1

Fundamentals of Plasma

1.1 INTRODUCTION

Low-pressure plasma, cold plasma, nonequilibrium plasma, and glow discharge are some of the synonymously used terms to designate the same type of process. The technologies using these plasma assisted processes are generally referred to as plasma processing and include such diverse approaches as plasma assisted chemical vapor deposition (PACVD), plasma enhanced chemical vapor deposition (PECVD), ionitriding, and plasma etching. Plasma assisted processing is a critical technology used in the production of advanced microelectronics and in the production of present and future generations of large-scale integrated circuits. It would not be possible to manufacture very-large-scale integrated circuits (VLSI) computer chips without deposition of thin films by plasma assisted chemical vapor deposition or without plasma assisted etching, which enables etching of submicron-size features with vertical walls in silicon, metals, and dielectrics. Plasma processing also made possible the development of special materials with unique properties such as amorphous silicon or diamondlike carbon.

Plasma chemistry takes place under nonequilibrium conditions, and the reactions can occur while the gas or parts exposed to it remain at relatively low temperatures. The advantages of plasma processing are being exploited in various areas besides microelectronics. For example, the plasma assisted chemical vapor deposition technique called *ionitriding* allows replacement and upgrade of a conventional technology for surface hardening of metals, done by thermal nitriding, and thus achieves much more efficient surface hardening. The ionitriding technique enables control and adjustment of the properties of the hardened surface layers, not manageable while using the conventional method of nitriding.

At the base of the mentioned technologies is the cold plasma, a phenomenon similar to that occurring in fluorescent bulbs or neon lights, that is, an electrical discharge in a gas at low pressure. The phenomena occurring in cold plasmas are very complex and not yet fully understood. However, it is possible with the present knowledge of plasma physics and chemistry to adjust and control the composition of the gas mixtures and the parameters of the discharge to achieve required results in terms of processing and materials properties. The plasma assisted techniques allow increased production rates, precise production, and devising of materials with unique properties which evolve from the chemistry of cold plasmas.

The present book aims to provide a broad introduction to the physics and chemistry of cold plasmas, to present various diagnostic techniques used for studies, of plasma, for monitoring and optimization of plasma operations, and to discuss the state-of-the-art applications of cold plasmas.

1.2 DEFINITION OF PLASMA

Taking into consideration the energy of the particles constituting it, plasma is energetically the fourth state of the matter, apart from the solid, liquid, and gas states. Figure 1-1 presents schematically the ranges of temperature, or particle energy, in which each of the four forms of matter occur in nature. For the plasma state, the temperature range reflects only the energy of the heavy particles (not of the electrons) for reasons to be explained later.

Langmuir and collaborators were the first to study phenomena in plasma in the early 1920's while working on the development of vacuum tubes for large

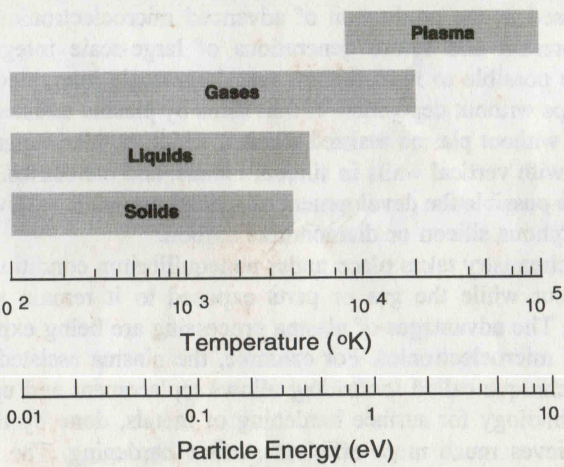


Fig. 1-1 State of matter versus temperature.

currents, and it was Langmuir who in 1929 used the term "plasma" for the first time [1] to describe ionized gases.

In a more rigorous way, a plasma can be defined as a *quasi-neutral gas* of charged and neutral particles characterized by a *collective behavior*.

Let us first define the collective property of the plasma. The behavior of a neutral gas is described by the kinetic theory of gases. According to this theory, in an ordinary neutral gas no forces act between the molecules of the gas (gravitational forces are considered negligible), and the particles travel in straight lines, with a distribution of velocities. The motion of the molecules is controlled by the collision among themselves and with the walls of the container. As a result of these collisions, the molecules of a neutral gas follow a random Brownian motion, as illustrated in Fig. 1-2 (a).

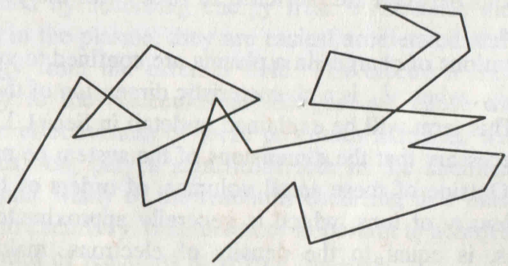
Assuming the particles of the neutral gas to be rigid spheres of radius r and their density n, the kinetic theory of the gases defines the *cross section for collision*, σ, and mean free path, λ, as

$$\sigma = \pi r^2 \tag{1.1}$$

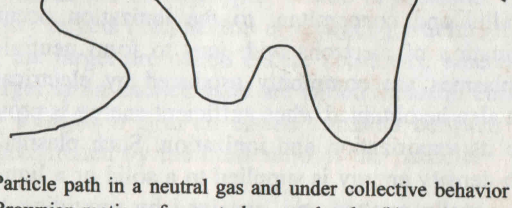
$$\lambda = \frac{1}{\sigma n} \tag{1.2}$$

The average number of collisions per second, called the *collision frequency*, ν, and the *mean time between collisions*, τ, are given by

$$\nu = \frac{\bar{v}}{\lambda} \tag{1.3}$$



(a)



(b)

Fig. 1-2 Particle path in a neutral gas and under collective behavior in a plasma: (a) Brownian motion of a neutral gas molecule; (b) motion of a charged particle in a plasma.

$$\tau = \frac{1}{\nu} = \frac{\lambda}{\bar{v}} \tag{1.4}$$

where $\bar{v}$ is the *average velocity* of the molecules in the gas which is determined by its temperature, T:

$$\bar{v} = \left(\frac{kT}{M}\right)^{1/2} \tag{1.5}$$

M is the mass of the molecule, and k is the Boltzman constant. If the temperature of the gas is constant, the *collisional mean free path* is inversely proportional to the pressure in the system:

$$\lambda = \frac{ct}{p} \tag{1.6}$$

where ct = a constant depending on the gas
p = pressure in the gas

In a plasma, contrary to the preceding description, the motion of the particles can cause *local concentrations of positive and negative electric charges.* These charge concentrations create long-ranged Coulombic fields that affect the motion of charged particles far away from the charge concentrations. Thus elements of the plasma affect each other, even at large separations, giving the plasma its characteristic collective behavior. A charged particle in a plasma moves along a path which on average follows the electric field. Such a path is illustrated in Fig. 1-2 (b). In some conditions, at low pressures, the effect of the long-range electromagnetic forces on the motion of the particles can be much stronger than the effect of the collisions between the particles. In such cases the plasma is called a *collisionless plasma.*

Local concentrations of charges in a plasma are confined to volumes of small dimensions of size λ_D, where λ_D is a characteristic dimension of the plasma, called the Debye length. This term will be explained in detail in Sec. 1.3.3. For a plasma to be stable, it is necessary that the dimensions of the system be much larger than the Debye length. Outside of these small volumes, of orders of tens of micrometers, the *charge density* of ions, which is generally approximately equal to the density of the ions, is equal to the density of electrons, making the plasma electrically neutral. As a result, the plasma is considered a quasi-neutral gas.

