

Part I
Introduction to Plasma Technology for Surface Functionalization

1 Introduction to Plasma and Plasma Technology

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1.1 Plasma: the Fourth State of Matter

The term *plasma* was first used by Lewi Tonks and Irving Langmuir in 1929 [1] to describe a collection of charged particles in their studies of oscillations in the inner region of an electrical discharge. Later, the definition was broadened to define a state of matter ('the fourth state of matter') in which a significant number of atom and/or molecules are electrically charged or ionized with the fundamental characteristic of exhibiting a collective behavior due to the long-range Coulomb interactions.

A rough but comprehensive definition of plasma is that of an ensemble of charged, excited, and neutral species, including some or all of the following: electrons, positive and negative ions, atoms, molecules, radicals, and photons. On average a plasma is electrically neutral, because any charge unbalance would result in electric fields that would tend to move the charges in such way as to neutralize charges of opposite sign.

It is estimated that more than 99.9% of the apparent universe is in the plasma state: gaseous nebulae, interstellar gas [2], stars, including our sun [3–5], have extremely high surface temperatures (from 2000 to 22 000 K) and they consist entirely of plasma. Our planet is not an exception to the presence of the plasma state. The earth's atmosphere (in the altitude range between 90 and 500 km, the thermosphere), is continuously bombarded by intense cosmic rays and solar wind radiation and as a consequence its components become electrically charged species leading to the formation of an atmospheric shell, called the '*ionosphere*' [6–9]. The solar UV radiation is almost completely absorbed by the ionosphere, producing the electrically charged particles (especially electrons) which are deflected and funneled by the magnetic field of the earth to the poles, which results in the northern hemisphere in the formation of spectacular 'northern lights' known as *Aurora Borealis* [10]. Lightning developed during thunderstorms is a natural plasma state as well. It is estimated that about 100 cloud–ground and cloud–cloud lightning strikes happen every second over the whole earth. Lightning is an intense transient electric discharge of extremely long path-length (often many kilometers).

Even though the mechanism of electric field development in clouds is incompletely understood, it is suggested that this phenomenon is associated with the freezing of water. It was found that in the absence of ice the field build-up is slow and lightning is rare. Colliding ice particles are believed to generate electric-field growth and their separation under gravity probably contributes to the development of charge transfer. The plasma state can be produced in laboratories and by raising the energy content of matter regardless of the nature of the energy source. Thus plasmas can be generated by mechanical (close to adiabatic compression), thermal (electrically heated furnaces), chemical (exothermic reactions), radiant (high energy electromagnetic and particle radiations, e.g., electron beams) and electromagnetic (arcs, coronas, direct current (DC), and radio frequency (RF), microwave (MW), electron cyclotron resonance (ECR) discharges) energies, and by the combination of them, as in an explosion, in which mechanical and thermal energies are present.

1.2

Historical Highlights

In the mid-nineteenth century the Czech medical scientist, Johannes Purkinje (1787–1869) used the Greek word plasma (which means ‘moldable substance’ or ‘jelly’) to denote the clear fluid which remains after removal of all the corpuscular material in blood.

Half a century later, in 1927, the Nobel prize winning American chemist Irving Langmuir first used this term to describe an ionized gas. Langmuir was reminded of the way blood plasma carries red and white corpuscles by the way an electrified fluid carries electrons and ions.

Langmuir, along with his colleague Lewi Tonks, was investigating the physics and chemistry of tungsten-filament lightbulbs, with a view to finding a way to greatly extend the lifetime of the filament. In the process, he developed the theory of plasma sheaths, the boundary layers which form between ionized plasmas and solid surfaces. He also discovered that certain regions of a plasma discharge tube exhibit periodic variations of the electron density, which we nowadays term *Langmuir waves*. In the 1920s and 1930s a few isolated researchers began the study of what is now called *plasma physics*. In the 1940s Hannes Alfvén developed a theory of hydromagnetic waves (now called *Alfvén waves*) and proposed that these waves would be important in astrophysical plasmas.

The creation of the hydrogen bomb generated a great deal of interest in controlled thermonuclear fusion as a possible power source for the future, since 1952. At first, this research was carried out secretly, and independently, by the United States, the Soviet Union, and Great Britain. But the ‘International conference on the peaceful uses of atomic energy’, held in Geneva in 1955 [11, 12], ratified the beginning of the studies on peaceful use of nuclear fusion. The constitution of the International Atomic Energy Agency (IAEA) was almost contemporaneous (1957). Nowadays the agency works with its member states and multiple partners worldwide to promote safe, secure, and peaceful nuclear technologies.

Fusion progress was slow through most of the 1960s, but by the end of that decade the empirically developed Russian tokamak configuration began producing plasmas with parameters far better than the lackluster results of the previous two decades. By the 1970s and 1980s many tokamaks with progressively improved performance were constructed and at the end of the twentieth century fusion break-even had nearly been achieved in tokamaks [13].

In the 1970s a new application of plasma physics appeared, and has developed as critical technique for the fabrication of the tiny, complex integrated circuits used in modern microelectronic devices. This application is now of great economic importance for industry, indeed plasma processing has been an enabling technology for the broader applications of microelectronics which has led to the actual information and communication society with radical changes in worldwide living habits.

Plasma processing is a technology used in a large number of industries, and whilst semiconductor device fabrication for computers is perhaps the best known, it is equally important in other sectors such as automotive, textile, food packaging, biomedical, polymers, and solar energy. A common theme in the applications is plasma treatment of surfaces. Plasma is an environmentally friendly process technology, producing an extremely low level of industrial by-products, especially when compared to more traditional wet chemical treatments.

The principal applications of plasma treatments concern the processes that induce a limited and selected transformation of the outermost surface layer (nanometric scale).

Many fundamental processes take place during surface treatment of a material: the surface undergoes bombardment by fast electrons, ions, and free radicals, combined with the continued electromagnetic radiation emission in the UV-Vis spectrum enhancing chemical-physical reactions in order to obtain the desired functional and aspect properties.

Many properties and functionalities can be obtained by plasma treatment, and they depend on the application: the plasma can be used to change the surface wettability which can be changed from hydrophilic to hydrophobic and vice versa, to enhance the barrier characteristics, adhesion, dye-ability, printability, or the oleophobicity.

For example, plasma treatment of textile fabrics and yarns (see Chapter 6) is investigated as an alternative to wet chemical fabric treatment and pre-treatment processes, for example, shrink resistance, water repellent finishing, or improvement of dye-ability, which tend to alter the mechanical properties of the fabric and are environmentally hazardous [14, 15].

In the food sector the application of plasma processing is interesting for many purposes, in particular to provide barrier effects on homopolymeric packaging for their recyclability (see Chapter 8) or on biodegradable films (polylactic or starch based compounds) to attain an extended shelf life by product preservation [16]. Food processing also requires surfaces with enhanced functionalities in terms of wear resistance, chemical inertness, controlled surface energy for adhesion control, and barriers against migration of heavy metals; whose properties are efficiently

achieved by deposition of coatings via plasma processing (see Chapter 9) or by surface plasma treatment.

In the biomedical sector plasma technology is used for cold sterilization [17] of instruments and prostheses as well as many thermolabile materials used in the biomedical technology sector for its particular advantages, including its moderate or negligible impact on substrate materials and use on nontoxic compounds). Low pressure plasma (LPP) processing is also being investigated for the production of non-fouling surfaces to prevent the formation of biofilms with promising results (as detailed in Chapter 7)

1.3

Plasma Fundamentals

Plasma is sometimes considered as the fourth state of matter, an expression that was first coined by Crooks in 1879 to describe the ionized medium created in a gas discharge. Though this attribute can be somehow misleading, it highlights the unique feature of the plasma phase. The concept of the fourth state of matter results from the idea that phase transitions occur by progressively providing energy to the matter, such as the one from the solid state to liquid up to the gas state.

A further 'phase transition' may be thought of as the one from the gas state to the plasma state, even if this state is reached gradually by providing more and more energy to the system. Therefore this process cannot be rigorously defined as a 'phase transition', because it lacks the signature of all real phase transitions: that is, an abrupt change (discontinuity) in the order parameter defining the thermodynamic phase.

Plasma can be seen as a particular ionized gas, which retains some unique features which distinguish it from an (ideal) gas. One of the main differences is that plasma particles do interact, because of the electromagnetic coupling between charged particles and electric and magnetic collective perturbations which constitute the plasma itself.

Another important difference from an ideal gas is found in nonthermal plasmas (NTPs) in which quite different temperatures are associated with different species, due to the out-of-equilibrium thermodynamic regime. Indeed, in cold plasmas, neutrals and ions may be at ambient temperature whereas electrons may reach temperatures close to 10^5 K. These plasma systems are of particular interest for molecular processing and surface treatment, because cold plasmas often produce 'activated' states of matter, capable of enhancing plasma–surface chemical reactions and physical processing which cannot be achieved under thermodynamic equilibrium conditions. Therefore molecular and surface micro/nano-structures can be fabricated by plasma processing in a way which is different from any other available method.

In the following sections we do not claim to provide a rigorous derivation of plasma fundamentals, which is available in several reference textbooks [18–21]; we rather aim at providing a comprehensive overview of the basic concepts and to offer

some helpful tools to better understand the plasma state and the different plasma regimes determining the processing conditions for surface functionalization.

1.3.1

Free Ideal Gas

An ideal gas is an ensemble of non-interacting rigid and negligible-size particles, each one undergoing frequent elastic scattering with other particles and with the physical boundaries of the system. Real gases (containing many particles) may be described in good approximation as ideal gases if they have a low density. Due to frequent (elastic) collisions the ideal gases obey the Maxwell–Boltzmann velocity distribution statistics, that is, the particles' velocities (or energies) are distributed according to the statistical curve depicted in Figure 1.1, which is named after the two physicists Maxwell and Boltzmann.

