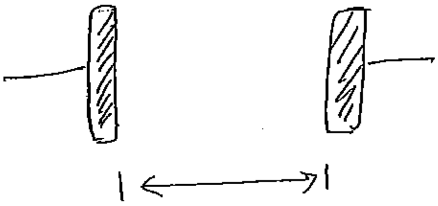




If $\lambda_{mfp} \gtrsim L$, then many electrons can move right across the plasma without a collision. Hence, the electric and magnetic fields (and <u>not</u> collisions) decide the electron properties such as the EEDF

If $\lambda_{mfp} << L$, then there are "many" e-n collisions, and these collisions are important in deciding the electron properties such as the eedf.

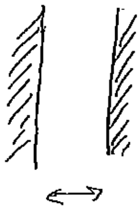
Examples DC plasma & PDP plasma (argon gas).



$L \sim 3\,cm.$

$p \sim 1$ Torr

DC plasma



$L \sim 10\,\mu m$

$p \sim 200$ Torr

PDP plasma

In the DC plasma at 1 Torr $\lambda_{mfp} \sim 1\,mm$ and so $\lambda_{mfp} \ll L$ ie. e-n collisions are very important. In the PDP plasma, $\lambda_{mfp} \sim 2\,\mu m$ and so $\lambda_{mfp} \sim L$. In this case, collisions are much less important in the plasma, compared with the DC plasma. The PDP plasma is at higher pressure, but the plasma size is so small that collisions are actually less important. actually, they still are important, but

The important point here is that, although it is necessary to study each collision separately, this is not sufficient. To understand the importance of each collision type, you have to compare it with other plasma characteristics, and determine its relative importance.

12. Surface Collisions/Reactions

Up until now we have considered various types of collisions and reactions which occur in a plasma. The collisions which were discussed in Sections 9, 10 and 11 were all collisions between particles in the gas phase. We also have to consider collisions of particles with the surfaces which surround the plasma. These reactions can be very important in many different types of plasma.

It is important to realize that these collisions and reactions are important for all types of plasmas. Of course, in processing plasmas, these reactions are extremely important, because these plasmas are used to modify surface properties. However, the collisions and reactions which are discussed in this chapter can occur in any type of plasma, and so they have to be understood.

The different processes are

(i) recombination

(ii) secondary electron emission

(iii) adsorption and desorption

(iv) fragmentation

(v) sputtering.

These reactions are discussed in the sub-sections below.

12.1 Recombination

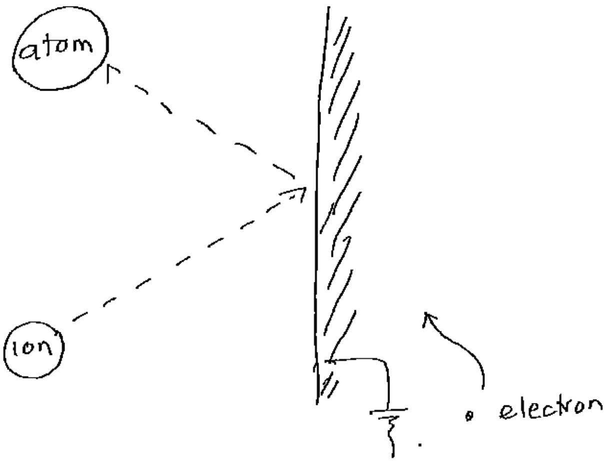
In a previous section, we noted that the recombination reaction [e + ion → atom] cannot occur because of energy and momentum conservation. The reaction [e + ion + particle → atom + particle] can occur, however. This reaction can occur in the gas phase, where the "particle" is a neutral atom or molecule, but it can also happen on a surface, where the surface particles play the role of the "particle". This reaction occurs very quickly – when an ion hits a wall, it is almost instantly converted into a neutral particle

recombination at a grounded metal surface

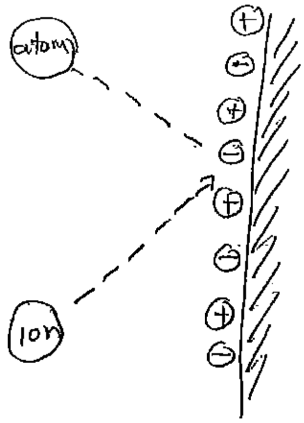
For the case where the surface is a grounded metal surface, such as a chamber wall, the wall is always at zero potential. Thus, when an electron hits the wall, it is "instantly" lost, as a current will flow to the ground. When an ion hits the surface, an electron from the ground comes up to the wall surface and attaches to the ion. This particle then leaves the surface as a neutral atom.

recombination at a floating surface.

For the case when the surface is not grounded, such as for insulating materials (ie. windows, wafers etc), the charged particles which hit the surface remain on the surface. Thus, when an ion hits the surface, an electron on the surface can attach to the ion and form a neutral particle.



reaction at a grounded surface



reaction at an insulated surface

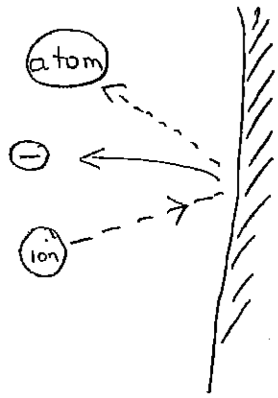
Comments

Recombination at surfaces is one of the most important reactions in a plasma. In a plasma, charged particles are always hitting the surfaces which surround the plasma. By recombination reactions at the surface, the charged particles are "lost". In some high pressure plasmas, recombination can occur in the gas, but this is extremely unlikely in a low pressure plasma. Just as it is very important to study ionization reactions (because these reactions create charged particles) it is also important to study recombination reactions, because charged particles are lost by this process.

Both the creation and loss of the charged particles is important

12.2 Secondary electron emission

The process where an ion from the plasma hits a surface, and causes an electron to be ejected from the surface, is called secondary electron emission. (Note that electrons produced by ionization are called primary electrons).



Combined recombination and secondary electron emission reactions

The number of secondary electrons which are produced for each incident ion is given by γ_{se}, which is called the secondary emission co-efficient. γ_{se} depends on the properties of both the incident ion and the surface atoms. A rough estimate of γ_{se} is given by

$$\gamma_{se} \sim 0.016\,(\mathcal{E}_{iz} - 2\mathcal{E}_\phi)$$

where $\mathcal{E}_{iz}$ is the ionization energy of the incident ion, and $\mathcal{E}_\phi$ is the "work function" of the surface material (the energy needed to release a particle from the surface.

One important point is that secondary emission occurs because the electric field on the ion interacts with the electrons in the surface material. It is <u>not</u> a direct transfer of energy from the ion to the surface (this is called sputtering). The electron emission occurs because the ion's electric field disturbs the surface material so that an electron can escape from the surface.

For nearly all materials $\mathcal{E}_f$ is between 4 and 6 eV. $\mathcal{E}_{12}$ varies for all atoms. Secondary emission, is therefore, most efficient (ie, γ_{se} is high) for noble gas ions (such as He^+ and Ar^+) striking surfaces, because $\mathcal{E}_{12}$ is high for these ions.