A plasma is usually obtained when sufficient energy, higher than the ionization energy, is added to atoms of a gas, causing ionization and production of ions and electrons. Parallel and concomitant to the ionization occurs the opposite process of recombination of electrons with ions to form neutral atoms or molecules. Although plasmas are commonly produced by electrical discharges in gases, a plasma can also be obtained when sufficient energy is provided to a liquid or a solid to cause its vaporization and ionization. Such plasma plumes can be obtained when high-density energy is supplied to a solid or a liquid by a laser. In a gas, a plasma is usually excited and sustained by providing to the gas electromagnetic energy in different forms: direct current, radio frequency, microwaves, and so on. Plasmas are often referred to as *gas discharges* because the most common way to produce plasma is by passing an electrical discharge through the gas.

1.3 PLASMA PARAMETERS

A plasma, especially one sustained in a mixture of molecular gases, contains a multitude of different neutral and charged particles. A group of identical particles in a plasma is commonly referred to as a *species*.

The plasma is broadly characterized by the following basic parameters:

- The *density of the neutral particles*, n_n.
- The *densities of the electrons and ions*, n_e and n_i. In the quasi-neutral state of plasma the densities of the electrons and of the ions are usually equal, $n_i = n_e = n$ and n is called the *plasma density*.
- The *energy distributions* of the neutral particles, $f_n(W)$; ions, $f_i(W)$; and electrons, $f_e(W)$.

The plasma density is an important parameter in plasma processing because the efficiency of the processes occurring in the plasma and their reaction rates are generally dependent directly on the density of the charged particles. As we shall see in Chapter 2, the electrons are the main factor responsible for the transfer of the energy from the external electric field to the discharge gas. Being electrically charged, both electrons and ions interact with the applied external electric field and are accelerated by absorbing energy from it. Because the electrons are the lightest particles in the plasma, they are easiest accelerated and absorb the largest amount of energy from the external field. The electrons then transfer through collisions energy to the molecules of the gas and cause their ionization and dissociation. The effectiveness of these processes increases with increasing electron density. Ions, too, play a significant role in the chemical reactions taking place in the plasma. Many of the reactions occurring in a plasma are controlled, or affected, by ion chemistry. It is therefore important to achieve high ion densities to increase the rates of reactions involving the ions.

As in any gaseous system, particles in the plasma are in continuous motion, inducing collisions between them. The collisions which take place between the particles in the plasma are of two types, elastic or inelastic. Collisions between electrons and heavy targets (i.e., neutral or charged particles) that do not result in an excitation of the target are called *elastic collisions*, whereas those collisions that leave the target in an excited state are called *inelastic collisions*.

The *energy transfer* W_{Tr} in an elastic collision between an electron and a heavy target is determined by the mass ratio of the particles

$$W_{Tr} = \frac{2m_e}{M} W \tag{1.7}$$

where M = mass of the heavy particle
W = energy of the electron
m_e = mass of electron

For an elastic collision of an electron with an argon atom, the fraction of transferred energy is therefore very small, about

$$\frac{W_{Tr}}{W} \approx \frac{1}{40{,}000} \tag{1.8}$$

On the other hand, a significant amount of energy is transferred in a collision between two electrons.

The electrons gain energy through acceleration by the electric field, which sustains the plasma and transfers that energy by inelastic collisions with the neutral gas molecules. The inelastic collisions between energetic electrons and the heavy species of the plasma result in excitation, ionization, or dissociation of the target if it is multiatomic. Energy transfer in an inelastic collision is not controlled by the mass ratio of the colliding particles. In an inelastic collision between two particles, the fraction of transferred energy is given by

$$\frac{W_{Tr}}{W} = \frac{M}{m_{in} + M} \tag{1.9}$$

where m_{in} is the mass of particle losing energy.

According to Eq. (1.9), in an inelastic collision between an electron and a heavy particle ($m_{in} = m_e \ll M$), the electron can transfer almost all its energy to the heavy particle, creating an energetic plasma species. The inelastic collisions therefore sustain the plasma by producing the particles that form it and giving the plasma its special features. Inelastic collisions involve energy transfer in amounts that vary from less than 0.1 eV (for rotational excitation of molecules) to more than 10 eV (for ionization).

Electron-electron collisions can also play a significant role in the energy transfer processes in the plasma. Their importance depends on the degree of ionization prevalent in the plasma. For degrees of ionization below 10^{-10}, the contribution of the electron-electron collisions to the energy transfer is negligible. However, in *electron cyclotron resonance* (*ECR*) plasmas, where the degree of ionization can be above 10^{-3}, electron-electron collisions dominate [2].

The relative contribution of each type of collision to the processes taking place in the plasma depends on additional plasma parameters, which will be discussed next and which derive from the previously described parameters.

1.3.1 The Degree of Ionization

The parameter that defines the density of the charged particles in the plasma is the *degree of ionization* of the gas. It specifies the fraction of the particles in the gaseous phase which are ionized. The degree of ionization, a, is defined as

$$\alpha = \frac{n_i}{n} \tag{1.10}$$

α

For plasmas sustained in low-pressure discharges, the degree of ionization is typically 10^{-6} to 10^{-3}. However, if the electrical discharge is assisted and confined by an additional magnetic field, the degree of ionization can reach values of 10^{-2} or higher, as for example, in an ECR plasma. Table 1-1 presents the range of values of the degree of ionization encountered in different low-pressure plasmas used for processing of solids.

TABLE 1-1 Ranges of Parameters for Various Low-Pressure Plasmas

Plasma Type	Pressure (torr)	Ion Density (cm^{-3})	Degree of Ionization
Deposition/etching	< 10	$< 10^{10}$	10^{-6}
Reactive ion Etching	10^{-2}–10^{-1}	10^{10}	10^{-6}–10^{-4}
Magnetron sputtering	10^{-3}	10^{11}	10^{-4}–10^{-2}
Electron cyclotron resonance	$< 10^{-4}$–10^{-2}	10^{12}	$< 10^{-1}$

The degree of ionization in a plasma is a function of the elements contained in the plasma. For example, in plasmas used in magnetron sputtering, the degree of ionization of the sputtered metal is higher than that of the process gas employed for the sputtering.