For ideal gases the kinetic theory of gases provides a very good theoretical description of microscopic and macroscopic physical state variables fully describing the gas behavior. The kinetic theory of gases must be modified if there are strong interactions or, more in general, where the conditions for an ideal gas no longer hold. For completeness sake we must say that strong interactions are indeed not the only cause for a non-ideal gas regime. Quantum correlation responsible for gas degeneracy can be another sufficient reason to give up the kinetic theory of gases. Anyway it is useful to recall the basis of the kinetic theory of gases in order to have a starting point from which we can move toward a satisfactory description of plasma physics.

If we think of the gas as an ensemble of N particles in a cubic box with volume V and edge length l , a single particle moving along a box direction, say x , will undergo scattering by another particle or the box (perpendicular) surface. If the particle collides onto the surface, its momentum change will be: $\Delta p_x = 2mv_x$, where m

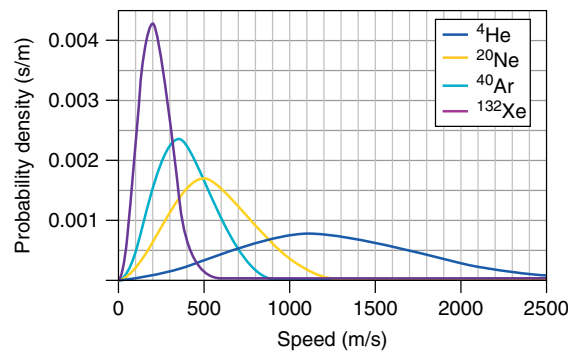


Figure 1.1 Maxwell–Boltzmann velocity distribution of some noble gases for a given system temperature (298.15 K). The x axis represents the velocity and the y axis reports the relative particles probability density, that is, the fraction of particles per infinitesimal speed interval.

is the particle mass and v_x its velocity. The force exerted by the particle will be then: $F_x = \Delta p_x / \Delta t$. By considering the motion of the particle along the whole box edge, we can consider the time during which momentum is changed as $\Delta t = l / v_x$. The force exerted by the i -th particle then results in: $F_i = 2mv_x^2 / l$. By summing up over all the particles (assumed to have the same mass) hitting the surface we may estimate the overall force exerted on the surface, and remembering that pressure is $p = F/A$, we get (Equation 1.1):

$$F_{tot} = \sum_{i=1}^N F_i = \sum_{i=1}^N \frac{2mv_i^2}{l}; \quad p_{tot} = \sum_{i=1}^N p_i = \sum_{i=1}^N \frac{2mv_i^2}{l^3} = \sum_{i=1}^N \frac{2mv_i^2}{V} \quad (1.1)$$

In order to evaluate the overall pressure on each face we can consider the velocity components along the three axes and assume that the particles' velocities are equally distributed on average along each direction (Pascal principle). The total pressure on the six faces of the box is then defined as:

$$p = N \frac{2m \langle v^2 \rangle}{6V} = N \frac{m \langle v^2 \rangle}{3V}, \quad \text{with } \langle v^2 \rangle = \frac{1}{N} \sum_{i=1}^N v_i^2 \quad (1.2)$$

or the average square velocity along one axis. By comparison of Equation (1.2), known as the *Joule–Clausius formula*, derived by microscopic considerations with the ideal gas law $pV = Nk_B T$, ($k_B \approx 1,381 \cdot 10^{-23} \text{ J/K}$) valid for macroscopic system quantities, it is possible to connect macroscopic physical variables with microscopic ones. In particular the temperature reads $T = m \langle v^2 \rangle / (3 k_B)$, and the total kinetic energy of the system is $\varepsilon_{tot} = 1/2 Nm \langle v^2 \rangle = 3/2 Nk_B T$, whence we obtain the (average) single particle kinetic energy $\varepsilon = 3/2 k_B T$ (m being the particle mass, k_B the Boltzman constant, and N the number of particles).

1.3.2

Interacting Gas

When considering a plasma – even if it is only partially ionized – it is necessary to take into account long-range particle interactions in the ensemble. Indeed, electrically charged particles feel electric Coulomb forces whose range is long compared with the characteristic scale length of the plasma. When charged species are in motion they generate electric currents inducing internal magnetic and electric fields which, in turn, interact with external fields. This dramatically complicates the modeling of such a system, which is self-consistent through a strong coupling between its dynamics and the electromagnetic configuration. Although intrinsically complex, this coupling allows one to control to some extent the dynamics of an ensemble of charged particles by biasing its collective behavior with external electromagnetic fields. A typical example of such plasma controlling by electromagnetic fields is its spatial confinement, which turns out to be very useful for technological applications and particularly for fusion.

Whereas an ideal gas (see Section 1.3.1) expands indefinitely in free space, a plasma can be temporarily confined in a small spatial region by applying suitable

electromagnetic fields. In order to describe the plasma while taking into account the particle interactions a new theoretical framework is needed.

Electromagnetic interactions are described by the Maxwell equations. Relevant fields entering the equations are \mathbf{E} and \mathbf{B} , the electric and magnetic field in vacuum, respectively.

Here, vacuum does not mean that the equations hold only for the low pressure regime, but that the relevant fields are outside the medium, that is, the particle ensemble. We do not need to describe fields inside the matter, because we are only interested in gas dynamics. In order to properly describe the dynamics of a population of many particles we need a statistical approach. The statistical information can be encoded in the distribution function $f(\mathbf{v}, \mathbf{r}, t)$ describing the population time evolution in phase space. It depends on velocity (\mathbf{v} , or momentum $\mathbf{p} = m\mathbf{v}$), position (\mathbf{r}), and time (t), and gives the statistical probability of the particles' velocity (momentum) and position at each time step. In other words, the distribution function contains the information on how many particles have momentum \mathbf{p} and position \mathbf{r} . For short range particle interactions the Boltzmann equation provides a good model for plasma dynamics, describing the time evolution of the distribution function of a particle population subject to external forces:

$$\frac{\partial f_\alpha}{\partial t} + \mathbf{v} \cdot \frac{\partial f_\alpha}{\partial \mathbf{r}} + \frac{\partial f_\alpha}{\partial \mathbf{v}} \cdot \frac{\mathbf{F}}{m} = \left. \frac{\partial f_\alpha}{\partial t} \right|_{coll} \quad (1.3)$$

In Equation 1.3 quantities in bold character are regarded as vectors (or space differential operators) and the subscript α refers to the different species to which the equation can apply, for example, electrons or ions. The first term is the free evolution term, the second one represents the diffusion term from regions of higher density to lower density regions, the third one represents the drift term (from higher to lower density regions in reciprocal space). The right hand side (RHS) of the equation is the term taking into account the collisions between particles. In a plasma the relevant force \mathbf{F} is represented by the Lorentz force (Equation 1.4):

$$\mathbf{F} = q_\alpha \cdot (\mathbf{E} + \mathbf{v} \times \mathbf{B}) \quad (1.4)$$

with q_α the electrical charge of particle type α . Different from the kinetic theory of ideal gases, the collisional term includes both elastic and inelastic scattering. Another important difference from the kinetic theory is that the Boltzmann equation holds also in the nonequilibrium regime. The Boltzmann equation is easily derived from the Liouville theorem ($\mathbf{D}f/\mathbf{D}t = 0$) as a consequence of matter and energy conservation, once the distribution function f is well defined.

Despite its intrinsic complexity due to the collective behavior of particles in plasma systems, some approximations of this collisional term have been proposed, leading to different forms of the Boltzmann transport equation which are valid in specific plasma regimes.

For example, for fully ionized plasmas (e.g., in thermal plasmas), the suitable collision term leads to the Fokker–Planck equation based on the fundamental assumption that long range Coulomb interactions produce large angle deflections

of particle trajectories due to the rapid succession of multiple collisions with distant particles. In the Fokker–Planck model the collision operator reads:

$$\left. \frac{\partial f}{\partial t} \right|_{coll} = \sum_i \frac{\partial}{\partial v_i} \left\langle \frac{\Delta v_i}{\Delta t} \right\rangle f(\mathbf{v}, t) + \frac{1}{2} \sum_{ij} \frac{\partial^2}{\partial v_i \partial v_j} \left[\left\langle \frac{\Delta v_i \Delta v_j}{\Delta t} \right\rangle f(\mathbf{v}, t) \right] \quad (1.5)$$

In Equation 1.5 the $\langle \rangle$ symbols denote the average change in velocity moments of the distribution function per time unit and the indexes i and j refer to the space coordinates. This form of the collisional term takes into account nonequilibrium thermodynamic behavior at first expansion order. The first term on the RHS takes into account acceleration or slowing down of a group of particles (for instance due to effects similar to friction). The second term on the RHS accounts for diffusion effects due to spreading of the distribution function.

For partially or weakly ionized plasmas, which are of greater interest for industrial plasma processing, short range interaction of ionized plasma particles with the neutral background dominates the other mechanisms such as diffusion and conductivity and a suitable formal representation of the two-body collisional operator is provided by Equation 1.6:

$$\left. \frac{\partial f_\alpha}{\partial t} \right|_{coll} = \sum_\gamma n_\gamma \int d\mathbf{V} \int d\Omega \frac{d\sigma}{d\Omega} |\mathbf{v} - \mathbf{v}_1| [f_\alpha(\mathbf{r}, \mathbf{v}', t) f_\gamma(\mathbf{r}, \mathbf{v}'_1, t) - f_\alpha(\mathbf{r}, \mathbf{v}, t) f_\gamma(\mathbf{r}, \mathbf{v}_1, t)] \quad (1.6)$$

where primed velocities refer to velocities of scattered particles and \mathbf{v}, \mathbf{v}_1 represent velocities of two particles approaching each other before scattering. $d\Omega$ is the solid angle element in velocity space, α and γ refer to the incident and target particle species and σ is the scattering cross-section, which quantifies the particles collision probability. However, the Boltzmann equation with the above collision operator is practically intractable for its intrinsic complexity and nonlinearity. For weakly ionized plasmas simplifying assumptions, which yield more tractable equations are possible, provided that we consider the time evolution of the distribution function as mainly determined by:

- average fields of charged particles included in a self consistent form;
- applied external electromagnetic fields, included in the Lorentz force (see Equation 1.4);
- collisions dominated by charged species with the neutral background.