$\therefore$ γ_{se} varies between ~0.01 and ~0.2 for most cases. Some values are shown in the table on the next page.

In some plasmas, secondary electron emission can be important because it is another source of electron creation. When you are considering the balance of electron creation and loss, you sometimes have to consider secondary electron emission

---

Secondary Emission Co-efficients

Solid	Work function (V)	Ion	Energy (V)	γ_{se}
Si (100)	4.90	He^+	100	0.168
		Ar^+	10	0.024
			100	0.027
Ni (111)	4.5	He^+	100	0.170
		Ar^+	10	0.034
			100	0.036
Mo	4.3	He^+	100	0.274
		Ar^+	100	0.115
		N_2^+	100	0.032
		O_2^+	100	0.026
W	4.54	He^+	100	0.263
		Ar^+	10	0.096
			100	0.095
		H_2^+	100	0.029
		N_2^+	100	0.025
		O_2^+	100	0.015

12.3 Adsorption and Desorption

Adsorption is the process in which a particle from the plasma is absorbed onto the wall surface. The particle becomes weakly bonded to the surface atoms. This reaction is usually written as

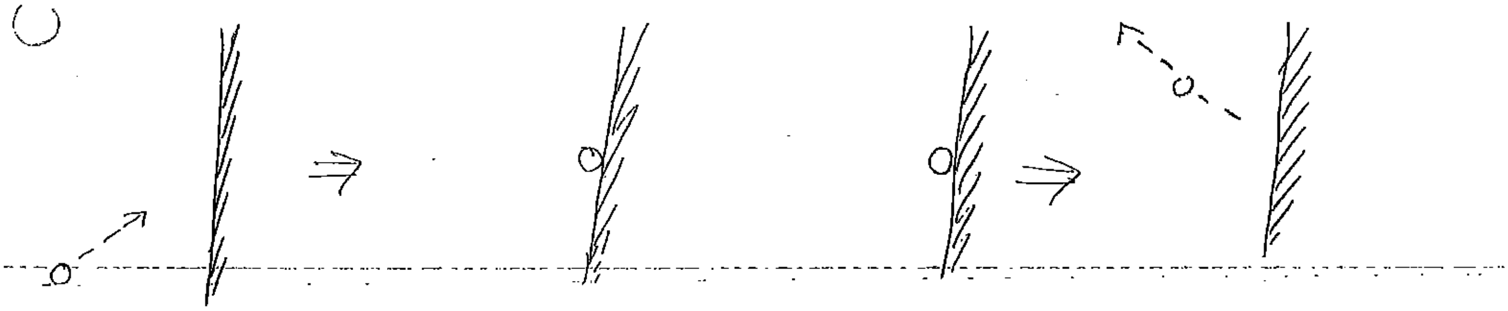
$$A \rightarrow A(s)$$

where the (s) means that the particle is on the surface.

(This reaction can also be written as $A + S \Rightarrow A:S$)

Desorption is the reverse process, in which a particle which is on the surface leaves the surface and goes back into the gas or plasma. It is written

$$A(s) \rightarrow A$$



adsorption desorption

* Note that, in the processes, the particle is still considered to be separate from the surface material. It

is resting on the surface, but has not actually become part of the surface.

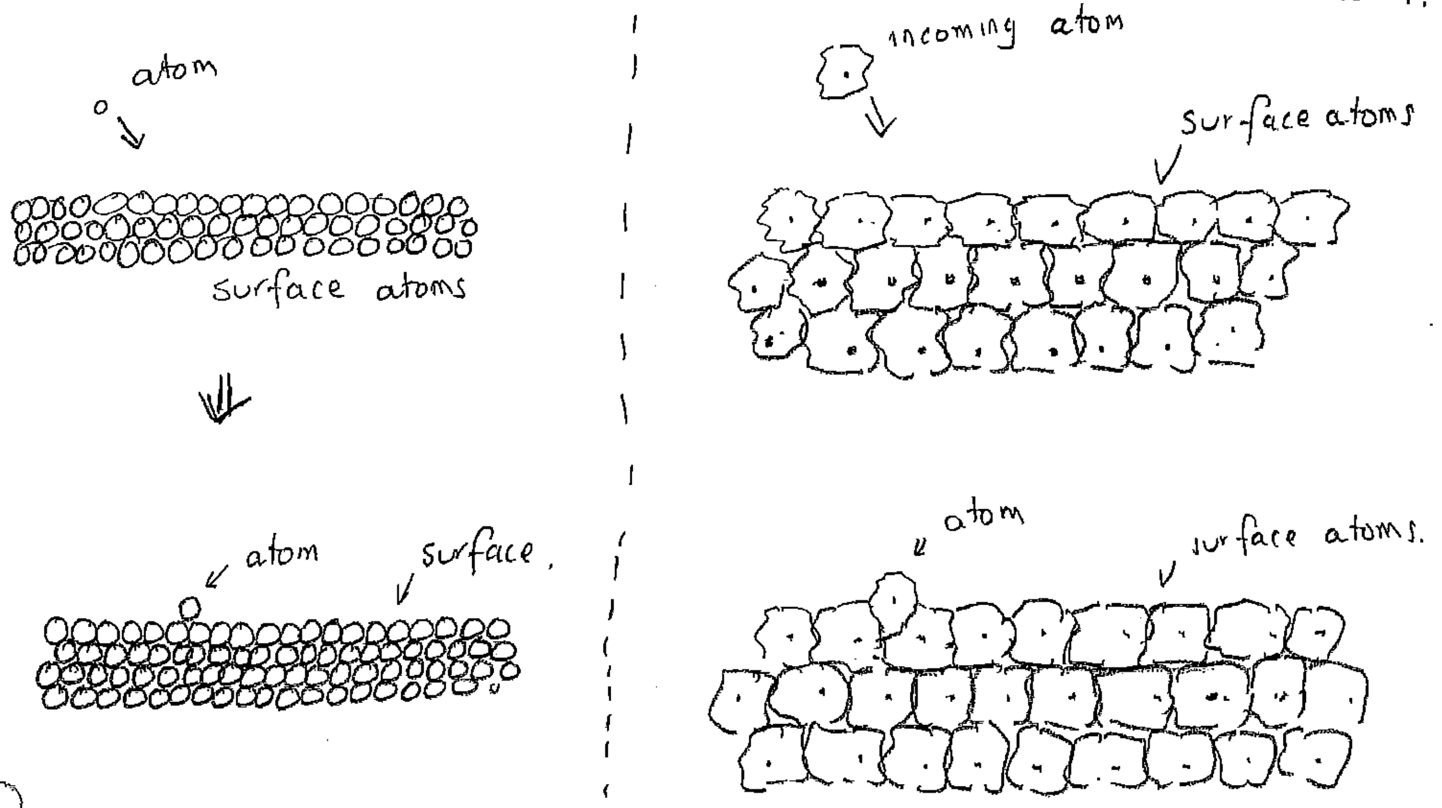
Adsorption is divided up into two types

(i) physical adsorption, which occurs when the particle just rests on the surface

(ii) chemical adsorption, which occurs when the incoming particle forms a loose chemical bond with a surface atom.