The value of the *critical ionization* is defined by [3]

$$a_c \approx 1.73 \times 10^{12}\, \sigma_{ea}\, T_e^2 \tag{1.11}$$

where σ_{ea} = electron-atom collision cross section at the average electron velocity, expressed in cm^2

T_e = electron temperature of the plasma, expressed in eV

The electron temperature will be defined later, in Sec. 1.3.2.1.

If the degree of ionization is much bigger than the critical ionization value, the charged particles behave as in a fully ionized gas.

1.3.2 Plasma Temperature

One of the physical parameters defining the state of a neutral gas in thermodynamic equilibrium is its temperature, which represents the *mean translational energy* of the molecules in the system. A plasma contains a mixture of particles with different electric charges and masses. At a first approximation, the plasma may be considered, thermally, as consisting of two systems: the first containing only electrons and the second containing the heavy species, that is, neutral atoms or molecules, ions, and neutral molecular fragments. 1 2 3

The electrons gain energy from the electric field, which energizes the plasma, and lose part of it by transfer to the second system through elastic or inelastic collisions. The system of heavy particles loses energy to the surroundings, either by radiation or by heat transfer to the walls of the vessel containing the plasma. 4

6 The electrons and the heavy species in the plasma can be considered approximately as two subsystems, each in its own thermal quasi-equilibrium.

7 The ions and electrons in the plasma can therefore be characterized by their specific different average temperatures: the *ion temperature*, T_i, and the *electron temperature*, T_e. Actually in some cases additional temperatures may characterize the particles in the plasma. For example, in the presence of a magnetic field, even a single plasma species, for example, the ions, is characterized by two different temperatures, one representing the translation of the ions parallel to the magnetic field, $T_{||}$, and one representing the translation perpendicular to the magnetic field, $T_{\perp}$. This is caused by the fact that the forces acting on the species parallel to the magnetic field are different from those acting perpendicular to it [4].

8 The situation is even more complicated, as the heavy species in the plasma can be characterized by several temperatures at the same time, even in the absence of a magnetic field [5]: the *temperature of the gas*, T_g, which characterizes the translatory energy of the gas; the *excitation temperature*, T_{ex}, which characterizes the energy of the excited particles in the plasma; the *ionization temperature*, T_{ion}; the *dissociation temperature*, T_d, which characterize the energy of ionization and dissociation; and the *radiation temperature*, T_r, which characterizes the radiation energy. Thermodynamic equilibrium will exist in the plasma only if the following equation is satisfied:

$$T_g = T_{ex} = T_{ion} = T_d = T_r = T_e \tag{1.12}$$

? Complete thermodynamic equilibrium cannot be achieved in the entire plasma because the radiation temperature, T_r, at the envelope of the plasma cannot equal the temperature in the plasma bulk. However, under certain laboratory conditions, it is possible to achieve local thermodynamic equilibrium in plasma in volumes of order of the mean free path length. If this happens, the plasma is called a *local thermodynamic equilibrium* (*LTE*) plasma. In low pressure plasmas, produced by direct current glow discharge or radio frequency excitation, the LTE conditions are generally not achieved. These plasmas are therefore called *non-LTE plasmas*.

In non-LTE plasmas the temperatures of the heavy particles are normally too small to promote chemical reactions in thermodynamic equilibrium. The electron temperature is therefore the most important temperature in non-LTE plasmas, among all those different temperatures mentioned previously. The fraction of electrons that will cause the different reactions in the plasma, the overall efficiency of the plasma processes, and the processing rates increase with increasing electron temperature. The electron temperature is discussed in further detail in the following section.

1.3.2.1 Electron Temperature

The *velocity distribution* function $f(v)$ for a system of particles is defined as the density of particles in the velocity space that satisfies the equation

$$n(cm^{-3}) = 4\pi \int_0^\infty f(v)v^2 \; dv \tag{1.13}$$

where v = velocity
$f(v)$ = velocity distribution function (density in velocity space)
n = the density of the particles in the geometrical space

If it is assumed that the velocity distribution of the electrons in the plasma is isotropic, that the effects of inelastic collisions act only as a perturbation to the isotropy, and that the effects of the electric fields are negligible, then the velocity distribution is Maxwellian. The *Maxwellian distribution* assumes that the temperature of the electrons equals the temperature of the gas, $T_e = T_g$.

If the distribution of the electron velocities can be considered Maxwellian, then it can be described by [4, 6]

$$f(v) = n_e \left(\frac{m_e}{2\pi kT_e}\right)^{3/2} \exp\left(-\frac{m_e v^2}{2kT_e}\right) \tag{1.14}$$

The *electron energy distribution* function $f(W)$ is related to the velocity distribution function $f(v)$ through the relation [6]

$$f(W) = \frac{4\pi}{m_e} v f(v) \tag{1.15}$$

Therefore, the Maxwellian energy distribution function for the electrons is given by

$$f(W) = 2.07 W_{av}^{-3/2} \; W^{1/2} \exp\left(\frac{-1.5W}{W_{av}}\right) \tag{1.16}$$

where W_{av} is the *average energy of electrons.*
It can be shown that the average energy of the electrons is related to their temperature by

$$W_{av} = \frac{3}{2} kT_e \tag{1.17}$$

Due to the simplifying assumptions, the Maxwellian distribution provides only a first approximation of the electron energy (or velocity) distribution in the plasma.

The assumptions made for the Maxwellian distribution can be replaced in low-pressure plasmas by the following assumptions:

1. The electric field strength in the plasma is sufficiently low such that one can neglect the inelastic collisions, but large enough for the electron temperature to be much higher than the ion temperature, $T_e \gg T_i$.
2. The electric field is of sufficiently low frequency, that is, it is of a frequency ω much lower than the frequency of collisions ν.
3. The collision frequency is independent of the electron energy.

Under these assumptions the distribution of the electrons in the plasma is given by a *Druyvesteyn distribution* [6]. The Druyvesteyn distribution function gives a better approximation than the Maxwellian one for the electron energy distribution in the non-LTE plasmas.

The Druyvesteyn energy distribution of the electrons in the plasma is given by

$$f(W) = 1.04 W_{av}^{-3/2} W^{1/2} \exp\left(-\frac{0.55W^2}{W_{av}^2}\right) \tag{1.18}$$

In the case of the Druyvesteyn distribution, the average electron energy and the electron temperature are functions of E_o/p, where E_o is the strength of the electric field and p is the pressure in the plasma. However, when the degree of ionization becomes large, the electron density also affects the energy distribution [6]. It should be emphasized that the Druyvesteyn distribution, as the Maxwellian one, gives only an approximation for a steady plasma. Numerical calculations have to be made to obtain a more accurate evaluation of the electron energy distribution.