The last condition assumes, contrary to the Fokker–Planck theory, that the collision duration is much shorter than the time lap in-between two collisions. Along with the previous assumptions the Boltzmann transport equation may be further simplified by using a mean-free-transit time (τ). This τ is the average time between collisions and is independent on the particle velocity. Hence, the collision integral reduces to Equation (1.7):

$$\left. \frac{\partial f}{\partial t} \right|_{coll} = \frac{f_o - f(\mathbf{r}, \mathbf{v}, t)}{\tau(|\vec{v}|)} \approx \frac{f_o - f(\mathbf{r}, \mathbf{v}, t)}{\tau} \quad (1.7)$$

The modified Boltzmann equation (sometimes referred to as the *Krook model*), becomes

$$\frac{\partial f_\alpha}{\partial t} + \mathbf{v} \cdot \frac{\partial f_\alpha}{\partial \mathbf{r}} + \frac{q_\alpha}{m} (\mathbf{E} + \mathbf{v} \times \mathbf{B}) \cdot \frac{\partial f_\alpha}{\partial \mathbf{v}} = -\frac{f_\alpha(r, v, t)}{\tau_\alpha} \quad (1.8)$$

Equation 1.8 accounts for the distribution function f_α evolution of the α -species (e.g., electrons, positive and negative ions) toward relaxation to the equilibrium distribution on local scale, which should be chosen as a local Maxwellian distribution function. Conservation of particles is assumed and the collision operator is considered as source or sink of particles. A final simplification named after Lorentz considers only the electrons as diffusing particles having collisions in a background of heavy particles described by an equilibrium statistical distribution.

1.3.3

The Plasma as a Fluid

Starting from the statistical treatment it is possible to derive macroscopic plasma quantities by averaging the distribution function and providing the (mass, momentum, and energy) continuity equations. These equations coupled with the Maxwell equations for electromagnetic fields provide a self consistent plasma model. The system of Equations 1.9 represents the plasma in the two-fluid theory. Electrons and ions are considered as two conducting fluids and are coupled through momentum transfer collisions (by a suitable definition of the collisional operator) and through Maxwell equations. In this representation we assume isotropy (the pressure tensor reduces to a scalar) and adiabatic conditions, providing energy conservation (Equation 1.9c).

$$\left\{ \begin{array}{l} \frac{\partial n_\alpha}{\partial t} + \nabla \cdot (n_\alpha \mathbf{u}_\alpha) = 0 \quad (1.9a) \\ m_\alpha n_\alpha \frac{\partial \mathbf{u}_\alpha}{\partial t} + m_\alpha n_\alpha \mathbf{u}_\alpha \cdot \nabla \mathbf{u}_\alpha = q_\alpha m_\alpha (\mathbf{E} + \mathbf{u}_\alpha \times \mathbf{B}) \\ -\nabla p_\alpha - \sum_\beta m_\alpha n_\alpha \nu_{\alpha\beta} (\mathbf{u}_\alpha - \mathbf{u}_\beta) \quad (1.9b) \\ \frac{\partial [p_\alpha \cdot (m_\alpha n_\alpha)^\gamma]}{\partial t} + \mathbf{u}_\alpha \cdot \nabla [p_\alpha \cdot (m_\alpha n_\alpha)^\gamma] = 0 \quad (1.9c) \\ \nabla \cdot \mathbf{E} = \frac{1}{\epsilon_0} \cdot \sum_\alpha q_\alpha n_\alpha \quad (1.9d) \\ \nabla \cdot \mathbf{B} = 0 \quad (1.9e) \\ \nabla \times \mathbf{B} = \frac{1}{\epsilon_0} \frac{\partial \mathbf{E}}{\partial t} + \mu_0 \sum_\alpha q_\alpha n_\alpha \mathbf{u}_\alpha \quad (1.9f) \\ \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \quad (1.9g) \end{array} \right.$$

The subscript α (or β) refers to the particle (conducting fluid) species.

A simplified and modified set of equations is provided by the three-fluid model (Equation 1.10) introduced in Chapter 10. The model is simplified in the sense that only the continuity equations of the three different species (electrons and both negative and positive ions) are included and only the electric field is taken into account, through the Poisson equation, which understands plasma quasi-neutrality

conditions (negative and positive charges are balanced).

$$\partial n_e / \partial t + \text{div} n_e \mathbf{w}_e = (v_i - v_a) n_e + v_d n_n, \quad (1.10a)$$

$$\partial n_p / \partial t + \text{div} n_p \mathbf{w}_p = v_i n_e, \quad (1.10b)$$

$$\partial n_n / \partial t + \text{div} n_n \mathbf{w}_n = v_a n_e - v_d n_n, \quad (1.10c)$$

$$\text{div} E = e(n_p - n_e - n_n) / \epsilon_0, \quad (1.10d)$$

In Equation 1.10 the indexes e , p , and n refer to electrons, positive, and negative ions, respectively, n_p , n_e , and n_n are the positive ion, electron, and negative ion number densities derived by the respective distribution functions integrated in the space domain, \mathbf{w}_p , \mathbf{w}_e , and \mathbf{w}_n their drift velocities, v_i , v_a , and v_d are the ionization, attachment, and detachment frequencies, e is the electronic charge and ϵ_0 is the permittivity of free space. The electron drift velocity and kinetic coefficients are to be determined from solving the electron Boltzmann equation Equation 1.8 for $\alpha = e$, the ion drift velocities are calculated using the known ion mobilities (see Equation 1.29 below).

1.3.4

Waves in Plasmas

Waves occurring in plasmas are described starting from the study of particle dynamics either by a statistical approach or through the fluid models. Complete description of waves in plasmas has been made extensively in dedicated works [22]. Waves in cold plasmas of interest for technological applications are described by considering the plasma as a dispersive dielectric medium (accounting for plasma inhomogeneities and anisotropies) for which the appropriate dielectric tensor may be defined.

Restricting our description of plasma waves relevant to applications described in this book (see Chapter 2), we consider the case of magnetized plasmas, in which it is possible to describe the cold plasma as collisionless by taking into account only electrons (ions and neutrals species are considered as an almost motionless particle background). For the sake of simplicity the external magnetic field is directed along the z axis and regarded as uniform and stationary (B_0).

Assuming harmonic time dependence of time varying quantities (n_α , p_α , \mathbf{u}_α , \mathbf{E} , \mathbf{B}) in the two-fluid model (Equation 1.9), and combining the last two Maxwell equations (Equation 1.9f,g) by taking the curl of Equation 1.9g it is possible to derive the wave equation (Equation 1.11):

$$\nabla \times \nabla \times \mathbf{E} = \frac{\omega^2}{c^2} \epsilon \cdot \mathbf{E} \quad (1.11)$$

where ϵ is represents the dielectric tensor. By taking the 3D Fourier transform of the same quantities with respect to space dependence, the vectorial Equation 1.12 leading to the dispersion relation is obtained:

$$-\mathbf{k} \times \mathbf{k} \times \hat{\mathbf{E}} = \frac{\omega^2}{c^2} \epsilon \cdot \hat{\mathbf{E}} \quad (1.12)$$

which can be written more explicitly as (Equation 1.13):

$$\begin{pmatrix} k_z^2 & 0 & -k_x k_z \\ 0 & k_x^2 + k_z^2 & 0 \\ -k_x k_z & 0 & k_x^2 \end{pmatrix} \begin{pmatrix} \hat{E}_x \\ \hat{E}_y \\ \hat{E}_z \end{pmatrix} = \frac{\omega^2}{c^2} \cdot \begin{pmatrix} \varepsilon_{\perp} & -j \cdot \varepsilon_x & 0 \\ -j \cdot \varepsilon_x & \varepsilon_{\perp} & 0 \\ 0 & 0 & \varepsilon_{\parallel} \end{pmatrix} \begin{pmatrix} \hat{E}_x \\ \hat{E}_y \\ \hat{E}_z \end{pmatrix} \quad (1.13)$$

The first term in parentheses of the RHS of Equation 1.13 is the explicit form of the plasma dielectric tensor.

For a non-collisional homogeneous plasma immersed in a steady uniform magnetic field the resulting tensor components read:

$$\begin{aligned} \varepsilon_{\perp} &= 1 - \frac{\omega_{pe}^2}{\omega^2 - \omega_{ce}^2} \\ \varepsilon_x &= \frac{\omega_{ce}}{\omega} \frac{\omega_{pe}^2}{\omega^2 - \omega_{ce}^2} \\ \varepsilon_{\parallel} &= 1 - \frac{\omega_{pe}^2}{\omega^2} \end{aligned} \quad (1.14)$$

with $\omega_{ce} = eB_0/m_e$ is defined as the electron cyclotron frequency, which corresponds to the gyration frequency of electrons along the magnetic field lines, $\omega_{pe} = (e^2 n / \varepsilon_0 m)^{1/2}$ is the electron plasma frequency, corresponding to undriven small amplitude electron oscillations. In the case of collisional plasma the plasma dielectric tensor components are given by (Equation 1.15):

$$\begin{aligned} \varepsilon_{\perp} &= 1 - \frac{\omega - j\nu_m}{\omega} \frac{\omega_{pe}^2}{(\omega - j\nu_m)^2 - \omega_{ce}^2} \\ \varepsilon_x &= \frac{\omega_{ce}}{\omega} \frac{\omega_{pe}^2}{(\omega - j\nu_m)^2 - \omega_{ce}^2} \\ \varepsilon_{\parallel} &= 1 - \frac{\omega_{pe}^2}{\omega(\omega - j\nu_m)} \end{aligned} \quad (1.15)$$

where ν_m represents the electron-neutral collision frequency. The last terms in Equation 1.14 and in Equation 1.15, corresponding to a direction parallel to the magnetic field (and transverse to the electric field) also represent the plasma dielectric constants in a nonmagnetized cold collisionless and collisional plasma, respectively. This simple case of transverse modes ($\mathbf{k} \cdot \mathbf{E} = 0$) leads to the following dispersion relation:

$$\omega^2 = \omega_{p,e}^2 + c^2 k^2 \quad (1.16)$$

Equation 1.16 for the dielectric permittivity exhibits a phenomenon called *cut-off*. Cut-off occurs when ε goes to zero. That is, when (Equation 1.17)

$$\omega^2 = \omega_{p,e}^2 = \frac{e^2 n_e}{\varepsilon_0 m_e} \quad (1.17)$$

which corresponds to the critical electron density $n_c = m_e \varepsilon_0 \omega^2 / e^2$. For MWs with a frequency of $f = 2.45$ GHz, (see Chapters 2 and 8) wave reflection occurs at the critical electron density $n_c = 7.5 \times 10^{16} \text{m}^{-3}$. This is quite crucial for MW-generated

plasmas in which a MW source may produce a plasma with a maximum electron density equal to n_c .