Physical adsorption

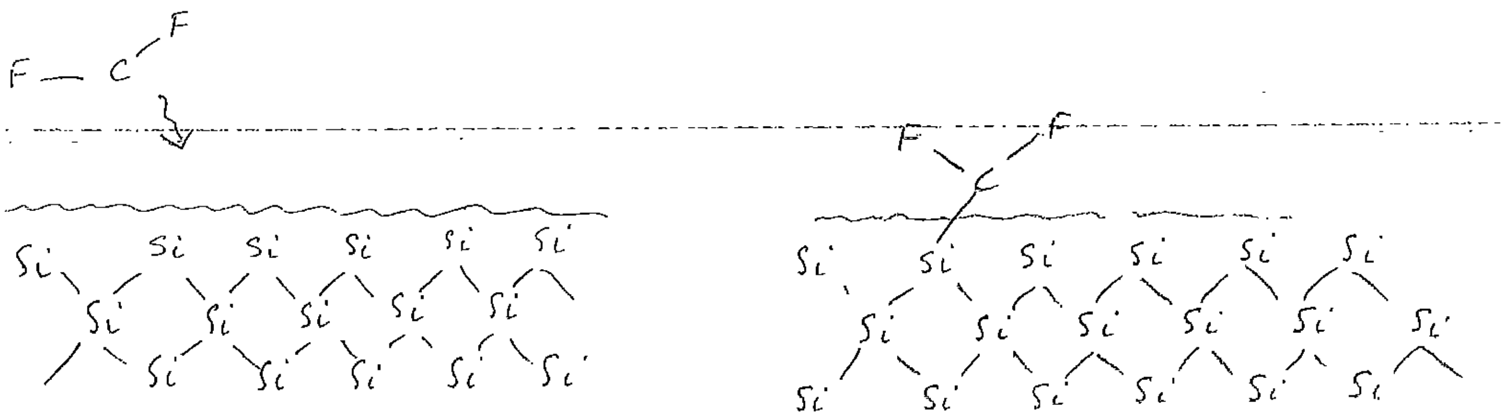
This process can be understood by looking at the two figures. The simplest description is shown on the left side, where the particle just rests on the surface. A more complicated, but more realistic picture is shown on the right side. The electron cloud of the incoming particle interacts with the electron cloud of the surface atoms. A small, very shallow potential well is formed, and the atoms rests in this potential well. Note that the atom on the surface is only very weakly connected to the surface. This is not a very stable situation.



2 different pictures of physical adsorption

Chemical adsorption

In this process, the incoming particle actually forms a chemical bond with one of the atoms in the surface. One example is shown below.

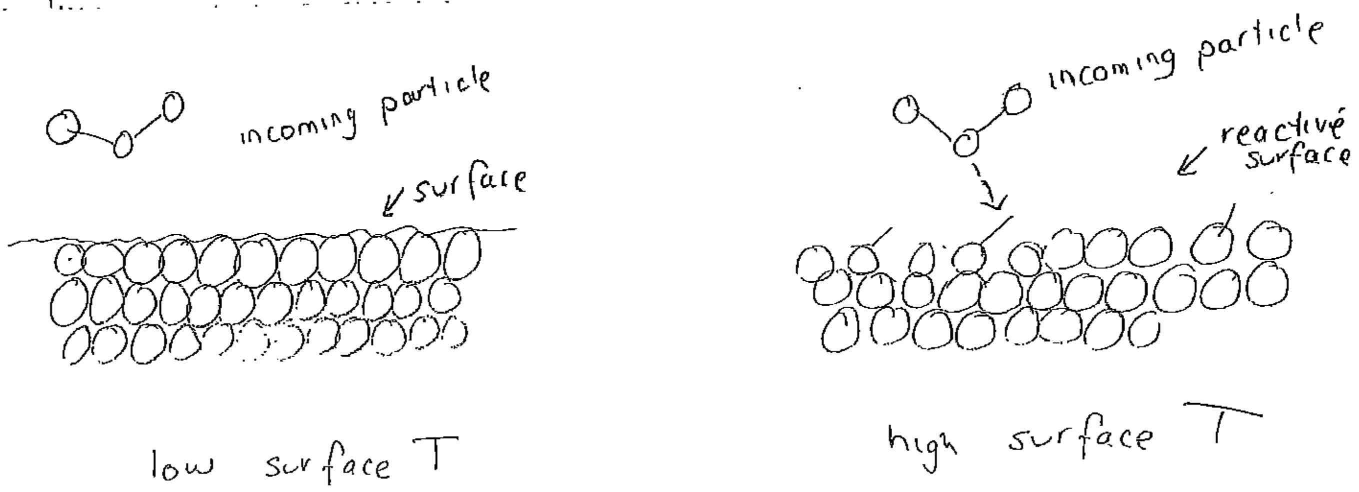


In this case, the particle is much more strongly bound to the surface than is the case for physical adsorption.

Temperature Effects (c).

In most cases, adsorption can be both the physical type and the chemical type, depending on other conditions, such as the temperature. For example, the type of bonding which occurs on the surface can depend on the surface temperature. At a low surface temperature, the surface atoms are ~~at~~ not very reactive, and so in this case, it is hard for the incoming particle to form a chemical bond. At higher surface temperature, however, the top layer of the surface can be much more reactive, and so an incoming particle can form a chemical bond.

(c)



Desorption

This is simply the reverse process to adsorption. It is written as

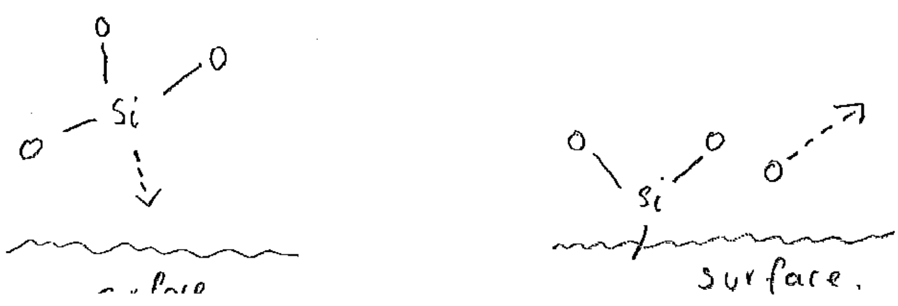
$$A(s) \rightarrow A$$

The rate at which particles are desorbed from a surface greatly depends on the surface temperature. This is especially true for particles which are only weakly bound to the surface. A small rise in the surface temperature can lead to a large rise in the amount of particles which are desorbed from the surface. (This is the principle behind the "baking" of vacuum chambers in order to clean the inner surfaces)

12.4 Fragmentation

When molecules hit a surface, it is possible for them to break up into smaller molecules or atoms. This is called fragmentation. ~~The smaller particles can then either be~~ adsorbed onto the surface, or move away from the surface.

eg/



12.5 Sputtering

When heavy particles, such as large ions, hit a surface, they can cause atoms to be ejected from the surface. This is called sputtering. A threshold energy is needed for this process, and so, in a plasma, it is usually the heavy ions which do the sputtering. Neutral particles also hit the surface but they usually don't have much energy, so they don't cause sputtering to occur.