Figure 1-3 illustrates Maxwellian and Druyvesteyn distributions for a sample of several average electron energies. As can be seen, the Druyvesteyn distribution is characterized by a shift toward higher electron energies, as compared to the Maxwellian one. As we shall see later, the reaction rates in the plasma are a function of interaction cross sections, which in turn depend on the energies of the particles. Some reactions in the plasma have an energetic threshold and will happen only if the energy of the participating electron is higher than the threshold value. An important fact illustrated by Fig. 1-3 is that both energy distributions are characterized by a *high-energy tail*. For an average electron energy of 5 eV, a significant amount of electrons have energies above 8 eV, reaching even values

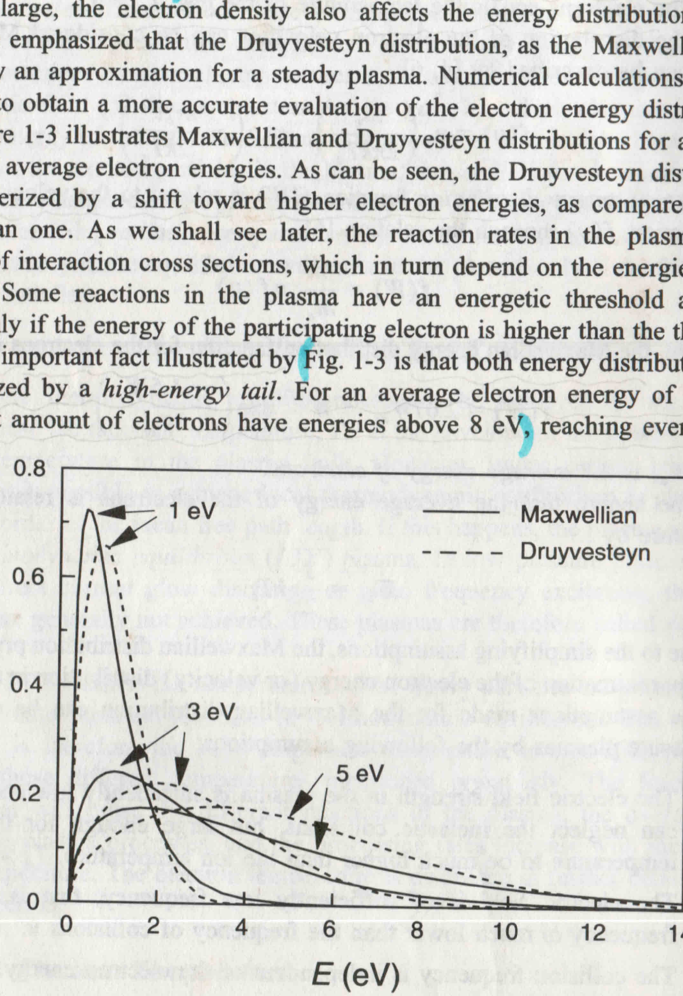


Fig. 1-3 Electron energy distributions according to Druyvesteyn and Maxwell. The numbers indicate the average electron energy for each distribution.

up to 14 eV. Thus the electrons in the high-energy tail of the distribution, though in small concentrations, have a significant impact on the overall reaction rates in the plasma. The Druyvesteyn distribution predicts a larger number of electrons to contribute to reactions requiring high energies.

As mentioned before, the different species in the plasma may be characterized by their distinct temperatures. The temperatures tend to equilibrate as the interaction between the two systems, that is, electrons and heavy particles, increases. This happens if either the pressure or the density of the electrons in the plasma increase, as shown in Fig. 1-4.

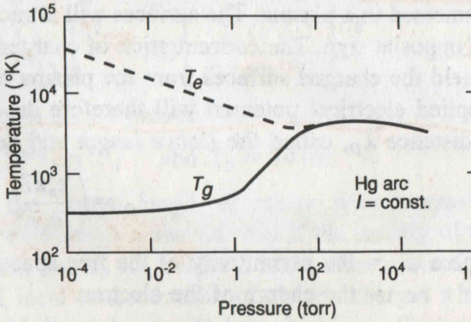


Fig. 1-4 Electron and ion temperatures as a function of pressure (from [7], reprinted with permission from R.F. Baddour and R.S. Timmins, *The Application of Plasmas to Chemical Pressing*, MIT Press, © 1967).

At low pressures, the electron temperature is much greater than the temperature of the gas, $T_e \gg T_g$. When the pressure in the plasma increases, the energy transfer from electron to neutrals increases, causing an increase in the temperature of the gas and decrease of the electron temperature (see Fig. 1-4). The electron and gas temperature converge to similar values at a pressure between 10 torr and 100 torr and the plasma becomes arclike. In arcs at atmospheric pressure the two temperatures are equal, $T_e = T_g$. When the two temperatures are about the same, the distribution of the species in the plasma can be described by equilibrium relations, while in the case when $T_e \gg T_g$, the distribution of active species is best represented by the electron temperature, T_e.

Although the temperatures of the electrons in the types of plasmas to be discussed in the following chapters are several times 10^4 °K (several electron volts), it does not imply that these plasmas are hot. Typical electron densities in these plasmas are about 10^{10} cm^{-3}, as compared to the density of particles in a gas at atmospheric pressure which is about $\sim 2.7 \times 10^{19}$ cm^{-3}. Due to the very low density and the very low heat capacity of the electrons, the amount of heat transferred by the electrons to the gas (heavy neutral and ionized particles) and to the walls of the container is very small. Thus, the term "cold plasma" derives its meaning from the small amount of heat transferred to the gas or solids in contact with it.

1.3.3 Debye Length

1 Another important parameter of a plasma is its *Debye length*. If an electric field is created in the plasma, the charged particles will react to reduce the effect of the field. The lighter, more mobile, electrons will respond fastest to reduce the electric
2 field. If a plasma had an excess of positive or negative particles, this excess would create an electric field and the electrons will move to cancel the charge.