1.3.5

Relevant Parameters that Characterize the State of Plasma

From the above theoretical framework it is possible to nail down some useful physical quantities and parameters which help in characterizing the plasma state and different plasma regimes.

In particular, for systems in thermodynamic equilibrium such as high temperature plasmas (thermal plasmas) a plasma temperature may be defined starting from the particle velocity (Maxwell) distribution. However also nonequilibrium plasmas can be described by parameters provided that there is local equilibrium, or that at least the equilibrium within each particle species is maintained. This means that it is possible to define different equilibrium regimes for each plasma species even if the whole system is not in equilibrium. In this case different temperatures may be defined for different particle populations, for cold plasmas typically electrons, ions, and neutrals. Thermal equilibrium within each species is due to the inefficient collisions among different particle populations. In this regime mutual collisions among species (e.g., electron–ion or electron–neutral) do not lead to significant energy losses (or gains) for any of the species involved in the interactions but collisions among particles of the same species are efficient in terms of energy exchange, providing fast thermalization and attainment of the equilibrium regime. A typical case is that in which electron, ion, and neutral temperatures may be defined separately. For each plasma species assumed to be in thermodynamic equilibrium a Maxwell distribution is associated in velocity space (obtained by integrating the particle distribution function over Euclidian space) and the selected plasma species temperature is related to the average kinetic energy of the particles derived from their velocity distribution function second order momentum; therefore ion (i) and electron (e) temperatures are defined as: $T_i = m\langle v_i^2 \rangle / (3 k_B)$ and $T_e = m\langle v_e^2 \rangle / (3 k_B)$.

Other characteristic physical parameters in space and time (frequency) domains are useful to characterize plasmas and for their classification.

The *Debye length* (λ_D) represents the distance over which the electric field of each charge carrier (usually electrons) is screened, representing the interaction range of single charged particles. It is given by Equation 1.18:

$$\lambda_D = \sqrt{\frac{\epsilon_0 k_B T_e}{n_e e^2}} \quad (1.18)$$

where n_e , T_e , and e are the electron density, temperature, and charge ($e = 1,602 \cdot 10^{-19}$ C), respectively, k_B the Boltzmann constant, and ϵ_0 the vacuum electric permeability ($\epsilon_0 = 8,859 \cdot 10^{-12}$ F/m).

If non-negligible size particles are considered, another useful parameter of gas dynamics is the so-called *mean free path*, representing the average distance traveled by particles in rectilinear motion between subsequent collisions within the gas box (see the free ideal gas model of Section. 1.3.1). Where d is the classical particle

diameter, T and p the gas temperature and pressure, the mean free path is evaluated by (Equation 1.19):

$$\lambda = \frac{k_B T}{\sqrt{2} \pi d^2 p} \quad (1.19)$$

The *plasma parameter* (g) is a nondimensional parameter defined through the Debye length and the plasma (equilibrium) density: it is the measure of the number of particles present in a Debye sphere (Equation 1.20):

$$g = \frac{1}{n_0 (\lambda_D)^3} \quad (1.20)$$

The plasma parameter has to be small for a many body system to be treated in the so-called '*plasma approximation*'. This means that the average potential energy of a particle is much less than its kinetic energy. Departure from this limit implies that the particles interaction energy to becomes more relevant and that the plasma may not be treated as an ideal gas (this holds typically in the case of highly charged particles density per Debye sphere).

The *thermal De Broglie wavelength* Λ is the average particle de Broglie length defined as Equation 1.21:

$$\Lambda = \sqrt{\frac{h^2}{2\pi m k_B T}} \quad (1.21)$$

where h is the Plank constant ($h \approx 6.626 \times 10^{-34}$ Js). To consider the plasma as a classical system the following relations must be satisfied: $\Lambda \ll \sqrt[3]{n_0}$; $\Lambda \ll e^2 / (k_B T)$, where the last term on the RHS in the two relations are the mean spacing among plasma particles and the distance of closest approach in Coulomb interactions, respectively. If the first inequality is violated, the binary collision among near neighbor particles can no longer be treated classically. If the second approximation relation does not hold, the system cannot be described by the Maxwell–Boltzmann statistics, since degeneracy occurs and a quantum statistics has to be adopted, either Fermi–Dirac (fermion gas) or Bose–Einstein (boson gas).

Concerning the frequency domain, the plasma frequency may be defined as:

$$\omega_{p,\alpha} = \sqrt{\frac{n_\alpha q_\alpha^2}{\epsilon_0 m_\alpha}} \quad (1.22)$$

When Equation (1.22) concerns the electron species ($\alpha = e$, where here q_e represents the electron charge) the *electron plasma frequency* is the rate of electron free oscillations (seen as a non-collisional plasma slab) over a background of almost steady still positive ions, when the system is perturbed by a small amplitude electric impulse. The plasma frequency may also be seen as a measure of the electron density and it is the parameter that influences the transmission (or damping) of specified frequency external electromagnetic waves. A similar quantity may be defined for ions when $\alpha = i$ and $q_i = Ze$ is the total ion charge, providing the *ion plasma frequency*.

In magnetized low density plasmas charged particle motion is characterized by spinning around the magnetic field lines, and the ion and electron *gyrofrequency* is defined as Equation (1.23):

$$\omega_{c,\alpha} = \frac{q_\alpha B}{m_\alpha} \quad (1.23)$$

where B denotes the intensity of the magnetic field. For $\alpha = e$ and $\alpha = i$ the electron and ion gyrofrequencies are defined, respectively. Due to the electron-to-mass ratio and to typical reactor dimensions, in plasma processing the electron gyrofrequency is of great interest, for example, in ECR plasmas (see Chapters 2 and 8). The corresponding gyration radius or gyroradius can be written as Equation (1.24):

$$r_c = \frac{v_{\perp,\alpha}}{|\omega_{c,\alpha}|} \quad (1.24)$$

where $v_{\perp,\alpha}$ represents the particle(s) of type- α speed component perpendicular to the magnetic field.

Regarding characteristic velocity parameters, it is worth mentioning the drift velocity of the guiding center of particles gyrating around magnetic field lines. The $\mathbf{E} \times \mathbf{B}$ *drift velocity* is due to the presence of perpendicular components of electric and magnetic fields in the plasma (Equation 1.25):

$$\mathbf{v}_{\text{ExB}} = \frac{\mathbf{E} \times \mathbf{B}}{B^2} \quad (1.25)$$

The $\mathbf{E} \times \mathbf{B}$ drift motion is of particular importance, for example, in the confinement of secondary electrons in magnetron sputtering sources as well as for the control of the arc spot on arc-physical vapor deposition (PVD) targets (see Chapter 2).

Considering electrostatic waves in plasmas the *adiabatic electron sound speed* accounts for the propagation of waves in plasma parallel to the electric field (which is possible in plasma but not in vacuum or in a conventional dielectric material) due to an exchange between thermal and electric energy (γ being the ratio of specific heats in Equation 1.26):

$$c_{e,\gamma} = \sqrt{\frac{\gamma k_B T_e}{m_e}} \quad (1.26)$$

In magnetized plasmas the Alfvén velocity represents the phase speed of transverse waves produced by oscillation of ions through a perpendicular magnetic field whose exerted force acts as a restoring force (Equation 1.27):

$$v_A = \frac{B}{\sqrt{\mu_0 n_0 m_i}} = \frac{\omega_{c,i}}{\omega_{p,i}} \cdot c \quad (1.27)$$

where n_i and m_i are the ion number density and mass, B is the magnetic field strength, μ_0 the vacuum magnetic permeability, and c the speed of light.

Regarding the *transport parameters*, when assuming only electron-neutral collisions and for low electric field frequencies (e.g., low frequency electric field perturbations) the *plasma resistivity* is defined as Equation (1.28):

$$\rho = \frac{m_e v_{m,e}}{n_e e^2} = \frac{v_{m,e}}{\varepsilon_0 \omega_p^2} \quad (1.28)$$

where $\nu_{m,e}$ is the electron collision frequency, n_e is the electron density, ω_p is plasma frequency, m_e is the electron mass. For kinetic transport the mobility (μ) and diffusion coefficients (D) of the species α through a background of neutral (steady) particles are given by Equation (1.29):

$$\mu_\alpha = \frac{q_\alpha}{m_\alpha \nu_{m,\alpha}}; D_\alpha = \frac{kT_\alpha}{m_\alpha \nu_{m,\alpha}} \quad (1.29)$$

where T_α and $\nu_{m,\alpha}$ are the species temperature and collision frequency with neutrals.