The amount of sputtering which occurs is given by a value called the sputtering co-efficient Y_{sputt}, where

$$Y_{sputt} \propto \frac{1}{\mathcal{E}_t} \frac{M_i}{M_i + M_t}$$

where $\mathcal{E}_t$ is the binding energy of the surface (which is a property of the material), M_i is the ion mass and M_t is the mass of the surface atoms.

Some values of Y_{sputt} are shown in the table, for Ar^+ incident ions. Note that for some materials, such as copper, more than one atom is ejected for every incident ion. So the sputtering process can be very efficient.

Sputtering Co-efficients

(for Ar^+ at 600V).

Target	$Y_{sputt.}$
Al	0.83
Si	0.54
Fe	0.97
Co	0.99
Ni	1.34
Cu	2.00
Ge	0.82
W	0.32
Au	1.18

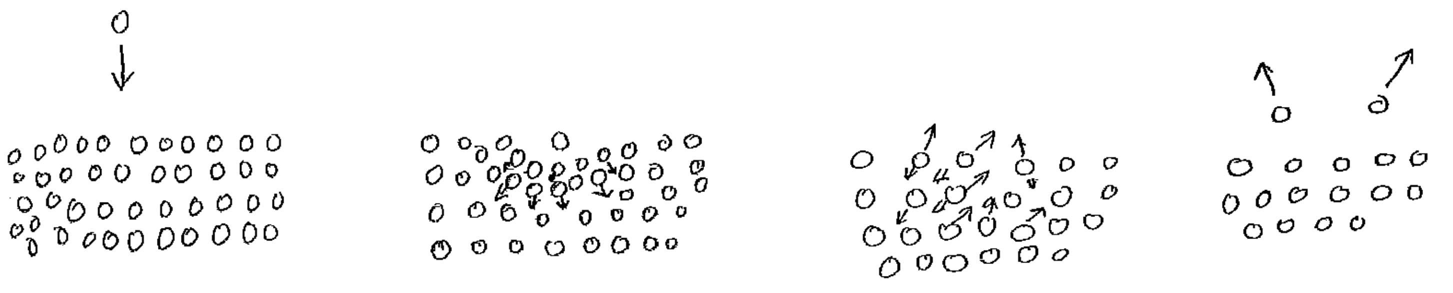
The actual sputtering process occurs as follows.

(i) the ion hits the surface

(ii) many surface atoms are affected by the ion impact

(iii) the surface atoms gain energy from the collision

(iv) some of the surface atoms are ejected.



(i) (ii) (iii) (iv).

12-6 Sticking Co-efficient

When a flux of molecules or atoms arrive at a surface, some of these particles will be adsorbed and some particles will not. The ratio of adsorbed particles to reflected particles is called s, the sticking co-efficient. (Note that this will be a function of temperature)

If s is close to one, then nearly all incoming particles will be adsorbed onto the surface. If s is nearly zero, then nearly all the particles will be reflected.

12.7. Importance of Surface Reactions

In this section, we have considered various kinds of surface reactions. Although many different reactions are ~~possible, it is important to remember that, in a stable plasma,~~ all the processes have to balance. So if many particles are adsorbed onto the walls, then an equal number of particles have to be desorbed back into the plasma. These kinds of processes have to balance each other

• The important point about surface reactions are that some reactions can occur at the surface which cannot occur in the plasma. So new particles can be created on the surface and then released into the plasma.

For example, the series of reactions shown here results in a new kind of particle. (the molecule A-B-C.).

$$AB \rightarrow AB(s).$$

$$AB(s) + C(s) \rightarrow ABC(s).$$

$$ABC(s) \rightarrow ABC$$

Because this kind of reaction can occur, it is important to always consider surface reactions as well as gas-phase reactions. Both types of reactions can be important in

~~determing plasma properties~~

13. Effects of Collisions/Reactions (2)

In Section 11, we considered the general effects of some important collision types. In this section, we will continue that discussion, but in much more detail. As well as being able to discuss effects in general terms, we also have to be able to discuss effects in specific, or quantitative, terms.

Another reason for this is it is impossible to estimate the importance of some collisions/reactions without considering other reactions too. It is only by considering the relative importance of different reactions that you can understand whether a reaction is important or not.

For example, consider a simple argon plasma, containing argon atoms, metastable argon atoms, excited atoms, ions and electrons. Some of the collisions/reactions are shown on the next page.

If we consider the ionization collision, (which creates ions and electrons) we also have to consider the loss reactions

Some reactions in an argon plasma.

1.	$e + Ar \rightarrow e + Ar$	elastic
2	$e + Ar \rightarrow e + Ar^+ + e$.	ionization
3	$e + Ar \rightarrow e + Ar_m$	metastable excitation
4	$e + Ar \rightarrow e + Ar^* \rightarrow e + Ar + h\nu$	excitation & emission
5	$e \rightarrow e(s)$	diffusion to walls
6	$Ar^+ \rightarrow Ar^+(s)$	diffusion to walls
7	$Ar^+(s) + e(s) \rightarrow Ar(s)$	recombination
8	$Ar(s) \rightarrow Ar$	desorption
9	$Ar^* + e \rightarrow Ar + e$ $Ar_m + e \rightarrow Ar + e$	collisional de-excitation

---

The loss reactions are Reactions 5, 6, 7.

If the ionization rate increases, we might expect the electron and ion density to increase. However, if the loss reaction rates <u>also</u> increase, then maybe the electron and ion density might be unchanged, or it might decrease. We can't understand the effect of ionization (Reaction 2) unless we also consider the other reactions too.

13.1 Rate Constant K

In order to understand about the relative importance of collision and reaction processes, it is necessary to compare reactions in some way. One way to do this is to use a property called the rate constant K. This indicates the number of collisions/reactions per second per unit density. (i.e., the collision frequency per unit density). It is given by

$$K = \sigma \bar{v}$$

where σ is the collision cross-section and $\bar{v}$ is the average velocity of the colliding species.

It is important to notice the difference between K and σ. σ, the collision cross-section, is a basic property of the collision, and does not depend on the plasma properties at all. K, however, does depend on plasma properties, because of the $\bar{v}$ dependence.

[Notice that K is called the rate constant, but it actually does depend on plasma properties. So the name "constant" is a little misleading.