The response of charged particles to reduce the effect of local electric fields
3 is called *Debye shielding* and the shielding gives the plasma its quasi-neutrality characteristic. Let us assume that an electric potential is applied between two surfaces immersed in a plasma. The surfaces will attract equal amounts of charged particles of opposite sign. The concentration of charged particles near the two surfaces will shield the charged surfaces from the plasma bulk, which will remain neutral. The applied electrical potential will therefore develop mostly near the surfaces, over a distance λ_D, called the *Debye length* and defined by

$$\lambda_D = \left(\frac{\varepsilon_o k T_e}{n_e e^2}\right)^{1/2} \tag{1.19}$$

where ε_o = the permittivity of the free space
e = the charge of the electron

To clarify the meaning of the Debye length, let's assume that a positive electric charge, q, is inserted in a plasma that is initially quasi-neutral. The charge will create an electric potential, which in free space would be [2]

$$V_o = \frac{q}{4\pi\varepsilon_0 d} \tag{1.20}$$

where d is the distance from the charge. In the plasma, the potential is affected by the plasma electrons and ions and its value can be obtained by solving Poisson's equation,

$$\nabla^2 V = -\frac{\rho}{\varepsilon_0} \tag{1.21}$$

where ρ is the total charge density in the plasma and is given by:

$$\rho = e(n_i - n_e) + q\delta(d) \tag{1.22}$$

where $\delta(d)$ is the Dirac δ function, indicating that q is a point charge.

The potential V changes the electron density, and assuming that the electrons are in thermodynamic equilibrium at temperature T, the density can be calculated as [2]:

$$n_e = n \exp\left(\frac{eV}{kT}\right) \tag{1.23}$$

As it can be assumed that $eV \ll kT$, the Poisson's equation can be rewritten using Eq. (1.22) as

$$\nabla^2 V = \frac{V}{\lambda_D} + q\delta(d) \tag{1.24}$$

with λ_D defined by Eq. (1.19). The solution of Eq. (1.24) is

$$V(d) = \frac{q}{4\pi\varepsilon_0 d}\exp\left(-\frac{d}{\lambda_D}\right) = V_0 \exp\left(-\frac{d}{\lambda_D}\right) \tag{1.25}$$

Equation (1.25) shows that the plasma changes the potential of free space, V_0, causing its attenuation with a decay length equal to the Debye length, λ_D. This attenuation of the potential produced by a local charge in the plasma is the Debye shielding effect.

For estimation purposes and taking into account that $T(°\mathrm{K}) = 11{,}600\ T(\mathrm{eV})$, it is convenient to calculate the Debye length from

$$\lambda_D(\mathrm{cm}) = 6.93\left[\frac{T_e(°\mathrm{K})}{n_e(\mathrm{cm}^{-3})}\right]^{1/2} = 743\left[\frac{T_e(\mathrm{eV})}{n_e(\mathrm{cm}^{-3})}\right]^{1/2} \tag{1.26}$$

An example of typical values found in a cold plasma is

$$T_e = 1\ \mathrm{eV}, \quad n_e = 10^{10}\ \mathrm{cm}^{-3}, \quad \text{and } \lambda_D = 74\ \mu\mathrm{m}$$

As indicated by Eq. (1.19), the Debye length decreases with increasing electron density. An ionized gas is considered a plasma only if the density of the charged particles is large enough such that $\lambda_D \ll L$, where L is the dimension of the system. If this condition is satisfied, local concentrations of electric charges which may occur in the plasma are shielded out by the Debye shielding effect over distances smaller than the Debye length. Outside these volumes of charge concentrations the plasma bulk is quasi-neutral. The Debye length, λ_D, is therefore the characteristic dimension of regions in which breakdown of neutrality (formation of local concentrations of charges) can occur in a plasma.

Another plasma parameter related to the Debye length is the *number of particles, N_D,* in a *Debye sphere*, that is, in a sphere of radius equal to λ_D. The solution of Poisson's equation given by Eq. (1.25) can be obtained only by assuming that the shielding effect is produced by a large number of electrons, or in other words, the shielding effect can occur only if the Debye sphere contains a large number of electrons. Due to the exponential decay of the potential, it can be assumed that the shielding is caused by the electrons in the Debye sphere, whose number is given by

$$N_D = \frac{4\pi}{3} n_e \lambda_D^3 = \frac{1.38 \times 10^3 T_e^{3/2}\ (°\mathrm{K})}{n_e^{1/2}} = \frac{1.718 \times 10^9 T_e^{3/2}\ (\mathrm{eV})}{n_e^{1/2}} \tag{1.27}$$

N_D has to be therefore much larger than unity to fulfill the collective characteristic of the plasma. For electron temperatures $T_e > 1$ eV and densities $n_e < 10^{12}$ cm^{-3}, the condition $N_D \gg 1$ is easily satisfied. In the cold plasmas N_D ranges from about 10^4 to 10^7 electrons in a Debye sphere.

1.3.4 Plasma Sheath

We shall proceed with a more detailed examination of what happens at a surface in contact with a plasma. Ions and electrons reaching the solid surface recombine and are lost from the plasma system. Electrons that have much higher thermal velocities than ions reach the surface faster and leave the plasma with a positive charge in the vicinity of the surface. An electric field that retards the electrons and accelerates the ions develops near the surface in such a way as to make the net current zero. As a result, the surface achieves a negative potential, relative to the plasma, or in other words, the surface is at a negative *self-bias* relative to the plasma.

The plasma is therefore always at a positive potential relative to any surface in contact with it. Because of the Debye shielding effect, the potential developed between the surface and the plasma bulk is confined to a layer of thickness of several Debye lengths. This layer of positive space charge that exists around all surfaces in contact with the plasma is called the *plasma sheath*.

The *sheath potential*, V_s, is the electrical potential developed across the plasma sheath. Only electrons having sufficiently high thermal energy will penetrate through the sheath and reach the surface, which, being negative relative to the plasma, tends to repel the electrons. The value of the sheath potential adjusts itself in such a way that the flux of these electrons is equal to the flux of ions reaching the surface. Its value is given for a planar surface by [8]

$$V_s = \frac{kT_e}{2e} \ln\left(\frac{m_e}{2.3m_i}\right) \tag{1.28a}$$

where V_s = sheath potential
m_i = mass of ion

For a spherical surface the expression changes to [9]

$$V_s = \frac{kT_e}{2e} \ln\left(\frac{\pi m_e}{2m_i}\right) \tag{1.28b}$$

Figure 1-5 shows a schematic diagram of a plasma sheath. As indicated in the figure, the plasma sheath is a region of positive *space charge*, almost devoid of negative charges. The *thickness of the plasma sheath*, d_s, is defined as the thickness of the region where the electron density is negligible and where the potential drop V_s occurs. As previously explained, the thickness of the plasma sheath is related to the Debye length. It also depends on the collisional mean free path in the plasma and is affected by external biases applied to the surface.