Another kinetic transport parameter relevant for electrically driven plasmas is the *ambipolar diffusion coefficient* (Equation 1.30) accounting for the diffusion process induced by the presence of static electric field:

$$D_A = \frac{\mu_i D_e + \mu_e D_i}{\mu_i + \mu_e} \quad (1.30)$$

where the subscripts i and e refer to ion and electron species, respectively. For magnetically driven and magnetized plasmas electron diffusion perpendicular to the magnetic field are described by the relative directional mobility and diffusion coefficients (Equation 1.31):

$$\mu_\perp = \frac{\mu_e}{1 + (\omega_{c,e}/\nu_{m,e})^2}; D_\alpha = \frac{kT_e}{m_\alpha \nu_{m,e}} \cdot \frac{1}{1 + (\omega_{c,e}/\nu_{m,e})^2} \quad (1.31)$$

Finally, we report Loschmidt's number, corresponding to the particle number density at standard pressure and temperature: $n_0 \approx 2.6868 \times 10^{25} \text{ m}^{-3}$, useful to gauge the variety of plasma densities in LPPs such as encountered in PVD or plasma enhanced chemical vapor deposition (PECVD) reactors. In atmospheric pressure plasma (APP) regimes, examples are plasma jets, dielectric barrier discharge (DBD), or plasma coronas.

1.4 Classification of Technological Plasmas

A first broad classification of plasmas may be done in terms of their thermodynamic properties: thermal plasmas (TPs) and non thermal plasmas (NTPs) also regarded as plasmas in thermodynamic equilibrium and nonequilibrium plasmas, respectively. The first class includes high pressure hot plasmas characterized by pressures (p) exceeding 10^3 Pa with high electron temperatures (T_e) in the order of 10^4 K and higher. In these systems the collision frequency among different plasma species is efficient: the collision frequency is high with respect to the particles transit time on the plasma scale length and allows the electrons to lose energy in favor of the ion species, providing thermalization of different particle species to the thermodynamic equilibrium temperature. The energy equipartition principle holds and energy content is evenly distributed among vibration, rotational, and translation energies. The ionization degree (number of ions over total plasma particles) is close or equal to 100%.

On the contrary cold NTPs are in a thermodynamic nonequilibrium state in which it is sometimes possible to define different temperatures for the different plasma species. The typical situation in plasma processing is to find relatively hot electrons with temperatures of the order of 10^4 K ($T_e \sim 10^4$ K) and cold ions and neutrals, often found at almost ambient temperature ($T_i \sim T_n \sim 10^4$ K). Nonthermal cold plasmas are associated with low degrees of ionization in the range 10^{-4} – 10^{-1} .

1.4.1

Hot (Thermal) Plasmas and Their Applications

Hot plasmas, such as electrical arcs, plasma jets of rocket engines, plasmas generated by thermonuclear reactions, and so on, have an extremely high energy content, which induces fragmentation of all organic molecules to atomic levels. As a consequence, these plasmas can only be used to generate extremely high caloric energy or to modify thermally stable inorganic materials (metals, metal oxides, etc.). The thermal plasma is obtained by generating an arc discharge in a gas submitted to electric fields of varied frequency. The bundle of gas ionized at very high temperature is able to remove, fuse or to thermally modify a material. The bundle can be compared to a tool, it is easily controllable and not in direct contact with the treated surface. The applications of thermal plasmas depend on temperature, gaseous reagents and tiny particles injected into the plasma (plasma spraying, synthesis) or exposed to plasma in the form of 'bulk materials' (fusion and refining in metallurgy).

The potential applications of thermal plasma processing technology cover a wide range of activities, such as the extraction of metals, the refining/alloying of metals/alloys, the synthesis of fine ceramic powders, spray coatings, and the consolidation and destruction of hazardous waste. In particular cases the thermal plasma finds applications in complicated chemical processes, for instance fast quenching chemistry or synthesis of nanoparticles.

In metal melting and remelting, the plasma is used primarily as an effective source of process heat, making use of the anode heat transfer characteristics of an arc between a cathode and the metal. The relatively long characteristic process times (from 0.1 second to minutes) reduce the importance of instability effects. In plasma cutting and welding, the use of a plasma is more economical than using a laser or an electron beam which may provide higher power flux densities. New approaches are driven by improvement of the product quality and process reliability. Examples are the expanded use of pulsing the weld current and of sensors for feedback control in automated welding.

Plasma sprayed coating has evolved extensively during the last 20 years, except for the basic design of the plasma gun (nozzle), which has not been changed significantly. The essential part of the gun is the nozzle that consists of a cone-shaped cathode located within a cylindrical anode, which usually extends beyond the cathode. Reactive or inert gases or mixtures of them traversing the space located between the electrodes are 'instantly' ionized and as a result the plasma state is generated. For coating purposes, powders can be injected into the plasma jet at

desired locations relative to the nozzle to control the caloric energy absorption of the materials for deposition and the pathways of the plasma-borne particles and droplets. The coating particles (powders) introduced into the jet are instantly molten and the resulting droplets are deposited and cooled on the target surfaces usually leading to strongly bound – though porous – coatings. In plasma waste treatment, the major advantages of using thermal plasmas are the fast heating rates, the high processing temperatures allowing the formation of stable vitrified slugs, and the low off-gas flow rates. Off-gas cleaning is a major economic factor in any waste processing installation, and the costs scale down with increasing gas flows. The major issue is the economics of the specific process, and all new developments have been directed toward improving the economics either by combining plasma processes with conventional incinerators to make use of the heating value of the wastes, or by using the waste heat to obtain a useful co-product.

1.4.2

Cold (Nonthermal) Plasmas and Their Applications

In common perception, plasmas are hot gases that emit light and conduct electricity. Indeed, plasmas often contain energetic electrons (at $E \cong 1 \text{ eV} = 1.1604 \times 10^4 \text{ K}$ or higher) that in turn transfer their energy to neutral molecules and excite radiating transitions. However, not all plasmas are hot. Cold plasmas, including low-pressure DC and RF discharges (silent discharges), discharges from fluorescent (e.g., neon) illuminating tubes, DBDs may be found both at low pressure or atmospheric pressure. Cold LPPs for surface processing are found in the range between 10^{-6} and 1 Pa , with a typical Debye length, corresponding to the electromagnetic screening distance, of 10^{-5} m , much less than the typical plasma scale length in the order of 10^{-1} – 1 m . Cold LPPs have neutrals densities between $10^{-5}n_0$ and $10^{-2}n_0$ (n_0 , being the Loschmidt number, as defined in Section 1.3.3), while cold APPs such as DBDs are characterized by electron number densities of the order of n_0 with an energy range of 1 – 10 eV .

Electrons, which are small and light particles, cannot heat the large and heavy molecules very efficiently, so in many cases the background gas remains almost at room temperature. In such nonequilibrium systems (often called *nonthermal plasmas* or *cold plasmas*), the complex plasma chemistry is driven by electrons. They perform ionization, necessary to sustain the plasma; in addition, they are responsible for atomic/molecular excitation, dissociation, and production of radicals and metastable molecular states. The result is an active gaseous medium that can be safely used without thermal damage to the surrounding materials. Such exceptional nonequilibrium chemistry is the base of plasma applications in lighting technology, exhaust gas treatment, and material processing. There are several methods to generate cold plasmas. When charged particles are in the minority, heating of neutral molecules is limited. This leads to diffuse plasmas where the fraction of ionized species is below $10^{-7}n_0$ and pressures reach 10^3 Pa . The effect of low pressure is double: in a rare gas ionization events are scarce, which keeps the charge density low. Moreover, the frequency of elastic collisions between

electrons and atoms/molecules is low, so electrons do not have much chance to convey their energy to the gas. LPPs are of great value in fundamental research as well as in plasma technology, but they have many serious drawbacks. These plasmas must be maintained in massive vacuum reactors, in which the chemistry is optimally controlled, but their operation is costly due to long pump down times, energy requirement, as well as the reactor maintenance burden. The access for observation or sample treatment is limited, and there are limitations for the materials to be treated because of degassing problems. Therefore, one of the recent trends focuses on developing new plasma sources, which operate at atmospheric pressure, and target to retain the properties of low-pressure media. Also these approaches are characterized by positive features such as substrate accessibility, high throughput, continuous or semi-continuous processing, but limitations are also found in the shapes of substrate to be treated, less precise control of plasma chemistry due to plasma pollution, different physical and chemical regimes posing limitations to surface processing such as to plasma polymerization of high boiling point precursors.

NTPs may be generated for processing purposes by using different principles where the energy input comes from diverse sources.

In **micro-plasmas** gas heating occurs in the plasma volume, and the energy is carried away by thermal diffusion/convection to the outside. If the plasma has a small volume and a relatively large surface, gas heating is limited.

Coronas are gas discharges where the electrode geometry controls and confines the ionization processes of gases in a high-field ionization environment, in the absence of insulating surfaces or when the dielectric surfaces are far away from the discharge zone. Corona discharges are often called *negative, positive, bipolar, AC, DC*, or high frequency (HF) coronas, according to the polarity of the stressed electrodes, to whether one or both positive and/or negative ions are involved into the current conduction, and to the nature of the driving field. What makes corona discharges unique in comparison to other plasmas is the presence of a large low field drift region located between the ionization zone and the passive (low field) electrode. Ions and electrons penetrating the drift space will undergo neutralization, excitation, and recombination reactions involving both electrons and neutral and charged molecular and atomic species. However, because of multiple inelastic collision processes in atmospheric pressure environments the charged active species escaping from the ionization zone (electrons, ions) will have energies lower than the ionization energies, and as a consequence, neutral chemistry (free radical chemistry) will characterize the drift region. According to various electrode configurations, point-to-plane, wire-cylinder, and wire-to-plane corona discharges can be identified.