Example 1. electrons having elastic collisions in argon.

$$e + Ar \rightarrow Ar + e$$

The collision frequency is

$$\nu_{el} = n_{Ar}\, \sigma_{el}\, \bar{v}_e$$

and the rate constant is

$$K_{el} = \sigma_{el}\, \bar{v}_e$$

In this case, we have used the average velocity of the electron, which is a plasma property. So K will be different for different plasma conditions.

Example 2 argon ions having charge-exchange collisions

$$Ar^+ + Ar \rightarrow Ar + Ar^+$$

In this case, the collision frequency is

$$\nu_{c-x} = n_{Ar}\, \sigma_{c-x}\, \bar{v}$$

and

$$K_{c-x} = \sigma_{c-x}\, \bar{v}$$

In this case, we use $\bar{v}$ where $\bar{v}$ is the average relative velocity of the ion and atom ($= V_R$, from a previous section) Sec 9, 10.

Averaging K over a velocity distribution.

You can see from the above discussion that K will be fairly accurate if $\bar{v}$ is truly indicative of the particle velocity. (ie, if most particles have velocity close to $\bar{v}$). However, in most cases, there is a wide range of velocity, and also, the cross-section has a velocity dependence. In these cases, the definition of ν and K above is not very useful. It is necessary to include the effect of the range of velocity, and not just use the average velocity

For example, in an argon plasma with electron temperate 2 eV, the average electron energy is about 3 eV. At $E_e = 3\,eV$, the cross-section for ionization is zero, so, by the above definition, $K_I = 0$ for this plasma, and $\nu_I = 0$ where K_I and ν_I are the ionization rate constant and frequency, respectively. However, ionization does occur in an argon plasma with $T_e = 2\,eV$, and so this calculation is clearly useless. It is definitely necessary to include both the ~~co~~ cross-section's velocity dependence and the distribution of velocity. Although sometimes this can be mathematically difficult, it is not too difficult if we assume

Maxwellian velocity distributions. We will consider the mathematical details of this calculation later.

13.2. Balancing different reaction/collisions

We have mentioned several times, so far, about how plasma properties are determined by the balance between different reactions. The rate at which the plasma properties change due to collisions/reactions is given by the reaction rate constants K. We can use this to calculate, mathematically, the different particle densities.

This is best shown by an example calculation. At the start of this section, a set of reactions was given for an argon plasma. This set of reactions can be compressed by combining the surface reactions (No 5, 6, 7, 8) into a single reaction, as shown on the next page.

Reaction set

	Reaction	Rate constant
1.	$e + Ar \rightarrow 2e + Ar^{+}$	K_1
2.	$e + Ar \rightarrow e + Ar_m$	K_2
3.	$e + Ar \rightarrow e + Ar^{*}$	K_3
4.	$e + Ar^{+} \rightarrow Ar$	K_4
5.	$Ar^{*} \rightarrow Ar + h\nu$	K_5
6.	$e + Ar^{*} \rightarrow Ar + e$	K_6
7.	$e + Ar_m \rightarrow Ar + e.$	K_7

The reactions which affect the electron density are 1 and 4.

So we can write

$$\frac{dn_e}{dt} = \text{electron creation} - \text{electron loss} = 0 \quad \text{in a stable plasma}$$

$$= n_e n_{Ar} K_1 - n_e n_{Ar^+} K_4$$

~~For metastable atoms, we can write~~

$$\frac{dn_{Ar_m}}{dt} = n_e n_{Ar} K_2 - n_e n_{Ar_m} K_7$$

The full set of equations ~~be~~ can be written.

electrons

$$\frac{dn_e}{dt} = n_e n_{Ar} K_1 - n_e n_{Ar^+} K_4 = 0$$

$$\frac{dn_{Ar^+}}{dt} = n_e n_{Ar} K_1 - n_e n_{Ar^+} K_4 = 0$$

$$\frac{dn_{Ar}}{dt} = n_e n_{Ar^+} K_4 - n_e n_{Ar}(K_1 + K_2 + K_3) = 0$$

$$\frac{dn_{Ar^*}}{dt} = n_e n_{Ar} K_3 - n_{Ar^*} K_5 - n_e n_{Ar^*} K_6 = 0$$

$$\frac{dn_{Ar_m}}{dt} = n_e n_{Ar} K_2 - n_e n_{Ar_m} K_7. = 0.$$

By solving these 5 equations, you can determine the 5 densities n_e, n_{Ar^+}, n_{Ar_m}, n_{Ar^*}, n_{Ar}.

Notice that (i) the K in these equations has to be properly calculated to consider the velocity distribution

(ii) this is only a crude set of equations, but the information gained by this type calculation can be a useful guide to plasma behaviour

K ✱✱ (iii) the relative importance of each reaction can be understood by comparing the terms in each equation

13.3 Comments

⊛ We started off this section by aiming to find some way to understand the relative importance of different reactions and collisions in a plasma.

⊛ In order to do this, we have to combine information about the reaction/collision properties <u>and</u> the plasma properties.

⊛ By constructing reaction sets, and then equation sets, the important reactions can be determined

⊛ By solving the rate equation sets, we can obtain information about particle densities which is a useful guide to the plasma properties.

<u>Also</u>

⊛ For many many cases, the collision cross-sections and rate constants are not known, and so calculation is very difficult. Only approximate calculations can be done

⊛ For these "rough" calculations, plasma information, such as the electron velocity and energy distributions is needed. Usually, this is not known well, so again, calculation is "rough" (ie, approximate).

14. Effect of Basic External Parameters

In Section 11, some general effects of different collision types were discussed. In Section 13, a method to estimate the importance of collisions and reactions was discussed. In those sections, we considered the effect of different collisions on the plasma properties. In this section, we will consider the effect of external parameters on the plasma properties

For every kind of plasma, there is a set of externally set conditions. The most important parameters are

(i) size
(ii) gas pressure
(iii) input power
(iv) application of B field.

Just by considering each of these, it is possible to make some general conclusions about the plasma properties. For examnple, a plasma with an applied magnetic field is very different to a plasma without an applied field. Thus, some general conclusions can be made

14-1 Plasma Size

There are many different size plasmas — very small plasmas like a PDP discharge, and very large plasmas like fusion plasmas. The important parameter, however, is not really the physical size, but the ratio of the size and the effective collision lengths. (This point was discussed in Section 11). Hence, plasmas can be categorized as

$$L \gg \lambda_{mfp}$$

or

$$L \lesssim \lambda_{mfp}$$

where L is the physical size of the plasma (perhaps the chamber size) and λ_{mfp} is the typical mean free path.

The difference between the two cases is that for $L \gg \lambda_{mfp}$, the chamber wall surfaces become relatively unimportant in determining the plasma properties. This is because particles in the center of the plasma are relatively unaffected by conditions at the chamber walls. In this case, gas-phase collisions will be most important in determining plasma properties.

For $L \lesssim \lambda_{mfp}$, the surfaces surrounding the plasma have an effect on the <u>entire</u> plasma. This is because particles from the walls can travel into the main part of the plasma.