At higher pressures, when the collisional mean free path is of the same order of magnitude as the thickness of the plasma sheath, the latter can be estimated from [10]

$$d_s \approx \eta^{2/3} \times \lambda_D \tag{1.29a}$$

with

$$\eta = \frac{e(V_p - V_B)}{kT_e} \tag{1.29b}$$

where d_s = thickness of plasma sheath
V_B = the bias on the considered surface (self- or external bias)
V_p = the plasma potential, which will be defined in Sec. 5.2

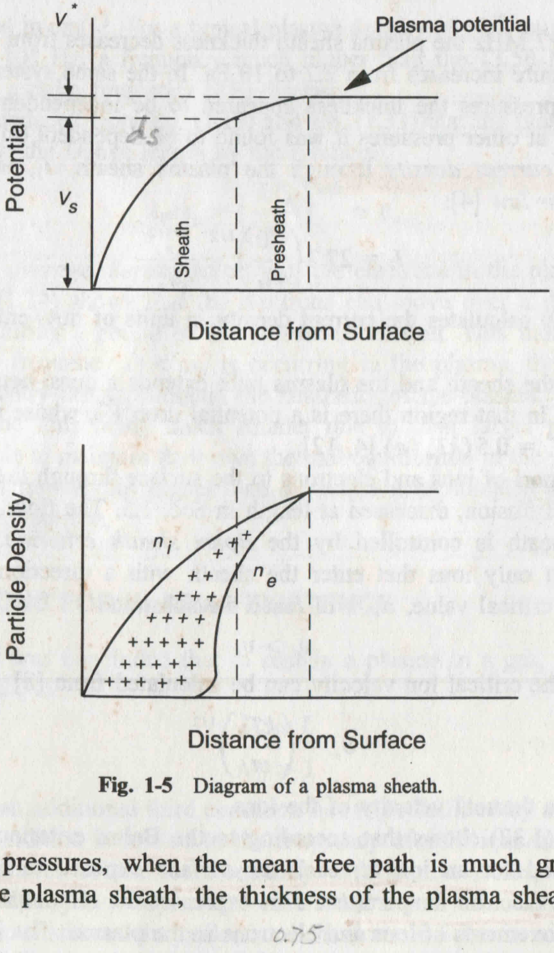


Fig. 1-5 Diagram of a plasma sheath.

At lower pressures, when the mean free path is much greater than the thickness of the plasma sheath, the thickness of the plasma sheath can be calculated from

0.75

$$d_s \approx 1.1\,\eta^{3/4} \times \lambda_D \tag{1.29c}$$

If the surface bias is small, of the order of magnitude of T_e, the sheath will only be a few Debye lengths thick. At pressures below ~ 0.05 torr the self-bias can reach values of tens to hundreds of volts, and the sheath thickness increases. If a bias of -100 V is applied to a surface in contact with an argon plasma in which $T_e \approx 1$ eV, the plasma sheath thickness is about $32\,\lambda_D$ [10].

It was experimentally found that the thickness of the plasma sheath is affected by more parameters than these figuring in Eq. 1.29. The relation between the thickness of the plasma sheath and those additional parameters is not clearly understood.

The thickness of the plasma sheath was found to be also dependent on the frequency of the electromagnetic field and the pressure in the system. For example, it was found in a certain system [11] that at 7 MHz, the plasma sheath thickness decreases from 12 mm to 7 mm when the pressure increases from 4 to

20 Pa, but at 27 MHz the plasma sheath thickness decreases from 6 mm to 4 mm when the pressure increases from 2.2 to 10 Pa. In the same system it was found that at some pressures the thickness appeared to be independent of the sheath voltage, while at other pressures it was found to be dependent on it [11].

The *ion current density* through the plasma sheath, J_i, is given by the *Child-Langmuir law* [4]:

$$J_i = 27.3\left(\frac{40}{m_i}\right)^{1/2} \frac{V_s^{3/2}}{d_s^2} \tag{1.30}$$

Equation (1.30) calculates the current density in units of $\mathrm{mA/cm^2}$ for V_s in kV and d_s in mm.

Between the sheath and the plasma bulk extends a quasi-neutral region called *presheath*. In that region there is a potential drop V^*, whose magnitude is of the order of $V^* = 0.5\,(kT_e/e)$ [4, 12].

The transport of ions and electrons to the surface through the sheath is done by ambipolar diffusion, discussed at length in Sec. 1.5. The flow of ions through the plasma sheath is controlled by the *Bohm sheath criterion*. This criterion establishes that only ions that enter the sheath with a directional velocity, v_i, greater than a critical value, v_c, will reach the substrate:

$$v_i > v_c \tag{1.31}$$

The value of the critical ion velocity can be calculated from [8]

$$v_c = \left(\frac{kT_e}{m_i}\right)^{1/2} \tag{1.32}$$

where v_c is the thermal velocity of the ions.

Equation (1.32) shows that according to the Bohm criterion, the minimum velocity required for an ion to reach the surface exposed to the plasma is a function of the electron temperature. This expresses the relationship which exists between the movements of ions and electrons in the plasma. The ions achieve the velocity v_i required by the the Bohm criterion by acceleration in the quasineutral presheath region.

If the conditions of the plasma are such that collisional mean free path, λ, is much larger than the Debye length ($\lambda \gg \lambda_D$), the plasma has a *collision-free sheath*.

1.3.5 Plasma Frequency

Although the plasma bulk is quasi-neutral, local perturbations from neutrality can occur in volumes smaller than the Debye sphere. Due to their low mass, the electrons will respond faster than the ions to the electric forces generated by the perturbation from neutrality. The response to the perturbation will be through oscillations. The frequency of these electron oscillations is called the *plasma*, or *Langmuir frequency*, ω_p, and is given by the relation [8]

$$\omega_p = \left(\frac{n_e e^2}{m_e \varepsilon_o}\right)^{1/2} = 18{,}000\ \pi n_e^{1/2}\ \mathrm{Hz} \tag{1.33}$$

for n_e expressed in cm^{-3}. For a typical plasma density of 10^{10} cm^{-3}, the plasma frequency is 9.10^8 Hz, a frequency much higher than the 13.56 MHz generally used to sustain a radio frequency (RF) discharge.

It can be deduced from Eq. (1.19) and Eq. (1.33) that the plasma frequency, ω_p, is related to the Debye length by the relation

$$\lambda_D \omega_p = \left(\frac{kT_e}{m_e}\right)^{1/2} \approx \bar{v}_e \tag{1.34}$$

Here, $\bar{v}_e$ is the *average thermal velocity* of the electrons in the plasma.

Equation (1.34) shows that the electrons can move over a distance of one Debye length during a period of the plasma oscillation. This indicates that if a perturbation of frequency $\omega < \omega_p$ is occurring in the plasma, the electrons can respond sufficiently fast to maintain the neutrality of the plasma. The oscillation frequency of the ions being much smaller due to their larger mass, only the electrons are able to maintain their own thermal equilibrium in the plasma. Plasma perturbations of frequencies higher than ω_p will not be shielded out through the response of the electrons.