Dielectric barrier discharges. These plasmas are typically generated between parallel metal plates, which are covered by a thin layer of dielectric or highly resistive material. Usually they are driven by a HF electric current (in the kHz range), but it is also possible to obtain a DBD by simple transformation of 50 Hz/220 V network voltage to about 10 kV to 40 kHz electric input. The dielectric layer plays an important role in suppressing the current (sparking due to streamers): the cathode/anode layer is charged by incoming positive ions/electrons, which reduces

the electric field and hinders charge transport toward the electrode. DBDs have typically low ionization degrees and currents in the order of mA. Besides, the electrode plates are quite large ($\sim 0.1 \text{ m}^2$, in some cases with a large aspect ratio of 10 : 1) and the distance between them usually does not exceed the millimeter range. Thus, DBD has a large surface-to-volume ratio, which promotes diffusion losses and maintains a low gas temperature (at most a few tens of degrees above the ambient). The only serious drawback of a DBD is its limited flexibility. Since the distance between the plates must be kept small, treatment of large and irregular (3D) samples is impossible, at least with conventional planar electrodes.

In **electron cyclotron resonance ion sources** (ECRISs), the plasma is confined in a special magnetic field configuration where an axial magnetic field is produced by, for example, two solenoid coils (magnetic mirror). Superimposed is a radial magnetic field usually produced by a permanent multipole magnet. This geometry leads to a minimum-B-structure, that is, from the geometrical middle the magnetic field increases in all directions. Electrons confined in that magnetic field gyrate around the magnetic field lines with the cyclotron frequency ($\omega_{c,e}$). The microwave energy is radiated into the plasma and electrons can be heated resonantly when the microwave frequency equals the cyclotron frequency. Every time an electron passes the resonance region it can gain 1–2 keV energy. Electrons from ECRIS can have energies up to several kiloelectronvolts and therefore a good magnetic plasma confinement is required. Ions are not accelerated due to their high mass and are confined electrostatically by the space charge of the plasma electrons. When electrons leave the plasma through the loss cone of the magnetic mirror, ions can follow and can then be extracted from the ion source by applying a high voltage. The maximum obtainable charge state depends on the confinement time of the ions and on the energy of the plasma electrons. These can be varied by tuning the ion source parameters like gas pressure, microwave power, magnetic field strength, and so on.

Microwave plasmas are sustained by microwave energy dissipated into the reaction media by coaxial cables or by waveguides in the case of higher powers. The physical dimensions of coaxial cables (cross-sections) and waveguides are selected according to the microwave frequency. Most materials efficiently absorb or reflect microwaves, and as a result microwave energy cannot be transported using conventional cables. Microwave discharges are more difficult to sustain under low-pressure conditions ($< 10^3 \text{ Pa}$). In a collisionless condition the energy gained by an electron during one cycle is too small to produce ionization. In collisional plasmas at constant power density and electric field, the average (RF) microwave power transferred from the driving field has a maximum value when the collision frequency equals the driving frequency. The absorption of microwave power depends on the collision frequency of the electrons which is controlled by the atomic and molecular species. At comparable plasma parameters, RF discharges most often fill the entire reactor, whose dimensions are usually smaller than the wavelength of the RF field (13.56 MHz corresponds roughly to 22 m). Microwave plasmas exhibit a strong peaking in field intensity at the coupling to the microwave cavity that diminishes gradually with increasing distance from the coupling, rather than being deposited throughout the discharge.

1.5

Reactive Plasmas

In this section we particularly focus on the reactivity of NTPs and the capability of promoting plasma–chemical reactions through intermediate steps in a way to exploit the plasma state as a very efficient environment as compared to conventional conditions where chemical reactions usually take place. The free electric charges – electrons and ions – make a plasma electrically conductive, internally interactive and strongly responsive to electromagnetic fields. Plasma is widely used in practice, in particular for surface processing, and NTPs offer three major features that are attractive for industrial applications:

- The temperature of at least some plasma components and the energy density can significantly exceed those in conventional chemical technologies (e.g., energetic electrons), abating the activation energy thresholds.
- Plasmas are able to produce very high concentrations of energetic and chemically active species (electrons, ions, atoms and radicals, excited and metastable states, and photons with different wavelengths which can interact with the processing surface).
- Cold plasmas are far from thermodynamic equilibrium, providing extremely high concentrations of the chemically active species while keeping the bulk temperature as low as room temperature, thus not affecting the properties of material to be treated other than the ones of the functionalized surface.

These plasma features allow significant intensification of traditional chemical processes, a dramatic increase of their efficiency and often successful promotion of chemical reactions which in conventional chemistry would require significant energy input and the use of additional chemical compounds such as catalysts. Moreover, plasma treatments are by definition dry processing methods, thus avoiding the use of water and solvents, minimizing emissions and the overall environmental burden, as discussed in detail in Chapter 12.

1.5.1

Elementary Plasma–Chemical Reactions

To reach the required degree of reactivity in a plasma not all particles need to be ionized; a common condition in plasma chemistry is that the gases are only partially ionized. The ionization degree in the conventional plasma-chemical systems spans a range of seven orders of magnitude (10^{-7} – 10^{-14}). When the ionization degree is close to unity, such a plasma is called *completely ionized plasma*, which is often the case in high temperature thermal plasmas. When the ionization degree is low, the plasma is called *weakly ionized plasma*, which is the main focus of plasma chemistry in the present context.

The total yield of the plasma–chemical processes is due to synergistic contributions of numerous different elementary reactions taking place simultaneously in a discharge system. The sequence of transformations of the initial chemical

substances and electric energy into products and thermal energy is usually referred to as the mechanism of *the plasma–chemical process*. Elementary reaction rates are determined by the microkinetic characteristics of individual reactive collisions (like, for example, collision cross-sections, i.e., elementary reaction probabilities) as well as by relevant kinetic distribution functions (see Section 1.3), like the electron energy distribution function (EEDF) and ion energy distribution function (IEDF), respectively defined generically as f_α in the previous sections, and by other distribution functions such as that of excited molecular states. Formally reactions rates (k) are calculated by means of the reaction cross-sections and interacting particle speeds as Equation (1.32):

$$k = \langle \mathbf{v} \cdot \sigma \rangle \quad (1.32)$$

where the $\langle . \rangle$ symbol stands for an averaged quantity over the distribution function and σ is the reaction cross-section, while \mathbf{v} is the relative velocities of the reacting particles.

Indeed, the elementary reaction rate is actually the result of integration of the reactive collision cross-section over the relevant distribution function and it is characterized by the energy or excitation state of the reactant.

The key process to sustain the plasma discharge and therefore to allow plasma-chemical reactions is ionization, which means conversion of neutral atoms or molecules into *electrons* and *positive ions*. Thus, ionization is the first processes to be considered.

In quasi-neutral plasmas, typically employed in surface processing, the number density of electron and positive ions species are comparable or equal ($n_e \approx n_i$) in case of high electron affinity of heavy particle species negative ions are also effectively formed and give rise to ‘electronegative’ plasmas. Mainly responsible for ionization are inelastic effective collisions. Therefore we dwell briefly on a quantitative description of collision phenomena principles and dynamics to get the main understanding of these processes.

Due to continuous impact of natural energetic cosmic rays on the neutral gas some free electrons are continuously generated and always available. When external (intense) electric fields are applied, an ionization avalanche process is started, providing more and more available free electrons. The latter are the first species gaining kinetic energy from electric fields, because of their low mass and high mobility with respect to other species such as ions. Those energetic free electrons transfer energy to all other plasma components, providing energy for ionization, excitation, dissociation, and other plasma chemical processes. The rates of such processes depend on how many electrons have enough energy to do the job. This can be quantitatively described by means of the EEDF, which is the probability density $f(\varepsilon)$ for an electron for having an energy ε . The EEDF strongly depends on the applied electric field and the gas composition in the plasma (especially in nonthermal discharges) and often can be very far from the equilibrium distribution.

1.5.2

Elastic Scattering and Inelastic Thomson Scattering: Ionization Cross-section

Electron–electron, electron–ion, and ion–ion scattering processes are so-called Coulomb collisions. Their cross-sections are quite high with respect to those of collision with neutral partners, but they are much less frequent in a discharge with a low degree of ionization. An important feature of Coulomb collisions is the strong dependence of their cross-section on the kinetic energy of the colliding particles. This can be demonstrated by a simple analysis, where two particles (considered as rigid spheres) have the same charge and, for the sake of simplicity, one collision partner is considered to be at rest. A scattering event takes place if the Coulomb interaction energy ($U \sim q^2/b$, where b is the impact parameter) is comparable to the kinetic energy ε of a moving particle. Then, the impact parameter $b \sim q^2/\varepsilon$ and the ionization reaction cross action σ can be estimated as $\sigma = \pi b^2$, in the classical hard spheres approximation.

In order to sustain a plasma and to provide its chemical reactivity, continuous ionization is necessary. Electron collisions with the background neutral species and ions provide the mechanism to determine these conditions when collisions are said to be non-elastic and a certain amount of collisional energy is spent to directly ionize or excite and subsequently ionize the molecules.

Starting with the Rutherford formula for differential cross-section from (classical) collision particle dynamics it is possible to derive the Thomson ionization cross-section:

$$\sigma_{iz}(\varepsilon) = \pi \left(\frac{e^2}{4\pi\varepsilon_0} \right)^2 \frac{1}{\varepsilon} \left(\frac{1}{\varepsilon_{iz}} - \frac{1}{\varepsilon} \right) \quad (1.33)$$

Equation 1.33 is valid for $\varepsilon > \varepsilon_{iz}$ and for $\varepsilon \leq \varepsilon_{iz}$ the ionization cross-section is identically zero: $\sigma_{iz}(\varepsilon) \equiv 0$.