These effects can be summarized as

"small plasma" → surface conditions affect the whole plasma

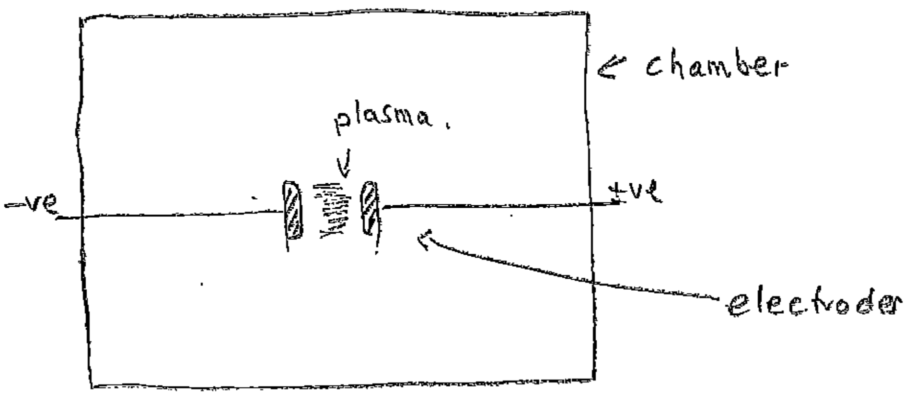
"large plasma" → surface conditions do not affect most of the plasma.

Some examples are given below

<u>Example 1</u>

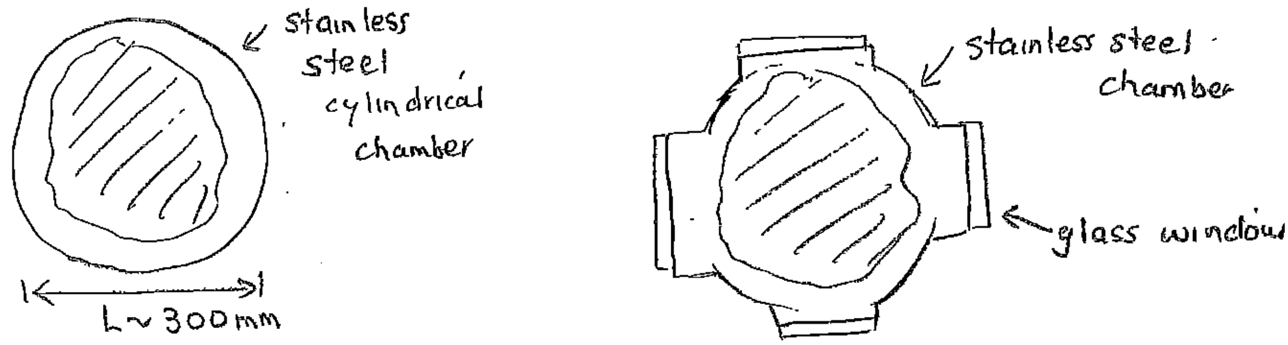
$L \sim 300\,mm$

Ar plasma
~ 1 Torr
$\Rightarrow \lambda_{mfp} \lesssim 1\,mm.$



In this case, a small plasma is in the center of a large chamber. The electrode materials will affect the plasma properties, because the plasma is close to the electrodes. The chamber wall material, however, should have no effect at all on the plasma.

Example 2



* Inductively coupled plasma at p ~ 0.5 mTorr.

* Chamber diameter ~ 300mm, λ_{mfp} ~ 100 cm.

In this case, clearly the wall surfaces and wall conditions will affect the plasma. However, consider the two cases above. In one case, the wall is all made of the same material (stainless steel). In the second case, big glass windows are present. The effect of the chamber walls will be different because the wall surfaces are different in each case.

14-2 Gas pressure.

The effect of gas pressure is similar to that of plasma size. In this case, pressure determines the mean free path for collisions, and we have to compare λ_{mfp} with the chamber or plasma size. Hence the same conclusions as made in 14-1 are true for gas pressure.

(Low pressure) $\lambda_{mfp} \gtrsim L$, then surface conditions are important

(High pressure) $\lambda_{mfp} \ll L$, then surface conditions not so important.

Other general conclusions can be made, however, based on the fact that high pressure usually means many collisions. These are

- high pressure $\rightarrow$ Maxwellian EEDF

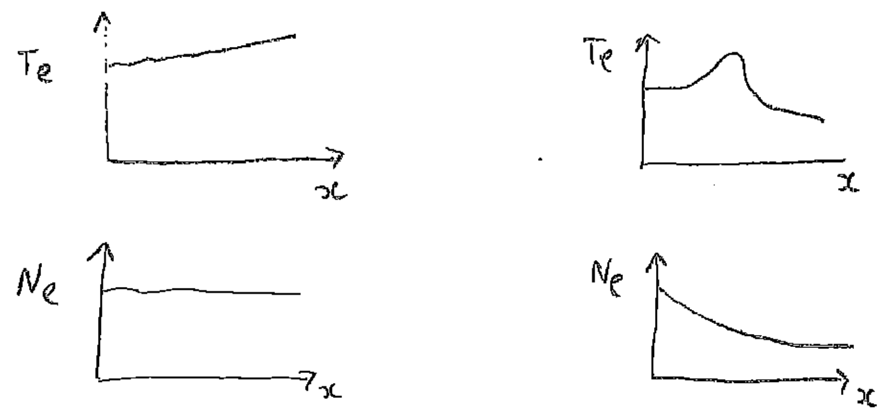
  This is because many e-n collisions tend to produce a Maxwellian EEDF (see Sect. 11).

- high pressure $\rightarrow$ strong spatial dependence.

  This is because one effect of many collisions is to "localize" phenomena in the plasma. Particles from one region in a plasma cannot move readily to other regions of the plasma. This produces strong spatial distributions of the plasma properties.

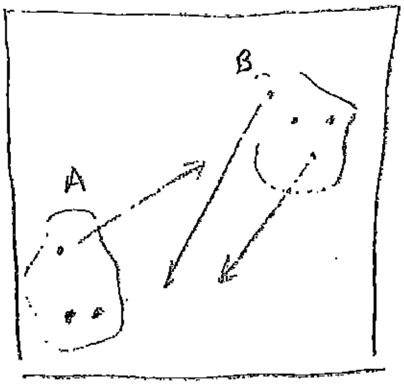
e.g

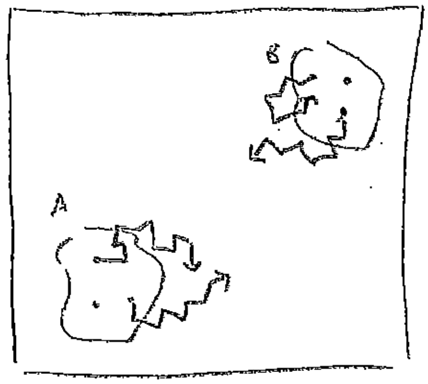
Low pressure | High pressure



low pressure | high pressure

e.g.





particles can move freely through the plasma, and so the properties of region A are similar to the properties of region B

particles in region A cannot easily move to region B, and so properties of the two regions might be completely different

⊙ High pressure ⟶ low T_e
low pressure ⟶ high T_e.