1.4 CONDITIONS FOR PLASMA EXISTENCE

In Sec. 1.3.3 it was concluded that to sustain a plasma in a gas, two conditions have to be met:

$$\lambda_D \ll L \tag{1.35}$$

$$N_D \gg 1 \tag{1.36}$$

However, an additional third condition has to be fulfilled by a gas to become plasma. This condition is related to the frequency of collisions in the plasma. If the charged particles collide too frequently with neutral atoms, their motion is controlled by ordinary hydrodynamic forces rather than by electromagnetic forces. Under these circumstances the collective behavior condition is not satisfied, and the gas is not behaving as a plasma. If τ is the mean time between collisions of charged particles with neutral atoms, the product $\omega\tau$ has to be bigger than 1 for the gas to behave like a plasma rather than a neutral gas.

The three conditions that have to be satisfied by a plasma are therefore given by Eq. (1.35), Eq. (1.36), and Eq. (1.37):

$$\omega\tau > 1 \tag{1.37}$$

1.5 DIFFUSION OF CHARGED PARTICLES IN PLASMA

It was so far implicitly assumed that the plasmas are homogeneous. However, any plasma has a density gradient and has to be considered as having a nonuniform distribution of ions and electrons in a dense background of neutrals. Because of the concentration gradients, the plasma particles will tend to move by diffusion toward regions of lower density. As the plasma spreads out as a result of concentration gradient and electric field forces, the individual charged particles diffuse by undergoing a random walk and collide frequently with the neutral atoms. The electrical conductivity of the plasma caused by the movement of the charged particles is therefore controlled by the diffusion of the charged particles through it.

1. At very low charge concentrations, like those existing near the breakdown in a direct current glow discharge (described in Sec. 2.1), where the Debye length is of the same order of magnitude as the diffusion distance or system dimension, L, the electrons and ions will diffuse independently, and their flux will be controlled by their individual *diffusivities*, D_e and D_i, respectively. However, this is
2. no longer true when the density of the charged particles increases above $n_e \approx n_i \geq 10^8\ \text{cm}^{-3}$ and the Debye length becomes much smaller than the dimensions of the system.

The *diffusion*, or *drift velocity*, v, of charged particles in an electric field is proportional to the field strength, E, and the proportionality factor is called the *mobility*, μ, of the particles:

3

$$\mu = \frac{v}{E} \tag{1.38}$$

The mobility of a charged particle is its drift velocity in an electric field of unity. Because of the much smaller mass of the electrons as compared to that of the ions, their mobility is much higher than the mobility of the ions in the plasma.
4 The mobilities, μ, of the charged particles are correlated to their diffusion coefficients, D, by the Einstein equation

$$\mu = \frac{|q|D}{kT} \tag{1.39}$$

where q = the electric charge of the considered particles.

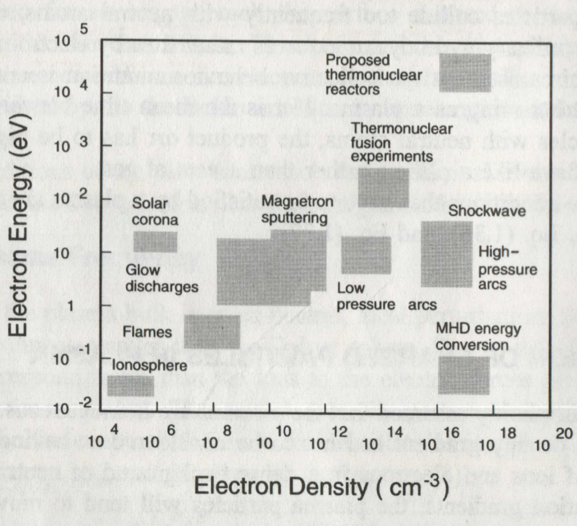


Fig. 1-6 Plasma types by electron density and temperature.

Due to the proportionality between the mobility and diffusion coefficient, as indicated by Eq. (1.39), the diffusion coefficient of the electrons is much higher than that of the ions. As a result, the electrons tend to diffuse toward regions of lower concentration much faster than the ions. This faster diffusion causes the formation of a space charge, which according to the Debye shielding effect (Sec. 1.3.3.) has to be contained over distances smaller than λ_D. A corresponding *space charge field*, E_{sc}, is formed.

The motion of the electrons is restrained by the space charge field, created by their tendency for faster diffusion. At the same time, the field that restrains the electrons causes the ions to diffuse faster than they would otherwise in the absence of the electrons. Consequently, both species of charged particles diffuse with the same velocity. Because it is also assumed that $n_e = n_i = n$, the *flux of the electrons*, Γ_e, is equal to the *flux of the ions*, Γ_i:

$$\Gamma_e = \Gamma_i = \Gamma \tag{1.40}$$

The described behavior is called *ambipolar diffusion* [13] because particles of opposite electric charges diffuse together due to their interaction.

The flux of charged particles is composed of two terms:

1. Flux associated with the motion induced by diffusion, caused by concentration gradients, ∇n; this term, $-D\nabla n$, is not affected by the electric charge of the particles.
2. Flux associated with the drift of the charged particles under the influence of the electric field; the sign of this term, $(\pm)n\mu E_{sc}$, depends on the charge of the particles.

The fluxes of the diffusing particles will therefore be given for electrons and ions, respectively, by

$$\Gamma_e = -D_e \nabla n_e - n_e \mu_e E_{sc} \tag{1.41}$$

$$\Gamma_i = -D_i \nabla n_i + n_i \mu_i E_{sc} \tag{1.42}$$

Assuming $n_e = n_i = n$ and $\Delta n_e = \Delta n_i = \Delta n$, Eq. (1.41) and Eq. (1.42) can be solved to give the value of the space charge field and the particle flux:

$$E_{sc} = -\left(\frac{D_e - D_i}{\mu_e + \mu_i}\right)\frac{\nabla n}{n} \tag{1.43}$$

$$\Gamma = -\left(\frac{D_i \mu_e + D_e \mu_i}{\mu_e + \mu_i}\right)\nabla n = -D_a \nabla n \tag{1.44}$$

The diffusion of the charged particle in the plasma is therefore not controlled by the individual diffusion coefficients of the electrons and ions but by the *ambipolar diffusion coefficient*, D_a:

$$D_a = \frac{D_e \mu_i + D_i \mu_e}{\mu_e + \mu_i} \tag{1.45}$$

As said before, the coefficient D_a reflects the interaction between plasma species of opposite electric charges.

Because $\mu_e \gg \mu_i$, Eq. (1.45) for the coefficient of ambipolar diffusion can be changed to

$$D_a = D_i\left(1 + \frac{D_e\mu_i}{D_i\mu_e}\right) \tag{1.46}$$

and using Eq. (1.39),

$$D_a = D_i\left(1 + \frac{T_e}{T_i}\right) \tag{1.47}$$

1.6 PLASMA TYPES

The plasma state exists in natural form in the cosmos or is created under unique conditions for specific purposes. The plasmas found in nature cover a very large range of electron densities and temperatures. As shown in Fig. 1-6, the plasma density, n_e, spans the range between 1 and 10^{20} cm^{-3}, while the electron temperature, T_e, can vary between 10^{-2} and 10^5 eV.