When considering typical scattering cross-sections at room temperature ($\sim 293 \text{ K} = 3.39 \times 10^{-2} \text{ eV}$) it is straightforward to realize that there is a gap of three orders of magnitude with respect to the scattering cross-section of electrons at a temperature of 1 eV ($\sim 1.16 \times 10^{-4} \text{ K}$), typical for electric discharges. Beside this we recall that for a charged particle scattering on a neutral molecule which has a permanent dipole moment (interaction energy $U \sim 1/r^2$) and an induced dipole moment (interaction energy $U \sim 1/r^4$), the ionization cross-sections are $\sigma_{ix}(\varepsilon) \sim 1/\varepsilon$ and $\sigma_{iz}(\varepsilon) \sim 1/\varepsilon^{1/2}$, respectively. Similar considerations may be made for electrons.

Moreover, energy transfer during an elastic collision (in the hard sphere scattering approximation) is possible only as a transfer of kinetic energy. However the average fraction γ of kinetic energy (Equation 1.34), transferred from one particle of mass m (m_e for electron mass) to another particle of mass M (m_i for ion mass), is equal to:

$$\gamma = \frac{2 m_e m_i}{(m_e + m_i)^2} \quad (1.34)$$

For elastic collisions of electrons with heavy neutrals or ions, $m_e \ll m_i$ and, hence, $\gamma \sim 2 m_e/m_i$, which means that the fraction of transferred energy is very

small ($\gamma \sim 10^{-4}$). In particular, this explains why the direct impact ionization due to a collision of an incident electron with a valence electron of an atom predominates (here $\gamma = 0.5$).

1.5.3

Molecular Ionization Mechanisms

Nondissociative and dissociative ionization of molecules by direct electron impact is presented here as an example for the complex mechanisms that occur in reactive plasmas. Such a process can be written, for the case of diatomic molecules AB respectively as:



Here, AB denotes a diatomic molecule, AB^+ an ionized diatomic molecule, B^+ an ionized atom as product of molecular dissociation, B^* an atom in an excited state after molecular dissociation.

The first of the listed processes (Equation 1.35) takes place when the electron energy does not greatly exceed the ionization potential. Some peculiarities of molecule ionization by electron impact can be seen from the illustrative potential energy curves for AB and AB^+ , shown in Figure 1.2, for collisions having a threshold energy ε_{iz} . For collisions having threshold energies higher than ionization, molecule dissociation occurs with excitation or further ionization of products (represented in states labeled as *c* and *b*, respectively in Figure 1.2).

The fastest internal motion of atoms inside molecules is their molecular vibration. But even molecular vibrations have a typical time period of $10^{-14} - 10^{-13}$ s, which is much longer than the interaction time between the plasma electrons and the molecules: $a_0/v_e \sim 10^{-16} - 10^{-15}$ s (where a_0 is the atomic unit of length and v_e is the mean electron velocity). This means that all kinds of electronic excitation processes under consideration, which are induced by electron impact, are much faster than the atomic motion inside the molecules. As a result, all the atoms inside a molecule can be considered to be frozen during the process of electronic transition, stimulated by electron impact. This fact is known as the *Frank-Condon principle*. The nondissociative ionization process (Equation 1.35) usually results in the formation of a vibrationally excited ion $(AB^+)^*$ and requires a little more energy than the corresponding atomic ionization. When the electron energy is relatively high and substantially exceeds the ionization potential, dissociative ionization can take place:



This ionization process (Equation 1.36) corresponds to electronic excitation into a repulsive state of the ion, $(AB^+)^*$, followed by a decay of this molecular ion. The energy threshold for the dissociative ionization is essentially greater than that for the nondissociative situation.

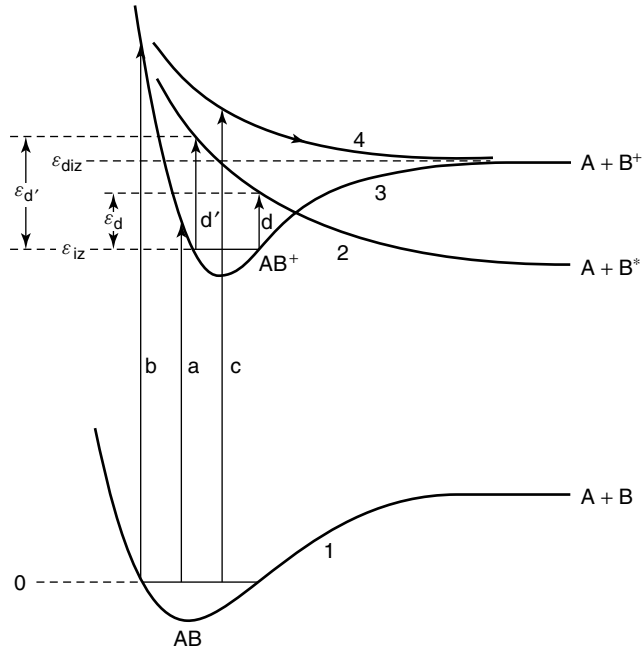


Figure 1.2 Qualitative representation of potential energy curves for ionization of molecules AB and AB^+ by electron impact. Energy input to a molecule by collisions may be comparable to or exceed the ionization energy ε_{iz} . In the case of comparable energy (a) the molecule AB is ionized into the AB^+ state; if higher energy is transferred to the molecule by electron impact, dissociation may occur (b and c).

In reactive plasmas many other similar two- and three-body processes, including association, dissociation, recombination, attachment, detachment, excitation transfer processes of increasing complexity may also occur.

1.5.4

Stepwise Ionization by Electron Impact

The efficiency of the ionization and excitation mechanisms associated with specific molecules (regarded as precursors in plasma processing) strongly influences the plasma reactivity.

However, the mechanisms previously described do not account for bridging the three orders of magnitude gap missing for the cross-section to explain why such efficient ionization processes sustain plasma discharges. To understand this and to see why the plasma state may provide such efficient reaction pathways we consider the molecular stepwise ionization process by electron impact.

When the plasma density and, therefore, the concentration of excited neutrals is high enough, the energy (ε_{iz}) necessary for ionization can be provided in two different ways. First, as in the case of direct ionization, it can be provided by

the energy of plasma electrons. Second, the high energy of preliminary electronic excitation of the neutrals can be converted in the ionization process, which is called *stepwise ionization*. If the level of electronic excitation is high enough, stepwise ionization is much faster and more efficient than direct ionization, because the statistical weight of electronically excited neutrals is greater than that of free plasma electrons. Hence, the probability that particle collisions are effective is higher for excitation than for direct ionization. Furthermore, the probability that the subsequent electron collisions are effective for ionization is higher, because the energy difference between the excited state and the unbound electron state is lower. We can consider the ionization process $e + A \rightarrow A^+ + e + e$, as the inverse to the three-body recombination event: $A^+ + e + e \rightarrow A^* + e \rightarrow A + e$, realized through a set of excited states. For quasi-equilibrium or thermal plasmas we may apply the principle of detailed equilibrium and consider the ionization process $e + A \rightarrow A^+ + e + e$ as if going through the set of electronically inverse excited states of the three-body recombination process, in this interpretation the ionization is regarded as a stepwise process.

For the ionization process we may define a rate coefficient k_{iz} (Equation 1.37), derived by the summation of partial rate coefficients $k_{iz,i}$, corresponding to the j -th electronically excited state, over all states of excitation, taking also into account their concentration:

$$k_{iz} = \sum_j^n k_{iz,j} \frac{N_j(\varepsilon_j)}{N_0} \quad (1.37)$$

Further, we assume that the electron excited states in the target atoms, radicals, or molecules, are in quasi equilibrium with plasma electrons, and apply the Boltzmann statistics describing the electronically excited states as having a defined electron temperature T_e , and by taking into account the statistical weights (g_j) of the states, their number density (N_j), Equation (1.38), and their energy (ε_n), become linked (note that the subscript '0' refers to the ground state):

$$N_j = \left(\frac{g_j}{g_0} \right) N_0 \cdot e^{\left(-\frac{\varepsilon_j}{k_b T_e} \right)} \quad (1.38)$$

From statistical thermodynamics $g_j = 2 g_{izj}^2$, where g_{iz} is the statistical weight of an ion.

Assuming effective (inelastic) electron neutral excitation collision, the energy transfer from the impinging electron to an electron bound to the neutral target particle undergoing excitation is about T_e . This means that excited particles with an energy of about $\varepsilon_j = \varepsilon_{iz} - T_e$ make the major contribution to the sum of Equation (1.37). Taking into account that $\varepsilon_j \sim 1/j^2$, the number of states with an energy of about $\varepsilon_j = \varepsilon_{iz} - T_e$ and a ionization potential of about $\varepsilon_{iz} = k_B T_e$ is of order j . Thus, from Equations (1.33) and 1.38 we can derive the reaction rates at each step:

$$k_{iz} = \left(\frac{g_{iz}}{g_0} \right) j^3 \cdot \langle \sigma_{iz} \cdot v \rangle \cdot e^{\left(-\frac{\varepsilon_{iz}}{k_b T_e} \right)} \quad (1.39)$$

By substituting the thermal velocity and ionization cross-section as a result, considering that from quantum mechanics $j^2 \approx \frac{Z^2 e^4 m}{(4\pi\epsilon_0)^2 \hbar^2 \epsilon_{iz}^2}$, the stepwise ionization rate coefficient can be expressed as:

$$k_{iz} \approx \left(\frac{g_{iz}}{g_0} \right) \frac{1}{(4\pi\epsilon_0)^5} \cdot \frac{m e^{10}}{\hbar^3 T_e^3} \cdot e^{\left(-\frac{\epsilon_{iz}}{k_b T_e} \right)} \quad (1.40)$$

Finally, comparing the stepwise- (Equation 1.40) and direct-ionization rate ($\bar{k}_{iz}(T_e)$) coefficients we obtain:

$$\frac{k_{iz}(T_e)}{\bar{k}_{iz}(T_e)} \approx \left(\frac{g_{iz} a_0^2}{g_0 \sigma_0} \right) \cdot \left(\frac{e^4 m}{(4\pi\epsilon_0)^2 \hbar^2 T_e^2} \right)^{\frac{7}{2}} \approx \left(\frac{\epsilon_{iz}}{T_e} \right)^{\frac{7}{2}} \quad (1.41)$$

From Equation (1.41) it is possible to argue that for $\sigma_0 \approx a_0$ and for $\epsilon_{iz}/T_e \approx 10$, as it is the case for a typical discharge, the stepwise ionization can be $10^3 - 10^4$ times faster than the direct one, as needed to sustain a plasma discharge.