This is a very generally true. There are probably some cases where it isn't valid, but usually it is true. The reason for this effect is related to the movements of electrons in the plasma, The electrons in the plasma can energy from electric fields in the plasma. At low gas pressures, the electrons can move relatively long distances without collisions. Hence, if there is an electric field, they can gain a large amount of energy before having a collision. Hence, the average electron energy, for low pressure plasmas, can be relatively high.

For high pressure plasmas, however, the electrons only move a short distance before having a collision. The collision will change the direction of the electron motion, and mates it harder for the electron to gain a large energy. Hence, higher pressure plasmas tend to have lower electron temperatures

[Note that there are other important effects which determine T_e, not just the pressure. Pressure, however, does have some effect]

14-3 Input Power

It is a very rough rule that higher input power means higher electron density. This is because ionization collisions require energy, and so if more energy is absorbed by electrons, then more ionization collisions can occur

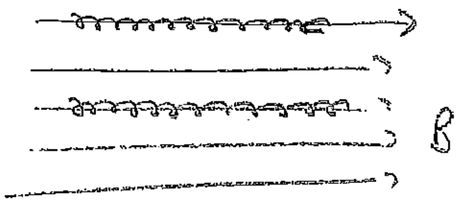
It is generally <u>not</u> true that higher power means higher electron temperature. The electron temperature is determined by a variety of factors, but mostly the gas pressure. The input power does not significantly affect the average electron energy. [Electrons <u>do</u> gain more energy at higher input power, but they lose this energy by collisions, such as ionization collision, The <u>average</u> energy is not really affected.

14-4 Magnetic Field

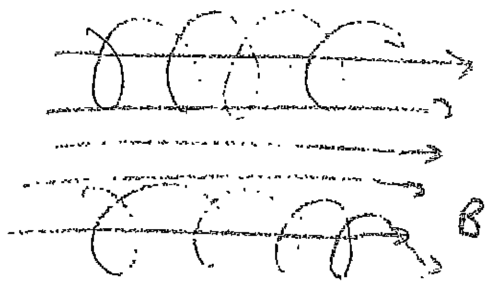
In an earlier section, we considered the effect of a magnetic field on the motion of the charged particles, electrons and ions. The conclusions there were

- electron motion is greatly affected
- ion motion is slightly affected, depending on the size of B.

(• the field causes the particles to have circular motion)



electron motion



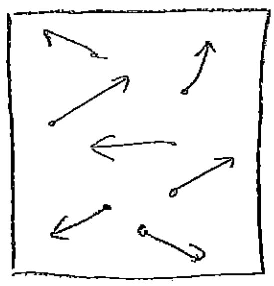
ion motion

An applied magnetic field, even a small one, can have a large effect on plasma properties because of its effect on the motion of the charged particles, particularly the electrons.

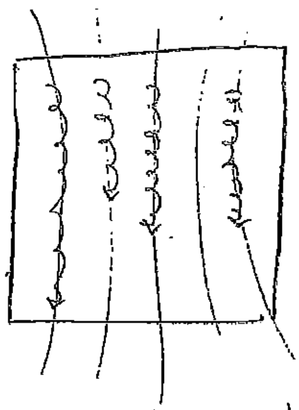
The effects of an applied B field can be summarized as follows.

(i) $\begin{cases} \text{No } B \rightarrow \text{particles have 3-D motion} \\ \text{large } B \rightarrow \text{particles have 1-D motion.} \end{cases}$

When there is a large B field, the charged particles cannot freely move. They tend to move in the same direction as the magnetic field (as shown in the previous diagrams). Hence, the plasma particles tend to have only a 1-D motion. The charged particles, especially the electrons, can't move long distances ⊥ to the B field



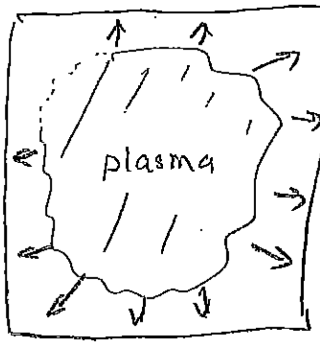
electron motion with no B



electron motion with a strong B.

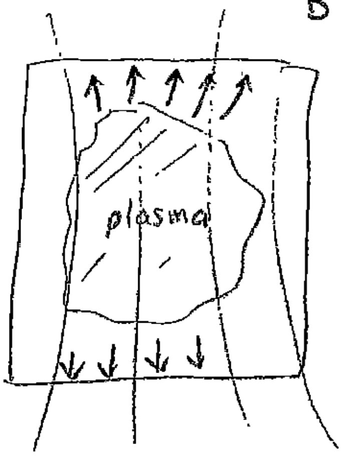
(ii) Loss of charged particles is greatly affected by B.

This is related to the first effect, described above. When there is no B, the charged particles will hit all of the chamber walls. When there is a large B, the particle loss is greatly reduced, as shown in the following figure



When there is no B, charged particles are lost to all surfaces.

B ↓



When there is a large B, only the top and bottom walls are hit by particles.

(iii) There are strong spatial dependencies when B is large.

This is also related to the two above effects. When B is large, the charged particles can't easily move $\perp$ to B. Hence the different regions of the plasma are separated from each other.

(iv) EEDF tends to be anisotropic when B is large.

This is similar to point (i). Because the electrons can move freely in the direction $\parallel$ B, but not in the direction $\perp$ B, the average energy of electrons $\parallel B$ and $\perp B$ will probably be different.

Important point.

Note that the effect of B is largest for low pressure plasmas, because the particles can move freely (and hence be affected by B). For high pressure plasmas, the effects of collisions tend to overcome the effects of B. For example, the particles will move $\perp$ to B because of frequent collisions — the EEDF will become isotropic because of frequent collisions etc ...

So magnetic fields are usually applied to lower pressure discharges. They don't have much effort for higher pressure plasmas (to be exact, they don't have much effect when $\lambda_{mfp} \ll r_{Larmor}$)

14-5 Summary

In this section, we considered the general effects of external plasma parameters. These can be summarized as.

	large	small
size	chamber walls don't have much effect	- chamber walls are important - surface reactions are important
pressure.	strong spatial dependence. maxwellian EEDF low T_e	fairly uniform plasma. (maybe) non-Maxwellian EEDF (maybe) high T_e.
input power.	high n_e	low n_e.
magnetic field	1-D plasma reduced election/ion loss strong spatial dependence. anisotropic EEDF	3-D plasma (for zero B). normal election/ion loss.

Please remember that these are general effects only. There are probably plasmas in which they are not valid. However, we <u>can</u> consider them to be <u>generally</u> true.

Thus, if we have a plasma with certain conditions. (for example, high pressure; small chamber, high input power, no B) then we <u>already</u> can make some general assumptions about the plasma properties, just using only this information.

14.6 Effects of Different Gases

Another effect that is important is the effect of different gases. Each gas has its own characteristic properties, but there are some general properties for some gases.