Solar winds are a continuous stream of charged particles with $n_e = 5$ cm^{-3} and $T_e = 50$ eV. The interstellar material contains a hydrogen plasma with a density of 1 cm^{-3}. The ionosphere, which extends approximately from 50 km upward from the earth's surface, is populated by a weak plasma with a density varying up to 10^6 cm^{-3} and an electron temperature of 0.1 eV, while the sun and stars have surface temperatures ranging from 5000 to more than 70,000 °K (0.5 to 7 eV). They consist entirely of plasma, the outer layer being partially ionized and the interior hot enough to be completely ionized. The temperature at the center of the sun is at about 2 keV.

In the quest for controlled thermonuclear fusion, it is necessary to create plasmas with electron temperatures above 10 keV and with ion densities of $(1-2) \times 10^{14}$ cm^{-3}. These values are required in order to obtain the nuclear fusion reaction between deuterium and tritium atoms, because reasonable cross-sections for the fusion reactions are obtained only for energies above 5 KeV. Central ions temperature of $T_i \approx 35$ KeV and electron temperature of $T_e = 15$ KeV have been reached in Tokomak fusion reactors [14].

Taking into account the wide ranges of parameters, the plasmas are classified into several categories:

- Plasmas in *complete thermodynamic equilibrium – CTE plasmas*. In a CTE plasma all temperatures discussed previously in Sec. 1.3.2 are equal. CTE plasmas exist only in stars or during the short interval of a strong explosion. They have no practical importance because they do not exist in controlled laboratory conditions.
- Plasmas in *local thermodynamic equilibrium – LTE plasmas*. These are plasmas in which all temperatures, except the radiation temperature, T_r, are

equal in each small volume of the plasma. The LTE plasmas are discussed in Sec. 1.6.1.

- Plasmas that are not in any *local thermodynamic equilibrium – non-LTE plasmas*. These plasmas, also named *cold plasmas*, are the subject of discussion in the following chapters.

The plasmas produced for research or manufacturing purposes are either LTE or non-LTE type plasmas, designated in daily use, respectively, as thermal and cold plasmas.

1.6.1 Thermal Plasmas

LTE plasmas can exist under two circumstances:

- When the heavy particles are very energetic, at temperatures of the order of 10^6–10^8 °K (10^2–10^4 eV)
- When the pressure is atmospheric, even at temperatures as low as 6000 °K

An increase of pressure in the plasma causes an increase in the number of collisions between the electrons and the heavy species. As a result, when the pressure in the system increases toward atmospheric pressure, the two systems tend to reach the same thermodynamic equilibrium, as shown in Fig. 1-4. For example, in electric arcs, or in plasma jets operating at pressures of about 1 atm, the temperature of the electrons is approximately equal to that of the gas, $T_e = T_g$. The temperature of the gas in the center of these plasmas can reach values of 20,000 to 30,000 °K. The high-intensity arc of plasma jets in inert gas atmosphere is used as a heating torch that is capable of delivering considerably higher temperatures and rates of heat transfer as compared to conventional torches.

Such LTE-plasmas at atmospheric pressure are called *thermal plasmas*. Their production and properties make them appropriate for deposition of coatings by plasma spraying processes and in extractive metallurgy, for reduction, or for smelting of ores.

The plasmas produced to create controlled thermonuclear fusion are LTE plasmas with very energetic heavy particles. The high energies can be obtained at low pressures of 10^{-8}–10^{-3} torr, and the main problem in heating these plasmas is to prevent the interaction of the energetic particles with the walls of the reactor. The interaction with the walls causes both loss of energy from the plasma and its contamination with particles sputtered from the walls of the plasma container. Continuous heating of the plasmas to the required temperatures of above 10 KeV (above 10^8 °K) and the confinement from interactions with the containing vessel are problems yet to be solved.

1.6.2 Cold Plasmas

As mentioned before, in low-pressure discharges, thermodynamic equilibrium is not reached, even at a local scale, between the electrons and the heavy particles, and these plasmas are of the non-LTE type. In the non-LTE plasmas the temperature of the electrons is much higher than that of the heavy particles and $T_e \gg T_i > T_g > T_{ex}$. The electrons can reach temperatures of 10^4–10^5 °K (1–10 eV), while the temperature of the gas, T_g, can be as low as room temperature. Therefore, such plasmas are called *cold plasmas*.

The cold plasmas have been developed specifically and purposefully based on their nonequilibrium properties and their capability to cause physical and chemical reactions with the gas at relatively low temperatures. Applications of cold plasmas are widespread and put to use in a variety of fields, from microelectronic fabrication to surface hardening of metals. In the following chapters we will concentrate on and examine in depth only the cold plasmas.

1.7 QUESTIONS

1. The value of the constant in Eq. (1.6) is $ct = 18.0 \times 10^{-3}$ cm.mbar for helium and $ct = 6.5 \times 10^{-3}$ cm.mbar for oxygen. Plot the mean free path versus pressure for both gases in the pressure range 10^{-5}–10 torr.
2. Plot the collision frequencies for the same conditions as in question 1, assuming that the gases are at room temperature.
3. The electron temperature in an argon plasma is 20,000 °K. Plot the energy distribution of the electrons assuming that it is a Druyvesteyn distribution.
4. a. Calculate the average energy of the electrons for the conditions stated in question 3.
   b. Calculate the fraction of electrons having energies higher than twice the average energy at those conditions.
   c. How will the values calculated in (a) and (b) change in an oxygen plasma at identical conditions?
5. a. Calculate the Debye length in a helium plasma having a density of 5.10^9 cm^{-3} and an average electron energy of 4 eV.
   b. How will the Debye length change if the plasma density increases to 10^{11} cm^{-3} and the electron temperature remains the same?
   c. What is the number of particles in a Debye sphere in each of the previous cases?
6. a. Calculate the sheath potential at a planar surface in contact with an argon plasma sustained at a pressure of 1 torr and having an electron temperature of 1 eV.
   b. What is the thickness of the plasma sheath if the plasma potential is 20 V?
   c. Calculate the thickness of the plasma sheath in a plasma sustained at 10^{-4} torr, assuming the same electron temperature and plasma potential as before.
7. What are the ion current densities in argon plasmas sustained at the conditions corresponding to questions 6 (b) and (c)?

8. What is the lowest density of a plasma that could be sustained in a reactor whose smallest dimension is 5 cm, at an electron temperature of 1 eV? How would that density change for an electron temperature of 10 eV?
9. In terms of thermodynamic equilibrium, what type of plasma exists
   a. inside the sun?
   b. in a controlled nuclear fusion device?
   c. in a low-pressure plasma for processing of solids?

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