1.6 Plasma Sheaths

Confined plasmas which enter into contact with materials are of particular interest for technical applications. A description of physical and chemical interactions between plasma and material surfaces is provided in Chapter 3 for processing applications. To understand the effective plasma regime at the plasma–substrate interface, the features of plasma sheaths are introduced in the following.

Plasmas which are quasi neutral ($n_i \approx n_e$), develop positively charged boundary layers called *sheaths* when approaching the material confining surfaces. This is due to the higher thermal velocity of electrons, $v_{th,e} = (2 k_B T_e / m_e)^{1/2}$, exceeding that of ions, $v_{th,i} = (2 k_B T_i / m_i)^{1/2}$, by two orders of magnitude because of the disproportioned mass ratio $m_e / m_i \ll 1$. Considering a simple (ideal) configuration of a plasma slab between two identical parallel grounded surfaces (walls), due to charge neutrality, the electric field would be zero everywhere. However, since in this configuration electrons are not confined by any electric field, due to their higher mobility they are rapidly lost to the walls, causing an abrupt change of charge concentration. Therefore at the plasma–wall interface charge neutrality is no longer satisfied and the electrical potential is found to be positive in the plasma (due to lack of negative charged particles) and rapidly decreasing within the plasma sheath space-domain, and approaching zero close to the walls within a few Debye lengths. The onset of this natural charge unbalance and consequent generation of potential barrier provides a self-confining mechanism for electrons that are then pulled into the plasma by the electric field directed from the plasma to the walls. Under these conditions ions approaching the plasma sheath are accelerated to the walls, causing ion bombardment. An important aspect of plasma sheaths is that their typical scale length is much smaller than the plasma spatial extension.

In fact, the sheath structure is more complex than just that of a boundary layer. Indeed, to satisfy the continuity of ion flux through the sheath, a pre-sheath

between the plasma and the sheath has to be assumed. Furthermore, sheath features are strongly dependent both on boundary conditions (applied external voltages: continuous, oscillating high/low voltage) and on the plasma characteristics (i.e., presence of electronegative ions, ion temperature, ionization degree).

For simplification, we consider a non-collisional plasma with Maxwellian electron temperature T_e , assuming cold ions such that ($T_e \gg T_i$) and quasi neutrality. Under these conditions at the plasma–sheath interface, considering a one-dimensional space dependence of quantities (1D-system) the momentum (ion-flux) and energy conservation along with the Maxwell Equation 1.9d read:

$$\begin{cases} n_i(x)u(x) = n_{i,s}(x)u_s & (1.42a) \\ \frac{1}{2}m_i u^2(x) = \frac{1}{2}m_i u_s^2 - e\varphi(x) & (1.42b) \\ \nabla^2 \varphi(x) = \frac{e}{\varepsilon_0}(n_e - n_i) & (1.42c) \end{cases}$$

where u is the ion speed and n_i and n_e the ion and electron densities in the plasma, respectively, $n_{i,s}$ and u_s are ion density and speed within the sheath, where ionization is assumed to be absent.

Given the electrons thermal equilibrium, the electron density is expressed by the Boltzmann relation $n_e(x) = n_{es} \exp[-e\varphi(x)/k_B T_e]$, with n_{es} the electron density within the sheath and k_B the Boltzmann constant. By solving Equations 1.42a and 1.42b with respect to u we find a relation for n_i as a function of $\varphi(x)$; which together with the former Boltzmann equation for n_e may be introduced into Equation 1.42c to give:

$$\frac{d^2 \varphi(x)}{dx^2} = \frac{en_s}{\varepsilon_0} \left\{ \exp[-e\varphi(x)/k_B T_e] - \left[1 - \frac{e\varphi(x)}{\varepsilon_s} \right]^{-\frac{1}{2}} \right\} \quad (1.43)$$

where $\varepsilon_s = 1/2m_i u_s^2$ and $n_s = n_{i,s} = n_{e,s}$ are the kinetic energy and density of ions within the plasma sheath. Equation (1.43) is the basic nonlinear equation governing the sheath potential and the ion and electron densities; it allows for a first exact integral obtained by multiplying Equation (1.43) by $d\varphi/dx$ and then integrating with respect to x with the field free plasma boundary conditions at $x = 0 : \varphi(0) = 0; [d\varphi/dx]_0 = 0$; thus yielding:

$$\frac{1}{2} \left[\frac{d\varphi(x)}{dx} \right]^2 = \frac{en_s}{\varepsilon_0} \left\{ k_B T_e \exp[-e\varphi(x)/k_B T_e] - k_B T + 2\varepsilon_s \left[1 - \frac{e\varphi(x)}{\varepsilon_s} \right]^{\frac{1}{2}} - 2\varepsilon_s \right\} \quad (1.44)$$

Equation 1.44 may be integrated numerically. However, analytical considerations provide some fundamental information on sheath features. The RHS of Equation (1.44) is positive-defined yielding to the consideration that the ion density within the sheath must always be larger than the electron density. Furthermore, by expanding up to the second order in $\varphi(x)$ we get the relation $e\varphi(x)^2/k_B T_e - e\varphi(x)^2/2\varepsilon_s \geq 0$, which may be satisfied for any value of x only if $2\varepsilon_s \geq k_B T_e$, leading to the Bohm

sheath criterion (Equation 1.45):

$$u_s \geq u_B \equiv \sqrt{\frac{k_B T_e}{m_i}} \quad (1.45)$$

From this condition the need is derived for an intermediate region between plasma (bulk) and plasma sheath in which ions are accelerated by electric an field to reach the speed u_s : this region is named *presheath*. Given the structural complexity of the plasma–wall interface matching (analytical and numerical) computational techniques are needed to provide solutions in specific configuration conditions and plasma regimes.

However, configurations in which a simple analytical solution is possible are still representative in some plasma regimes and often applied in surface functionalization processes. This is the case of high negative voltage biasing of one of the electrodes connected to the substrate to be plasma-treated or plasma-coated (see for instance PVD processes dealt with in Chapters 2 and 9) imply driving high negative voltages to one of the electrodes. In this case the sheath voltage is high and the related energy is large compared with the electron thermal energy, $e\varphi(x)^2 \gg k_B T_e$, allowing Equation (1.44) to be simplified by neglecting the exponential term on the RHS. This is the case of the so called *matrix sheath* in which only ions are present in the plasma sheath, with constant density $n_i(x) \equiv n_i = n_s$. In this one-dimensional configuration the Poisson equation deriving from the Gauss theorem (Equation 1.9d) has a simple source term: $d^2\varphi(x)/dx^2 = en_s/\varepsilon_0$, which leads to the analytical solution: $\varphi(x) = -(en_s/2\varepsilon_0)x^2$ from which for the boundary condition $\varphi(s) = -V_0$, (where $-V_0$ is the applied bias voltage) the sheath thickness s may be derived as a function of the plasma characterizing parameters:

$$s = \lambda_{De} \cdot \sqrt{\frac{2eV_0}{k_B T_e}} \quad (1.46)$$

Equation 1.46 confirms that the sheath scale length is much shorter than the plasma spatial extension. Considering the situation in which the kinetic energy of ions entering the sheath region is small compared with the plasma sheath potential energy the momentum (ion flux), energy conservation and Gauss theorem (Equations 1.9b, c and d) simplify to:

$$\begin{cases} en_i(x)u(x) = J_0 \\ \frac{1}{2}m_i u^2(x) = -e\varphi(x) \\ \frac{d^2\varphi(x)}{dx^2} = -\frac{en_i(x)}{\varepsilon_0} \end{cases} \quad (1.47)$$

where J_0 represents the constant ion current. By simultaneous solution of the three equations in Equation (1.47) it is possible to obtain a new differential equation for the sheath potential, which further multiplied by its first derivative $d\varphi(x)/dx$ and finally integrated by setting the following boundary conditions:

$d\varphi(x)/dx \equiv 0$ and $\varphi(x) \equiv 0$; leads to the solution:

$$\varphi(x) = -\sqrt[3]{\left(\frac{3}{2}\right)^4} \sqrt[3]{\frac{m_i}{2e} \left(\frac{J_0}{\varepsilon_0}\right)^2} \sqrt[3]{(x)^4} \quad (1.48)$$

By imposing the following boundary conditions $\varphi(s) \equiv -V_0$ in Equation (1.48), and solving for J_0 we get the well-known Child's law:

$$J_0 = \frac{4}{9} \frac{\varepsilon_0}{s^2} \sqrt{\frac{2 e V_0^3}{m_i}} \quad (1.49)$$

In particular, Equation (1.49) provides a more refined relation between plasma sheath potential and sheath thickness than Equation (1.46):

$$s = \frac{\sqrt{3}}{2} \lambda_{De} \sqrt[4]{\left(\frac{2 e V_0}{k_B T_e}\right)^3} \quad (1.50)$$

For collisional sheaths and other plasma sheaths regimes not falling into the considered simplified configurations, a dedicated analysis is necessary, as reported in Ref. [18].

1.7

Summary

In this chapter we have provided some fundamental and introductory concepts to develop a more rigorous and comprehensive understanding of the plasma state as well as providing basic tools to better appreciate the technical content of this book. Characterizing parameters and scaling quantities are provided in order to facilitate the parameterization of different plasma states and to allow classification of processing plasmas used for industrial applications.

Statistical and fluid description of plasmas are presented to better understand the fundamentals of plasma reactivity and plasma-surface interactions as the characterizing features of technological plasmas for surface functionalization.

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