Two ways of classifying gases are shown below.

(i)

Atomic Gases	Molecular Gases
He, Ne, Ar, Kr, Xe	N_2, O_2, F_2, Cl_2, Br_2, H_2 CF_4, CH_4, BCl_3 ... etc

(ii)

Non-Reactive	Moderately Reactive	Very Reactive
He, Ne, Ar, Kr, Xe	N_2, H_2, O_2, CH_4 etc. (gases not including F, Cl, Br, ...)	F_2, Cl_2, Br_2 BCl_3, CF_4 etc (gases that include F, Cl, Br, ... etc)

In this section, we will mainly consider the difference between atomic and molecular gases.

Point 1 Number of species

Plasmas that contain only atomic gases, such as He and Ar, have only a small number of particle types. Plasmas with molecular gases can have very many different particle types.

For example

	Ar plasma	O_2 plasma	CF_4 plasma
Neutral species	Ar Ar^* Ar_m	O_2 O O_3 O^*, O_2^* O_M, O_{2m}	CF_4 CF_3 CF_2 CF F, F_2, C, C_2 CF_3^*, CF_2^* C_2F_4, C_2F_6 C_3F_8
Positively charged particles	Ar^+	O_2^+ O^+	CF_3^+, CF_2^+, CF^+ F_2^+ F^+
Negative charged particles	e^-	e^- O_2^-, O^-	e^- CF_3^-, CF_2^-, CF^- F^- F_2^-

Nearly all processes in a plasma become more complicated and more difficult to understand when the number of particles becomes large.

eg. ionization processes
collision processes
diffusion
loss of charged particles

Point 2 Types of Wall/surface reactions

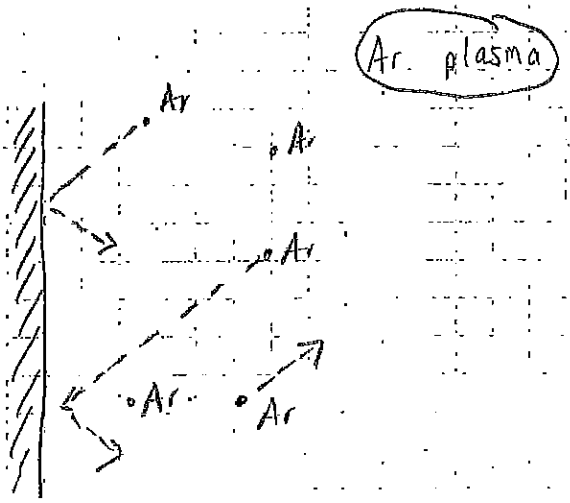
Different gases have very different reactivities with wall materials, and so just knowing the gas type gives you some information about wall/surface reactions.

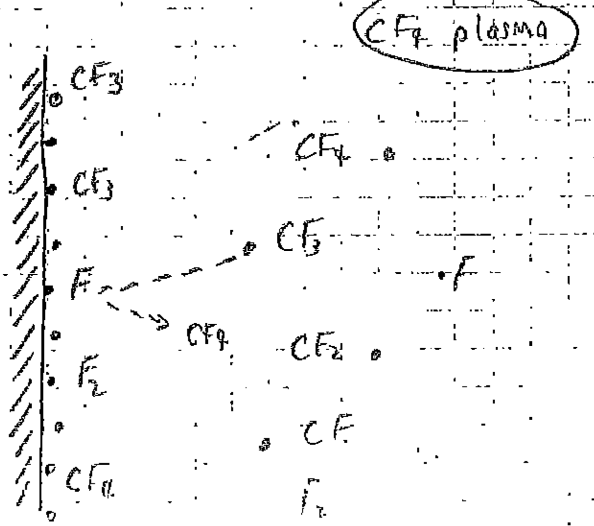
Atomic gases

- gas particles do not react with walls/surfaces
- only recombination reactions are important. $(Ar^+ + e^- \xrightarrow{wall} Ar)$

Molecular gases

- some gas particles do react with wall materials
- many types of surface reactions
- many particles are attached to walls





Point 3   EEDFs – (electron energy).

One general difference between plasmas with atomic gases and plasmas with molecular gases is that the EEDF is usually very different. One easy way to say this is

simple gas = simple EEDF

complicated gas = complicated EEDF.

This can be seen in the examples below. The main reason is that there are many more collision processes in molecular plasmas. These affect the EEDF.

Types of electron collisions

electron energy	He plasma	Ar plasma	CF_4 plasma
0 eV	coulomb e-n elastic	coulomb e-n elastic	Coulomb collision e - neutral elastic collisio negative ion formation dissociation for excitation (vibrationa rotationa
10 eV		+ excitation	+ excitation (electronic
15 eV		+ ionization	+ ionization
20 eV	excitation		
25 eV	ionization		

Hence, the EEDF is affected greatly by the type of gases in the plasma. This is because

more types of electron collisions = more types of electron energy loss

Point 4 Electron Density

The value of electron density is influenced by the type of gas. A simple rule is that a molecular gas plasma will have a lower n_e than an atomic gas plasma. This is for the same reason as above

more electron collisions = more electron energy loss

This can be understood by considering the "power balance" that we discussed much earlier in Section 4.

In a plasma, the power input to the plasma is absorbed by electrons, which then lose this energy is various collisions/reactions. One of these collisions is ionization collisions, which produce electrons. If there are many collision types, then there is less energy for ionization collisions.

For example, consider the Ar and CF_4 plasmas in the previous section. Both gases have ionization energy of ~ 15 eV. The power balance, however, is different. ~~Ke~~

Ar plasma

Power in = Power loss due to [e-n elastic collisions + e-n excitation collisions + e-n ionization collisions]

+ power loss when electrons hit chamber walls

CF_4 plasma

Power in = Power loss due to [e-n elastic collisions + e-n rotational excitation + e-n vibrational excitation

+ e-n dissociation + e-n electronic excitation

+ e-n ionization]

+ power loss when electrons hit chamber walls/surfaces

In the CF_4 plasma, there is less energy for ionization collisions so n_e is less than for an argon plasma.

" Please remember these are general statements. For example, He has ionization energy of 26 eV compared with ~15 eV for CF_4. "

For the same input power, He and CF_4 plasmas probably have similar n_e, even though He plasma is "simple" and CF_4 plasma is "complicated".

For most other gas types, however, this conclusion is generally true.

15. Summary of the Course until now

The sections until now have been.

1. General Image of Plasma
2. General Plasma Properties
3 General Behaviour of Different Particles
4 Particle and Energy Balance
5. Sheaths, Electric Fields, Potential
6. Electron Energy and Temperature.
7. Other basic information

Basic Plasma Theory

8. Basic Collision Theory
9 Electron Collisions
10 Ion and Neutral Collision
12 Surface Reactions

Collisions and Reactions

11. Effects of Collisions (1)
13 Effects of Collisions (2)
14 Effects of External Parameters

Important Effects.